Anal. Calcd. for $C_{10}H_7N_5$: C, 60.9; H, 3.6; N, 35.5. Found: C, 60.3; H, 3.6; N, 35.2.

2,3-Dicyano-7-hydroxy-5-methylpyrazole[2,3-*a*]pyrimidine.—A solution of 13.0 g. of 5-amino-3,4-dicyanopyrazole in 56 ml. of ethyl acetoacetate was heated at 150–160° until no more vapor was evolved. The mixture was then cooled and diluted with 100 ml. of ethanol, and the 2,3-dicyano-7-hydroxy-5-methylpyrazolo-[2,3-*a*]pyrimidine was collected, yield 13.3 g. (71%), m.p. >300°. An analytical sample was prepared by recrystallization from dimethylformamide–acetic acid.

Anal. Calcd. for $C_9H_5N_5O$: C, 54.3; H, 2.5; N, 35.2. Found: C, 54.4; H, 2.7; N, 35.0.

3-Chloro-4(5)-cyano-5(4)-carbamylpyrazole.—Sodium nitrite (14.0 g.) was added to 100 ml. of concentrated sulfuric acid, and the resulting mixture was heated with stirring at 70° until solution was complete. The solution was then cooled in ice and a suspension of 24 g. of 5-amino-3,4-dicyanopyrazole in 280 ml. of glacial acetic acid was added while the temperature was kept eblow 20°. After the mixture had been stirred for 30 min., a solution of 20 g. of cuprous chloride in 200 ml. of concentrated hydrochloric acid was added slowly. The resulting solution was stirred for an additional hour and diluted with 1 l. of water; the resulting solution was extracted with three 300-ml. portions of ethyl acetate. The ethyl acetate extracts were combined, washed with water, dried over magnesium sulfate, and evaporated to dryness. The yield of chloroamide after recrystallization from water was 7.4 g., m.p. 233–235°.

Anal. Calcd. for $C_5H_3N_4OCl$: C, 35.2; H, 1.7; N, 32.8; Cl, 20.8. Found: C, 35.1; H, 1.5; N, 32.8; Cl, 20.7.

3,4-Dicyanopyrazole.—The diazotization was carried out exactly as in the preparation of the chlorocyanopyrazolecarboxamide except that one-fourth the quantities were used. The solution of the diazonium compound was slowly added to 100 ml. of ethanol that contained 0.50 g. of copper sulfate and had been preheated to 60°. The resulting solution was boiled for 30 min., diluted with 400 ml. of water, and extracted with three 150-ml. portions of ethyl acetate. The ethyl acetate extracts were combined, dried over magnesium sulfate, and evaporated to dryness to give 3.1 g. of tan solid. The 3,4-dicyanopyrazole was difficult to purify further, and an analytical sample was prepared by recrystallization one time each from water and benzene and then by sublimation. After repeating this process, the melting point was 196–197°.

Anal. Calcd. for $C_5H_2N_4$: C, 50.8; H, 1.7; N, 47.5. Found: C, 50.9; H, 1.8; N, 47.4.

5(3)-Amino-3(5), 4-dicyano-1-methylpyrazole.—To a solution of 11.5 g. of sodium hydroxide in 50 ml. of water was added 33.3 g. of 5-amino-3,4-dicyanopyrazole, and 42 g. of dimethyl sulfate immediately after the pyrazole had dissolved. After 15 min., the solid that formed was collected and washed with water, yield 22.5 g. The filtrate deposited more solid upon standing and this (B) was collected, yield 5.5 g., m.p. 110–120°. The 22.5-g. sample was heated with 100 ml. of ethanol and filtered hot to remove the undissolved solid. This solid (18.0 g.) melted at 243–245° and the melting point was unchanged after recrystallization from dioxane.

Anal. Calcd. for $C_6H_5N_5$: C, 49.0; H, 3.4; N, 47.6. Found: C, 49.2; H, 3.6; N, 47.3.

B was recrystallized several times from ethanol and the melting point was raised to 128–130°. A mixture melting point determination with the tetracyanoethylene–methylhydrazine product (Table I) showed no depression of the melting point.

Acknowledgment.—We wish to acknowledge the discussion with Dr. W. J. Middleton which contributed to this work.

The Synthesis of 1*H*,3*H*-Thieno[3,4-*c*]thiophene[1,2]

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In order to study the effect of ring strain (Mills–Nixon effect) on the properties of five-membered heteroaromatics, the title compound, I, has been synthesized using a highly improved thiophene ring synthesis.

Although the Mills–Nixon[4] or ring-strain effect in indane derivatives recently[5,6] has been shown to be of little actual importance in changing the properties of the benzene ring, it seemed reasonable to expect a much larger effect by fusing the five-membered ring to a five-membered heterocyclic system. One fundamental question which might be resolved and which has received conflicting answers[6,7] thus far concerns in essence the bond order of the bond common to both rings.

To investigate the chemical and physical properties of some five-membered heteroaromatic systems fused to five-membered (or four-membered) rings, the synthesis of several compounds of type I and II has been undertaken.

I II

X = S, O, NR
Y = S, SO_2, NR, CR_2, O

This paper describes the synthesis of two compounds of type I, namely, 1*H*,3*H*-thieno[3,4-*c*]thiophene (I, X = Y = sulfur) and a derivative of 1*H*,3*H*-thieno-[3,4-*c*]thiophene 2,2-dioxide (I, X = S; Y = SO_2) by the reaction sequence outlined in eq. 1.

The reaction between biacetyl and diethyl thiodiacetate has been described[8] but furnished in our hands under the reaction conditions specified a nearly intractable tar. The desired diester could not be isolated, although 10–20% yields of the dibasic acid (IIIe) were realized. We discovered recently, however, in other work in progress in this laboratory,[9] that the reaction of α-diketones with glutaric ester analogs to furnish furans, thiophenes, and pyrroles[10]

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(1) Part I of a series of papers entitled "Steric effects in heterocyclic systems."

(2) Presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(3) Predoctoral Fellow of the Netherlands Organization for Pure Scientific Research (Z. W. O.).

(4) W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 2510 (1930).

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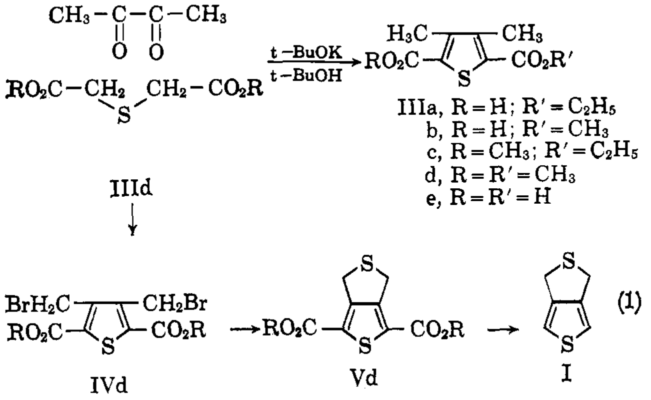


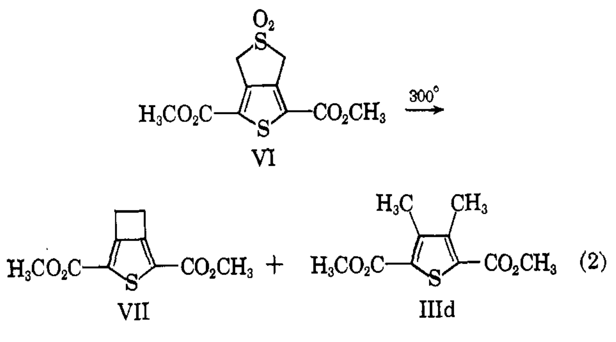
(1)

is a Stobbe-type[11] condensation proceeding *via* a δ-lactone intermediate. Utilizing the Stobbe–Johnson[11] conditions, *viz.*, potassium *t*-butoxide in *t*-butyl alcohol for a short (15–45 min.) time at room temperature, the monoester (IIIa) could be isolated in nearly quantitative yield by extraction with ammonia and acidification. The structure of the pure monoethyl ester, m.p. 232°, was supported by the elementary analysis and its conversion in high yield into the monomethyl monoethyl ester (IIIc), m.p. 93°. The n.m.r. spectrum of IIIc (see Experimental) was consistent with the structure assigned.

N-Bromosuccinimide bromination of the dimethyl ester (IIId) furnished the crystalline dimethyl 3,4-bisbromomethyl-2,5-thiophenedicarboxylate (IVd), m.p. 125°, in 71% yield. The latter could be cyclized to dimethyl 1*H*,3*H*-thieno[3,4-*c*]thiophene-4,6-dicarboxylate (Vd) using a freshly prepared sodium sulfide solution in anhydrous methanol. The thienothiophene, m.p. 163°, isolated in 58% yield as a pink[12] solid was converted to the dicarboxylic acid (Ve), m.p. >350°, by hydrolysis. The latter (Ve), also a pink solid and showing yellow fluorescence in alkaline solution, was decarboxylated using copper powder at 325° to furnish 1*H*,3*H*-thieno[3,4-*c*]thiophene (I), m.p. 61–62°. Its elemental analysis, n.m.r. spectrum in acetone (two singlets at τ 6.12 and 3.02, area ratio 2:1), and ultraviolet spectrum ($\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 232 mμ, ϵ 6100) are in accord with the structure assigned.

Oxidation of Vd with hydrogen peroxide in acetic acid gave the sulfone (VI), m.p. 199–200°, in 55% yield.

Initial attempts at conversion of VI and VII using methods described in the literature[13] were not successful, although the presence of 3,4-dimethyl thiophene-2,5-dicarboxylate (IIId) indicated that sulfur dioxide had been expelled.



(2)

In order to be able to compare the spectral properties of I with those of an appropriate model compound, 3,4-bis[(ethylthio)methyl]thiophene (VIII) was prepared according to the general scheme shown in eq. 1 (see Experimental for details).

Discussion

Since the publication in 1930 by Mills and Nixon[5] of the hypothesis of bond fixation in hydrindanes, considerable work has been done to substantiate or dispute this contention. Substitution reactions,[4] coupling reactions,[14] lactone formation,[15] ozonolysis,[16] hydrogenation,[17] epoxidation,[17] bromination,[18] and dehydrogenation[19] are all examples of reactions used to investigate the theory. In addition to the chemical reactivity, the studies have included an investigation of chelation behavior,[20,21] p*K* values of phenols,[22,23] and dipole moments.[24] Electron diffraction patterns,[25] oxidation–reduction potentials,[26] heats of hydrogenation,[27] and ultraviolet absorption measurements[28] have been made. Several quantum mechanical treatments have been given.[7,29] It is evident from a review of these studies that no single theory satisfactorily explains the many experimental results obtained. This is not surprising since some phenomena are a measure of differences in the stability or reactivity in the ground state, others of the transition state, while still others compare the (electronically) excited states. Furthermore, since it appears that the ring-strain effect one attempts to evaluate is, at best, a rather small effect, additional parameters such as entropies of activation and solvation influences may well obscure any trend. In certain recent cases, however, steric effects in π-electron systems have markedly altered the properties of the conjugated system as evidenced

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(11) W. S. Johnson and G. H. Daub, *Org. Reactions*, **6**, 1 (1951).

(12) Analytically pure diester (Vd) retained this characteristic pink ($\lambda_{\max}$ *ca.* 500 mμ in CH_2Cl_2) color, even after sublimation and chromatography.

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(16) L. Long and L. F. Fieser, *J. Am. Chem. Soc.*, **62**, 2670 (1940); J. P. Wibaut and F. P. K. de Jong, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **59B**, 285 (1956).

(17) E. Giovannini and H. Wegmüller, *Helv. Chim. Acta*, **41**, 933 (1958); **42**, 1142 (1959).

(18) N. MacLeish and N. Campbell, *J. Chem. Soc.*, 1103 (1937).

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(23) R. T. Arnold and R. L. Evans, *J. Am. Chem. Soc.*, **62**, 556 (1940).

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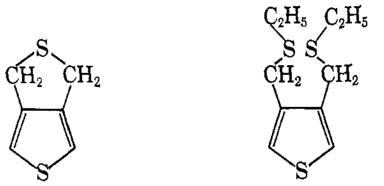
(29) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942); F. Seel, *Angew. Chem.*, **60**, 300 (1948); B. Pullman, *Bull. soc. chim. France*, **14**, 337 (1947); G. Berthier and A. Pullman, *ibid.*, **17**, 88 (1950).

by chemical reactivity[30] or spectral behavior,[31] thus encouraging further research in this direction.

The pertinent physical properties of the two compounds are listed below. Chart I shows that although the effects are not large they are consistent with the hypothesis that the five-membered ring in the thienothiophene has perturbed the aromaticity of the thiophene ring. The hypsochromic shift from the characteristic thiophene absorption at 245–250 mμ towards that of a diene chromophore and the weakening of the ring current effect as evidenced by the n.m.r. absorption at higher field both indicate that this perturbation may well be caused by diminished π-orbital overlap.

CHART I[a]



[a] Ultraviolet, $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ mμ (ε): 232 (6100) and 246 (5600), respectively. N.m.r. (acetone), aromatic protons (sweep width 50 c. p. s.): τ 3.02 and 2.75, respectively.

Experimental

N.m.r. spectra were determined on a Varian A-60 using tetramethylsilane (TMS) (τ 10) as internal standard, ultraviolet spectra in 95% alcohol using a Zeiss PMQ II, infrared spectra on a Perkin-Elmer Infracord or Model 125. Microanalyses were made by W. M. Hazenberg of this department. Melting points are uncorrected.

3,4-Dimethylthiophene-2,5-dicarboxylic Acid Monoethyl Ester (IIIa).—Using the apparatus for carrying out Stobbe condensations under nitrogen described by Johnson and Daub,[11] 77.0 g. of diethyl thiodiacetate [0.375 mole, b.p. 135–136° (10 mm.)] and 48.2 g. of diacetyl (0.56 mole, b.p. 88°) were added simultaneously as rapidly as possible to a stirred solution containing 30.0 g. of potassium (0.77 g.-atom) in 0.5 l. of dry *t*-butyl alcohol; during the addition the reaction mixture was cooled in an ice bath. The solution turned dark almost at once. Stirring was continued for 45 min. While cooling in ice the solution was acidified with 120 ml. of dilute (1:1) hydrochloric acid and most of the alcohol was removed *in vacuo*. Water was added, the organic material was extracted with ether, and the ether was extracted with five 200-ml. portions of 2.5% ammonia solution. Acidification with dilute hydrochloric acid furnished a tan solid which was removed by filtration and dried, yielding 86.0 g. of IIIa (~100%), m.p. 175–200°. Recrystallization from acetic acid gave 43.0 g. (50% based on thiodiacetate) of almost pure monoester, m.p. 228–230°. The analytical sample melted at 231–232.5° after further crystallizations from acetic acid and from chloroform; ultraviolet absorption: $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 209, 280 mμ (ε 11,000, 15,800).

Anal. Calcd. for $C_{10}H_{12}O_{,}S$ (mol. wt. 228.86): C, 52.60; H, 5.30; S, 14.05. Found: C, 52.4, 52.6; H, 5.0, 4.9; S, 13.9, 13.9.

The structure was confirmed by conversion to the methyl ethyl ester (IIIc) with diazomethane. A sample, recrystallized from methanol, melted at 93–94°; n.m.r. spectrum (in chloroform): two sharp singlets at τ 7.56 and 6.15, one triplet (τ 8.76, 8.64, 8.52), one quadruplet (τ 5.84, 5.72, 5.61, 5.49), area ratio 6:3:3:2; ultraviolet spectrum: $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 209, 280 mμ (ε 12,000, 17,500).

Anal. Calcd. for $C_{11}H_{14}O_4S$ (mol. wt. 242.29): C, 54.55; H, 5.82; S, 13.22. Found: C, 54.5, 54.7; H, 5.7, 5.6; S, 13.1, 13.1.

The dimethyl ester (IIId) was prepared from the monoethyl ester by passing a stream of dry hydrogen chloride through a solution containing 22.8 g. (0.10 mole) of the monoester in 0.5 l. of absolute methanol for 4 hr. The reaction was completed by heating the solution for 2 hr. under reflux. Cooling furnished a solid which was removed by filtration and recrystallized from carbon tetrachloride yielding 17.5 g. (77%) of the dimethyl ester (IIId), m.p. 170–171°; n.m.r. spectrum: two sharp singlets at τ 7.56 and 6.15 (chloroform), area ratio 1:1; ultraviolet spectrum: $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 209, 280 mμ (ε 11,400, 16,500).

Anal. Calcd. for $C_{10}H_{12}O_4S$ (mol. wt. 228.26): C, 52.60; H, 5.30; S, 14.05. Found: C, 52.8; 52.8; H, 5.4, 5.3; S, 13.6, 13.6.

Using dimethyl thiodiacetate, the monomethyl ester (IIIb), m.p. 230–231.5°, was prepared as described above in 51% yield (~100% crude yield) and converted to the dimethyl ester (IIId), m.p. 170–170.5°, in 94% yield, using diazomethane.

3,4-Bis(bromomethyl)thiophene-2,5-dicarboxylic Acid Dimethyl Ester (IVd).—The diester (IIId, 22.8 g., 0.10 mole) was dissolved in 200 ml. of dry, hot carbon tetrachloride and 35.6 g. (0.20 mole) of N-bromosuccinimide[32] (NBS) was added, followed by 0.3 g. of dibenzoyl peroxide. The mixture was heated to boiling on a steam bath and shaken occasionally. After 40 min., the NBS had disappeared and succinimide was suspended in the organic layer. It was removed by filtration of the warm solvent. Concentration of the solvent furnished 27.4 g. (71%) of IVd, m.p. 124.5–126°, as colorless crystals after recrystallizations from methanol and from petroleum ether (b.p. 60–80°); n.m.r. spectrum: two sharp singlets at τ 4.98 and 6.05 (in chloroform), area ratio 2:3; ultraviolet spectrum: $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 234, 282.5 mμ (ε 19,900, 12,100).

Anal. Calcd. for $C_{10}H_{10}BrO_4S$ (mol. wt. 386.09): C, 31.11; H, 2.61; Br, 41.40; S, 8.30. Found: C, 31.5, 31.3; H, 2.6, 2.6; Br, 41.7, 41.5; S, 8.6, 8.4.

1*H*,3*H*-Thieno[3,4-*c*]thiophene-4,6-dicarboxylic Acid Dimethyl Ester (Vd).—Using 2.53 g. (0.11 g.-atom) of sodium dissolved in 50 ml. of dry methanol, a dry sodium sulfide solution was prepared in the usual manner.[33] To the boiling solution was added during 1 hr. a warm solution of the dibromide (19.3 g., 0.05 mole) in 400 ml. of dry methanol. The solution was heated under reflux for an additional 1.5 hr. whereupon the solid was removed from the cooled mixture. Recrystallization from tetrahydrofuran–ether (3:1) furnished 7.5 g. (58%) of pink[12] needles, m.p. 163–164°, of pure Vd; n.m.r. spectrum: two singlets at τ 5.85 and 6.12 (in chloroform), area ration 2:3; ultraviolet spectrum: $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 205, 278 mμ (ε 14,000, 21,000).

Anal. Calcd. for $C_{10}H_{10}O_4S_2$ (mol. wt. 258.31): C, 46.49; H, 3.90; S, 24.83; Found: C, 46.4, 46.2; H, 3.9, 3.9; S, 24.3, 24.4.

The free dicarboxylic acid (Ve, R = H), m.p. >350°, was obtained as a pink solid upon hydrolyzing the ester (Vd, R = CH_3) by refluxing for 5 hr. with potassium hydroxide solution to which 5% methanol was added. The alkaline solution showed yellow fluorescence.

1*H*,3*H*-Thieno[3,4-*c*]thiophene (I).—The pink dicarboxylic acid (Ve, 460 mg., 2 mmoles) was mixed with 150 mg. of copper powder and the mixture was heated to 325° in a sublimation apparatus. A colorless solid deposited on the cold finger (cooled with a Dry Ice–acetone mixture) and was purified by a second sublimation at 55° (0.2 mm.), furnishing 88 mg. (31%) of 1*H*,3*H*-thieno[3,4-*c*]thiophene (I), m.p. 61–62°; n.m.r. spectrum: two singlets at τ 6.12 and 3.02 (in acetone), area ratio 2:1; ultraviolet spectrum: $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 232 mμ (ε 6,100); infrared spectrum: strongest absorption at 784 cm.⁻¹ (KBr).

Anal. Calcd. for $C_6H_6S_2$ (mol. wt. 142.24): C, 50.67; H, 4.25; S, 45.08. Found: C, 50.9, 50.9; H, 4.3, 4.2; S, 45.0.

3,4-Bis[(ethylthio)methyl]thiophene (IX).—The sodium salt of ethyl mercaptan was prepared by adding under ice cooling, 3.10 g. [0.05 mole, b.p. 34.5–35° (760 mm.)] of ethyl mercaptan to a solution containing 1.15 g. (0.05 g.-atom) of sodium in 50 ml. of absolute methanol. A solution of 7.72 g. (0.02 mole) of 3,4-bis(bromomethyl)thiophene-2,5-dicarboxylic acid dimethyl ester (IVd) in 100 ml. of dry benzene was added in the cold. Sodium bromide precipitated from the solution which was heated under reflux for 1 hr. after the addition was complete. After removal of the salt by filtration and of the solvent by

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(30) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **84**, 3789 (1962).

(31) H. Wynberg, A. de Groot, and D. W. Davies, *Tetrahedron Letters*, **No. 17**, 1083 (1963).

(32) Freshly prepared according to the direction of L. Horner and E. H. Winkelmann ("Neuere Methoden der präp. org. Chemie," Vol. III, Verlag Chemie, Berlin, 1961, p. 98).

(33) R. W. Bost and M. W. Conn, *Org. Syn.*, **15**, 72 (1935).

evaporation, the residue was washed thoroughly with water. These aqueous extracts contained monoester, m.p. 137–139°, and dibasic acid, m.p. 235–240°. The water insoluble portion was recrystallized from methanol–water (4:1) to furnish 3.81 g. (55%) of **3,4-bis[(ethylthio)methyl]thiophene-2,5-dicarboxylic acid dimethyl ester**, m.p. 79.5–80.5°; n.m.r. spectrum ($CHCl_3$): singlets at τ 5.67 and 6.10, triplet at τ 8.62, 8.75, and 8.88, and quadruplet at τ 7.28, 7.40, 7.52, and 7.63, area ratio 2:3:3:2; ultraviolet spectrum: $\lambda_{max}^{95\%\ EtOH}$ 218, 277 mμ (ϵ 22,000, 17,000).

Anal. Calcd. for $C_{14}H_{20}O_4S_3$ (mol. wt. 348.51): C, 48.25; H, 5.78; S, 27.61. Found: C, 47.8, 48.1; H, 5.9, 5.8; S, 27.3, 27.3.

After hydrolysis to the decarboxylic acid, m.p. 235–240°, the decarboxylation was carried out by heating 6.50 g. (0.0203 mole) of the diacid with 2 g. of copper powder in 50 ml. of quinoline. Carbon dioxide evolution commenced at 220°. Removal of the quinoline (from the distillate) with hydrochloric acid and distillation furnished 2.30 g. of VIII as a straw-colored liquid, b.p. 182–183° (15 mm.), $n^{20}{}_D$ 1.5840. 3,4-Bis[(ethylthio)methyl]-thiophene (VIII) was obtained as a colorless liquid, $n^{20}{}_D$ 1.5823, after passage over alumina; n.m.r. spectrum: singlets at τ 6.26 and 3.02, triplet at τ 8.68, 8.80, and 8.92, and quadruplet at τ 7.44, 7.55, 7.70, and 7.80; area ratio 2:1:3:2 (in CCl_4); ultraviolet spectrum: $\lambda_{max}^{95\%\ EtOH}$ 246 mμ (ϵ 5,600); infrared spectrum: strongest absorption 801 cm.$^{-1}$ (neat).

Anal. Calcd. for $C_{10}H_{16}S_3$ (mol. wt. 232.44): C, 51.67; H, 6.94; S, 41.39. Found: C, 52.2; H, 6.9; S, 40.9.

A mercurichloride derivative, m.p. 111–112° (70% ethanol), was prepared in 90% yield.

1*H*,3*H*-Thieno[3,4-*c*]thiophene-4,6-dicarboxylic Acid Dimethyl Ester 2,2-Dioxide (VI).—A solution containing 2.58 g. (0.01 mole) of Vd in 30 ml. of glacial acetic acid was heated with 3.06 ml. (0.03 mole) of a 30% hydrogen peroxide solution. The solution was refluxed for 30 min., causing disappearance of the pink color. Upon addition of water to the reaction mixture VI precipitated. Recrystallization of the solid (1.5 g., 55% yield) from benzene–petroleum ether (4:1) furnished the sulfone (VI) as colorless crystals, m.p. 199–200°; n.m.r. spectrum ($CHCl_3$): singlets at τ 5.52 and 6.08, area ratio 2:3.

Anal. Calcd. for $C_{10}H_{10}O_6S_2$ (mol. wt. 290.31): S, 22.09. Found: S, 21.7.

Pyrolysis of VI at 350° in a sublimation apparatus using copper powder or over a heated coil (500°)[13] furnished as the only identifiable product 3,4-dimethylthiophene-2,5-dicarboxylic acid dimethyl ester (infrared spectrum identical with that of IIIc, undepressed mixture melting point).

Mechanisms of Photochemical Reactions in Solution. XXIV.[1] Photochemical and Catalytic Decomposition of Diazoacetophenone

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Diazoacetophenone has been decomposed under a variety of conditions. The sensitized and direct photochemical decomposition both appear to produce the triplet ketocarbene which adds to *cis*- and *trans*-2-butene in a nonstereospecific manner. The ketocarbene is relatively unreactive and exhibits radical properties as characterized by the large amounts of bicyclohexenyl and acetophenone produced in the direct and sensitized photolysis of diazoacetophenone in cyclohexene. Phenacyl chloride was formed in addition to the expected cyclopropanes when metal chlorides were used to catalyze the reaction of diazoacetophenone with olefins.

When diazomethane is photochemically decomposed in solutions the resulting methylene reacts in a stereospecific manner with olefins[4,5] and gives indiscriminate insertion to hydrocarbons.[6,7] These properties are consistent with assigning the singlet state to methylene produced under these conditions. The singlet–triplet decay of methylene has not yet been observed in solution because of the extreme reactivity of methylene, but this decay has been postulated for the gas phase photolysis of diazomethane to explain both spectroscopic[8] and chemical results.[9] The only manner in which triplet methylene has been prepared in solution is by the photosensitized decomposition of diazomethane.[7]

In this process, benzophenone is selectively excited to a singlet state, whereupon intersystem crossing takes place to produce excited triplet benzophenone with the nearly unit efficiency. The triplet benzophenone can then transfer its energy (with conservation of spin angular momentum) to ground singlet diazomethane molecules to generate diazomethane in the excited triplet state. The triplet diazomethane then decomposes to give methylene which reacts as predicted for triplet methylene.

The synthetic importance of the photochemical decomposition of substituted diazomethanes (diazo ketones) has been recently emphasized by Meinwald's synthesis of D-norsteroids[10] and the reinvestigation of the photolysis of diazocamphor.[11]

The photochemical decomposition of diazo ketones is intriguing because of the possibility that the triplet ketomethylene could be produced upon direct irradiation. The result is predicted as a consequence of the high rates of intersystem crossing by carbonyl compounds in general.

Results and Discussion

The photolysis of diazoacetophenone in solution gave only traces of the dilactone (m.p. 268–270°) which Wiberg[12] obtained from the photolysis of solid diazoacetophenone. This is reasonable since the postulated mechanism for the formation involves the bimolecular reaction of either diazoacetophenone or the corresponding ketomethylene with phenylketene. The principal products from the direct and sensitized photolysis of diazoacetophenone in cyclohexene were 3,3′-bicyclohexenyl, acetophenone (70% yield), and 7-norcaryl

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