HETEROCYCLES, Vol. 20, No. 9, 1983

ARENE SYNTHESES BY EXTRUSION OF HETEROATOMS FROM 7-HETEROATOM-BICYCLO[2.2.1]HEPTENE SYSTEMS

Henry N.C.Wong*[1]

Department of Chemistry
The Chinese University of Hong Kong
Shatin, New Territories,
Hong Kong

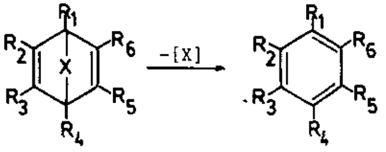
Tang-Kei Ng and Tai-Yuen Wong

Department of Applied Science
Hong Kong Polytechnic
Hung Hom, Kowloon,
Hong Kong

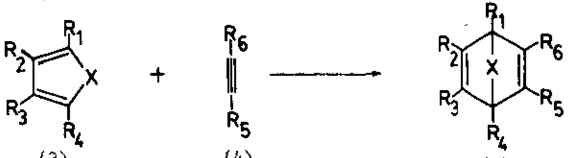
Abstract - Thermal and chemical extrusion of bridges containing O, S, N, P, Si, Ge, Sn, Co, Ir and Rh from the 7-heteroatom-bicyclo[2.2.1]heptenes are potentially important methods for constructing arenes with appropiate substituents.

Introduction

The extrusion of a heteroatom (e.g. X = S or O) or a carbon moiety (e.g. X = CO or CO_2) from the bicyclo[2.2.1]hepta-2,5-diene systems (1) formulates straightforward and viable method for the construction of arenes (2). This route appears particularly promising because (1) can be conveniently prepared in one step through Diels-Alder reaction between the heterocyclic compound (3) and the dienophile (4). The shortcoming of this methodology lies in the fact that some of the heterocyclic systems (3) (e.g. thiophenes and pyrroles) generally undergo Diels-Alder reaction reluctantly. Nevertheless, by resorting to the use of forcing reaction conditions and exceptionally powerful dienophiles, acceptable yields of the compounds (1) can still be realised. Another remedy to heal the disappointing reactivity of the heterocycle (3) is to deliberately link the hetero atom to an appropiate substituent, which enables the originally electron delocalised cyclic



(1) (2)



(3) (4) (1)

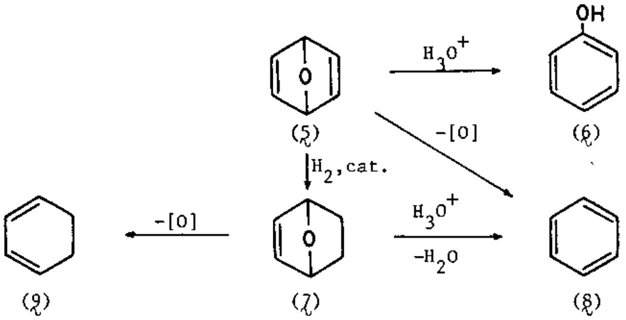
system (3) to resume most of its 1,3-diene character. Hence, by selecting heterocycles (3) and dienophiles (4) with suitable substituents, one can, at one's disposal, prepare a large number of bicyclo[2.2.1]heptene systems (1), which can then be subjected to their respective extrusion conditions.

It is interesting to point out that the approximate order of ease of extrusion of X atom from the cyclic system (1) is $N_2 > CO_2 > CO \geqslant SO > SO_2 > O_2 \geqslant S > O$.[2] The elimination of carbon dioxide[3] and carbon monoxide[4] bridges are subjects of numerous research papers and a number of reviews and therefore are not discussed here. The extrusion of ethylene[5] from compound (1) ($X = CH_2CH_2$) does not involve heterocyclic compounds and would not be reviewed. However, this special example of retro-Diels-Alder reaction deserves a mention because the debridging can be effected simply by heat, and has already been applied to the synthesis of many useful aromatic compounds.[5]

In this review, we would restrict our discussion only on the thermal or chemical extrusion of bridges constructed by O, S, SO_2, N, P, Si, Ge, Sn, Co, Ir as well as Rh. This extrusion strategy can by utilised for the syntheses of benzene-ring containing intriguing unnatural compounds and natural products, whose syntheses would be otherwise difficult to achieve.

Extrusion of Oxygen Bridge

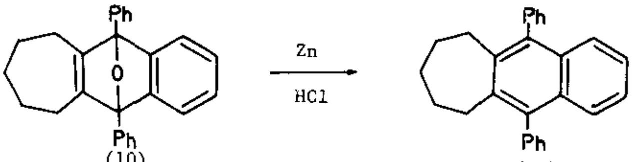
As synthetic target molecules, the 7-oxabicyclo[2.2.1]hepta-2,5-diene (5) are readily available due to the typical 1,3-diene behaviour of furans [(3), X = O]. Endoxides (5) are acid labile compounds, and would lead to phenolic compounds (6) when exposed to acidic conditions.[6] Therefore, strongly acidic deoxygenation reagents are not suitable for the debridging of the oxygen atom of (5). In addition, it has been mentioned earlier that the elimination of oxygen atom is perhaps one of the most difficult reaction according to the order of ease of extrusion.[2] It is hence not surprising that there is still no universal reagent for the deoxygenation of the endoxide (5) to the arene (8).



Alternatively, the endoxide (5) can be catalytically hydrogenated to (7), which would also afford the arene (8) upon treatment with acid.[7] This route is nonetheless confined to those compounds which do not contain acid sensitive groups. On the other hand, the endoxide (7) can be converted to the synthetically important cyclohexadiene (9) through also a deoxygenation reaction.

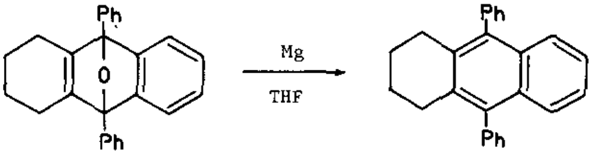
Despite the implicit difficulty and complication, the deoxygenation of the endoxide (5) has received considerable attention during the past few years and several research papers have appeared in the literature.

Wittig's pioneering reports on strained cycloalkynes and its Diels-Alder adducts with furans simultaneously also recorded some examples of deoxygenation reaction. Wittig found out that zinc in acid was effective for deoxygenating endoxides which were extensively conjugated with aromatic systems. The following is a typical example. The Diels-Alder adduct (10), upon deoxygenation by zinc in hydrochloric acid, gave the diphenylnaphthalene (11).[8]

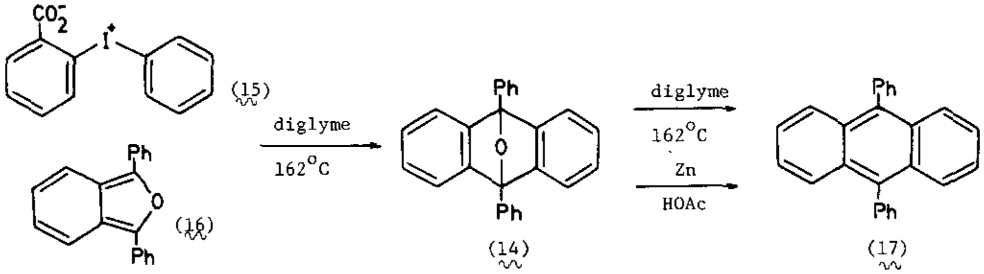


(10) (11)

On the other hand, Wittig also reported that magnesium was also seemingly capable of deoxygenating the endoxide (12) to the diphenylnaphthalene (13),[9] albeit in rather disappointing yield (8.6%). It is thus generally accepted that when endoxides are extensively conjugated with aromatic systems, the deoxygenation can be rendered rather easy. Consequently, 9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene (14), which was prepared via the betaine (15) and 1,3-diphenylisobenzofuran (16), could be converted to 9,10-diphenylanthracene (17) in 21% yield simply by heating in diglyme at 162°C for 2 hours.[10] The compound (17) can also be prepared by treatment of the endoxide (14) with zinc in acetic acid.[9]

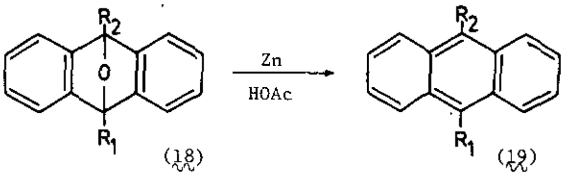


(12) (13)



(15) (16) (14) (17)

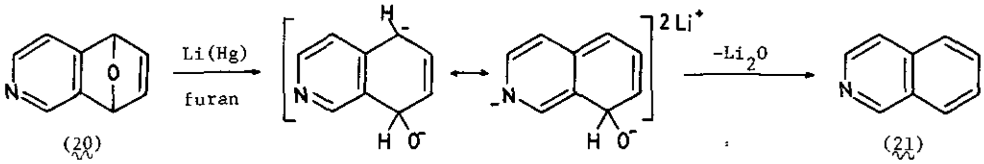
Similarly, the substituted polycyclic ethers (18) can be deoxygenated by reaction with zinc and acetic acid to give the substituted anthracene (19).[11]



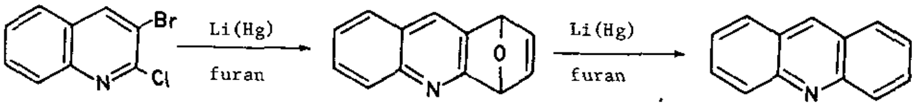
(18) (19)

(a) R_1=Ph, R_2=Ph (b) R_1=Ph, R_2=Me (c) R_1=Et, R_2=Ph (d) R_1=Ph, R_2=^{i}Pr

In general, lithium amalgam can deoxygenate endoxides which are fused to a pyridine ring. An example of these was recorded, in which the 5,8-dihydroisoquinoline-5,8-epoxide (20), was readily deoxygenated by lithium amalgam in furan to give isoquinoline (21) in 50% yield.[12] Heteroaromatic *o*-dihalogeno compounds reacted in similar manner with lithium amalgam in furan, resulting in the oxygen-free heteroaromatic compounds. Thus, 2-chloro-3-bromoquinoline (22) in furan was converted to acridine (23) in 4% yield by treatment with lithium amalgam at room temperature.[12]

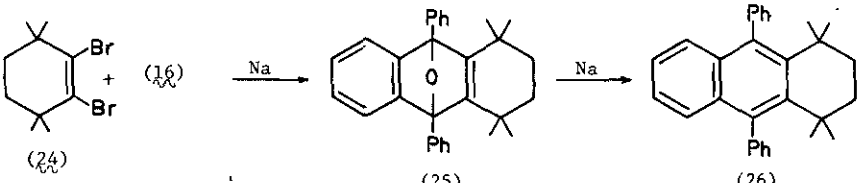


(20) (21)



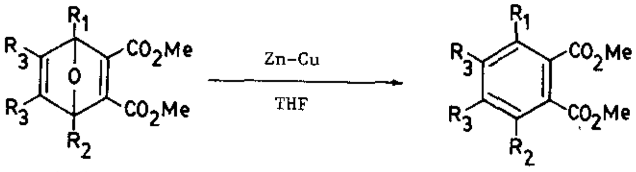
(22) (23)

Sodium has also been proved to be capable of eliminating an oxygen atom from endoxides. Thus, 3,3,6,6-tetramethyl-1,2-dibromocyclohexene (24) would be debrominated by sodium in the presence of 1,3-diphenylisobenzofuran (16), giving the intermediate compound, namely, 1,2,3,4,9,10-hexahydro-1,1,4,4-tetramethyl-9,10-diphenyl-9,10-endoxoanthracene (25). The intermediate compound (25) was then deoxygenated under the action of sodium to give the compound (26), whose total yield was merely 7%.[13]



(24) (25) (26)

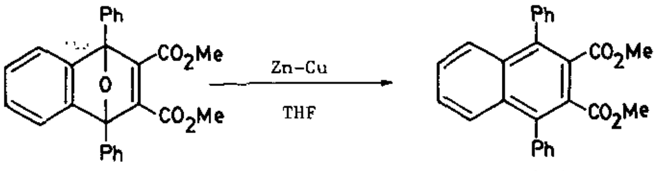
The activated form of Zn-Cu couple was recently found to be able also to deoxygenate compounds (27) and (29) to (28) and (30) respectively.[14] (Table 1)



(27) (28)

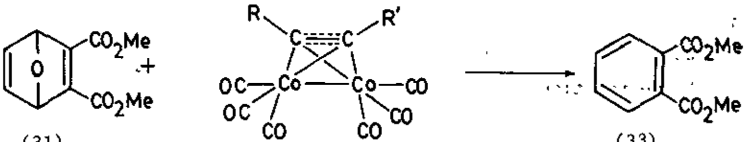
Table 1

Endoxide	R_1	R_2	R_3	Product	Yield
(27a)	H	Me	H	(28a)	40%
(27b)	Me	Me	H	(28b)	36%
(27c)	H	H	CO_2Me	(28c)	12%



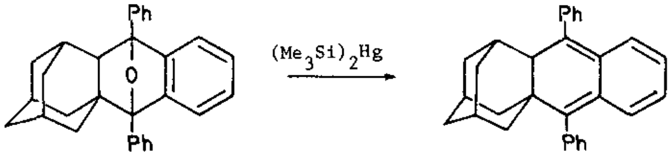
(29) (30)

Other metal complexes, such as those of cobalt and mercury, would also effect the deoxygenation. For example, the formation of dimethyl phthalate (33) was unexpectedly achieved by reaction of the endoxide (31) with acetylene hexacarbonyldicobalt complex (32).[15]



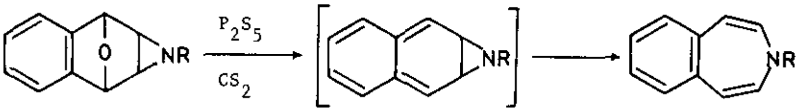
(31) (32) (33)

The diphenylisobenzofuran adduct (34) was readily transformed to the hydrocarbon (35) in the presence of *bis*(trimethylsilyl)mercury.[16]



(34) (35)

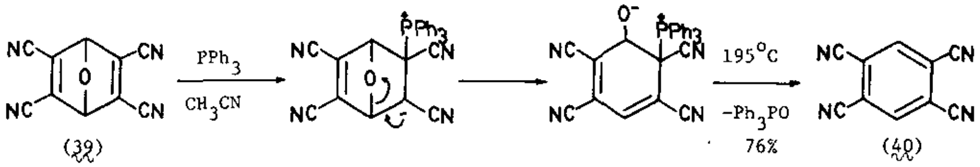
The aziridine (36) has recently been treated with P_2S_5 to give N-phthalimido-3-benzazepine (38).[17] The reaction was proposed to be a deoxygenation reaction, going through the intermediate (37).[17]



R=phthalimido

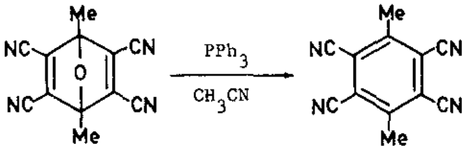
(36) (37) (38)

The deoxygenation of endoxide which is activated by cyano groups can be effected by triphenylphosphine. The extrusion of an oxygen atom can be accomplished by elimination of triphenylphosphine oxide at 195°C. The oxygen-bridged compound (39) could therefore be converted to 1,2,4,5-tetracyanobenzene (40) in acceptable yield.[18] This method was also applicable to 1,4-dimethyl-



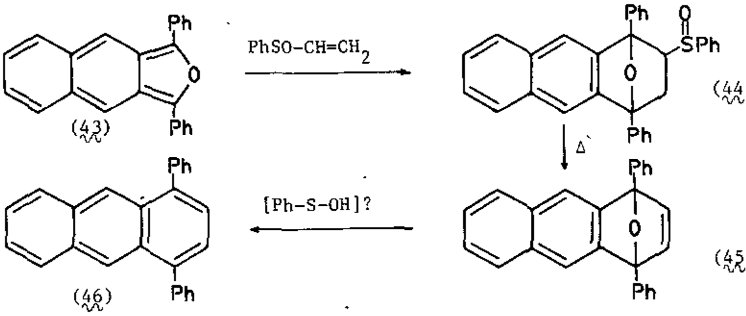
(39) (40)

2,3,5,6-tetracyano-7-oxabicyclo[2.2.1]hepta-2,5-diene (41) which afforded tetracyano-*p*-xylene (42) in 52% yield. The thermal cleavage process was not necessary in this reaction.[18]



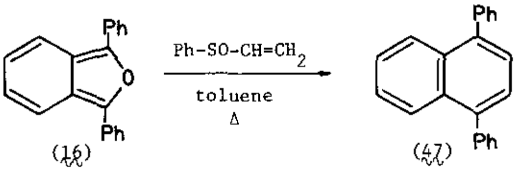
(41) (42)

When 1,3-diphenylnaphtho[2,3-*c*]furan (43) was allowed to react with phenyl vinyl sulphoxide *in toluene at 40°C for 6 hours, the adduct (44) was isolated.* When the compound (44) was heated to reflux in toluene, 1,4-diphenylanthracene (46) was isolated in good yield,[19] via the intermediate (45). It was suggested that the eliminated Ph-SOH was responsible for the deoxygenation of (45) to (46), but details of the reaction mechanism have not been pursued further.[19]



(43) (44) (45) (46)

Diphenylisobenzofuran (16) was converted in similar route to 1,4-diphenylnaphthalene (47) in 93% yield.[19]



(16) (47)

Deoxygenation reaction has also been observed for the Diels-Alder adducts between 2,5-*bis*(trimethylsiloxy)furan (48) and dimethyl acetylenedicarboxylate (49). The products obtained, after removal of the trimethylsilyl groups, were found to be the quinones (50) and/or the hydroquinones (51). The ratio of (50) and (51) was controlled by the reaction temperature as well as the substituents on the furan (48). For example, (48b) and (49) gave only the quinone (50b), but when the temperature was raised to 80°C, deoxygenation took place, making (51b) as major product.[20] (Table 2)

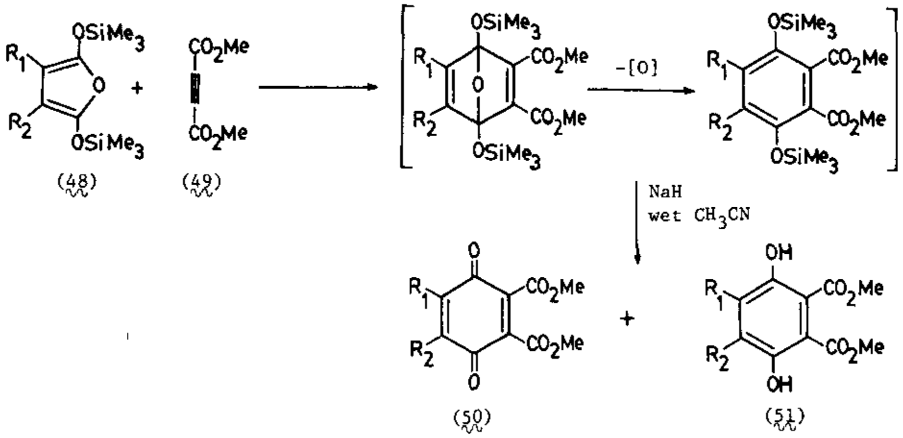
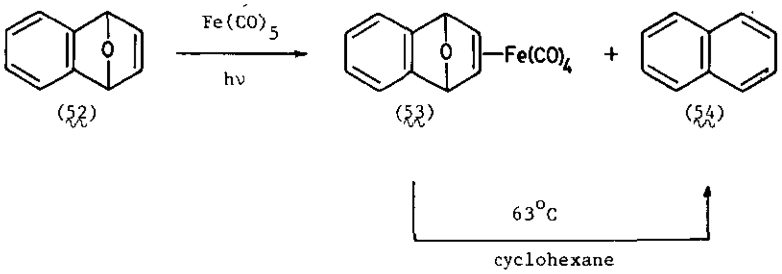


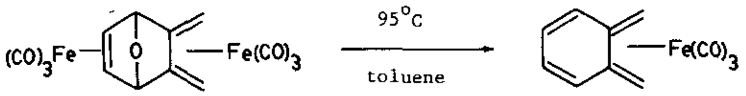
Table 2

Furan	R_1	R_2	Condition	Product and Yield
(48a)	H	H	Ph-H, 80°C	(50a) 50%
			CCl_4, 50°C	5:4 mixture of (50a) & (51a) 86%
			neat, r.t.	4:1 mixture of (50a) & (51a), (50a) 53%
(48b)	Me	H	CCl_4, 80°C	1:5 mixture of (50b) & (51b), (51b) 73%
			CCl_4, 50°C	(50b) 100%
			neat, r.t.	6:1 mixture of (50b) & (51b) 100%
(48c)	$-(CH_2)_4-$		CCl_4, 50°C	(50c) 84%
(48d)	$-CH_2CH=CHCH_2-$		neat, r.t.	5:2 mixture of (50d) and dimethyl 1,4-diphenyl-naphthalene-2,3-dicarboxylate

Iron carbonyl complex has also been found to be capable of aromatising endoxides. When a solution of the endoxide (52) and iron pentacarbonyl in pentane under nitrogen was irradiated for 6 hours, 50% yield of naphthalene (54) was obtained.[21] If a solution of the complex (53) was independently heated at 63°C for 10.5 hours, quantitative yield of naphthalene (54) was isolated.[21]

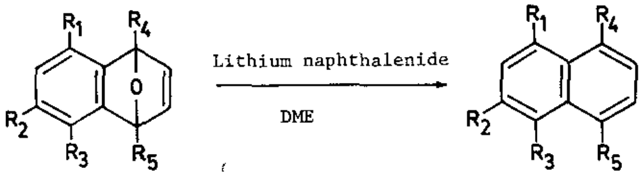


It was recently found out that the iron carbonyl complex (55) would eliminate an oxygen atom to yield an o-quinodimethane iron carbonyl complex (56) when heated to 95°C in toluene.[22]



(55) (56)

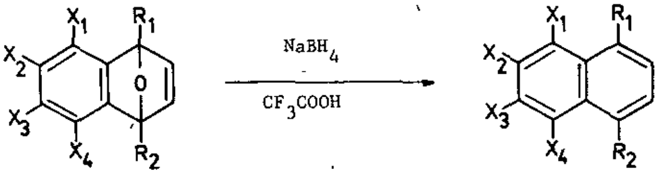
Lithium naphthalenide has been used to aromatise endoxides. The oxygen-bridged compound (57) can be converted to the naphthalene compound (58) by reaction with lithium naphthalenide in dry DME or THF under argon. The results are listed in Table 3.[23] The use of equivalent amount of lithium naphthalenide in this reaction makes this method rather unfavourable, because the work-up after the reaction would involve isolation of the naphthalene (58) obtained from equivalent amount of naphthalene.



(57) (58)

Table 3	R_1	R_2	R_3	R_4	R_5	Condition	Yield
	^{t}Bu	H	^{t}Bu	H	H	(a) DME, 1 hr at r.t.	61%
						(b) THF, 1 hr at r.t.	50%
	^{t}Bu	^{t}Bu	H	^{t}Bu	^{t}Bu	DME, 2 hr at r.t.	53.5%

Halogen-substituted naphthalene (60) can be obtained from the endoxides (59) by deoxygenation with sodium borohydride in trifluoroacetic acid. The yields are given in Table 4.[24]



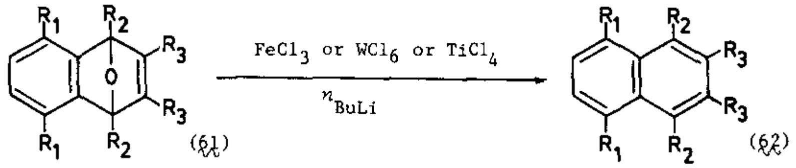
(59) (60)

Table 4	Endoxide	R_1	R_2	X_1	X_2	X_3	X_4	Product	Yield A	Yield B
	(59a)	Me	Me	H	H	H	H	(60a)	69%	90%
	(59b)	Me	Me	F	H	H	H	(60b)	97%	-
	(59c)	Me	Me	F	H	F	H	(60c)	92%	-
	(59d)	Me	Me	F	F	F	F	(60d)	64%	-
	(59e)	Me	Me	F	Cl	F	Cl	(60e)	57%	-
	(59f)	H	H	H	H	H	H	(54)	7%	59%
	(59g)	H	Me	H	H	H	H	(60g)	-	61%

A: A solution of (59) in Et_2O or CH_2Cl_2 was added to a mixt. of $NaBH_4$ in CF_3COOH at 15°C under N_2.

B: A solution of (59) and $NaBH_4$ in THF was allowed to react with a solution of CF_3COOH in THF at 0-5°C under N_2.

The low valent forms of iron, tungsten or titanium prepared by treatment of the corresponding metal chloride at -78°C with *n*-butyllithium, have been proved to be effective in removing the oxygen atom from the endoxides (61) and (63) to afford arenes (62) and (64) respectively.[25] (Table 5)



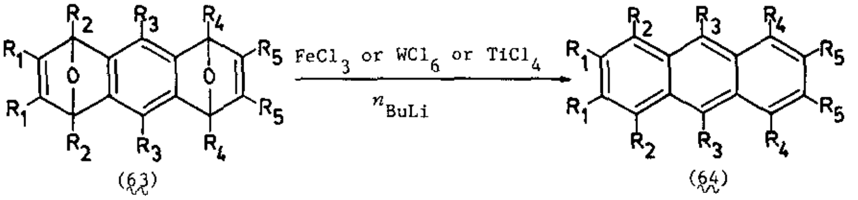
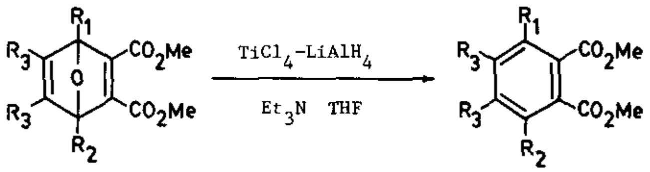


Table 5

Endoxide	R_1	R_2	R_3	R_4	R_5	Time(hr)	Product	Yield(%)		
								$FeCl_3$	WCl_6	$TiCl_3$
(61a)	H	Me	H	-	-	6	(62a)	81	88	81
(61b)	Me	Me	H	-	-	6	(62b)	83	-	-
(61c)	H	Me	Me	-	-	5	(62c)	-	89	55
(63a)	H	H	Me	H	H	10	(64a)	56	-	-
(63b)	H	H	Me	Me	H	9	(64b)	40	16	79
(63c)	Me	Me	Me	Me	Me	10	(64c)	-	-	50
(63d)	H	H	OMe	H	H	6	(64d)	20	89	-
(63e)	H	Me	OMe	Me	H	24	(64e)	-	47	-
(63e)	H	Me	OMe	Me	H	18	(64e)	60	-	54
(63f)	Me	Me	OMe	Me	Me	90	(64f)	61	-	-

So far, only the deoxygenation of endoxides conjugated with benzene-rings, or activated by powerful electron-withdrawing groups have been discussed. It is of particular interests to investigate the aromatisation of endoxides which contain no such activating factors. The low valent form of titanium generating by the reduction of $TiCl_4$ with $LiAlH_4$ seems to be the reagent of choice. This reagent has the potential of being developed into a universal deoxygenation reagent applicable for all types of endoxides. The following reactions are typical examples. $TiCl_4$-$LiAlH_4$-Et_3N in THF would deoxygenate the endoxides (31), (27a) and (27b) to the corresponding phthalates (33), (28a) and (28b) respectively.[26] (Table 6)

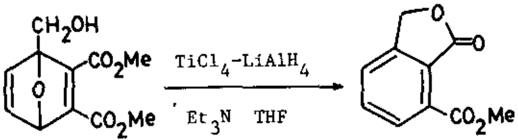


see Table 6

Table 6

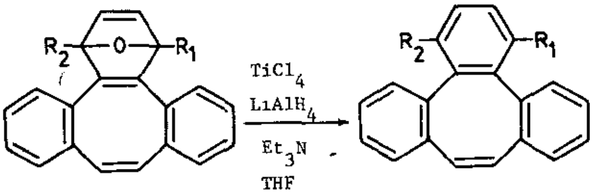
Endoxide	R_1	R_2	R_3	Product	Yield
(31)	H	H	H	(33)	64%
(27a)	H	Me	H	(28a)	77%
(27b)	Me	Me	H	(28b)	54%
(27c)	H	H	CO_2Me	(28c)	59%
(65a)	H	Me	CO_2Me	(66a)	50%
(65b)	Me	Me	CO_2Me	(66b)	30%

Similarly, the compounds (27c), (65a) and (65b) could also be converted to (28c) (66a) and (66b) respectively by treatment with $TiCl_4$-$LiAlH_4$-Et_3N in THF.[27] On the other hand, the phthalide (68) was unexpectedly isolated as the sole product from the reaction of the alcohol (67) with low valent titanium.[27]



(67) (68)

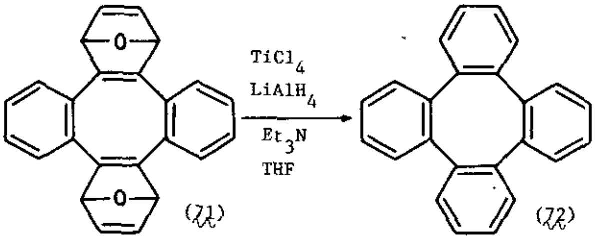
The usefulness of the low valent titanium generated from $TiCl_4$-$LiAlH_4$ was convincingly demonstrated by the deoxygenation of the unconjugated compound (69) to the substituted tribenzo[*a*,*c*,*e*]-cyclooctene (70),[28] (Table 7) which eluded formal synthesis for almost four decades since the first preparation of their parent compound (70a).[29] By using the same reagent mixture, tetraphenylene (72) was isolated in moderate yield from the endoxide (71).[26]



(69) (70)

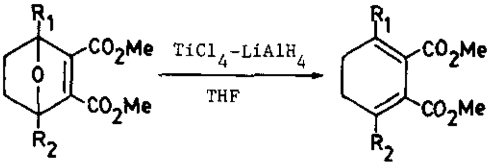
Table 7

Endoxide	R_1	R_2	Product	Yield
(69a)	H	H	(70a)	57%
(69b)	Me	Me	(70b)	75%
(69c)	H	CO_2Me	(70c)	27%
(69d)	H	CH_2OMe	(70d)	27%
(69e)	H	Me	(70e)	34%



(71) (72)

In the absence of triethylamine, the endoxide (73) would be converted to the cyclohexadiene (74) by reaction with low valent titanium.[30] This reaction is of particular importance because it reveals the mild condition of the reagent, which is not capable of aromatising the endoxide (73) [*viz.* (7)→(8)]. On the other hand, aromatisation took place in the presence Et_3N. The mechanism of this transformation and the role of Et_3N are at present not clear.[30] (Table 8)



(73) (74)

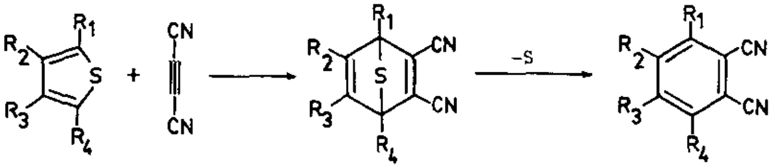
Table 8

Endoxide	R_1	R_2	Product	Yield
(73a)	H	H	(74a)	69%
(73b)	Me	H	(74b)	67%
(73c)	Me	Me	(74c)	57%

Extrusion of Sulfur Bridge

Although thiophene is inert to most dienophiles at room temperature, it would react with very powerful dienophiles such as dicyanoacetylene[31] and tetrafluorobenzyne[32] at moderate temperature, as well as with other weaker dienophiles at very high temperature.[33]

The Diels-Alder reaction of the thiophene (75) with dicyanoacetylene (76) gave the bicyclic intermediate (77), which was readily transformed to the corresponding phthalonitrile (78).



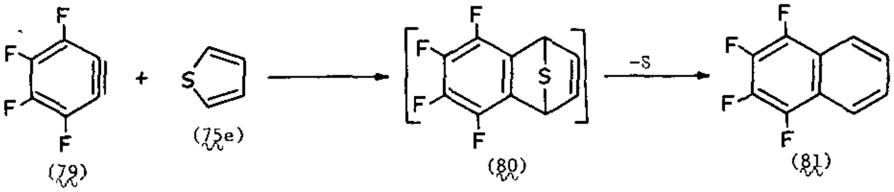
(75) (76) (77) (78)

The extrusion of sulfur was believed to be effected by heat. The overall yields are depicted in Table 9.[31]

Table 9

Thiophene	R_1	R_2	R_3	R_4	Condition	Product	Yield
(75a)	Me	^{t}Bu	H	Me	60°C, 10hr	(78a)	51%
(75b)	Me	H	H	Me	100°C, 12hr	(78b)	49%
(75c)	H	Ph	Ph	H	100°C, 12hr	(78c)	18%
(75d)	Me	H	H	H	80°C, 44hr	(78d)	9%
(75e)	H	H	H	H	120°C, 48hr	(78e)	8%

Tetrafluorobenzyne (79) reacted with thiophene (75e) to give 1,2,3,4-tetrafluoronaphthalene (81), presumably via the intermediate (80), suffering the subsequent extrusion of a sulfur atom.[32] At temperature well over 150°C, 2,5-dimethylthiophene (75b) and thiophene (75e) are able to react with dienophiles (82) to provide sulfur-bridged compounds (83), whose sulfur atoms can be extruded by the effect of heat to furnish compounds (84).[33] (Table 10)



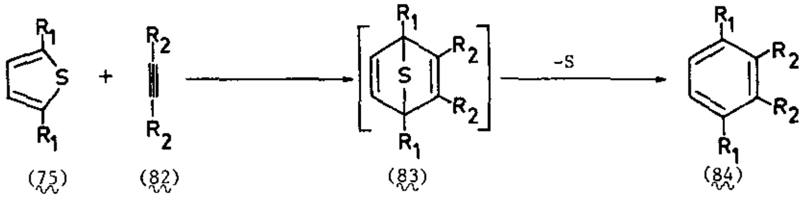
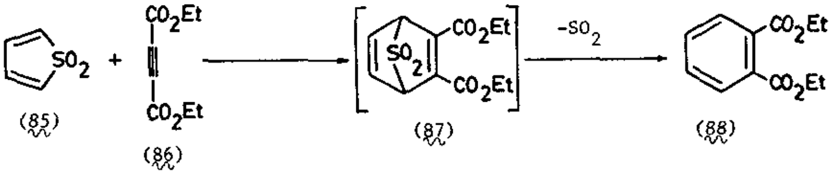
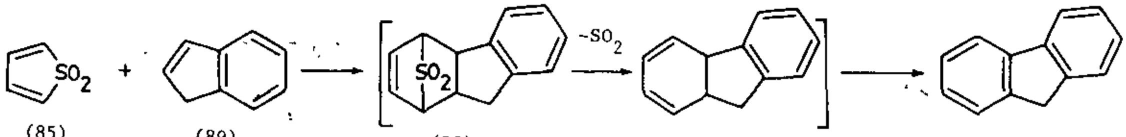


Table 10

Thiophene	R_1	R_2	Temperature	Time	Yield
(75b)	Me	CO_2Me	*ca.* 180°C	24hr	42%
(75b)	Me	CO_2Me	165°C	48hr	14%
(75b)	Me	Me	*ca.* 300°C	24hr	2%
(75e)	H	Ph	200-280°C	44hr	38%
(75e)	H	CO_2Me	*ca.* 165°C	24hr	56%

Thiophene 1,1-dioxide (85) behaves as a better 1,3-diene than thiophene itself. Thiophene 1,1-dioxide (85) and diethyl acetylenedicarboxylate (86) would form an unstable intermediate (87), which eventually eliminated the sulfur dioxide bridge to afford *diethylphthalate* (88) in 18% yield.[34] Furthermore, thiophene 1,1-dioxide (85) also readily underwent Diels-Alder reaction with indene (89) to give the sulfur dioxide-bridged compound (90), which lost sulfur dioxide to form 4*a*,9*a*-dihydrofluorene (91). The dihydrofluorene (91) could not be isolated and would be instead oxidised by coming into contact with air to give fluorene (92) in 3% yield.[34]

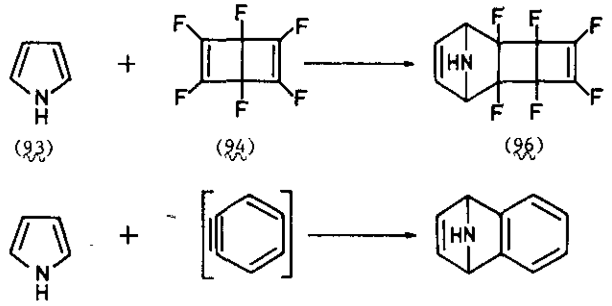




(85) (89) (90) (91) (92)

Extrusion of Nitrogen or Phosphorus Bridge

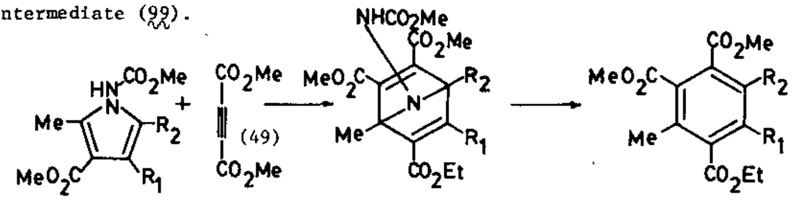
Pyrrole (93) behaves as a very poor 1,3-diene, and indeed it only undergoes Diels-Alder cycloaddition with very reactive dienophiles, i.e. 1,2,3,4,5,6-hexafluorobicyclo[2.2.0]hexa-2,5-diene (94)[35] and benzyne (95)[36] to yield the nitrogen-bridged compounds (96)[35] and (97)[36] respectively.



(93) (94) (96)

(93) (95) (97)

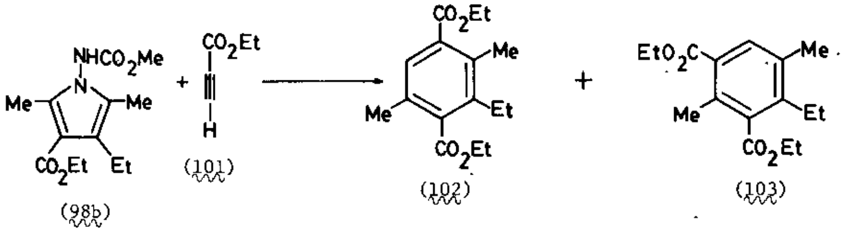
Alternatively, N-carbomethoxyaminopyrrole (98) serves as a normal 1,3-diene and it has been shown that (98) would react with excess dimethyl acetylenedicarboxylate (49) in refluxing toluene for 48 hours to give the compound (100) in good yield,[37] via possibly the nitrogen-bridged intermediate (99).



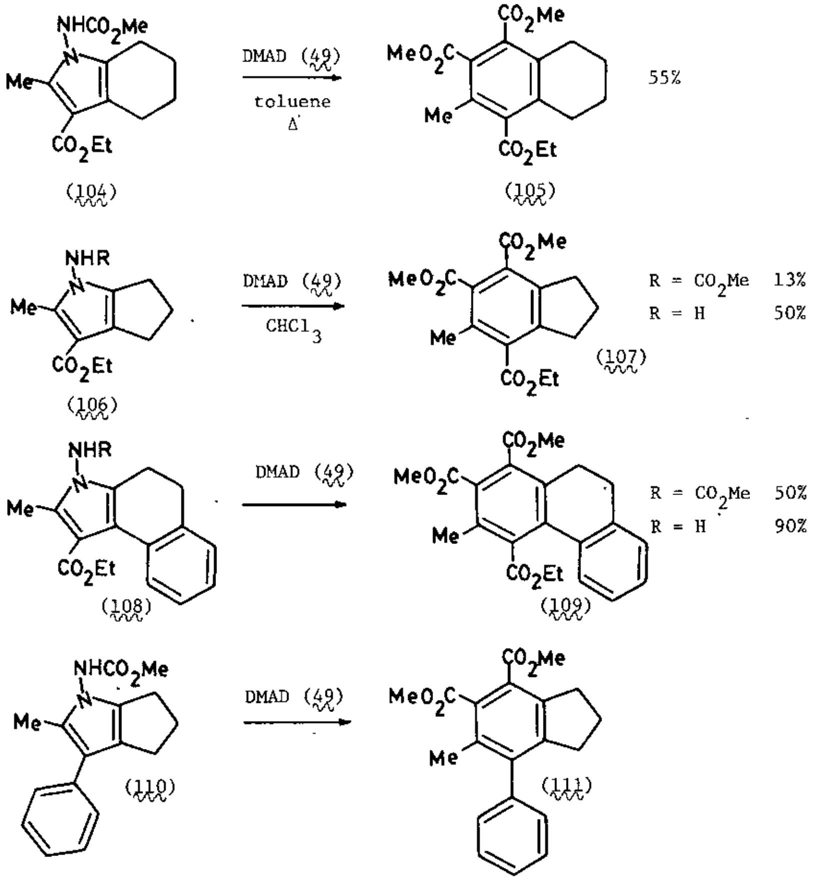
(98a) R_1=Me,R_2=Et (99) (100)

(98b) R_1=Et,R_2=Me

N-Carbomethoxyaminopyrrole (98b) also reacted with ethyl propiolate (101) to give a mixture of (102) and (103),[37] which were believed also to result from the elimination of the nitrogen bridge from the intermediate nitrogen-bridged compound.[37]

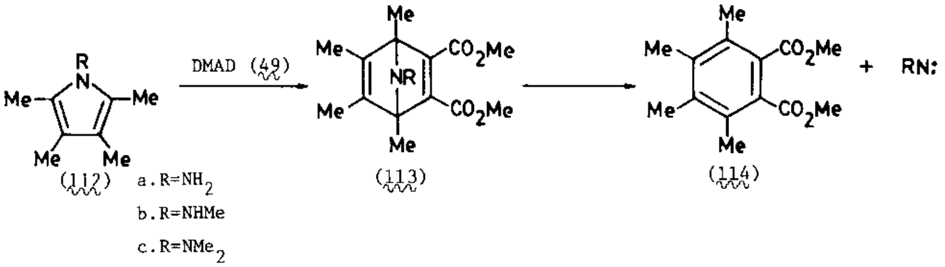


By using the same method, N-amino compounds (104), (106), (108) and (110) could be transformed to (105), (107), (109) and (111) respectively by reaction with dimethyl acetylenedicarboxylate (49).

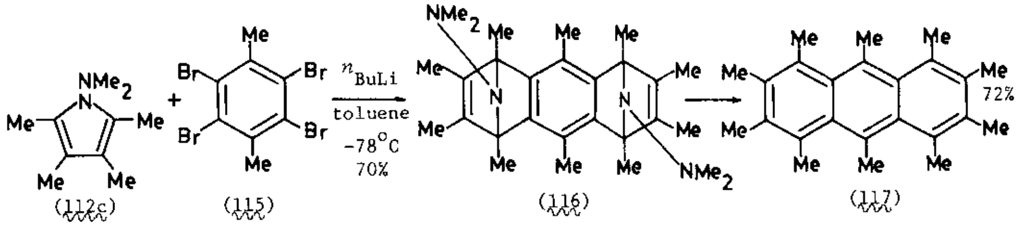


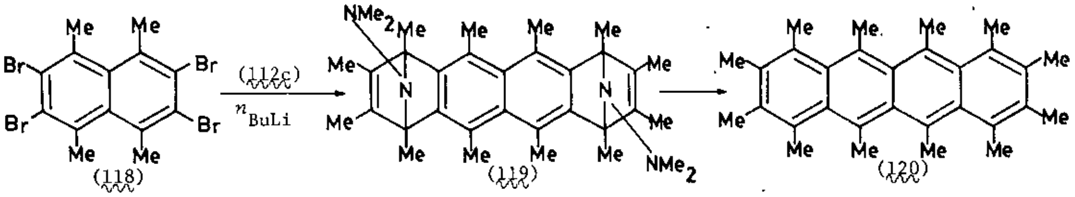
Interestingly, the yields of (107) and (109) were increased to 50% and 90% respectively when the R groups of (106) and (108) were H, and the yields were duly reduced when R is an electron withdrawing carbomethoxy group.[37]

Systematic investigation on the effect of alkyl substituents on the N-amino group has also been conducted. It is noteworthy that the observed rate of cycloaddition [*viz.* (112)→(113)] increased in the order (112c)<(112b)<(112a), whereas the observed rate of nitrogen extrusion [*viz.* (113)→(114)] followed the order (113c)>(113b)>(113a).[37]

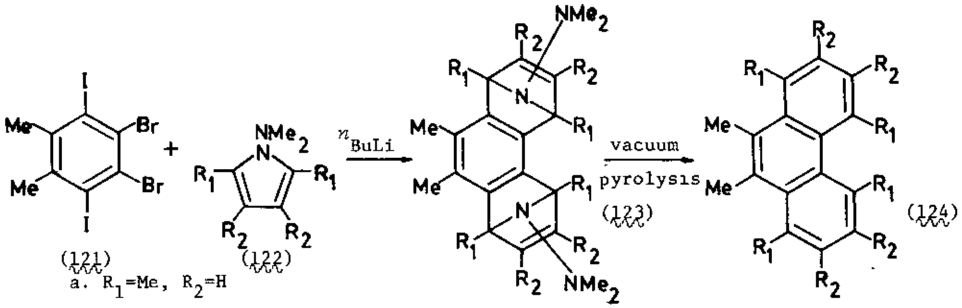


Hart and coworkers have reported the trapping of bisaryne,[38] which could be generated from the tetrabromide (115) by debromination with *n*-butyllithium. The intermediate bisaryne could be trapped with various 1,3-dienes. The cycloaddition of particular interest was the trapping of the





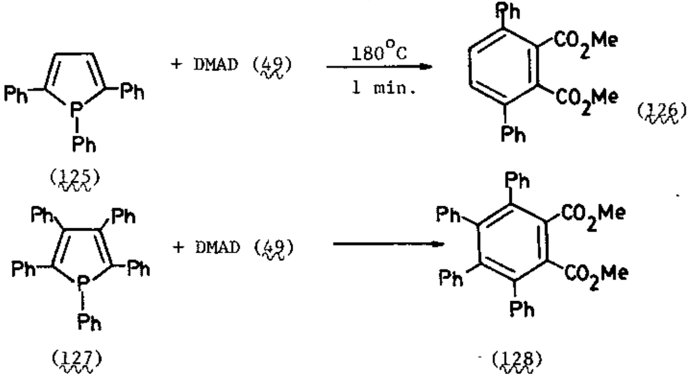
bisaryne with the N,N-dimethylaminopyrrole (112c), whose reaction product was the nitrogen-bridged compound (116).[38] The nitrogen bridge of (116) was eliminated by reaction with *m*-chloroperbenzoic acid (MCPBA) to yield decamethylanthracene (117).[38] The tetrabromide (118) was converted to dodecamethyltetracene (120) via (119) in a similar fashion.[38] An extension of this bisaryne work led Hart and coworks to the unequivocal synthesis of various phenanthrenes.[39] Thus, the halide (121) and the pyrrole (122) reacted in the presence of *n*-butyllithium to yield the nitrogen-bridged compound (123), which underwent debridging by vacuum pyrolysis to give the phenanthrenes (124).[39]

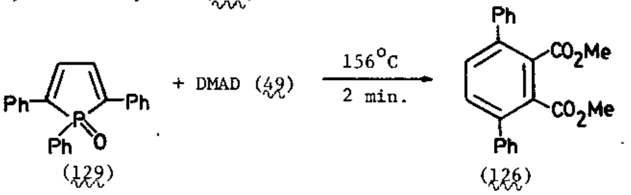


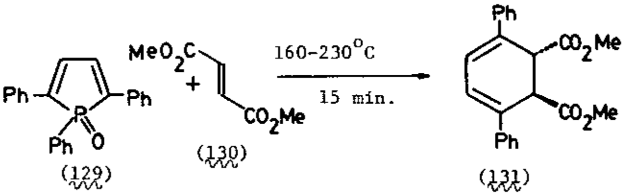
a. R_1=Me, R_2=H

b. R_1=H, R_2=Me

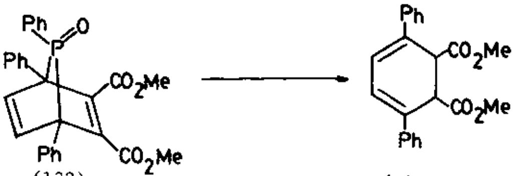
1,2,5-Triphenylphosphole (125) underwent Diels-Alder reaction at 180°C with dimethyl acetylenedicarboxylate (49) and lost the P-Ph bridge to give dimethyl 3,6-diphenylphthalate (126) in 40% yield.[40] Pentaphenylphosphole (127) also reacted to give dimethyl tetraphenylphthalate (128).[41] Comparatively, the phosphole oxide (129), when treated with (49), also afforded (126) in 71% yield.[40] Moreover, if (49) was replaced by dimethyl fumarate (130), higher temperature was required to extrude the phosphorus bridge, and 73% yield of dimethyl 3,6-diphenylcyclohexa-3,5-diene-*trans*-1,2-dicarboxylate (131) was obtained.[40]



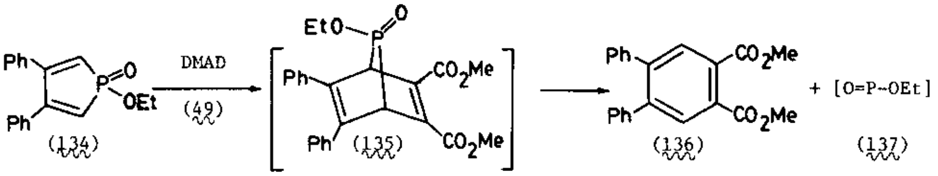




A similar extrusion was reported, in which the phosphabicyclo[2.2.1]heptene (132) yielded dimethyl 3,6-diphenyl-1,2-dihydrophthalate (133) upon thermal reaction with trichlorosilane or triphenylsilane in benzene.[42] The stereochemistry of (133), however, has not been indicated.

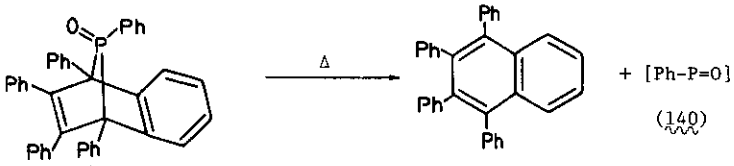

(132) (133)

1-Ethoxy-3,4-diphenylphosphole 1-oxide (134) would react with dimethyl acetylenedicarboxylate (49) to give dimethyl 4,5-diphenylphthalate (136) and elements of monomeric metaphosphite (137).[43] The phosphorus-bridged compound (135) was supposed to be the reactive intermediate.[43]



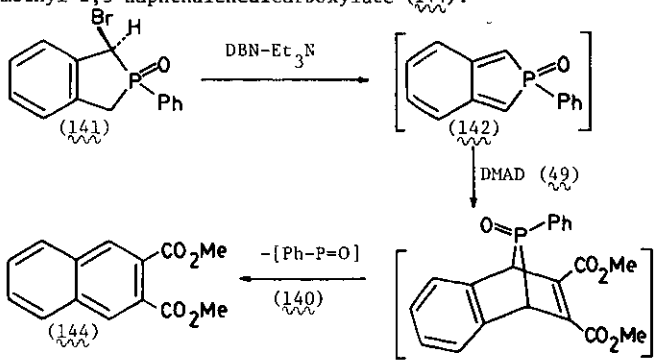
(134) (135) (136) (137)

2,3-Benzo-1,4,5,6,7-pentaphenyl-7-phosphabicyclo[2.2.1]hept-5-ene oxide (138) was prepared in 92% yield by the cycloaddition of *in situ* generated benzyne (95) to pentaphenylphosphole oxide.[44] Thermal extrusion of the reactive phenylphosphinidene oxide (140) from (138) led to 1,2,3,4-tetraphenylnaphthalene (139).[44]



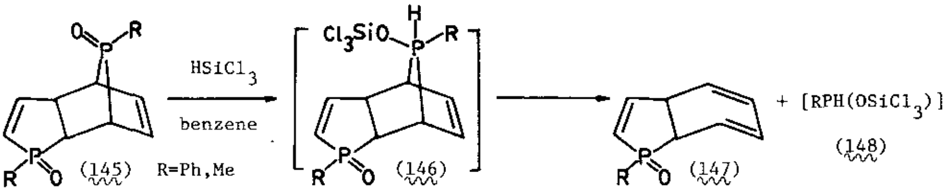
(138) (139) (140)

Dehydrobromination of the bromide (141) by DBN or Et_3N yielded the unstable benzophosphole oxide (142), which was trapped by dimethyl acetylenedicarboxylate (49) to give the phosphorus-bridged compound (143).[45] The compound (143) spontaneously lost phenylphosphinidene oxide (140) to afford dimethyl 2,3-naphthalenedicarboxylate (144).[45]

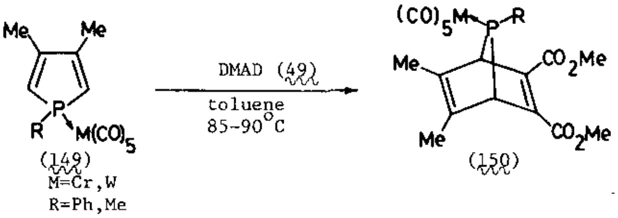


(141) (142) (144)

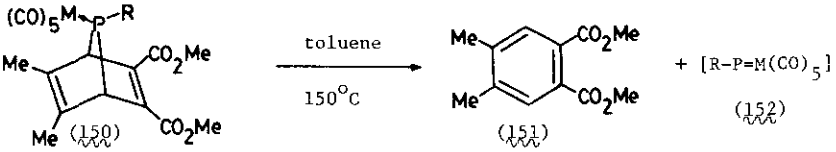
The reaction between trichlorosilane and (145) in benzene led to complete elimination of the phosphorus bridge. This reaction was due to the formation of the intermediate (146), which reacted further in accord to the retro-McCormack cycloaddition to form the cyclohexadiene (147) and the trivalent phosphorus moiety (148).[46]



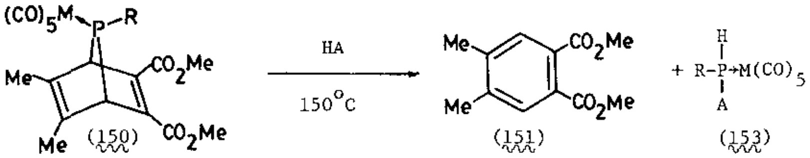
The 7-phosphanorbornadiene (150) was prepared from the phosphorus-metal complex (149) and dimethyl acetylenedicarboxylate (49) in toluene at 85-90°C.[47]



The compound (150) easily lost the phosphorus bridge upon heating in toluene at 150°C to yield dimethyl 4,5-dimethylphthalate (151) and the fugitive terminal phosphinidene complex (152), which could be trapped by 2,3-dimethylbuta-1,3-diene or diphenylacetylene.[48]



The complex (150) could also afford (151) and the complex (153) by solvolytic reaction with water, alcohols or amines.[48] The stepwise mechanism of these reactions have been discussed in details.[48]

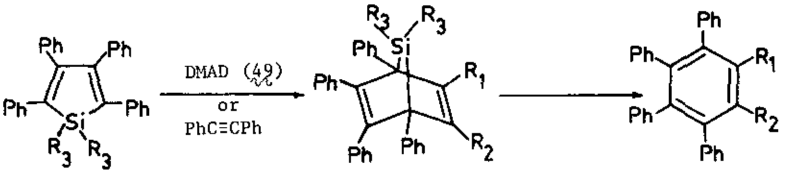


HA = HOMe, HOH, HNR'_2

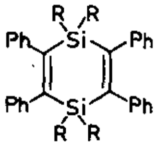
Extrusion of Silicon, Germanium or Tin Bridge

The research effort in the debridging of sila-, germa- and stanna-norbornanes is indebted to the enthusiasm in the chemistry of silylenes, germylenes as well as stannylenes. We however focus our attention mainly on other products of these reactions, namely, arenes.

The cycloaddition reaction of the silole (154) with dienophiles furnished the silanorbornadiene (155), which would readily loss the silylene to give the arene (156)^{49,50} (Table 11). The reactive silylene could be trapped by diphenylacetylene to yield 1,4-disilacyclohexadiene (157)$^{49-51}$ or could polymerise to the amorphous dimethylsilyl polymer (158)$^{49-51}$ in the absence of diphenylacetylene.



(154) (155) (156)



(157)

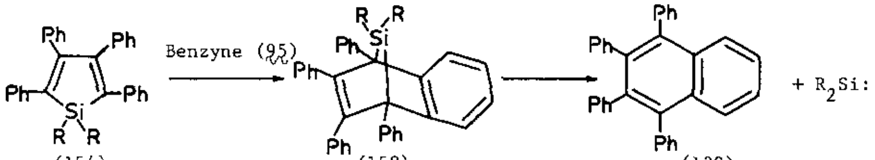
$[Me_2Si]_n$

(158)

Table 11

Silanorbornadiene	R_1	R_2	R_3	Condition	Yield	Reference
(155a)	CO_2Me	CO_2Me	Ph	Basic Al_2O_3	96%	50
(155b)	CO_2Me	CO_2Me	Me	EtOH	-	49
(155c)	Ph	H	Me	300°C, 3hr with PhC≡CPh	84.3%	49

Similar results demonstrated that when the silole (154) was allowed to add to benzyne (95), the silicon-bridged compound (159) could be isolated. The compound (159) would also loss dialkylsilylene rather easily on several occasions$^{49-51}$ to give 1,2,3,4-tetraphenylnaphthalene (139) (Table 12). Consequently, 7-silanorbornanes are important precursors for silylene generation.^{52}

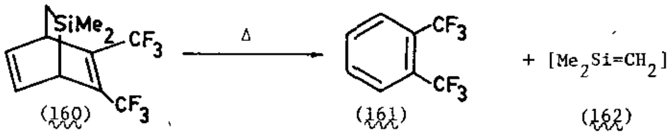


(154) (159) (139)

Table 12

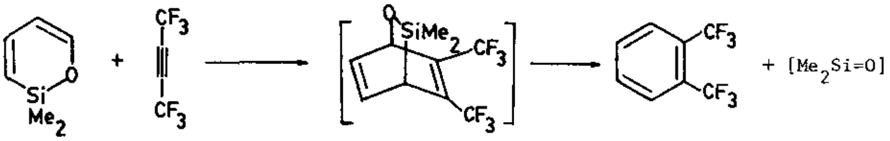
Silanorbornadiene	R	Condition	Yield	Reference
(159a)	Ph	300°C, 3hr	79%	50
(159a)	Ph	300°C, 3hr with PhC≡CPh	100%	50,51
(159a)	Ph	$LiAlH_4-Et_2O-THF$ reflux, 1hr	100%	50
(159b)	Me	300°C, 3hr	88%	49
(159b)	Me	300°C, 3hr with PhC≡CPh	72%	49,51

Pyrolysis of the fluorinated compound (160) under various conditions yielded cleanly *o-bis*(trifluoromethyl)benzene (161) as well as reactive 2-methyl-2-silapropane (162), which dimerised rapidly.[53]



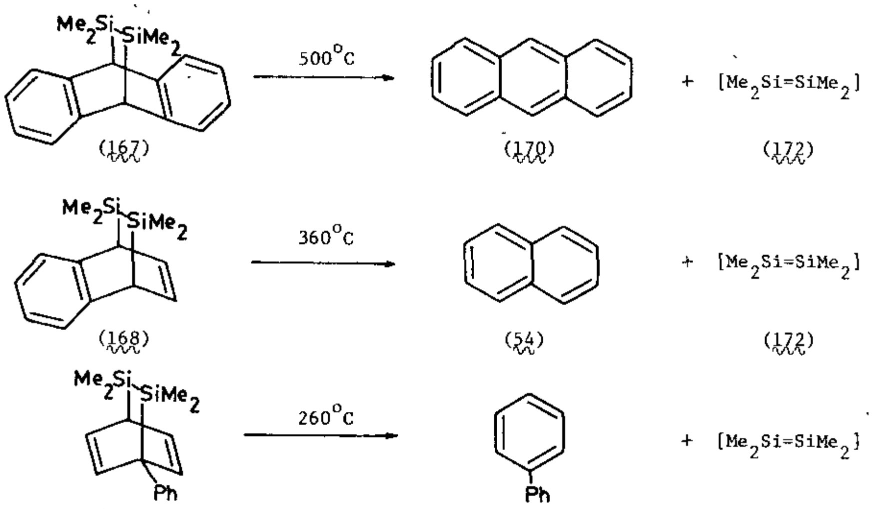
(160) (161) (162)

o-bis(Trifluoromethyl)benzene (161) has also been isolated when 2,2-dimethyl-1-oxa-2-silacyclohexa-3,5-diene (163) was allowed to react with perfluoro-2-butyne (164) at room temperature. The initial Diels-Alder adduct (165) has not been observed, but the extrusion of the unstable silanone bridge (166) was evidenced by trapping experiments.[54]



(163) (164) (165) (161) (166)

The interests in disilene chemistry led to the preparation of the disilene precursors (167), (168) and (169), which were found to decompose thermally to provide quantitative yields of anthracene (170), naphthalene (54) and biphenyl (171) respectively.[55] The extruded tetramethyldisilene (172) was believed to suffer polymerisation.[55]



(167) (170) (172)

(168) (54) (172)

(169) (171) (172)

Diels-Alder reaction of the germole (174) with the benzyne (173) yielded the crystalline 7-germanorbornadiene (175), which debridged to give the naphthalene (176) in moderate yields (Table 13). The extruded dialkylgermylene (177) could be trapped by diphenylacetylene or 2,3-dimethylbuta-1,3-diene. The transformation was proposed to go through radical mechanism.[56]

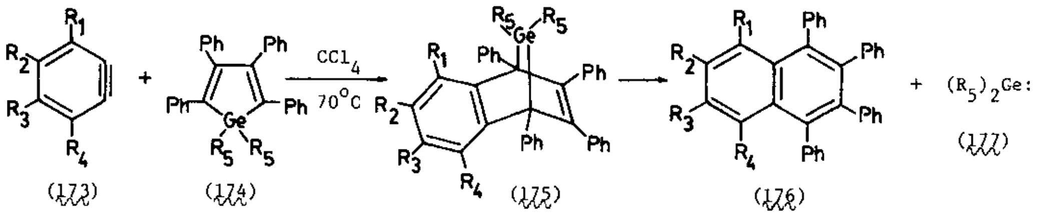
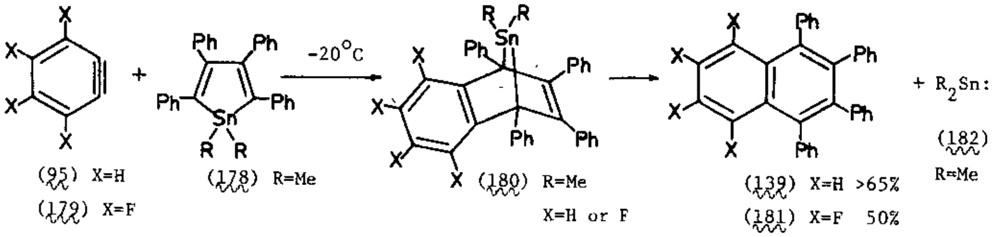


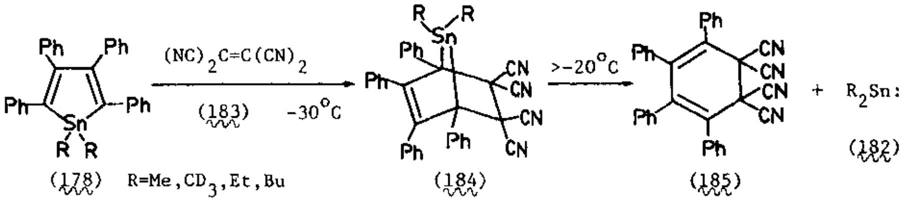
Table 13

Germanorbornadiene	R_1	R_2	R_3	R_4	R_5	Yield
(175a)	H	H	H	H	Me	65%
(175b)	H	Me	H	H	Me	65%
(175c)	H	Me	Me	H	Me	65%
(175d)	H	H	H	Me	Me	70%
(175e)	Me	H	Me	Me	Me	80%
(175f)	Me	Me	Me	Me	Me	80%
(175g)	Me	H	Me	Me	Ph	70%

The stannole (178) reacted with benzyne (95) and tetrafluorobenzyne (179) to generate the intermediate (180) at -20°C. Eventually, the intermediate (180) would eliminate the dimethylstannylene (182) and resulted in the isolation of (139) and (181) respectively.[57]

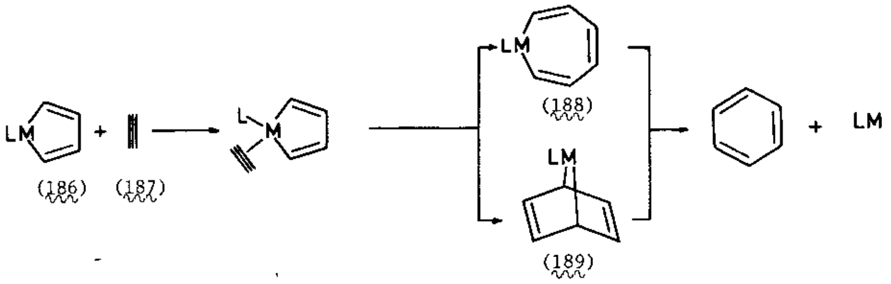


Similarly, the stannole (178) reacted also with tetracyanoethylene (183) at -30°C to give the Diels-Alder adduct (184). At above -20°C, (184) decomposed to afford 5,5,6,6-tetracyano-1,2,3,4-tetraphenyl-1,3-cyclohexadiene (185) and the dialkylstannylene (182).[57,58] The mechanism of this reaction was supposed to involve radical intermediates. The generated stannylenes could be trapped by various reagents.[57,58]

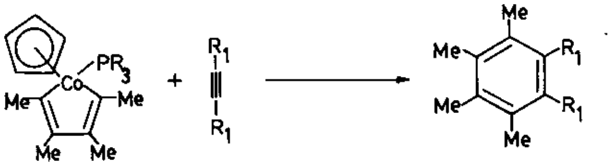


Extrusion of Cobalt, Iridium or Rhodium Bridge

Metalole (186) usually reacted with alkynes (187) to produce arenes. Two different mechanisms have been suggested for this reaction type, i.e. (A) insertion of the alkyne to give a metalocycloheptatriene (188), (B) generation of the intermediate bicyclic compound (189) through Diels-Alder cycloaddition.



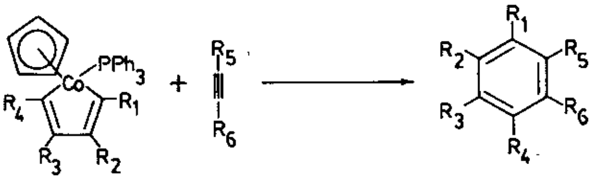
Triethylphosphinecyclopentadienylcobalt-2,3,4,5-tetramethylcyclopentadiene (190a) reacted with 2-butyne (187) in benzene at 120°C to yield hexamethylbenzene (191).[59] Comparatively, the trimethyl analogue (190b) reacted with (49) stoichiometrically at room temperature to lead to dimethyl tetramethylphthalate (114).[59]



(190a) R=Et (187) R_1=Me (191) R_1=Me

(190b) R=Me (49) R_2=CO_2Me (114) R_1=CO_2Me

Other cobaltacyclopentadiene complex (192) also added smoothly to acetylene derivatives (193) in refluxing benzene. The yields of the substituted benzenes (194) obtained are listed in Table 14.[60]



(192) (193) (194)

Table 14

R_1	R_2	R_3	R_4	R_5	R_6	Yield
Ph	Ph	Ph	Ph	CO_2Me	CO_2Me	17%
Ph	Ph	Ph	Ph	H	CO_2Me	22%
Ph	Me	Me	Ph	CO_2Me	CO_2Me	13%
Ph	Me	Me	Ph	H	CO_2Me	26%
Ph	Me	Me	Ph	Ph	CO_2Me	59%
CO_2Me	Me	CO_2Me	Me	Ph	Ph	16%
Ph	CO_2Me	Me	CO_2Me	Ph	Ph	36%

By using olefins (195) instead of alkynes (193), cobaltacyclopentadienes (192) were also able to produce cyclohexadienes (196).[60,61] The reaction took place by two different routes, depending on the reaction conditions, Method A: direct production of (196) when (192) and (195) were heated at 150°C in toluene; Method B: at 110°C in benzene, (192) and (195) reacted to form cobalt complex (197) or (198), which yielded also (196) when exposed to Ce^{4+} in benzene-ethanol at room temperature.[60,61] The yields of (196) are given in Table 15.[60,61]

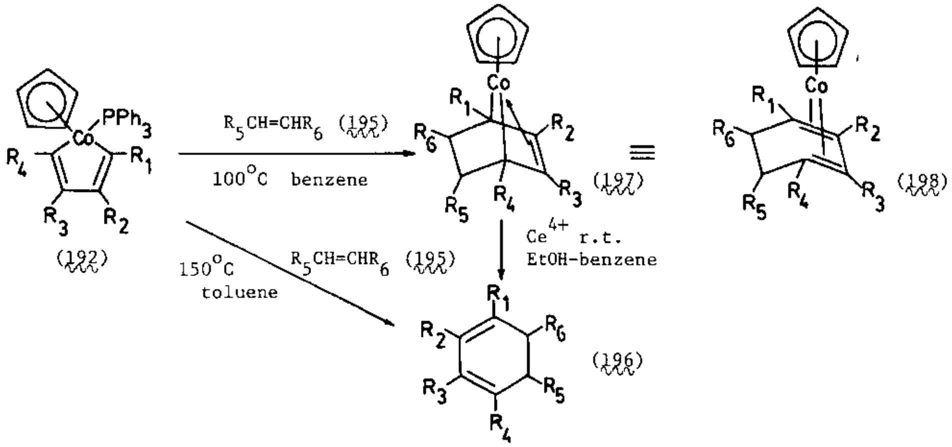
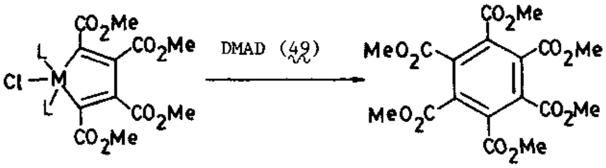


Table 15

R_1	R_2	R_3	R_4	R_5	R_6	Method	Yield
Ph	Ph	H	*p*-MePh	H	H	A	93%
Ph	Ph	CO_2Me	Ph	H	H	A	33%
Ph	Ph	H	CO_2Me	CO_2Me	CO_2Me	B	36%
Ph	CO_2Me	CO_2Me	Ph	H	H ,	B	33%

Metalocyclopentadienes of iridium and rhodium also reacted with acetylene derivatives to form substituted benzenes. Iridocycle (199a) and dimethyl acetylenedicarboxylate (49) underwent cycloaddition in refluxing toluene to furnish hexacarbomethoxybenzene (200)[62,63] in fair yield, whereas rhodocycle (199b) behaved similarly but required lower temperature to afford (200).[62,63]



(**199a**) M=Ir L=PPh_3
(**199b**) M=Rh L=$AsPh_3$

(**200**)

Conclusion

Due to the sporadicalness and enormity of results in this particular research area, a thorough literature review is by no means possible. We have tried only to present an introductory view of the extrusion reactions, which are mainly applicable to the syntheses of arenes. The practicality of constructing arenes from 7-heteroatom-bicyclo[2.2.1]heptene systems depends very much on the accessibility to the heterocyclopentadienes as well as their relative reactivities. The most ironical fact is that the furans are readily available and behave as typical 1,3-dienes, but the oxygen atom of the 7-oxabicyclo[2.2.1]hepta-2,5-dienes are difficult to extrude. On the other hand, most of the metalobicyclo[2.2.1]heptenes would spontaneously loss the metal bridges, but metaloles are synthetically difficult to realise and sometimes even require special precautions in their handling.

In view of the high regioselectivity of Diels-Alder reaction, this Diels-Alder cycloaddition-extrusion approach seems to provide the advantage of controlling the positions of the substituents on the benzene ring. We would like to point out here that more efforts ought to be carried out before the usefulness of this extrusion methodology in synthesising arenes could be fully understood. Nevertheless, this strategy is an extremely attractive and promising way towards the syntheses of many intriguing benzenoidal natural as well as unnatural compounds.

REFERENCES AND NOTES

1. Also known as Nai Zheng Huang, to whom correspondence should be addressed.
2. B.P.Stark and A.J.Duke, 'Extrusion Reactions', Pergamon Press, Elmsford, N.Y., 1967.
3. N.P.Shusherina, Russ.Chem.Rev., 1974, 851
4. C.F.H.Allen, Chem.Rev., 1945, **37**, 209; C.F.H.Allen, Chem.Rev., 1962, **62**, 653; W.M.Schubert and R.R.Kintner, 'The Chemistry of the Carbonyl Group', eds. by S.Patai, Interscience, London, 1966, pp. 743-747; R.Huisgen, R.Grushey and J.Sauer, 'The Chemistry of Alkenes', eds. by S.Patai, Interscience, London, 1964, pp.889-891.
5. Y.Arai, T.Kamikawa and T.Kubota, Tetrahedron Lett., 1972, 1615; G.M.Rubottom and D.S.Krueger, Tetrahedron Lett., 1977, 611; P.A.Harland and P.Hodge, Synthesis, 1982, 223.
6. E.Wolthuis, B.Bossenbroek, G.DeWall, E.Geels and A.Leegwater, J.Org.Chem., 1963, **28**, 148; L.Contreras and D.B.MacLean, Can.J.Chem., 1980, **58**, 2573, 2580.

7. R.Weiss and A.Beller, *Monatsh.Chem.*, 1932, **61**, 143; W.Tochtermann, K.Oppenländer and U.Walter, *Chem.Ber.*, 1964, **97**, 1329; J.De Wit and H.Wynberg, *Recl.Trav.Chim.Pays-Bas*, 1973, **92**, 281; H.N. C.Wong and F.Sondheimer, *Tetrahedron*, 1981, **37**(S1), 99; N.Z.Huang, *Chem.Ind.(London)*, 1981, 364; C.Schmitz, J.M.Aubry and J.Ridaudy, *Tetrahedron*, 1982, **38**, 1425; L.A.Levy and Sashi Kumar,V.P., *Tetrahedron Lett.*, 1983, **24**, 1221.
8. G.Wittig and R.Pohlke, *Chem.Ber.*, 1961, **94**, 3276; G.Wittig, E.Knauss and K.Niethammer, *Justus Liebigs Ann.Chem.*, 1960, **630**, 10.
9. G.Wittig and U.Mayer, *Chem.Ber.*, 1963, **96**, 329.
10. F.M.Beringer and S.J.Huang, *J.Org.Chem.*, 1964, **29**, 445.
11. G.S.Reddy and M.V.Bhatt, *Tetrahedron Lett.*, 1980, **21**, 3627.
12. T.Kaufmann, *Angew.Chem.*, 1965, **77**, 557; *Angew.Chem.Int.Ed.Engl.*, 1965, **4**, 543.
13. D.E.Applequist, P.A.Gebauer, D.E.Gwynn and L.H.O'Connor, *J.Am.Chem.Soc.*, 1972, **94**, 4272.
14. Y.D.Xing, Q.Q.Gong and N.Z.Huang, *Acta Chim.Sinica*, in press.
15. P.L.Pauson and I.U.Khand, *Annals of the New York Academy of Sciences*, 1977, **295**, 2
16. J.I.G.Cadogan and R.Leardini, *J.Chem.Soc.,Chem.Commun.*, 1979, 783,
17. K.Narasimhan and P.Raja Kumar, *J.Org.Chem.*, 1983, **48**, 1122.
18. C.D.Weis, *J.Org.Chem.*, 1962, **27**, 3520.
19. L.A.Paquette, R.E.Moerck, B.Hirirchian and P.D.Magnus, *J.Am.Chem.Soc.*, 1978, **100**, 1597.
20. P.Brownbridge and T.-H.Chan, *Tetrahedron Lett.*, 1980, **21**, 3423.
21. L.Lombardo, D.Wege and S.P.Wilkinson, *Aust.J.Chem.*, 1974, **27**, 143.
22. P.Vioget, P.Vogel and R.Raulet, *Angew.Chem.*, 1982, **94**, 454; *Angew.Chem.Int.Ed.Engl.*, 1982, **21**, 430.
23. S.B.Polovsky and R.W.Franck, *J.Org.Chem.*, 1974, **39**, 3010.
24. G.W.Gribble, W.J.Kelly and M.P.Sibi, *Synthesis*, 1982, 143.
25. H.Hart and G.Nwokogu, *J.Org.Chem.*, 1981, **46**, 1251.
26. Y.D.Xing and N.Z.Huang, *J.Org.Chem.*, 1982, **47**, 140.
27. Q.Q.Gong, N.Z.Huang and Y.D.Xing, to be published.
28. X.L.Hou, M.Sc.Thesis, Shanghai Institute of Organic Chemistry, Academia Sinica, 1983.
29. R.G.Shuttleworth, W.S.Rapson and E.-T.Stewart, *J.Chem.Soc.*, 1944, 71.
30. N.Z.Huang, Y.D.Xing and D.Y.Ye, *Synthesis*, 1982, 1041.
31. R.Helder and H.Wynberg, *Tetrahedron Lett.*, 1972, 605.
32. D.D.Callander, P.L.Coe and J.C.Tatlow, *J.Chem.Soc.,Chem.Commun.*, 1966, 143.
33. H.J.Kuhn and K.Gollnick, *Chem.Ber.*, 1973, **106**, 674.
34. W.J.Bailey and E.W.Cummins, *J.Am.Chem.Soc.*, 1954, **76**, 1940.
35. M.G.Barlow, R.N.Hazeldine and R.Hubbard, *J.Chem.Soc.,Chem.Commun.*, 1969, 301.
36. G.Wittig and B.Reichel, *Chem.Ber.*, 1963, **96**, 2851.
37. A.G.Schultz and M.Shen, *Tetrahedron Lett.*, 1979, 2969.
38. H.Hart, C.-y.Lai, G.Nwokogu, S.Shamouilian, A.Teuerstein and C.Zlotogorski, *J.Am.Chem.Soc.*, 1980, **102**, 6649.
39. H.Hart and S.Shamouilian, *J.Org.Chem.*, 1981, **46**, 4874.
40. I.G.M.Campbell, R.C.Cookson, M.B.Hocking and A.N.Hughes, *J.Chem.Soc.*, 1965, 2184.
41. E.H.Braye, W.Hübel and I.Caplier, *J.Am.Chem.Soc.*, 1961, **83**, 4406.
42. U.Schmidt, I.Boie, C.Osterroht, R.Schröer and H.-F.Grützmacher, *Chem.Ber.*, 1968, **101**, 1381.
43. F.B.Clarke III and F.H.Westheimer, *J.Am.Chem.Soc.*, 1971, **93**, 4541.
44. J.K.Stille, J.L.Eichelberger, J.Higgins and M.E.Freeburger, *J.Am.Chem.Soc.*, 1972, **94**, 4761.

45. T.-H.Chan and K.T.Nwe, Tetrahedron Lett., 1973, 4815.
46. L.D.Quin and K.A.Mesch, J.Chem.Soc.,Chem.Commun., 1980, 959.
47. A.Marinetti, F.Mathey, J.Fischer and A.Mitschler, J.Chem.Soc.,Chem.Commun., 1982, 667.
48. A.Marinetti, F.Mathey, J.Fischer and A.Mitschler, J.Am.Chem.Soc., 1982, 104, 4484; A.Marinetti and F.Mathey, Organometallics, 1982, 1, 1488.
49. H.Gilman, S.G.Cottis and W.H.Atwell, J.Am.Chem.Soc., 1964, 86, 1596.
50. H.Gilman, S.G.Cottis and W.H.Atwell, J.Am.Chem.Soc., 1964, 86, 5584.
51. W.H.Atwell and D.R.Weyenberg, J.Am.Chem.Soc., 1968, 90, 3438.
52. *Inter alia* see P.P.Gaspar, 'Silylenes' in 'Reactive Intermediates', eds. by M.Jones and R.A. Moss, Wiley, New York, 1978.
53. T.J.Barton and E.Kline, J.Organomet.Chem., 1972, 42, C21.
54. G.Hussmann, W.D.Wulff and T.J.Barton, J.Am.Chem.Soc., 1983, 105, 1263; T.J.Barton and W.D. Wulff, J.Am.Chem.Soc., 1979, 101, 2735.
55. D.N.Roark and G.J.D.Peddle, J.Am.Chem.Soc., 1972, 94, 5837.
56. W.P.Neumann and M.Schriewer, Tetrahedron Lett., 1980, 21, 3273.
57. C.Grugel, W.P.Neumann and M.Schriewer, Angew.Chem., 1979, 91, 578; Angew.Chem.Int.Ed.Engl., 1979, 18, 543.
58. L.-W.Gross, R.Moser, W.P.Neumann and K.-H.Scherping, Tetrahedron Lett., 1982, 23, 635.
59. D.R.McAlister, J.E.Bercaw and R.G.Bergman, J.Am.Chem.Soc., 1977, 99, 1666.
60. Y.Wakatsuki, T.Kuramitsu and H.Yamazaki, Tetrahedron Lett., 1974, 4549.
61. Y.Wakatsuki and H.Yamazaki, J.Organomet.Chem., 1977, 139, 169.
62. J.P.Collman, J.W.Kang, W.F.Little and M.F.Sullivan, Inorg.Chem., 1968, 7, 1298.
63. J.P.Collman, Acc.Chem.Res., 1968, 1, 136.

Received, 13th June, 1983