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Bis-(polyfluoroalkyl)-acetylenes. V. Addition of Bis-(trifluoromethyl)-1,2-dithietene to Olefins and Acetylenes¹

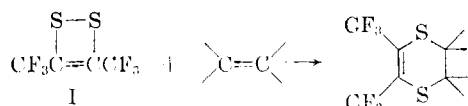
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Addition of bis-(trifluoromethyl)-1,2-dithietene to olefins has been found to give dihydro-*p*-dithiins. This dithietene adds to acetylenes to form *p*-dithiins, thiophenes and dihydro-*p*-dithiino-*p*-dithiins, with the products formed dependent on reaction temperature and electronegativity of substituents on the acetylenic bond. Bis-(trifluoromethyl)-1,2-dithietene also combines with mercury to form a reactive mercuric salt.

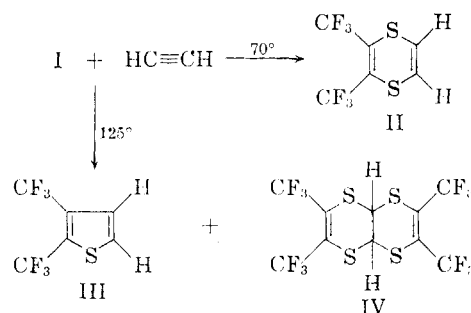
In the course of synthesis of bis-(trifluoromethyl)-1,2-dithietene (I) it was shown that the sulfur-sulfur linkage is weak and can be broken by a weak base to give dimer, or by heat to effect addition to hexafluoro-2-butyne.² These findings led us to attempt to add the dithietene to olefins and to other acetylenes. The addition was found to be a smooth one, particularly with olefins and acetylenes having a high density of loosely bound electrons, and the reaction is quite general.

For example, I reacts readily with ethylene at 150° to form 2,3-bis-(trifluoromethyl)-5,6-dihydro-*p*-dithiin as the only product. Substitution of alkyl or aryl groups for hydrogen results in increased reactivity of the olefin so that such olefins react at only 100°, giving the corresponding dihydro-*p*-dithiin as the sole product. Since tetramethylethylene with I gives a 47% yield of 2,3-bis-(trifluoromethyl)-5,5,6,6-tetramethyl-5,6-dihydro-*p*-dithiin at 100°, restriction of the reaction by steric hindrance is not as important as the electron density about the olefinic bond. The importance of electron distribution is borne out by the high reactivity of ethyl vinyl ether; when mixed with I at 25°, this olefin gives a vigorously exothermic reaction that leads to the expected dihydro-*p*-dithiin.



That dithietenes other than I will give similar adducts with unsaturated compounds is shown by the reaction of bis-(2-chlorotetrafluoroethyl)-1,2-dithietene with butyl vinyl sulfide. The only product isolated is again the dihydro-*p*-dithiin.

The ease of addition of I to acetylenes is also controlled by the availability of electrons at the triple bond. In this case, however, the products vary with reaction temperature and with substituents on the triple bond. Acetylene and I react readily at 125°, but the primary addition product II is not obtained. Due to the instability of the *p*-dithiin ring at elevated temperatures,² sulfur is eliminated with the formation of 2,3-bis-(trifluoromethyl)-thiophene (III). The double bond bearing hydrogen in II is reactive toward addition of I at 125°, so that a bicyclic compound IV is also formed. A lower reaction temperature of 70° results in a much slower addition of I to acetylene, but II is stable at



this temperature and can be isolated in low yield as the only product.

The presence of two electron-donating alkyl groups in 3-hexyne renders its triple bond more susceptible to attack than that of acetylene, so reaction of 3-hexyne with the dithietene I occurs at only 25° to give a *p*-dithiin. The double bond bearing ethyl groups in this *p*-dithiin is also reactive toward I, resulting in a bicyclic product as well.

Dimethyl acetylenedicarboxylate, on the other hand, reacts with I at about 70° to form only a *p*-dithiin. On further heating, this product loses sulfur to form 2,3-dimethoxycarbonyl-4,5-bis-(trifluoromethyl)-thiophene. This series of reactions is the same as that observed for I with hexafluoro-2-butyne; the electronegative groups attached to the triple bond are especially effective in preventing addition of the second molecule of I.²

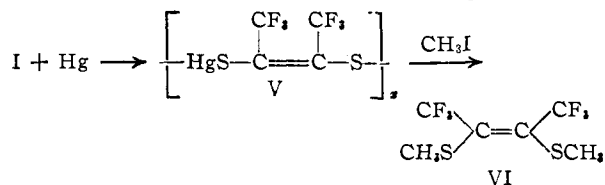
While the experimental data fit an electrophilic attack on a multiple bond by I, details of the reaction mechanism are not known. Since I has essentially no free radical character at 25°, the reaction does not proceed by initial homolytic cleavage of the disulfide bond at low temperatures. An association of I and the unsaturated compound, as in the Diels-Alder reaction, is more likely. Subsequent reaction steps of such a complex would be expected to result in *cis* addition of the sulfur atoms to an ethylenic bond, so that adducts of I with olefins such as *trans*-stilbene are believed to have the *trans* arrangement of substituents on the ring. *cis*-Olefins like the *p*-dithiin II would similarly retain the *cis* configuration while reacting to form IV. The existence of II in predominantly the boat form³ should ensure a *cis* arrangement at the juncture of the two rings in IV, since the structure of the transition state would be very close to that of the *cis* product IV.

(1) C. G. Krespan, B. C. McKusick and T. L. Cairns, *J. Am. Chem. Soc.*, **82**, 1515 (1960).

(2) C. G. Krespan, *ibid.*, **83**, 3131 (1961).

(3) W. E. Parham, H. Wynberg, W. R. Hasek, P. A. Howell, R. M. Curtis and W. N. Lipscomb, *ibid.*, **76**, 4957 (1954), have established that *p*-dithiin itself has the boat configuration.

Compound I also reacts with mercury, slowly at 25° and rapidly at higher temperatures. This reactivity is much greater than that of fluorinated disulfides such as bis-(trifluoromethyl) disulfide, which require irradiation to bring about reaction with mercury.⁴ The mercuric salt V of 1,2-dimercapto-1,2-bis-(trifluoromethyl)-ethylene, obtained from I and mercury, is a high melting solid that is insoluble in non-polar solvents, in contrast to bis-(trifluoromethylthio)-mercury. The properties of V coupled with the reluctance of mercury to enter into small rings points to a linear or large ring polymeric structure for V. Moreover, the *cis* arrangement about the double bond in I should be preserved in a low temperature reaction with mercury at the sulfur-sulfur bond, so the mercury salt is assumed to have the *cis* configuration. As further evidence for the mercaptide salt structure for V, it was converted to 1,2-bis-(methylthio)-1,2-bis-(trifluoromethyl)-ethylene (VI) by reaction with methyl iodide. The presence of a strong C=C band at 6.48 μ in the infrared spectrum of VI is good evidence that VI, and hence V, are *cis* compounds.



Experimental⁵

2,3-Bis-(trifluoromethyl)-5,6-dihydro-*p*-dithiin.—Reaction of 22.6 g. (0.10 mole) of 3,4-bis-(trifluoromethyl)-1,2-dithietene with 5 g. (0.18 mole) of ethylene in 20 ml. of cyclohexane at 150° for 12 hours under autogenous pressure gave 6.2 g. (24% yield) of 2,3-bis-(trifluoromethyl)-5,6-dihydro-*p*-dithiin, b.p. 106° (25 mm.), m.p. 29°.

Anal. Calcd. for C₈H₄F₆S₂: C, 28.35; H, 1.59; F, 44.84; S, 25.22. Found: C, 28.69; H, 1.63; F, 45.57; S, 25.28.

The infrared spectrum showed a band for C=C at 6.39 μ . Absorption in the ultraviolet occurred at $\lambda_{\text{max}}^{\text{acetone}}$ 223 m μ (ϵ 5,520), 295 m μ (ϵ 8330), shoulder at 302 m μ . The nuclear magnetic resonance spectra contained peaks for CF₃ at -1048 c.p.s. and CH₂ at +93 c.p.s.

2,3-Bis-(trifluoromethyl)-5,5,6,6-tetramethyl-5,6-dihydro-*p*-dithiin.—A mixture of 11.3 g. (0.05 mole) of 3,4-bis-(trifluoromethyl)-1,2-dithietene and 4.6 g. (0.055 mole) of tetramethylethylene was heated on a steam-bath for 20 hours. Distillation of the crude product afforded 7.3 g. (47% yield) of 2,3-bis-(trifluoromethyl)-5,5,6,6-tetramethyl-5,6-dihydro-*p*-dithiin, b.p. 84° (4 mm.), m.p. 21–22°.

Anal. Calcd. for C₁₀H₁₂F₈S₂: C, 38.70; H, 3.90; F, 36.74; S, 20.66. Found: C, 38.61; H, 3.92; F, 36.93; S, 21.26.

The infrared spectrum had a band for C=C at 6.45 μ . Absorption in the ultraviolet occurred at $\lambda_{\text{max}}^{\text{acetone}}$ 226 m μ (ϵ 4330), 288 m μ (ϵ 7440), 297 m μ (ϵ 7130). The nuclear magnetic resonance spectra contained single peaks for CF₃ at -1160 c.p.s. and for CH₂ at +193 c.p.s.

2,3-Bis-(trifluoromethyl)-6-ethoxy-5,6-dihydro-*p*-dithiin.—When 11.3 g. (0.05 mole) of 3,4-bis-(trifluoromethyl)-1,2-dithietene was mixed with 4.3 g. (0.06 mole) of ethyl vinyl ether, an exothermic reaction ensued that was moderated

(4) R. N. Haszeldine and J. M. Kidd. *J. Chem. Soc.*, 3219 (1953).

(5) Melting and boiling points are uncorrected. Nuclear magnetic resonance spectra were obtained by means of a high resolution nuclear magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates, operating at 56.4 mc./sec. and approximately 14,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the F¹⁹ resonance of trifluoroacetic acid and H¹ resonance of water. Negative frequency displacements are for resonances occurring at lower field than the references.

by external cooling. Distillation of the mixture gave 7.4 g. (50% yield) of 2,3-bis-(trifluoromethyl)-6-ethoxy-5,6-dihydro-*p*-dithiin, b.p. 79° (2 mm.).

Anal. Calcd. for C₈H₈F₆OS₂: C, 32.21; H, 2.70; F, 38.22; S, 21.50. Found: C, 32.35; H, 2.82; F, 38.83; S, 21.75.

An infrared band for C=C was found at 6.40 μ . Absorption in the ultraviolet occurred at $\lambda_{\text{max}}^{\text{acetone}}$ 222 m μ (ϵ 3550), 285 m μ (ϵ 6490), 296 m μ (ϵ 6410).

2,3-Bis-(trifluoromethyl)-5,6-tetramethylene-5,6-dihydro-*p*-dithiin.—When a mixture of 2.26 g. (0.010 mole) of 3,4-bis-(trifluoromethyl)-1,2-dithietene and 0.90 g. (0.011 mole) of cyclohexene was heated on a steam-bath for 15 hours and then cooled, 1.12 g. (36% yield) of colorless crystals precipitated. Recrystallization from aqueous ethanol gave analytically pure 2,3-bis-(trifluoromethyl)-5,6-tetramethylene-5,6-dihydro-*p*-dithiin, m.p. 67–68°.

Anal. Calcd. for C₁₀H₁₀F₆S₂: C, 38.96; H, 3.27; F, 36.98; S, 20.80. Found: C, 39.16; H, 3.50; F, 37.12; S, 20.29.

The infrared spectrum contained a band for C=C at 6.38 μ (KBr wafer). Absorption in the ultraviolet occurred at $\lambda_{\text{max}}^{\text{acetone}}$ 228 m μ (ϵ 3940), 293 m μ (ϵ 6680), 299 m μ (ϵ 6710). The nuclear magnetic resonance spectra in carbon tetrachloride solution showed a single CF₃ peak at -1151 c.p.s., a C-H peak at +70 c.p.s., and a CH₂ peak at +161 c.p.s. The proton resonances were in a 1:4 ratio and both had fine structure.

2,3-Bis-(trifluoromethyl)-5,6-diphenyl-5,6-dihydro-*p*-dithiin.—Reaction of 11.3 g. (0.05 mole) of 3,4-bis-(trifluoromethyl)-1,2-dithietene with 9.0 g. (0.05 mole) of *trans*-stilbene in 10 ml. of heptane on a steam-bath for 30 hours gave a solid product on cooling. Recrystallization from heptane gave 7.3 g. (36% yield) of 2,3-bis-(trifluoromethyl)-5,6-diphenyl-5,6-dihydro-*p*-dithiin, m.p. 160–162° (subl.). Absorption occurred in the ultraviolet at $\lambda_{\text{max}}^{\text{acetone}}$ 298 m μ (ϵ 8150), several shoulders in 210–270 m μ region.

Anal. Calcd. for C₁₈H₁₂F₆S₂: C, 53.20; H, 2.98; F, 28.05; S, 15.78. Found: C, 53.24; H, 3.09; F, 28.06; S, 15.67.

2,3-Bis-(2-chlorotetrafluoroethyl)-6-butylthio-5,6-dihydro-*p*-dithiin.—A mixture of 6.2 g. (0.017 mole) of 3,4-bis-(2-chlorotetrafluoroethyl)-1,2-dithietene and 2.3 g. (0.02 mole) of butyl vinyl sulfide⁶ was heated to 100° for 20 hours. Distillation of the product gave 2.5 g. (31% yield) of 2,3-bis-(2-chlorotetrafluoroethyl)-6-butylthio-5,6-dihydro-*p*-dithiin, b.p. 125–127° (1 mm.).

Anal. Calcd. for C₁₂H₁₂Cl₂F₈S₂: F, 31.98; S, 20.23. Found: F, 31.98; S, 20.65.

Reaction of Acetylene with 3,4-Bis-(trifluoromethyl)-1,2-dithietene at 125°.—A mixture of 22.6 g. (0.10 mole) of 3,4-bis-(trifluoromethyl)-1,2-dithietene, 5.0 g. (0.20 mole) of acetylene and 20 ml. of cyclohexane was heated at 125° for 8 hours under autogenous pressure. Distillation of the reaction mixture gave 2.1 g. (10% yield) of 2,3-bis-(trifluoromethyl)-thiophene (III), b.p. 69–70° (150 mm.).

Anal. Calcd. for C₈H₂F₆S: C, 32.73; H, 0.92; F, 51.78; S, 14.56. Found: C, 32.57; H, 1.10; F, 51.91; S, 14.55.

Infrared absorption for unsaturation occurred at 6.39 μ with other weak absorption in the 6.0–6.7 μ region. The nuclear magnetic resonance spectra contained CF₃ peaks at -1314 c.p.s. and -1112 c.p.s., and peaks for aromatic hydrogen at -117 and -110 c.p.s.

From the distillation residue there was obtained by recrystallization from methanol and sublimation at 110° (40 mm.) 7.2 g. (30% yield) of 2,3,6,7-tetrakis-(trifluoromethyl)-4a,8a-dihydro-*p*-dithiino[2,3-*b*]-*p*-dithiin (IV), m.p. 125–126° (subl.).

Anal. Calcd. for C₁₀H₂F₁₂S₄: C, 25.11; H, 0.42; F, 47.66; S, 26.81; mol. wt., 478. Found: C, 25.24; H, 0.66; F, 47.64; S, 26.65; mol. wt., 490 (b.p. benzene).

The infrared spectrum contained a band for C=C at 6.21 μ (KBr wafer). Absorption in the ultraviolet occurred at $\lambda_{\text{max}}^{\text{acetone}}$ 222 m μ (ϵ 10,000), 328 m μ (ϵ 3680), shoulders at 235, 320 m μ . The nuclear magnetic resonance spectra contained single peaks for CF₃ at -1211 c.p.s. and tertiary hydrogen at +2 c.p.s. (acetone solution).

(6) Butyl vinyl sulfide, b.p. 65–67° (50 mm), was prepared according to the general directions of W. Reppe and F. Nicolai, *Ger. Patent* 617,543 (1935).

2,3-Bis-(trifluoromethyl)-*p*-dithiin (II).—A mixture of 45.2 g. (0.20 mole) of 3,4-bis-(trifluoromethyl)-1,2-dithietene, 13 g. (0.50 mole) of acetylene and 50 ml. of benzene was heated under pressure at 50° for 45 hours, then at 70° for an additional 15 hours. Distillation of the reaction mixture gave 16.7 g. (37%) of recovered 3,4-bis-(trifluoromethyl)-1,2-dithietene and a residue of 10 g. (22%) of its crude dimer, along with 1.5 g. (3% yield) of 2,3-bis-(trifluoromethyl)-*p*-dithiin, b.p. 48° (10 mm.).

Anal. Calcd. for C₆H₂F₆S₂: C, 28.57; H, 0.80; F, 45.20; S, 25.42. Found: C, 28.29; H, 1.07; F, 45.25; S, 25.62.

The infrared spectrum contained bands for C=C at 6.28 μ and 6.47 μ . Absorption in the ultraviolet occurred at $\lambda_{\text{max}}^{\text{isooctane}}$ 261 m μ (ϵ 3630), 269 m μ (ϵ 4490), 278 m μ (ϵ 3960); 330 m μ (ϵ 400), shoulder at 255 m μ . Nuclear magnetic resonance peaks were found for CF₃ at -1091 c.p.s. and unsaturated C-H at -78 c.p.s.

Adducts of 3-Hexyne with 3,4-Bis-(trifluoromethyl)-1,2-dithietene.—3,4-Bis-(trifluoromethyl)-1,2-dithietene (11.3 g., 0.05 mole) and 3-hexyne (4.5 g., 0.055 mole) were allowed to react at 25° for 17 days to give on distillation 2.3 g. (15% yield) of yellow 2,3-diethyl-5,6-bis-(trifluoromethyl)-*p*-dithiin, b.p. 77-79° (4 mm.).

Anal. Calcd. for C₁₀H₁₀F₆S₂: C, 38.96; H, 3.27; F, 36.98; S, 20.80; mol. wt., 308. Found: C, 39.48; H, 3.27; F, 36.93; S, 20.21; mol. wt., 291 (b.p. benzene).

A band in the infrared for C=C came at 6.34 μ . Absorption in the ultraviolet occurred at $\lambda_{\text{max}}^{\text{isooctane}}$ 221 m μ (ϵ 4870), 260 m μ (ϵ 4810), 323 m μ (ϵ 460). Nuclear magnetic resonance showed a single peak for CF₃ at -1157 c.p.s.; and proton peaks for one kind of ethyl group; a quadruplet at +129, +137, +145 and +153 c.p.s. for CH₂; and a triplet at +209, +217 and +225 c.p.s. for CH₃.

Recrystallization of the distillation residue from methanol afforded 0.9 g. (7% yield) of 4a,8a-diethyl-2,3,6,7-tetrakis-(trifluoromethyl)-4a,8a-dihydro-*p*-dithiino[2,3-*b*]-*p*-dithiin, m.p. 132-133° (subl.).

Anal. Calcd. for C₁₄H₁₀F₁₂S₄: C, 31.46; H, 1.89; F, 42.66; S, 23.99. Found: C, 31.58; H, 2.02; F, 42.74; S, 23.96.

Infrared showed a band for C=C at 6.23 μ (KBr wafer). Absorption in the ultraviolet occurred at $\lambda_{\text{max}}^{\text{isooctane}}$ 225 m μ (ϵ 8870), 297 m μ (ϵ 3310), 318 m μ (ϵ 2830). Nuclear magnetic resonance showed a single CF₃ peak and a single ethyl group to be present.

2,3-Dimethoxycarbonyl-4,5-bis-(trifluoromethyl)-thiophene.—3,4-Bis-(trifluoromethyl)-1,2-dithietene (11.3 g., 0.05 mole) and 7.8 g. (0.055 mole) of dimethyl acetylenedicarboxylate were allowed to react in 15 ml. of refluxing methanol for 8 hours. The dithiadene that was apparently formed lost sulfur during distillation to give a mixture of

sulfur and a thiophene, b.p. 76-78° (0.5 mm.). Recrystallization of the product from petroleum ether, with a filtration step included to remove free sulfur, gave 5.4 g. (32% yield) of 2,3-dimethoxycarbonyl-4,5-bis-(trifluoromethyl)-thiophene, m.p. 49°.

Anal. Calcd. for C₁₀H₆F₆O₄S: C, 35.72; H, 1.80; F, 33.91; S, 9.54. Found: C, 36.09; H, 2.06; F, 33.62; S, 9.71.

The infrared spectrum contained carbonyl bands at 5.70 and 5.75 μ , thiophene ring bands at 6.42 and 6.72 μ . Nuclear magnetic resonance revealed quadruplets for CF₃ groups at -1293, -1283, -1273 and -1263 c.p.s., and at -1160, -1150, -1140 and at -1130 c.p.s.; a methyl peak came at +62 c.p.s.

Mercuric Salt of 1,2-Dimercapto-1,2-bis-(trifluoromethyl)-ethylene (V).—A mixture of 56.5 g. (0.25 mole) of 3,4-bis-(trifluoromethyl)-1,2-dithietene and 80.2 g. (0.40 mole) of mercury was heated with agitation at 85° for 16 hours. The resulting solid was washed well with petroleum ether and with carbon disulfide. The residual solid was dissolved in methanol, and then the solution was filtered and diluted with water. The precipitate, 84.1 g. (79% yield) of pale yellow mercuric salt of 1,2-dimercapto-1,2-bis-(trifluoromethyl)-ethylene, m.p. >300°, was insoluble in most organic solvents, indicating a high molecular weight. An analytical sample was prepared by another precipitation from methanol.

Anal. Calcd. for C₄F₆HgS₂: F, 26.71; Hg, 47.01; S, 15.02. Found: F, 26.57; Hg, 46.55; S, 14.97.

The infrared spectrum contained a band for C=C at 6.15 μ (KBr wafer). Absorption in the ultraviolet occurred at $\lambda_{\text{max}}^{\text{ethanol}}$ 325 m μ (ϵ 2310 based on a mol. wt. of 427), shoulders at 220, 285 m μ . The nuclear magnetic resonance spectrum had a single sharp peak in the CF₃ region (methanol solution).

Reaction of 12.5 g. (0.03 gram-mole) of the mercury salt and 9.9 g. (0.07 mole) of methyl iodide in 10 ml. of ethanol occurred at 25°. After 2 days the solution was decanted from mercuric iodide that had precipitated. Distillation gave 4.4 g. of oil, b.p. 67-74° (20 mm.), that was shaken with mercury and redistilled. There was thus obtained 3.2 g. (42% yield) of 1,2-bis-(methylthio)-1,2-bis-(trifluoromethyl)-ethylene (VI), b.p. 73° (20 mm.).

Anal. Calcd. for C₆H₆F₆S₂: C, 28.12; H, 2.36; F, 44.49; S, 25.02. Found: C, 28.44; H, 2.63; F, 44.56; S, 24.89.

A band in the infrared for C=C came at 6.48 μ . Absorption in the ultraviolet occurred at $\lambda_{\text{max}}^{\text{isooctane}}$ 294 m μ (ϵ 5,760). Nuclear magnetic resonance peaks were found for CF₃ at -1112 c.p.s. and for CH₃ at +143 c.p.s.

[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, THE FACULTY OF ENGINEERING, KYOTO UNIVERSITY, YOSHIDA, KYOTO, JAPAN]

Kinetics of the Epoxidation of Substituted α -Methylstilbenes

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The epoxidation of α -methylstilbene and ring-substituted α -methylstilbenes by peroxybenzoic acid in benzene solution has been studied kinetically. The rates are proportional to the product of the concentrations of stilbene and peroxyacid. The effect of substituents in the α -methylstilbenes and stilbenes⁴ have been discussed in terms of an asymmetric attack of peroxyacid on the double bond and the accessibility of the reagent or the magnitude of the resonance effect of the substituent. Also the effect of substituents on the peroxybenzoic acid has been estimated and these effects have been discussed in terms of the reactivity-selectivity relationships and the resonance contribution in the transition state.

Second-order kinetics have been observed for peroxyacid epoxidation of ethylenic compounds.¹ The reaction is subject to general acid catalysis

(1) (a) S. Medvedev and O. Blokh, *J. Phys. Chem. USSR*, **4**, 721 (1933); (b) D. Swern, *J. Am. Chem. Soc.*, **69**, 1692 (1947); (c) Ya. K. Syrkin and I. I. Moiseef, *Prog. Chem. USSR*, **29**, 425 (1960); (d) D. Swern, *Chem. Revs.*, **45**, 1 (1949); (e) S. L. Friess, *J. Am. Chem. Soc.*, **71**, 2571 (1949); see also D. Swern, "Organic Reactions," Vol. 7, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 378.

and a mechanism involving an attack of the peroxy acid molecule is preferable to that of OH⁺,^{2,3} because of the small salt effect and the dependence of product and/or rate on the nature of the peroxy acid. For peroxybenzoic acid (PBA), where no

(2) A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1574 (1948).
(3) F. L. Weisenborn and D. Taub, *J. Am. Chem. Soc.*, **74**, 1329 (1952).