# CYANOKETENES. CYCLOADDITIONS OF TERT-BUTYLCYANO- AND CHLOROCYANOKETENE TO SULFER DIIMIDES

Dorothy M. Goldish*, Barry W. Axon, and Harold W. Moore**

* Department of Chemistry, California State University, Long Beach, California

**Department of Chemistry, University of California, Irvine, California 92717

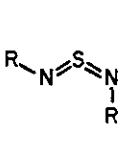
Abstract - A number of unusual transformations were observed when di-t-butyl and diphenylsulfur diimide were treated with t-butylcyano- and chlorocyanoketene. These include the formation of reactive thione-S-imines, which subsequently lead to 3-isothiazolidinones and benzisothiazoles. Other products include a cyclic thioimidate and a β-lactam.

Reported here is an investigation of the cycloadditions of tert-butylcyanoketene (TBCK) and chlorocyanoketene (CCK) to diphenyl- (1a) and di-tert-butylsulfur diimide (1b). The results of this study are of interest with respect to the unusual chemistry of the electron-deficient cyanoketenes[1] since the observed products generally differ from those reported for other ketene/sulfur diimide cycloadditions.[2]

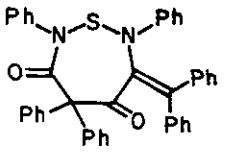
For the purpose of comparison, a brief summation of the previously reported cycloadditions of ketenes to sulfur diimides is outlined below. Diphenylsulfur diimide and diphenylketene cycloadd at low temperature (6-8°C) to yield a 1:2 adduct 2, and at higher temperature (80°C) a 1:1 adduct 3a.[2a] Additionally, the former is converted to the latter in refluxing benzene. On the other hand, di-tert-butylsulfur diimide gives 4 when treated with diphenylketene at 0°C, and this adduct ring expands to 3b in refluxing hexane. Both sulfur diimides 1a and 1b react with phenylketene below -50°C to give 5a,b and 6a,b as the major products.[2b] However, when phenylchloroketene is employed, its reaction with 1a results in 7. When alkylketenes are utilized, e.g., pentamethyleneketene, both sulfur diimides give acylic adducts, 8a and 8b, respectively, rather than cycloaddition products. Although detailed mechanistic studies are lacking, it is generally assumed that these transformations proceed from an initially formed zwitterionic intermediate 9.

TBCK and CCK react with the sulfur diimides 1a and 1b to give unanticipated products based upon the above analogies. The results are outlined below.

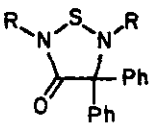
tert-Butylcyanoketene[3] was generated from 2,5-diazido-3,6-di-t-butyl-1,4-benzoquinone in refluxing benzene in the presence of 0.5 equivalent of di-tert-butylsulfur diimide, (1b). The reaction was followed by ir spectroscopy which showed the gradual disappearance of the azide absorption (2150 $cm^{-1}$) and the appearance of a new strong absorption at 2300 $cm^{-1}$, due to the formation of tert-butylisocyanate. After 1.5 h the solvent was removed and the reaction mixture subjected to flash-chromatography (silica gel) to yield 48% of 2,4,5-tri-t-butyl-4,5-dicyano-3-isothiazolidinone (12):



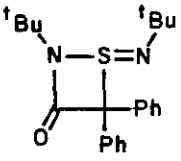
1



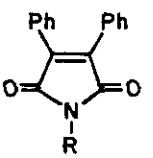
2



3

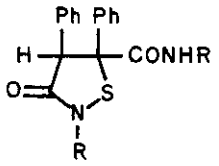


4

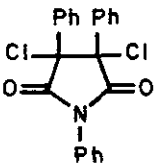


5

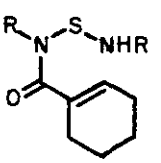
a) R = Ph
b) R = $^{t}$Bu



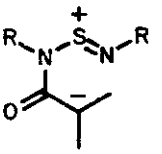
6



7

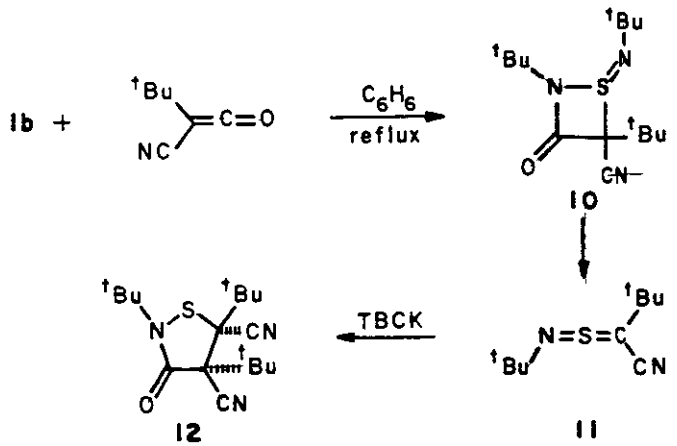


8



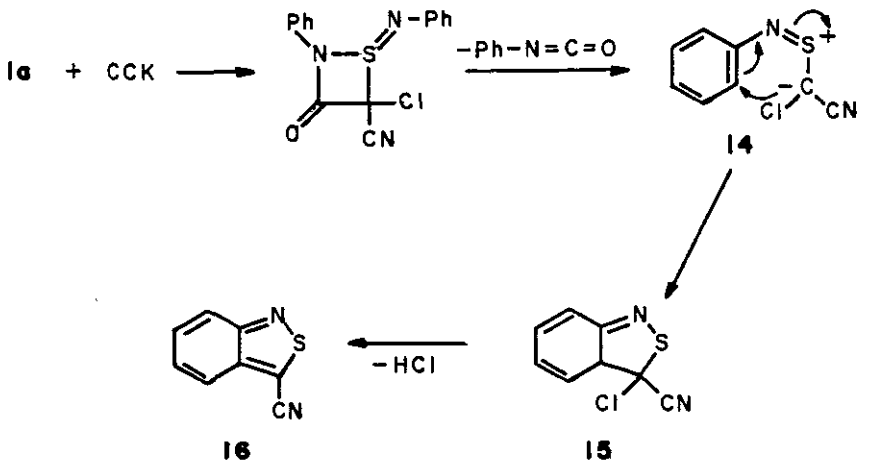
9

mp 101-102°C; ir (nujol, $cm^{-1}$) 1696; $^{1}$H nmr ($CDCl_3$,δ) 1.43 s (9H), 1.49 s (9H); 1.52 s (9H); $^{13}$C nmr ($CDCl_3$,δ) 162.8, 125.3, 118.0, 85.3, 83.9, 52.4, 51.4, 49.3, 34.7, 29.8, 28.5; mass spec (CI) 322 (92%), 266 (100%), 239 (44%), 183 (53%); anal $C_{17}H_{27}N_3OS$: C, 63.36; H, 8.87; N, 13.27; S, 10.11. These data are all in agreement with the assigned structure. Of particular note is the presence of an amide absorption in the ir spectrum (1696 $cm^{-1}$) and the amide carbonyl carbon in the $^{13}$C nmr spectrum (δ, 162.8).



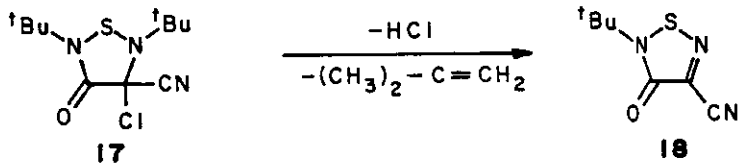

This transformation is viewed as proceeding via an initial 2 + 2 cycloaddition to give 10 which subsequently cleaves to t-butyl isocyanate and the thione-S-imide 11. This unusual heterocumulene, 11, is then trapped by an additional TBCK molecule to give the observed product 12. The stereochemistry of 12 is not yet known, but is assumed to be the E-isomer on the basis of steric considerations.

An analogous thione-S-imide, 14, is apparently formed when CCK[4] was generated in the presence of diphenylsulfur diimide (1a). However, in this case the thione-S-imide undergoes intramolecular cyclization before it reacts with an additional ketene molecule. Specifically, 14 ring closes to 15 and undergoes subsequent loss of HCl to give the observed product, 3-cyano-2,1-benzisothiazole (16) in 67% yield: mp, 99-100°C(lit.[5] mp 98-101°C); ir (nujol, $cm^{-1}$) 2208; $^1H$ nmr ($CDCl_3$,δ) 161.2, 137.7, 129.9, 128.1, 122.7, 120.3, 110.9; mass spec (CI) 160 (100%). Diphenylurea, a product from the hydrolysis of phenyl isocyanate, was also isolated from the above reaction, providing additional evidence for the proposed fragmentation of 10 and 13 to 11 and 14, respectively.

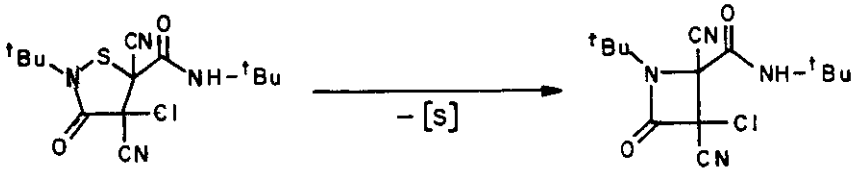



Treatment of diphenylsulfur diimide with TBCK gave a complex mixture of products which were not resolved. However, the reaction of di-t-butylsulfur diimide with CCK resulted in a most interesting transformation. The ketene (1 eq) was generated in refluxing benzene in the presence of 1b (2 eq). Here the major product (51%) is 18 and the minor product is tentatively assigned the β-lactam structure 20: 18, mp 131-132°C; ir(nujol, $cm^{-1}$) 1675; $^{1}H$ NMR ($CDCl_3$,δ) 1.69 s; $^{13}C$ nmr 160.6, 130.1, 111.6, 61.8, 27.6; mass spec (CI) 184 (100%); anal $C_7H_9N_3OS$: C, 45.92; H, 5.12; 20, mp, 132-133°C; ir(nujol, $cm^{-1}$) 3380, 1810, 1716, $^{1}H$ nmr ($CDCl_3$,δ) 1.45 s (9H); 1.52 s (9H); 8.62 b (1H) exchangable; $^{13}C$ nmr ($CDCl_3$,δ) 157.3, 153.2, 114.1, 110.9, 63.4, 62.8, 58.9, 54.3, 28.3, 27.4; mass spec (CI) 311 (100%); anal $C_{14}H_{19}ClN_4O_2$: C 53.89; H, 6.34. Although the structural assignment of 20 is tentative, the above data are in accord with its constitution. Most revealing are the carbonyl absorptions in the ir and the $^{13}C$ nmr spectrum which shows the correct carbon atom count, including two amide carbonyls (δ, 157.3, 153.2) and two cyano groups (δ, 114.1, 110.9).

Compound 18 is viewed as arising from an initial cycloaddition of CCK to 1b to give 17 followed by loss of isobutylene and HCl. The more unusual product, 20, may arise from the intermediate 19, the formation of which has a precedent in the cycloadditions of phenylchloroketene to sulfur diimides.[2a] Desulfurization of 19 under the reaction conditions would appear to be unique, but this would result in the β-lactam 20.

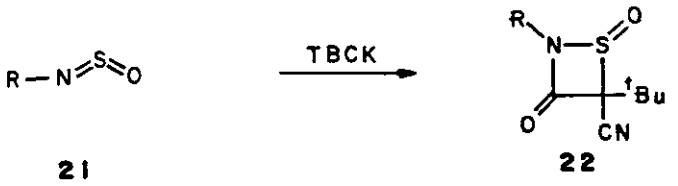



17 18



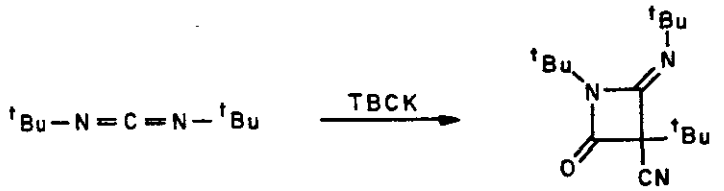

19 20

The cycloadditions of TBCK to N-t-butyl- and N-phenylsulfinylamines as well as di-t-butylcarbodiimide were also studied to see if the initial 2 + 2 adducts would undergo a cleavage reaction analogous to that proposed for 10 and 13. However, TBCK was observed to cycloadd to the sulfinylamines, 21a and 21b, to give, respectively, 22a (86%) and 22b (90%), and these products were found to be resistant to cleavage in refluxing benzene. Characteristic spectral properties follow: 22a, mp 96-97°C; ir(nujol, $cm^{-1}$) 1756; $^1H$ nmr ($CDCl_3$,δ) 1.35 s (9H); 1.52 s (9H); $^{13}C$ nmr (CDCl,δ), 157.1, 111.1, 88.5, 59.1, 36.5, 28.2, 26.5; mass spec (CI) 243 (100%), anal. $C_{11}H_{18}N_2O_2S$: C, 54.75; H, 7.86: 22b, mp 100-101°C; ir(nujol, $cm^{-1}$) 1785; $^1H$ nmr ($CDCl_3$,δ) 7.42 m (5H); 1.36 s (9H); $^{13}C$ nmr ($CDCl_3$,δ) 155.6, 134.5, 129.9, 128.5, 120.6, 110.5, 90.6, 37.0, 26.6; mass spec (CI) 263 (100%); anal. $C_{13}H_{14}N_2O_2S$: C, 59.68; H, 5.46. Analogously, TBCK cycloadds to di-t-butylcarbodiimide to give 23 (88%) which was also stable in refluxing benzene: mp 73-74°C; ir (nujol, $cm^{-1}$) 1815, 1710; $^1H$ nmr ($CDCl_3$,δ) 1.27 s (9H), 1.35 s (9H), 1.51 s (9H); $^{13}C$ nmr ($CDCl_3$,δ) 162.9, 135.7, 115.0, 67.2, 57.7, 55.4, 36.3, 31.1, 27.6, 27.0; mass spec (CI) 278 (10%); anal. $C_{16}H_{27}N_3O$: C, 69.52; H, 10.15.




21 22

a) R = $^t$Bu; b) R = Ph




23

ACKNOWLEDGEMENT: The authors wish to thank the National Science Foundation (CHE-8025567) and the Public Health Service (AI-15651) for financial support of this work.

REFERENCES

1. H.W. Moore and M.D. Gheorghiu, Chem. Soc. Rev., 1981, 10, 289
2. a) T. Minami, K. Yamataka, Y. Ohshiro, T. Agawa, N. Yasuoka, and N. Kasai, J. Org. Chem., 1972, 37, 3810; b) T. Minami and T. Agawa, ibid., 1974, 39, 1210; c) H. Grill and G. Kresze, Tetrahedron Lett., 1970, 1427; d) H.H. Horhold and H. Eibisch, Tetrahedron, 1969, 25, 4277.
3. W. Weyler, W.G. Duncan, and H.W. Moore, J. Am. Chem. Soc., 1975, 97, 6187
4. D.M. Kunert, R. Chambers, F. Mercer, L. Hernandez, and H.W. Moore, Tetrahedron Lett., 1978, 929.
5. T. Onaka and T. Oikawa, Itsuu Kenkyusho Nempo, 1971, 16, 53

Received, 23rd August, 1982