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FREE RADICAL ADDITIONS OF BIS(TRIHALOMETHYL) SULFONES TO OLEFINS.[1]

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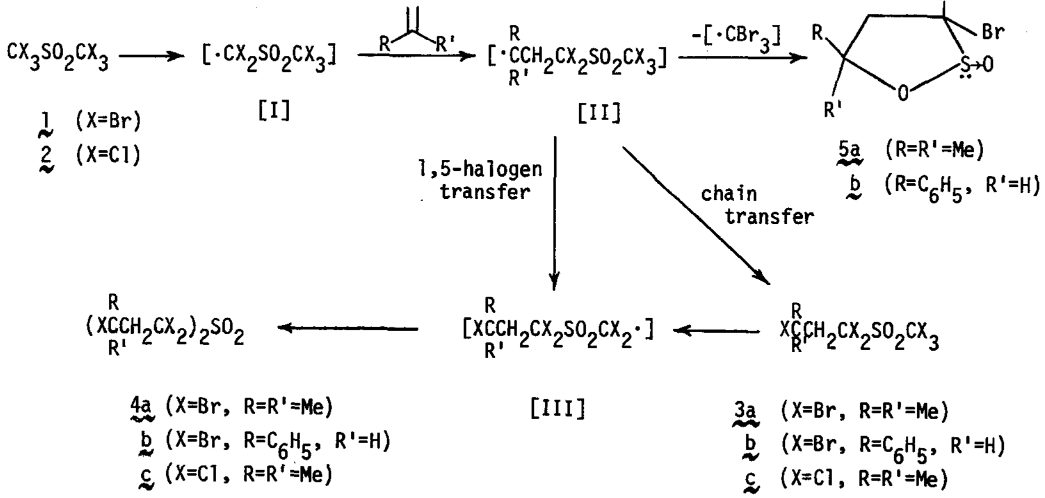
The recent report of the alkylation and subsequent debromination of bis(tribromomethyl) sulfone, 1, with trivalent phosphorus reagents provides an elegant route to dialkyl thiirene dioxides[2] and thus to dialkyl acetylenes.[2-4] The success of this method prompts us to to report an additional method for the alkylation of 1[5] and of its chlorine analog, bis(trichloromethyl) sulfone,[7] 2. We also report further chemistry of 1 and its alkylated derivatives.

The additions of bis(trihalomethyl) sulfones 1 and 2 to terminal olefins results in the formation of mono-, 3, and diadducts, 4. By analogy to the additions of carbon tetrahalides to olefins under similar conditions,[8] the additions of 1 and 2 should proceed through the intermediacy of free radicals I-III.



The reaction of 1 with isobutylene (C_6H_5Cl solution) proceeds in a sealed tube at room temperature initiated by light alone, as do the additions of CBr_4 to olefins.[8b] While the diadduct, 4a appears to be the chief product of this reaction, it did not crystallize even after chromatography.[9] Treatment of crude 4a with triethylamine in acetone led to the reductive removal of bromine atoms alpha to the sulfone.[10] Triethylamine acts as a soft base[11] by accepting a bromonium ion and liberating an α-sulfonyl carbanion which in this case is subsequently protonated. The diastereomeric sulfones 6 and 7 $[(Me_2BrCCH_2CHBr)_2SO_2]$ produced in this reaction were separated by liquid chromatography (2-3% ether)[9] in >50% yield (based on 1) and were fully characterized. The initially eluted isomer, 6, mp 162-63°

(EtOH), is the meso-isomer as evidenced by an (ABX)(A'B'X') pattern of 12 doublets in its ^1H nmr spectrum for the $-CH_2CHBr-$ portions of the molecule. The subsequently eluted isomer, **7**, mp 80-82°, has a simple ($A_2B_2X_2$) pattern of 6 doublets for the corresponding protons and is the racemic isomer.[12]

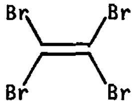
The reaction of **1** with styrene—initiated thermally in heptane (100°/3 hr)—proceeds to give a tarry mixture of products from which small amounts of styrene dibromide, **8**, can be separated by sublimation. The major products include **3b**, **4b**, telomeric materials and the unique 3,3-dibromo-5-phenyl-1,2-oxathiolane-2-oxide, **5b**. However, none of these products was obtained in pure form by chromatography of the crude mixture. After the mixture was treated in a basic medium (see below), transformation products derived from **3b** and **4b** were isolated along with unchanged **5b**. The isolation and characterization of **5b** and the identification of its ir (KBr) S→O stretching band at 1148 cm^{-1} allowed the observation of ir bands for both **5a** and **5b** in certain chromatographic fractions from the reactions of **1** with isobutylene and styrene respectively.[14] Further properties used to characterize **5b** are the following: mp 119-20° (hexane); sublimes (0.01 mm); ^1H nmr (60 MHz, $CDCl_3$) δ 3.25 (d, 2H, J=8 Hz), 7.32 (s, 5H, C_6H_5); ms:[16] m/e (rel. intensity) 278 (16), 276 (32), 274 (16) [$M-SO_2$],[14] 197 (46), 195 (47) [$M-SO_2Br$], 116 (97), 115 (100), 106 (18), 105 (40), 78 (15), 77 (46), 64 (13), 58 (18), 57.5 (34), 51 (30).

The most convenient rationalization for the formation of **5** is the cyclization of radical intermediate II by addition to the O←S bond. The subsequent liberation of the highly stabilized tribromomethyl radical provides the driving force for this unusual cyclization. Optimization of the yield of **5** was not attempted, but decreases in the concentration of both **1** and olefin would be expected to prolong the lifetime of II in solution thereby increasing the probability of its cyclization to **5**.

The comparable additions of **2** to olefins require a free-radical initiator. The sealed tube reaction of **2** with isobutylene (solvent) in the presence of 2-5% of AIBN and light gives mixtures of unreacted **2**, **3c**, mp 59-60°, and **4c**, mp 75.6°, which can be separated by chromatography (1/2% ether).[9] In one run the ratio of **3c** to **4c** was 10:1 with 27% of unreacted **2** recovered. This high ratio of mono- to diadduct suggests that a 1,5-chlorine atom transfer, i.e., II→III, is not, as would be expected,[17] a significant mechanistic pathway. As with CCl_4,[8b] the addition of **2** to styrene produced mostly telomers.

In an attempt to form carbon-carbon bonds through the elimination of bromine[2,18] from α-perbromo sulfones, we investigated the reaction of **1** and its styrene adducts with some soft bases. The treatment of **1** with triethylamine in CH_2Cl_2 gave the immediate precipitation of a salt, $Et_3\overset{+}{N}CBr_2SO_2CBr_3\cdot Br^-$, **9**, mp 170-71°, in 60% yield. Chromatography of the residue and sublimation allowed the isolation of tetrabromoethylene, **10**, in 5% yield, a finding which verifies the possibility of C-C bond formation by this method. The treatment of **1** with excess LiH in DMF[19] (85°, 52 hr) gave **10** in 17% yield.

Treatment of the mixture of styrene adducts of **1** with LiH in DMF (85°, 9 hr) gave a new mixture of products which chromatography showed to contain a trace of **10**, 1,1,2-tribromo-4-phenylbutadiene, **11** (6% based on **1**), trans-cis-trans-3,4-dibromo-1,6-diphenylhexatriene, **12**, (15%) mixed with a little **8** (all eluted with hexane), an orange, bromine-containing hydrocarbon (*ca.* 10%) which was not purified by rechromatography (1% ether), 5b (5%; 2-3% ether), and a gross mixture of sulfones (*ca.* 35%) several of which contained fewer than four α-bromine atoms by ir and nmr criteria (eluted with 4-10% ether).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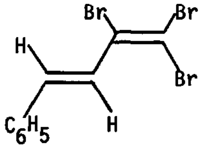
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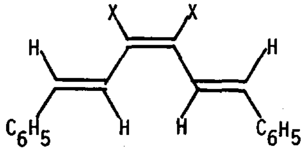
12 (X=Br)
13 (X=H)

Compound 11 is a colorless liquid [ir (film) 950 cm^{-1} (*trans* -CH=CH-), 832; ^1H nmr (CCl_4) δ 7.12 (s, 2H, vinyl), 7.1-7.5 (m, C_6H_5)] which discolored on standing. This substance was further identified by a quartet of parent ions (*m/e* 370, 368, 366, 364) and a doublet base peak (*m/e* 208, 206 [$M-Br_2$]) in its mass spectrum. Compound 12 is a yellow solid with two crystalline forms, mp 165-8° (EtOH) and 175-7° (CCl_4 or cyclohexane). It was identified by the following spectral parameters: ir (KBr) 954 cm^{-1} (trans -CH=CH-); ^1H nmr (CCl_4) δ 7.13, 7.62 (2d, *J*=15 Hz) superimposed on 10-proton phenyl multiplet; ms: *m/e* (rel. intensity) 392 (18), 390 (41), 388 (18) [M^+, triplet], 230 (100), 229 (75), 228 (35), 227 (11), 226 (15), 115 (71), 114.5 (13), 114 (24), 113 (13); uv (cyclohexane) λ_{max} ($\varepsilon \times 10^{-4}$) 270 nm (1.5), 277 (1.7), 350 (2.5), 367 (3.0), 386 (2.0).

The literature contains uv spectra for all-*trans* 1,6-diphenylhexatriene and its two isomers containing single *cis* double bonds, *i.e.* the Δ^1-*cis*, and the Δ^3-*cis* isomer, 13.[20] The original stereochemical assignments of Δ^1-*cis* and the Δ^3-*cis* compounds have been questioned, however.[21] Since the dibromo compound 12 has both peripheral double bonds *trans* by ir and nmr criteria, only the stereochemistry of the central double bond is open to question. Polyenes which possess a center of symmetry have no absorption maxima in the 260-280 nm region.[22] Therefore, the all-*trans* configuration must be ruled out for 12, which possesses two bands in this region. Thus, 12 must have the Δ^3-*cis* structure. The striking similarity of the fine structure in the uv spectrum of 12 with that in the spectrum assigned to 13 upholds the original assignment[20] in the face of the later revision.[21]

Footnotes and References

(1) Taken from the Ph.D. Thesis of C. J. Kelley, Indiana University, 1970. *Diss. Abstr. Int. B*, 31, 7187 (1971). For complete experimental section see Thesis, pp. 38-48.

(2) L. A. Carpino and J. R. Williams, *J. Org. Chem.*, 39, 2320 (1974).

(3) L. A. Carpino, L. V. McAdams, R. H. Rynbrandt and J. H. Spiewak, *J. Am. Chem. Soc.*, 93, 476 (1971).

(4) (a) Our interest in acetylene synthesis through the intermediacy of thiirene dioxides dates from the Ph.D. Thesis of Frank Scholnick[4b] who clearly stated the necessity for such an intermediate to explain the formation of phenylacetylene during the hydroxide-induced rearrangement of benzyl dibromomethyl sulfone. (b) F. Scholnick, Ph.D. Thesis, University of Pennsylvania, 1955. *Diss. Abstr.*, 15, 708 (1955).

(5) The preparation of 1 by bromination of DMSO[6a] is superior to the previous method.[6b]

Recrystallization of **1** from boiling hexane as was reported[6b] results in its partial decomposition. Only foul-smelling, oily crystals could be obtained from this solvent. Recrystallization from MeOH gives crystals of **1** lacking the reported[6b] "hypobromite" smell.

(6) (a) H. Johnson, U. S. Patent 3,051,757; *Chem. Abstr.*, **58**, 8908 (1963). (b) W. V. Farrar, *J. Chem. Soc.*, 508 (1956).

(7) W. R. James, U. S. Patent 2,628,982; *Chem. Abstr.*, **48**, 1411 (1953).

(8) (a) J. I. G. Cadogan and M. J. Perkins in "The Chemistry of Alkenes," S. Patai, ed., New York, Interscience Publishers, 1964, p. 585. (b) M. S. Kharasch, E. V. Jensen and W. H. Urry, *J. Am. Chem. Soc.*, **69**, 1100 (1947).

(9) All separations were carried out by liquid chromatography on silica gel with 1-10% ether in hexane as the eluents.

(10) (a) M. Carmack and K. Smith, unpublished observations, 1963. (b) L. A. Paquette, L. S. Wittenbrook, and V. V. Kane, *J. Am. Chem. Soc.*, **89**, 4487 (1967).

(11) R. G. Pearson, *J. Chem. Ed.*, **45**, 581 (1968).

(12) In the *meso*-isomer, **6**, the sulfur atom is a prochiral center while in the racemic isomer, **7**, it is a center of C2 symmetry.[13] The additional dissymmetry of **6** generates its more complex ^{1}H nmr spectrum.

(13) W. B. Jennings, *Chem. Rev.*, **75**, 307 (1975).

(14) Ir data and loss of SO$_2$ in the ms agrees with lit.[15] data for 1,2-oxathiolane-2-oxides.

(15) (a) R. M. Dodson, P. D. Hammen and R. A. Davis, *J. Org. Chem.*, **36**, 2693 (1971). (b) N. K. Sharma, F. Jung and T. Durst, *Tetrahedron Lett.*, 2863 (1973).

(16) Mass Spectra were obtained in an AEI MS-9 Spectrometer at 70 ev.

(17) L. K. Montgomery and M. S. Matta, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Penna., March 1966, 22K.

(18) An example of this variant of the Ramberg-Bäcklund reaction has been reported: F. G. Bordwell, B. C. Jarvis and P. W. R. Corfield, *J. Am. Chem. Soc.*, **90**, 5298 (1968).

(19) The use of N,N-dimethylformamide dried over and distilled from CaH$_2$ undoubtedly introduced some dimethylamine into the reaction mixture, thereby obscuring the exact base which attacks the α-bromo sulfone.

(20) K. Lunde and L. Zechmeister, *J. Am. Chem. Soc.*, **76**, 2308 (1954).

(21) J. Para and L. S. Forster, *Trans. Faraday Soc.*, **57**, 87 (1961).

(22) For a discussion of this point see the following: H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," New York, John Wiley and Sons, 1962, Chapter 11.