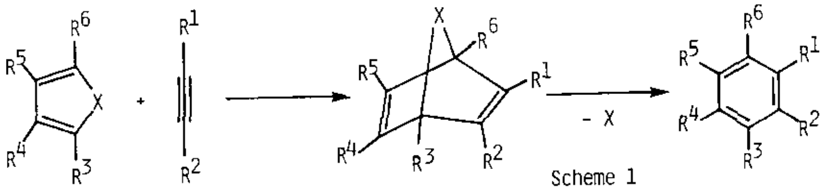
HETEROCYCLES, Vol. 24, No. 5, 1986

PREPARATION OF NAPHTHALENE DERIVATIVES BY REACTION OF BENZYNES WITH THIOPHENE-1,1-DIOXIDES

Juzo Nakayama,* Masami Kuroda,[1] and Masamatsu Hoshino
Department of Chemistry, Faculty of Science, Saitama University,
Urawa, Saitama 338, Japan

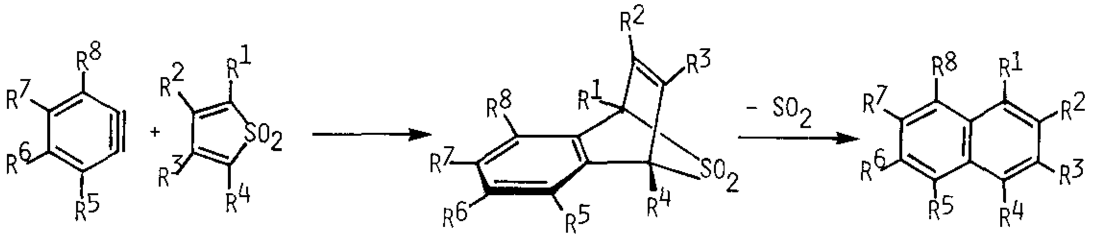
Abstract —— The reaction of benzynes with thiophene 1,1-dioxides affords the Diels-Alder cycloadducts which spontaneously lose sulfur dioxide to give the corresponding naphthalene derivatives in moderate yields. Further reaction of benzyne with naphthalenes yielding dibenzobarrelenes is observed in a few cases.

The Diels-Alder reaction of carbo- and heterocyclic dienes with acetylenic dienophiles and the removal of a bridging group X from the resulting adducts provide a convenient method for preparation of aromatic hydrocarbons (Scheme 1).



Scheme 1

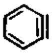
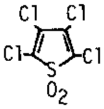
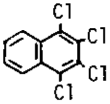
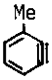
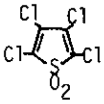
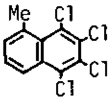
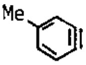
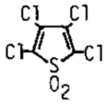
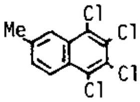
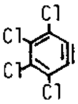
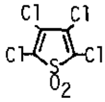
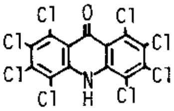
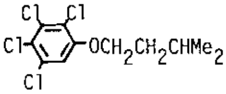
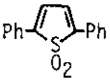
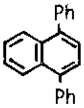
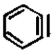
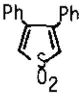
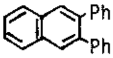
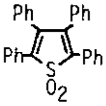
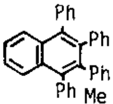
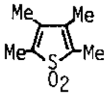
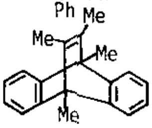
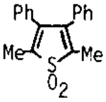
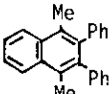
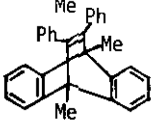
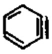
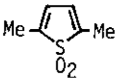
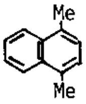
Benzyne is an excellent dienophile and was often employed in this synthesis. Furans[2] and pyrroles[3] act as a diene on benzyne and afford the cycloadducts in good yields. However, further elaboration is required for construction of an aromatic nucleus by the removal of the bridging group X from these adducts.[2,3] Tetraphenylcyclopentadienone is the most frequently used excellent benzyne acceptor and the resulting adduct spontaneously loses carbon monoxide to give 1,2,3,4-tetraphenylnaphthalene.[4] Cyclopentadienone and its derivatives are apt to dimerize, however, and therefore available cyclopentadienone monomers are limited.[5] Thiophene-1,1-dioxides are more stable than the corresponding cyclopentadienones. They are known to behave as a reactive diene and some adducts resulting from the reaction with acetylenic dienophiles lose sulfur dioxide under the applied conditions to give the corresponding aromatic hydrocarbons.[6] Herein we report the first naphthalene synthesis by reaction of benzynes with thiophene 1,1-dioxides (Scheme 2).[7]



Scheme 2

Thiophene 1,1-dioxides were prepared in moderate yields by oxidizing the corresponding thiophenes with m-chloroperoxybenzoic acid.[8,9] Benzyne was generated by thermal decomposition of 2-carboxybenzenediazonium chloride in the presence of propylene oxide.[10] 3-Methyl-, 4-methyl-, and 3,4,5,6-tetrachlorobenzynes were generated by aprotic diazotization of 3-methyl-, 5-methyl-, and 3,4,5,6-tetrachloroanthranilic acids, respectively.[11] The reaction was thus carried out either by refluxing a mixture of a thiophene 1,1-dioxide, 2-carboxybenzenediazonium chloride, and propylene oxide in 1,2-dichloroethane or by slow addition of a solution of a substituted anthranilic acid in dioxane to a refluxing solution of isoamyl nitrite and a thiophene 1,1-dioxide in 1,2-dichloroethane. Results are summarized in Table 1. All of the thiophene 1,1-dioxides examined are less reactive toward benzynes and hence 3 equivalents of benzyne precursors were employed. The yields of naphthalenes are low to moderate, though conversion yields are generally good. Tetrachlorothiophene 1,1-dioxide does not react with tetrachlorobenzyne, the former being recovered quantitatively (entry 4). This is probably due to the electron-deficient (electrophilic) nature of the both reactants. Perchloroacridone[12] and isoamyl tetrachlorophenyl ether[13] are produced by reactions of tetrachlorobenzyne with tetrachloroanthranilic acid and isoamyl alcohol, respectively. No expected 1,2,3,4-tetramethylnaphthalene was obtained (entry 8), but tetramethyldibenzobarrelene was formed instead. The barrelene is the product of the reaction of benzyne with tetramethylnaphthalene. Hart et al. actually reported the preparation of this barrelene by the above reaction.[14] These results show that tetramethylnaphthalene is more reactive than tetramethylthiophene 1,1-dioxide toward benzyne. The same reaction was also observed (entry 9). These two examples open a new route for the preparation of dibenzobarrelenes.

Table 1. Reaction of Benzynes with Thiophene 1,1-Dioxides

Entry	Benzynes[a]	Thiophene 1,1-dioxides	Products	Yields (Conv. yields) %	mp (°C)
1				72 (94)	196-199
2				65 (96)	201-202[c]
3				40 (97)	125.5-127[c]
4				23	363-367
				51	46-47
5	 [b]			9 (18)	135-136
6				23 (36)	88-88.5
7				64 (95)	202-204
8				23 (78)	176.5-179
9				25 (45)	146-148
				29 (51)	160-162[c]
10				19 (46)	oil[d]

a) Unless otherwise stated, 3 equivalents of benzyne precursors were employed. b) 4 Equivalents of 2-carboxybenzenediazonium chloride were used. c) These are new compounds and exhibit spectral characteristics consistent with assigned structures. d) Although dimethyldibenzobarrelene (ca. 4%) was formed, it could not be isolated in a pure crystalline form.

REFERENCES

1. Research paticipant from Fuji Electric Corporate Research and Development, Ltd.
2. G. Wittig and L. Pohmer, *Chem. Ber.*, 1956, **89**, 1334; J. E. Anderson, R. W. Franck, and M. L. Mandella, *J. Am. Chem. Soc.*, 1972, **94**, 4608; J. Nakayama, A. Sakai, and M. Hoshino, *J. Org. Chem.*, 1984, **49**, 5084.
3. G. W. Griblle, R. W. Allen, P. S. Anderson, M. E. Christy, and C. D. Colton, *Tetrahedron Lett.*, 1976, 3673; H. Hart and A. Teuerstein, *Synthesis*, 1979, 693.
4. R. W. Hoffmann, 'Dehydrobenzene and Cycloalkynes,' Academic Press, New York, 1967, Chapter 3.
5. 5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene serves as a 2,3,4,5-tetrachlorocyclopentadienone equivalent; J. W. Wilt and E. Vasiliauskas, *J. Org. Chem.*, 1970, **35**, 2410. Incidentally α-pyrone reacts with benzyne to give naphthalene in 36% yield with loss of carbon dioxide; G. Wittig and R. W. Hoffmann, *Chem. Ber.*, 1962, **95**, 2718.
6. M. S. Raasch, *J. Org. Chem.*, 1980, **45**, 856 and references cited therein; S. Rajappa in 'Comprehensive Heterocyclic Chemistry,' C. W. Bird and G. W. H. Cheeseman, Eds., Pergamon Press, London, Vol. 4, 1984, p. 841.
7. Benzynes react with thiophenes to give either naphthalenes by Diels-Alder reaction with loss of sulfur or benzo[b]thiophenes by 1,3-cycloaddition with loss of acetylenes: D. D. Callander, P. L. Coe, and J. C. Tatlow, *Chem. Commun.*, 1966, 143; P. L. Coe, G. M. Pearl, and J. C. Tatlow, *J. Chem. Soc.* (*C*), 1971, 604; D. Del Mazza and M. G. Reinecke, *Heterocycles*, 1980, **14**, 647; D. Del Mazza and M. G. Reinecke, *J. Chem. Soc., Chem. Commun.*, 1981, 124.
8. J. L. Melles and H. J. Backer, *Recl. Trav. Chim. Pays-Bas*, 1953, **72**, 314.
9. 2,3,4,5-Tetramethylthiophene 1,1-dioxide, mp 116-117.5 °C, ^{1}H-NMR (CDCl$_3$) δ 1.93 (6H, s, 2Me) and 2.00 (6H, s, 2Me) and 2,5-dimethyl-3,4-diphenylthiophene 1,1-dioxide, mp 213-215 °C, ^{1}H-NMR (CDCl$_3$) δ 2.13 (6H, s, 2Me) and 6.8-7.4 (10H, m, 2Ph) are new sulfones.
10. B. H. Klanderman and T. R. Criswell, *J. Org. Chem.*, 1969, **34**, 3426.
11. L. Friedman and F. M. Logullo, *J. Org. Chem.*, 1969, **34**, 3089.
12. R. Howe, *J. Chem. Soc.* (*C*), 1966, 478; H. Heaney and J. M. Jablonski, *ibid.*, 1968, 1895.
13. H. Heaney, J. M. Jablonski, and C. T. McCarty, *J. Chem. Soc., Perkin I*, 1972, 2903.
14. H. Hart, J. B.-C. Jiang, and M. Sasaoka, *J. Org. Chem.*, 1977, **42**, 3840.

Received, 25th January, 1986