An Unusual Acid-Catalyzed Dehydrative Expulsion of Sulfur Dioxide from a Thietane Dioxide[1]

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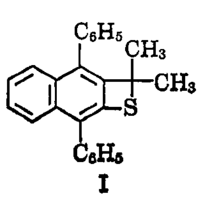
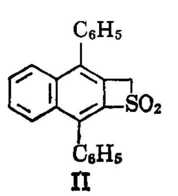
The reaction of the thietane dioxide III with polyphosphoric acid at room temperature results in a remarkable dehydrative expulsion of sulfur dioxide and the formation of a hydrocarbon dimer, the structure of which has been established by chemical and physical means. A mechanism for this transformation is suggested and tested. A synthesis of the parent 2H-naphtho[2,3-*b*]thiete 1,1-dioxide molecule has been achieved.

A synthetic approach to fused aromatic derivatives of thiete I and thiete sulfone II involving Diels–Alder reaction of isobenzofurans to thiete 1,1-dioxides, followed by acid-catalyzed dehydration of the resulting endoxy adduct, has recently been described.[3,4] An interesting problem associated with such molecules was the question of whether the fusion of a four-membered sulfur-containing ring to the 2,3-position of a naphthalene system would cause significant double-bond fixation.[5] Cava, Hwang, and Van Meter[6] have recently presented evidence for a substantial degree of bond fixation in a naphtho[*b*]cyclobutadiene and have demonstrated that such a phenomenon can be readily diagnosed by n.m.r. spectroscopy. Thus, when the single bond character of the 2a–8a bond (see IV) is significantly increased, the resonance lines associated with the protons at positions 3 and 8 undergo an upfield shift of *ca.* 0.4 p.p.m. which removes them positionally from the normal aromatic proton envelope (*ca.* δ 7).

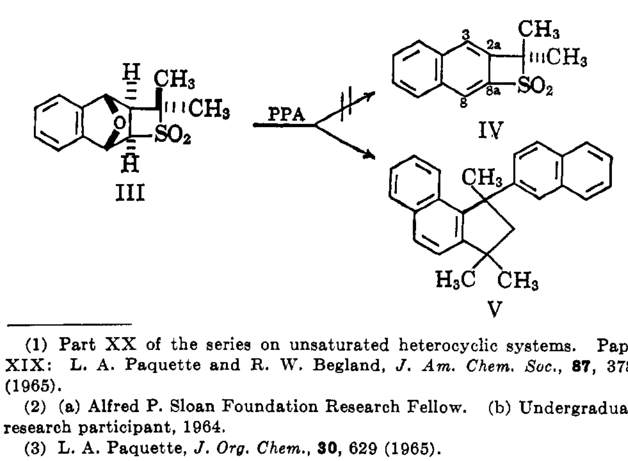


I

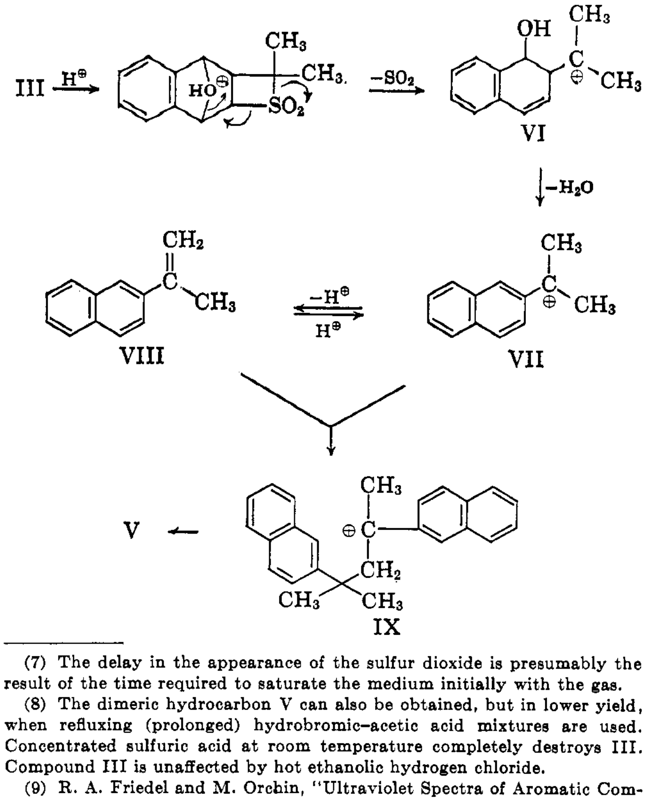


II

Because of the simplicity of the n.m.r. method, our attention was initially directed to the acid-catalyzed dehydration of III,[3] because the expected product IV would possess the two protons required for the spectral examination. However, admixture of a sample of III with about six times its weight of polyphosphoric acid (PPA) at room temperature resulted, after about 30 min., in the copious evolution of sulfur dioxide[7] and gave rise, on appropriate work-up, to a dimeric hydrocarbon, $C_{26}H_{24}$, m.p. 122–124°, in 41% yield.[8] This substance exhibited the following n.m.r. chemical shifts (in CCl_4): three methyl singlets at δ 1.34, 1.38 (somewhat overlapping), and 2.04, an AB quartet (J = 13 c.p.s., 2 protons) centered at δ 2.34, and a complex aromatic region (13 protons). Significantly, therefore, the transformation in question resulted in the conversion of one of the four methyl groups (from a composite of two molecules of III) into a methylene moiety. Furthermore, the ultraviolet spectrum of the hydrocarbon (see Experimental Section) indicated the presence of two *nonconjugated* naphthalene rings.[9] On the basis of the above and ensuing data, we have formulated the hydrocarbon as V, which can presumably arise *via* the mechanistic pathway shown in Scheme I. Protonation of III at the endoxy bridge can lead to the expulsion of sulfur dioxide by the proper migration of electrons which may or may not be synchronous, but



SCHEME I



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[1] Part XX of the series on unsaturated heterocyclic systems. Paper XIX: L. A. Paquette and R. W. Begland, *J. Am. Chem. Soc.*, **87**, 3784 (1965).

[2] (a) Alfred P. Sloan Foundation Research Fellow. (b) Undergraduate research participant, 1964.

[3] L. A. Paquette, *J. Org. Chem.*, **30**, 629 (1965).

[4] D. C. Dittmer and F. A. Davis, *Tetrahedron Letters*, 3809 (1964).

[5] It is well known that the α,β-bonds of naphthalene have appreciably more double bond character than the β,β-bonds: see, for example, L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p. 880.

[6] M. P. Cava, B. Hwang, and J. P. Van Meter, *J. Am. Chem. Soc.*, **85**, 4032 (1963).

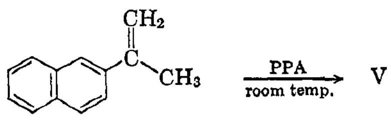
[7] The delay in the appearance of the sulfur dioxide is presumably the result of the time required to saturate the medium initially with the gas.

[8] The dimeric hydrocarbon V can also be obtained, but in lower yield, when refluxing (prolonged) hydrobromic–acetic acid mixtures are used. Concentrated sulfuric acid at room temperature completely destroys III. Compound III is unaffected by hot ethanolic hydrogen chloride.

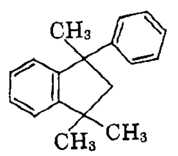
[9] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951; see especially spectra 287 and 288.

which ultimately affords the tertiary carbonium ion VI. Intermediate VI is without doubt rapidly dehydrated to attain the additional resonance energy of the naphthalene system. This new carbonium ion VII, which exists in equilibrium with its nonprotonated form VIII, undergoes electrophilic attack on VIII to produce IX which cyclizes to V.

Strong corroborative evidence for the above mechanistic scheme was obtained by submitting 2-isopropenylnaphthalene to the same reaction conditions. A dimeride was obtained which was identical with V by all the usual criteria.[10]



The structural assignment of V was further substantiated by examination of the n.m.r. spectrum of the dimer of α-methylstyrene (X)[13] which exhibited similar absorptions in CCl_4 at δ 1.00, 1.32, and 1.65 (three methyl groups), an AB quartet centered at δ 2.23 (two protons), and a rather sharp aromatic line at δ 7.06.

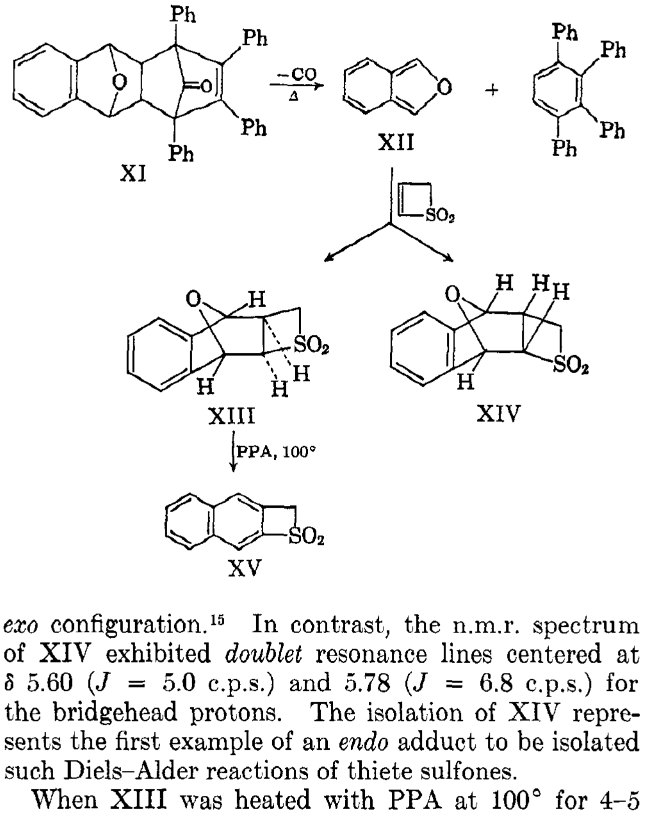


X

The synthesis and dehydration of XIII was next studied, for a similar ring-opening process would, of necessity, result in the formation of a primary carbonium ion. A critical test of the proposed mechanistic reasoning was therefore at hand; the highly unfavorable energetics which are involved in primary carbonium ion formation would be expected to permit a different reaction sequence (perhaps the desired dehydration pathway) to be favored.

Generation of isobenzofuran (XII) by the thermal decomposition of XI in hot diglyme[14] containing an approximate equivalent of thiete sulfone served to produce a mixture of *exo*-XIII (68%) and *endo*-XIV (15%) (see Scheme II). The two isomers differed greatly in their solubility characteristics and were easily separated by fractional crystallization. The stereochemistry of the adducts was readily deduced from their n.m.r. spectra (determined in dimethyl-d_6 sulfoxide solution). The bridgehead protons of XIII were displayed as *singlets* at δ 5.55 and 5.38; the absence of coupling of these protons with the neighboring cyclobutane protons can only be accommodated by the *exo* configuration.[15] In contrast, the n.m.r. spectrum of XIV exhibited *doublet* resonance lines centered at δ 5.60 (J = 5.0 c.p.s.) and 5.78 (J = 6.8 c.p.s.) for the bridgehead protons. The isolation of XIV represents the first example of an *endo* adduct to be isolated such Diels–Alder reactions of thiete sulfones.

SCHEME II



When XIII was heated with PPA at 100° for 4–5 hr.,[16] 2H-naphtho[2,3-*b*]thiete 1,1-dioxide (XV) was obtained as the sole identifiable product. Thus, the normal dehydrative sequence does occur in the case of XV, presumably because of the reasons discussed above. The n.m.r. spectrum of XV in dilute dimethyl-d_6 sulfoxide solution displayed the α-sulfonyl protons as a singlet at δ 5.50 and the aromatic protons as a complex multiplet below δ 7.4. Such evidence is indicative of the lack of bond fixation in XV and demonstrates that the fusion of the thiete sulfone ring to the 2,3 bond of naphthalene does not significantly alter the ground state of the aromatic moiety. This is also reflected in the great degree of similarity in the ultraviolet spectra of XV (see Experimental Section) and methyl 2-naphthyl sulfone.[17]

Experimental Section[18]

2,3-Dihydro-1,3,3-trimethyl-1-(2-naphthyl)-1H-benz[*e*]indene (V). A. Reaction of III with Polyphosphoric Acid.—A mixture of 12.25 g. (0.05 mole) of finely powdered *exo*-III[3] and 75 ml. of polyphosphoric acid was allowed to stand at room temperature for 2.5 days. After about 30 min., copious evolution of sulfur dioxide was observed, and the mixture gradually darkened. The black syrup was poured into water, and the organic components were extracted with methylene chloride. The resulting brown viscous oil was chromatographed on basic alumina (elution with hexane) and there was obtained 3.41 g. (40.5%) of white solid, m.p. 118–120°. Recrystallization from hexane fur-

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[10] Although acid-catalyzed dimerizations of such 2-naphthyl derivatives have not been reported, dimerides derived from 1-isopropenylnaphthalene,[11] 1-propenylnaphthalene,[11a] and α-methylstyrene[11a,12] are known in the literature.

[11] (a) C. S. Schoepfle and J. D. Ryan, *J. Am. Chem. Soc.*, **52**, 4021 (1930); (b) J. W. Cook, *J. Chem. Soc.*, 456 (1932); (c) W. V. Mayneord and E. M. F. Roe, *Proc. Roy. Soc.* (London), **A152**, 299 (1935); (d) Yw. S. Zal'Kind and S. A. Zonis, *J. Gen. Chem. USSR*, **6**, 988 (1936); (e) S. A. Zonis, *ibid.*, **7**, 637 (1939).

[12] H. Staudinger and F. Breusch, *Ber.*, **62**, 450 (1929); F. S. Dainton and R. H. Tomlinson, *J. Chem. Soc.*, 151 (1953); K. T. Serijan and P. H. Wise, *J. Am. Chem. Soc.*, **73**, 4766 (1951).

[13] The authors are indebted to Mr. Richard Nadolsky for this spectrum.

[14] L. F. Fieser and M. J. Haddadin, *J. Am. Chem. Soc.*, **86**, 2081 (1964).

[15] For a more extensive discussion of this topic, see ref. 3.

[16] No reaction was observed at room temperature.

[17] $\lambda_{\max}^{\mathrm{EtOH}}$ 229 mμ (ϵ 85,000), 277 (4470), 311 (1000), and 325 (1380); inflections in the curve were not reported but are obvious in the published spectrum [V. A. Koptyug and V. A. Plakhov, *Russ. J. Phys. Chem.*, **35**, 434 (1961)].

[18] Melting points are uncorrected. The n.m.r. spectra were obtained in the solvents specified with a Varian A-60 spectrometer utilizing tetramethylsilane as internal standard (TMS = δ 0). Ultraviolet spectra were determined in 95% ethanol on a Cary 14 recording spectrometer. The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

nished hard white prisms: m.p. 122–124°; λ_{max}^{EtOH} 222 mμ (ε 276,000), 265 sh (10,600), 275 (13,350), 278 (13,200), 283 (12,300) 291 sh (9320), 307 (2320), 313 (1700), and 321 (2660).

Anal. Calcd. for $C_{26}H_{24}$: C, 92.81; H, 7.19; mol. wt., 336. Found: C, 92.92; H, 7.32; mol. wt. (ebullioscopic in $CHCl_3$), 332.

Elution of the chromatographic column with ether afforded a small amount of a sulfur-containing (not a sulfone) compound which was not further identified.

B. Acid-Catalyzed Dimerization of 2-Isopropenylnaphthalene.—A mixture of 5.0 g. (0.03 mole) of 2-isopropenylnaphthalene[19] and 25 ml. of polyphosphoric acid was allowed to stand overnight at room temperature. The reaction was completed by heating on a steam bath for 0.5 hr. accompanied by occasional swirling with a glass rod. The mixture was poured into water, and the product was extracted twice with chloroform. The combined organic phases were washed with water, dried, filtered, and evaporated. The resulting viscous oil was purified by chromatography on neutral alumina (elution with hexane) and recrystallization from hexane. There was obtained 1.35 g. (27.0%) of white solid, m.p. 121–122°, identical by the usual criteria with the above sample.

2a,3,8,8a-Tetrahydro-3,8-epoxy-2H-naphtho[2,3-*b*]thiete 1,1-Dioxide (XIII and XIV).—A solution of 26.4 g. (0.05 mole) of XI[14] and 5.0 g. (0.048 mole) of thiete sulfone[20] in 125 ml. of diglyme was heated under reflux with stirring for 16 hr. The major portion of the diglyme was distilled under reduced pressure, and the residual material was chromatographed on neutral alumina. Elution with hexane–benzene (3:1) afforded, after recrystallization from benzene–hexane, 17.85 g. (97.4%) of 1,2,3,4-tetraphenylbenzene, m.p. 190–191.5°. Elution with benzene–methanol (19:1) gave 9.6 g. (90.7%) of white solid, m.p. 150–210°. Recrystallization of this material from a large volume of ethyl acetate furnished 7.2 g. of the *exo* isomer XIII, m.p. 218–219°. The analytical sample was obtained as white needles from ethyl acetate, m.p. 219° dec.

Anal. Calcd. for $C_{11}H_{10}O_3S$: C, 59.44; H, 4.54; S, 14.43. Found: C, 59.29; H, 4.58; S, 14.41.

From the mother liquor of the above purification, there was isolated 1.6 g. of solid, m.p. 150–170°. Three recrystallizations of this material from ethyl acetate–hexane gave pure *endo* isomer XIV, m.p. 165–167°.

Anal. Found: C, 59.37; H, 4.48; S, 14.34.

2H-Naphtho[2,3-*b*]thiete 1,1-Dioxide (XV).—A mixture of 11.2 g. (0.05 mole) of the *exo* isomer XIII and 100 ml. of polyphosphoric acid was heated on a steam bath for 3 hr. with stirring and allowed to stand at room temperature overnight. The mixture was poured into 900 ml. of water, and the product was extracted with chloroform. The combined organic layers were washed with water, dried, filtered, and evaporated to give 5.70 g. (52.8%) of a grayish white solid, m.p. 184–200°. Pure XV could be obtained by recrystallization from benzene–hexane, or preferably from dimethyl sulfoxide: m.p. 226°; λ_{max}^{EtOH} 214 mμ sh (ε 30,600), 233 (69,000), 272.5 sh (5470), 284 (4630), 289 (4440), 294 (4240), 313 (1640), 319 sh (1110), and 327 (1550).

Anal. Calcd. for $C_{11}H_{18}O_2S$: C, 64.68; H, 3.95; S, 15.70. Found: C, 65.00; H, 3.99; S, 15.39.

Acknowledgment.—We gratefully thank the National Science Foundation for partial support of this work. The authors are also indebted to Mr. Robert Davisson for his assistance in preparing the sample of compound XI.

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[19] Prepared by the action of triphenylphosphinemethylene on 2-acetonaphthone, m.p. 52–54° [see L. H. Klemm, W. C. Solomon, and A. J. Kohlik, *J. Org. Chem.*, **27**, 2777 (1962)].

[20] D. C. Dittmer and M. E. Christy, *ibid.*, **26**, 1324 (1961).

Reaction Paths in the Kolbe Synthesis

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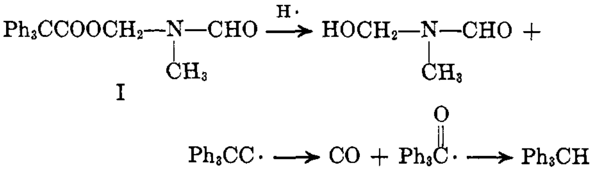
The products from the electrolysis of phenylacetic, diphenylacetic, mesitylacetic, and 2,4,6-triisopropylphenylacetic acids provide evidence for the formation of the Kolbe hydrocarbon at both electrodes. The formation of an ester and then a reductive cleavage at the cathode is suggested as the route for the unexpected hydrocarbon synthesis at the cathode.

One of the main products expected from the electrolysis of a carboxylic acid is a hydrocarbon.[1] It has been established that this reaction, the Kolbe synthesis, proceeds through a one-electron transfer at the anode, decarboxylation of the acyloxy radical, and coupling of the resulting alkyl radicals.

$$R{-}COO^- \xrightarrow{-e} R{-}COO\cdot \longrightarrow CO_2 + R\cdot \xrightarrow{R\cdot} R{-}R \quad (1)$$

More recently, attention has been directed toward those acids which yield substances other than the usual hydrocarbons. Most of these products, ethers, alcohols, and esters, depend on the solvent and can be reconciled with radical intermediates. There is convincing evidence[2] that in certain cases, however, carbonium ions resulting from a two-electron transfer at the anode account for some of the compounds produced. Some of the probable reaction paths are summarized in Chart I.

In an earlier article,[3] we reported that the electrolysis of triphenylacetic acid in dimethylformamide afforded a good yield of N-methyl-N-(triphenylacetoxymethyl)-formamide (I). This ester, after prolonged electrolysis, underwent reductive cleavage at the cathode as shown in eq. 2.


I

$$Ph_3CCOOCH_2{-}\underset{CH_3}{\underset{|}{N}}{-}CHO \xrightarrow{H\cdot} HOCH_2{-}\underset{CH_3}{\underset{|}{N}}{-}CHO +$$

$$Ph_3CC\cdot \longrightarrow CO + Ph_3\overset{O}{\overset{\|}{C}}\cdot \longrightarrow Ph_3CH \quad (2)$$

Since the half-esters of dicarboxylic acids often are successfully utilized in the Kolbe synthesis, it was of interest to determine if the cleavage illustrated in eq. 2 was a general reaction. Under conditions similar to those employed for the electrolysis of triphenylacetic

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[1] Several reviews of this reaction are (a) B. C. L. Weedon, *Quart. Rev.* (London), **6**, 380 (1952); (b) B. C. L. Weedon, *Advan. Org. Chem.*, **1**, 1 (1960); (c) M. J. Allen, "Organic Electrode Processes," Reinhold Publishing Corp., New York, 1958, pp. 95–115; (d) A. P. Tomilov and M. Ya. Fioshin, *Russ. Chem. Rev.*, **32**, 30 (1963).

[2] (a) W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **86**, 4686 (1964); (b) W. A. Bonner and F. D. Mango, *J. Org. Chem.*, **29**, 430, 1367 (1964); (c) E. J. Corey, N. L. Bauld, R. T. LaLonde, and J. Casanova, Jr., *J. Am. Chem. Soc.*, **82**, 2645 (1960); (d) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 581; (e) L. Eberson, *Acta Chem. Scand.*, **17**, 1196, 2004 (1963).

[3] L. Rand and A. F. Mohar, *J. Org. Chem.*, **30**, 3156 (1965).