that these manipulations served to separate quantitatively sodium *p*-nitrobenzoate and the starting *p*-nitrobenzoate esters. At the end of the kinetic runs, weighed samples of internal standards were added to the remaining reaction solutions and the mixtures were partitioned between ether and aqueous sodium carbonate. After the ether layers had been dried and concentrated, they were analyzed by gas chromatography.[19] To obtain the first-order rate constants of these solvolyses, plots of time *vs.* log of the *p*-nitrobenzoate concentration were prepared and the slopes were determined graphically. The values given are average values obtained from two different runs.

B. 9β-(4-Nitrobenzoyloxy)-3-azabicyclo[3.3.1]nonane (11).—The average first-order rate constant was $1.2 \pm 0.4 \times 10^{-6}$ sec^{-1}. The only neutral or basic product detected by gas chromatography[19] and thin layer chromatography[26] was the β-hydroxyamine **15**. The crude product from a solvolysis mixture was partitioned between ether and aqueous hydrochloric acid and then the aqueous phase was made basic with sodium hydroxide and extracted with ether. After this ethereal extract had been dried and concentrated, sublimation of the residue afforded the pure amino alcohol **15**, mp 93–93.5°, which was identified with an authentic sample by a mixture melting point determination and by comparison of infrared and mass spectra. A weighed amount of internal standard (*p*-dimethoxybenzene) was added to the crude product from a reaction which had gone to 91% of completion. The yield of amino alcohol **15** was calculated from the gas chromatograph of this mixture to be 79%.

C. 9α-(4-Nitrobenzoyloxy)-3-azabicyclo[3.3.1]nonane (8).—The average first-order rate constant was $4.4 \pm 0.9 \times 10^{-7}$ sec^{-1}. The only neutral or basic product detected by gas chromatography[19] was the α-hydroxyamine **16**; a sample of this product **16**, isolated as was described in the previous experiment, melted at 92.5–94°, and was identified with an authentic sample by a mixture melting point determination and by comparison of infrared and mass spectra. The calculated[19] yield (*p*-dimethoxybenzene internal standard) of the amino alcohol **16** from a reaction which had gone to greater than 99% completion was 82%.

D. 9α-(4-Nitrobenzoyloxy)-9β-methyl-3-azabicyclo[3.3.1]nonane (9).—The average first-order rate constant was $1.2 \pm 0.1 \times 10^{-5}$ sec^{-1}. An additional reaction was run under the exact conditions of a kinetic run except that a weighed amount of naphthalene was added as an internal standard. The crude neutral and basic materials present in the reaction mixture were analyzed by gas chromatography.[19] The calculated yields of products were dimethylamine **19** (first eluted), 35%; monomethylamine **18** (second eluted), 48%; β-hydroxyamine **17** (eluted third), 1%; and α-hydroxyamine **20** (eluted fourth), 16%. A minor unidentified component (eluted fifth) was also detected but neither of the benzylamines **36** or **37** nor unsaturated amine **49** was detected. The analogous crude product mixture from one of the kinetic runs (which did not contain an internal standard) had a similar composition,[19] namely, **19** (38%), **18** (41%), **17** (3%), and **20** (16%). Three additional unidentified minor components (total 2%) were also detected. Collected[19] samples of each of the amines **17–20** were identified with previously described authentic samples by comparison of gas chromatographic retention times and infrared and mass spectra. In a subsequent experiment to learn the effect of excess triethylamine on the amount of tertiary amine **19**, an aqueous dioxane (4:6 by volume) solution which was 0.010 *M* in the *p*-nitrobenzoate **9** and 0.030 *M* in triethylamine was heated to 89° for 117 hr at which time the solvolysis of the ester **9** was at least 98% complete. The crude mixture of basic and neutral products contained[19] 54% dimethylamine **19**, 43% monomethylamine **18**, and 3% amino alcohol **20**; the calculated yields were 34% **19**, 27% **18**, and 2% **20**.

E. 9β-(4-Nitrobenzoyloxy)-9α-methyl-3-azabicyclo[3.3.1]nonane (12).—The average first-order rate constant was $2.8 \pm 0.6 \times 10^{-6}$. After a weighed amount of naphthalene (as an internal standard) had been added to the reaction mixture from one of the kinetic runs, the crude mixture of basic and neutral products was separated and analyzed by gas chromatography.[19] The calculated yields were bicyclic amine **49** (eluted first), 39%; dimethylamine **19** (eluted second), 13%; β-hydroxyamine **17** (eluted third), 20%; and α-hydroxyamine **20** (eluted fourth), 2%. Thus, the composition[19] of the product mixture was **49**, 53%; **19**, 17%; **17**, 20%; and **20**, 3%. In another run where no internal standard was present, the composition[19] of the product mixture was **49**, 39%; **19**, 13%; **18**, 7%; **17** and **20** (not resolved), 41%. Collected samples of amines **49**, **19**, and **17** were identified with previously described authentic samples by comparison of gas chromatographic retention times and infrared and mass spectra.

F. 9β-(4-Nitrobenzoyloxy)-9α-phenyl-3-azabicyclo[3.3.1]nonane (13).—The average first-order rate constant was $2.1 \pm 0.1 \times 10^{-3}$ sec^{-1}. The crude basic and neutral product from one run contained[19] a minor unidentified component (eluted first), 1%, the dimethylamine **22** (eluted second), 20%, and the monomethylamine **21** (eluted third), 79%, but neither of the aromatic derivatives **42** or **43** was detected. The calculated yields[19] from another run containing an internal standard (biphenyl) were 20% **22** and 79% **21**. Collected[19] samples of the two unsaturated amines **21** and **22** were identified with previously described samples by comparison of gas chromatographic retention times and infrared, mass, and nmr spectra.

G. 9α-(4-Nitrobenzoyloxy)-9β-phenyl-3-azabicyclo[3.3.1]nonane (10).—The average first-order rate constant was $3.2 \pm 0.6 \times 10^{-3}$ sec^{-1}. The crude basic and neutral product from one run contained[19] 43% of the dimethylamine **22** and 52% of the monomethylamine **21** as well as 5% of two more rapidly eluted, unidentified components. As in the previous case, neither of the benzylamines **42** or **43** was detected. From another run containing an internal standard (biphenyl), the calculated[19] yields were 12% **22** and 88% **21**. Collected[19] samples of each of the amines **21** and **22** were identified with previously described authentic samples by comparison of gas chromatographic retention times and infrared and mass spectra.

(26) The thin layer chromatograms were obtained on plates coated with silicic acid and eluted with methanol–ethyl acetate mixtures.

The 1,2-Dithiolium Cation. VI.[1a] New Dithioles and No-Bond Resonance Compounds

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New evidence is presented on the condensation of dithiolium salts with carbonyl compounds. Chlorination of the products is discussed. Compound XIII may represent a new class of thiothiophthene derivative. Spectral and chemical evidence indicates a new form of no-bond resonance stabilization in the anions of XII and XIII.

An earlier paper in this series describes the condensation of 1,2-dithiolium salts with aryl methyl and aryl benzyl ketones to give acylmethylenedithioles (II) convertible to thiothiophthenes (III) by reaction with phosphorus pentasulfide. In the mechanism suggested for the condensation reaction, acylmethyldithioles (I) are formed, but not isolated, since they undergo immediate dehydrogenation to II at the expense of additional dithiolium salt.[1b] The proposed formation

(1) (a) Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 29, 1966; paper V, E. Klingsberg, *J. Heterocyclic Chem.*, **3**, 243 (1966); (b) paper IV, E. Klingsberg, *J. Am. Chem. Soc.*, **85**, 3244 (1963).

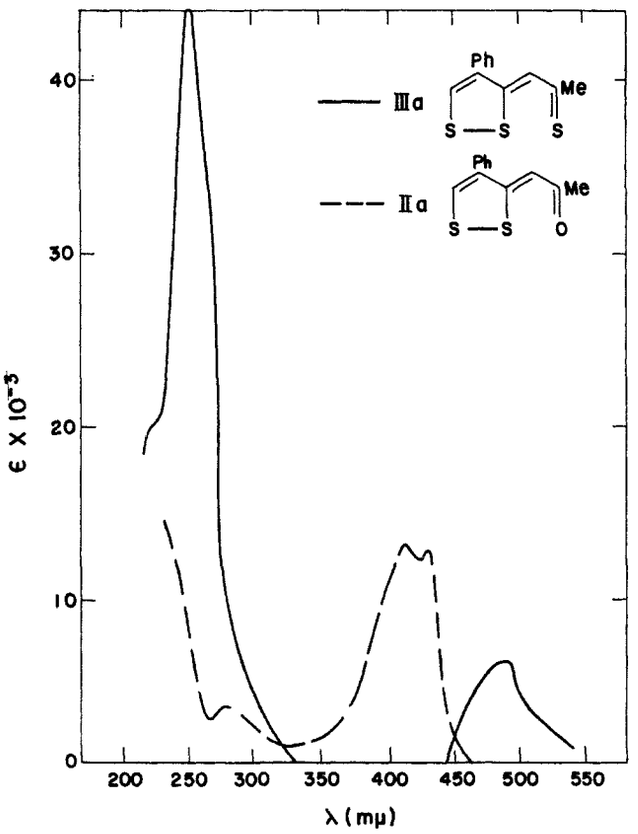


Figure 1.—Ultraxiolet spectra of IIa and IIIa in alcohol.

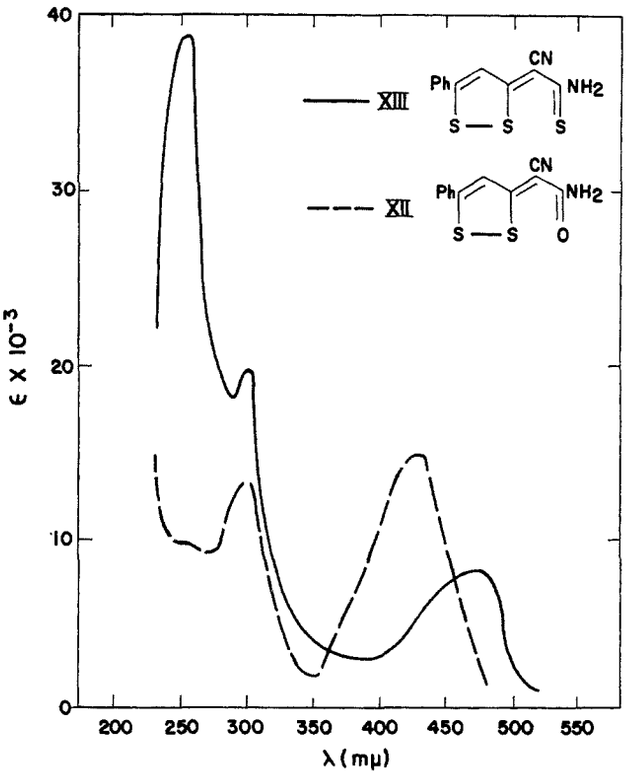
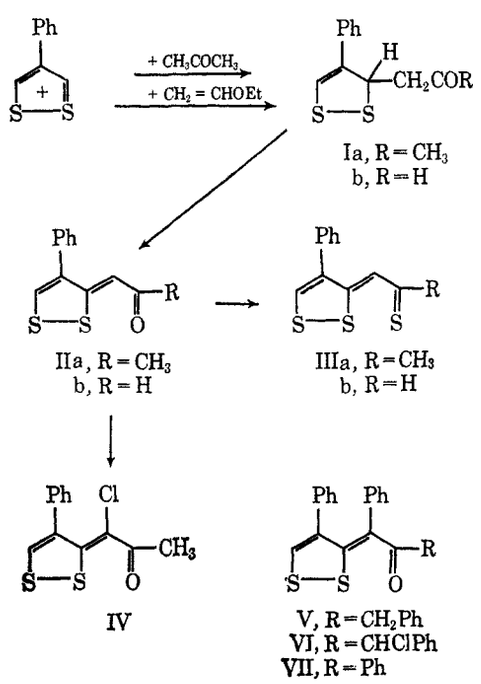


Figure 2.—Ultraviolet spectra of XII and XIII in alcohol.

and dehydrogenation of compounds of structure I have now been confirmed.

The condensation of 4-phenyl-1,2-dithiolium salts with acetone (unlike aryl ketones) is not accompanied by dehydrogenation. The product (Ia) is stable under

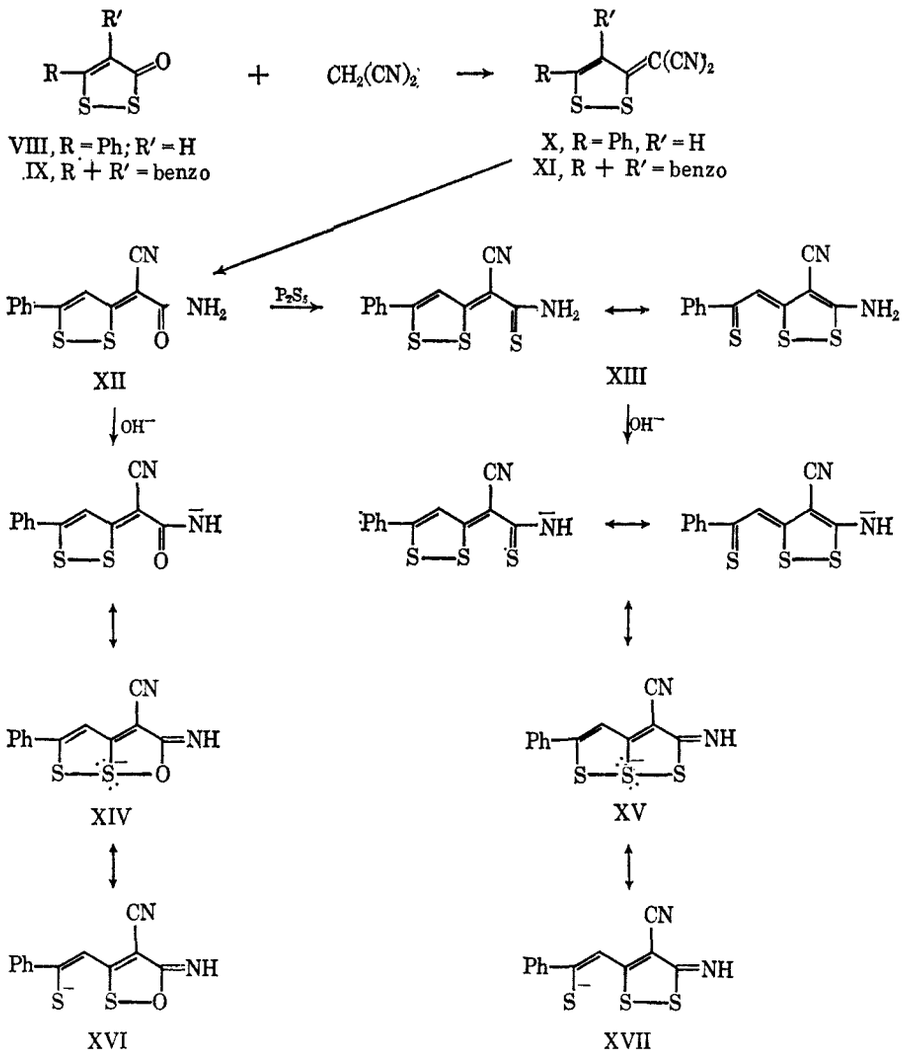


the conditions of the reaction but is smoothly dehydrogenated to IIa by chloranil, which can be employed *in situ* if desired. The dehydrogenation extinguishes the strong 6-μ carbonyl band shown by Ia; like other acylmethylenedithioles, IIa lacks normal infrared carbonyl absorption. It does, however, readily form a 2,4-dinitrophenylhydrazone; in this it resembles an aldehyde rather than an aryl ketone in the series. It reacts smoothly with P_2S_5 in benzene to give the thiothiophthene IIIa. This shows the typical electronic absorption, with a strong peak in the ultraviolet at 252 mμ (ϵ 44,400) and a weaker peak in the visual at 484 mμ (ϵ 6300). The precursor IIa absorbs much more weakly in the 250-mμ region, and more strongly in the visual but at lower wavelength than IIIa, with a double peak at 410 mμ (ϵ 13,300) and 427 mμ (ϵ 12,900). The two spectra (Figure 1) conform closely to the pattern that is evidently characteristic of the series.[2,3]

Acetaldehyde would not condense with dithiolium salts, but ethyl vinyl ether, which is, of course, a derivative of the enolic form of acetaldehyde, condensed smoothly with 4-phenyl-1,2-dithiolium hydrogen sulfate in aqueous solution, giving Ib. This reaction is known in the tropylium series.[4] Like Ia, the aldehyde Ib is smoothly dehydrogenatd by chloranil with loss of carbonyl absorption in the infrared. The product (IIb) reacts smoothly with P_2S_5 in benzene to give the phenylthiothiophthene IIIb; this resembles IIIa in its absorption, with peaks at 260 and 483 mμ.

Thiothiophthenes have not been successfully halogenated, but their acylmethylenedithiole precursors are smoothly chlorinated by sulfuryl chloride at room temperature if a position α to the carbonyl group is available. The position of substitution is easily shown by proton nmr. Compound IIa absorbs at δ 2.18 (relative area 3, methyl protons), 6.59 (relative area 1, olefinic proton), and 7.71 (relative area 1, heterocyclic proton).

(2) H. Behringer, M. Ruff, and R. Wiedenmann, *Chem. Ber.*, **97**, 1732 (1964).
(3) H. Behringer and D. Weber, *ibid.*, **97**, 2567 (1964).
(4) M. E. Vol'pin, I. S. Akhrem, and D. N. Kursanov, *Zh. Obshch. Khim.*, **30**, 159 (1960); *Chem. Abstr.*, **54**, 22535*h* (1960).



In V, which lacks the olefinic proton, absorption occurs at δ 7.77 (relative area 1, heterocyclic proton) and 3.65 (relative area 2, methylene protons). Now the chlorination product of IIa is IV, since the olefinic proton absorption disappears, while the methyl (δ 2.35, relative area 3) and heterocyclic (δ 7.79, relative area 1) protons are almost unchanged. The chlorination product of V is VI, since the heterocyclic proton is almost unchanged (δ 7.85, relative area 1) and the methylene absorption is replaced by a downfield methine peak (δ 5.58, relative area 1).

The attempt to introduce a second chlorine atom into VI was unsuccessful. The triphenyl compound VII, with no α position, also resists chlorination; it was recovered unchanged after treatment with sulfuryl chloride. Thiothiophthenes such as IIIa are converted under these conditions to intractable pitch, and the attempt to obtain a chlorinate thiothiophthene from IV was also unsuccessful; it was recovered unchanged after treatment with P_2S_5 in benzene.

A group of related compounds has been obtained from 5-phenyl-1,2-dithiol-3-one (VIII). Condensation with malononitrile in phosphorus oxychloride gave the dinitrile (X). (The corresponding reaction with benzoylacetonitrile has been reported.[1b]) 4,5-Benzodithiol-3-one (IX) similarly gave XI. Alkaline hydrolysis of X gave the amide XII, with absorption maxima at 303 mμ (ϵ 13,500) and 425 mμ (ϵ 15,350), respectively. Reaction of XII with P_2S_5 gave the thioamide (XIII), with maxima at 252 mμ (ϵ 39,100), 297 (19,600), and 465 (8200), respectively. The two spectra are shown in Figure 2; the pattern resembles Figure 1 so closely as to suggest that XIII represents a new class of no-bond resonance compounds, *i.e.*, an amine of the thiothiophthene series. Functionally, the compound is acidic rather than basic and is unexpectedly stable to aqueous alkali at the boil. It seems plausible that no-bond resonance contributes, *via* sulfur d-orbital expansion (XV), to electron delocalization favoring acidity and resistance to hydroxide ion attack. The acidity of the amide XII is even more anomalous; it is likewise stable to boiling alkali. Ultraviolet absorption spectra suggest a similar explanation, electron delocalization *via* structure XIV. The spectra of XII and XIII are entirely different (Figure 2) and are unchanged by acid but completely changed by base and now resemble each other closely (Figure 3). Each has one peak at 405 mμ; ϵ for XII is 17,400 and for XIII is 14,200. The similarity is exceptional if not unprecedented for sulfur–oxygen isologs of any known type and suggests an anionoid no-bond resonance system that admits an oxygen atom interchangeably with sulfur (XIV, XV). Other forms (XVI, XVII) might contribute but could hardly account for the base stability or spectral similarity.[5] In thiothiophthene, replacement of a sulfur atom

(5) Replacement of O by S in ordinary heteroaromatic systems causes distinct spectral shifts; *cf.* A. Cerniani and R. Passerini, *J. Chem. Soc.*, 2261 (1954).

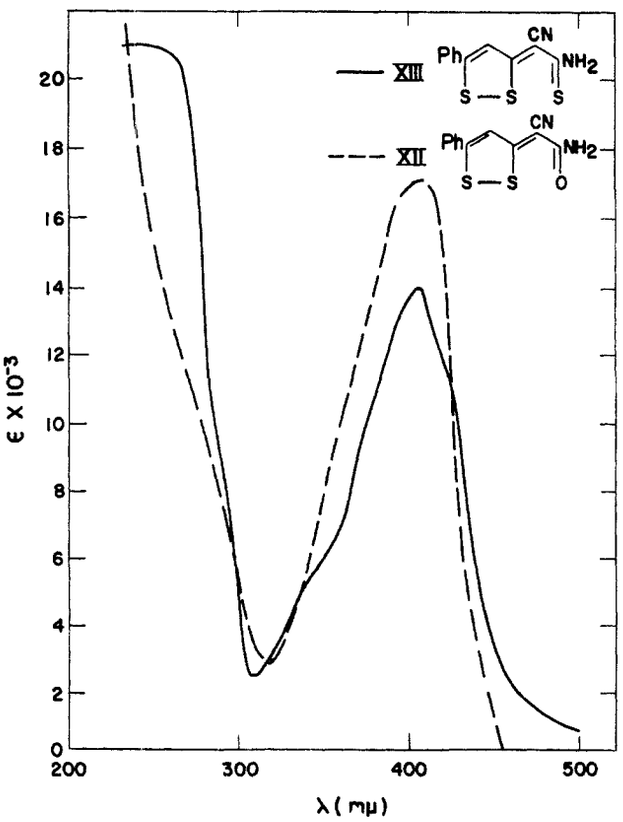


Figure 3.—Ultraviolet spectra of XII and XIII in 0.01 *N* alcoholic NaOH.

by oxygen causes a deep-seated change shown by bond distances[6a] and spectra (Figure 1).[2,3] As in the thiothiophthene case, X-ray determinations of bond distances are of course needed for conclusive demonstration of the structures of XII, XIII, and their anions. In a recent communication,[6b] Behringer and Wiedenmann have reported a different synthesis of XIII and proposed that it is a thiothiophthene derivative.

Experimental Section

Melting points are corrected. Ultraviolet and visible spectra were measured at 10-mg/l. concentration in alcohol; pmr spectra were measured in deuteriochloroform or carbon tetrachloride.

4,6-Epidithio-5-phenyl-5-hexenone-2 (Ia).—4-Phenyl-1,2-dithiolium hydrogen sulfate[7] (4.0 g, 0.014 mole) was refluxed for 2.5 hr in 300 ml of acetone and 250 ml of isopropyl alcohol. Evaporation to dryness at room temperature followed by crystallization from hexane gave 1.8 g (53%) of yellow product, mp 77.5–78.5°. This compound shows a strong carbonyl absorption at about 1680 cm^{-1}.

Anal. Calcd for $C_{12}H_{12}OS_2$: C, 61.01; H, 5.12; S, 27.10. Found: C, 61.04; H, 5.01; S, 27.48.

Yields were lower when the reaction was run on a larger scale.

4,6-Epidithio-5-phenyl-3,5-hexadienone-2 (IIa).—4-Phenyl-1,2-dithiolium hydrogen sulfate (10.0 g, 0.036 mole) was refluxed for 2.5 hr in 750 ml of acetone and 550 ml of isopropyl alcohol. Chloranil (8.8 g, 0.035 mole) was then added, refluxing was continued 0.5 hr longer, and the mixture was evaporated to dryness at room temperature. The orange product was isolated by Soxhlet extraction with petroleum ether (bp 35–60°) or hexane and then crystallized from isopropyl alcohol, mp 118–119°, yield 5.0 g (60%). It shows no absorption in the carbonyl region above 1600 cm^{-1}.

Anal. Calcd for $C_{12}H_{10}OS_2$: C, 61.54; H, 4.30; S, 27.33. Found: C, 61.50; H, 4.50; S, 27.57.

The yellow-brown 2,4-dinitrophenylhydrazone was prepared in methanol containing a little concentrated HCl and crystallized from ethanol, mp 162–164°.

Anal. Calcd for $C_{18}H_{14}N_4O_4S_2$: C, 52.18; H, 3.41; N, 13.52; S, 15.44. Found: C, 52.12; H, 3.52; S, 15.35; N, 13.54.

The proton nmr spectrum of IIa showed absorption at δ 2.18 (relative area 3, methyl protons), 6.59 (relative area 1, olefinic proton), 7.39 (relative area 5, phenyl protons), and 7.71 (relative area 1, heterocyclic proton).

Meribicyclo-4,6-epidithio-5-phenyl-3,5-hexadienethione-2 (IIIa).—A mixture of 4.0 g (0.017 mole) of 4,6-epidithio-5-phenyl-3,5-hexadienone-2, 3.8 g (0.017 mole) of phosphorus pentasulfide, and 150 ml of benzene was stirred and refluxed for 1.25 hr, filtered, and evaporated. Crystallization from hexane gave 2.7 g (63%) of brick-red product, mp 81–84°. A second crystallization from hexane sharpened the melting point to 82.5–83.5°.

Anal. Calcd for $C_{12}H_{10}S_3$: C, 57.60; H, 4.03; S, 38.37. Found: C, 57.29; H, 4.00; S, 38.51.

3,5-Epidithio-4-phenyl-4-pentenal (Ib).—A solution of 2.8 g (0.010 mole) of 4-phenyl-1,2-dithiolium hydrogen sulfate in 200 ml of water, on the addition of 15 ml of ethyl vinyl ether, soon turned yellow and turbid. It was stirred overnight and then filtered, yielding 1.9 g (86%) of crude product which was suitable for chloranil dehydrogenation. Crystallization from 150 ml of hexane gave 1.35 g (61%) of bright yellow solid, mp 60–64°. A specimen, crystallized again from hexane, melted at 63–63.5°.

Anal. Calcd for $C_{11}H_{10}OS_2$: C, 59.46; H, 4.54; S, 28.81. Found: C, 59.73; H, 4.89; S, 29.36.

The yellow-orange *p*-nitrophenylhydrazone was prepared in refluxing ethanol and crystallized from acetonitrile, mp 134–138°.

Anal. Calcd for $C_{17}H_{15}N_3O_2S_2$: C, 57.14; H, 4.23; N, 11.76; S, 17.95. Found: C, 57.50; H, 4.36; N, 11.70; S, 17.68.

3,5-Epidithio-4-phenyl-2,4-pentadienal (IIb).—A mixture of 2.00 g (9.0 mmoles) of crude 3,5-epidithio-4-phenyl-4-pentenal and 2.20 g (9.0 mmoles) of chloranil in 20 ml of benzene was heated to the boil, kept warm on a steam bath for 30 to 40 min, cooled to room temperature, and filtered. Evaporation of the benzene filtrate gave 1.65 g (78%) of yellow product, mp 110–112°. Crystallization from 150 ml of hexane gave 1.10 g (55%), mp 115.5–117°.

Anal. Calcd for $C_{11}H_8OS_2$: C, 60.00; H, 3.66. Found: C, 59.50; H, 3.65.

The purple 2,4-dinitrophenylhydrazone was prepared in methanol containing a little concentrated HCl and crystallized from acetic acid, mp 248–250°.

Anal. Calcd for $C_{17}H_{12}N_4O_4S_2$: C, 51.00; H, 3.02; S, 15.99. Found: C, 50.87; H, 2.81; S, 15.91.

Meribicyclo-3,5-epidithio-4-phenyl-2,4-pentadienethial (IIIb).—A mixture of 0.60 g (2.7 mmoles) of 3,5-epidithio-4-phenyl-2,4-pentadienal and 0.60 g (2.7 mmoles) of phosphorus pentasulfide in 12 ml of benzene was stirred and refluxed for 20 min, cooled to room temperature, and filtered. Evaporation of the filtrate gave a red oil which crystallized to a purple solid (0.30 g, 47%), mp 56–63°. Hexane gave purple crystals, mp 61–63°.

Anal. Calcd for $C_{11}H_8S_3$: C, 55.94; H, 3.41; S, 40.65. Found: C, 55.45; H, 3.71; S, 41.00.

3-Chloro-4,6-epidithio-5-phenyl-3,5-hexadienone-2 (IV).—A solution of 0.81 ml (1.35 g, 0.0100 mole) of sulfuryl chloride in 3–4 ml of dichloromethane was added at 0° to a solution of 2.34 g (0.0100 mole) of IIa in 35 ml of dichloromethane. The resulting solution was left overnight at room temperature and then evaporated to give 2.65 g (99%) of brown product, mp 97–101°. Crystallization from 100 ml of hexane gave 1.70 g (63%) of orange-yellow needles, mp 101–105°. A second crystallization raised the melting point to 108–109°.

Anal. Calcd for $C_{12}H_9ClOS_2$: C, 53.62; H, 3.38; Cl, 13.19; S, 23.86. Found: C, 53.85; H, 3.59; Cl, 12.78; S, 23.94.

The proton nmr showed absorption at δ 2.35 (relative area 3, methyl protons), 7.29 (relative area 5, phenyl protons), and 7.79 (relative area 1, heterocyclic protons).

1-Chloro-4,6-epidithio-1,3,5-triphenyl-3,5-hexadienone-2 (VI).—To a solution of 1.93 g (5.0 mmoles) of VI in 15 ml of ice-cold dichloromethane was added 0.41 ml (0.69 g, 5.1 mmoles) of sulfuryl chloride. The solution was left overnight at room temperature and then evaporated to give 2.05 g (97%) of brown solid, mp 155–158°. Methanol gave yellow crystals, mp 160–161°; the product also crystallizes from hexane.

(6) (a) M. Mammi, R. Bardi, G. Traverso, and S. Bezzi, *Nature*, **192**, 1282 (1961); (b) H. Behringer and R. Wiedenmann, *Tetrahedron Letters*, 705 (1965).

(7) E. Klingsberg, *J. Am. Chem. Soc.*, **83**, 2934 (1961).

Anal. Calcd for $C_{24}H_{17}ClOS_2$: C, 68.45; H, 4.07; Cl, 8.42; S, 15.23. Found: C, 68.55; H, 4.18; Cl, 8.42; S, 14.93.

The proton nmr showed absorption at δ 5.58 (relative area 1, methine proton) and 7.85 (relative area 1, heterocyclic proton), with complex phenyl proton absorption in the range 6.6–7.1 (relative area 15). The starting material (V) shows methylene absorption at δ 3.65 (relative area 2), heterocyclic proton absorption at δ 3.65 (relative area 2), heterocyclic proton absorption at 7.77 (relative area 1), and complex phenyl proton absorption at 6.7–7.2 (relative area 15).

5-Phenyl-1,2-dithiole-$\Delta^{3,\alpha}$-malonitrile (X).—A solution of 40.0 g (0.206 mole) of 5-phenyl-1,2-dithiol-3-one (VIII[7]) and 20 g (0.30 mole) of malononitrile in 100 ml of phosphorus oxychloride was heated on a steam bath for 5.5 hr, cooled, and carefully decomposed with ice. The product was filtered, washed, and dried. It was digested with carbon disulfide at room temperature and filtered; the operation was repeated with dioxane, yielding 45 g (90%), mp 208–214° dec. Dioxane (20 ml/g) gave golden brown crystals, mp 229° dec, in a recovery of 70–75%.

Anal. Calcd for $C_{12}H_6N_2S_2$: C, 59.51; H, 2.50; N, 11.57; S, 26.43. Found: C, 59.56; H, 2.60; N, 11.39; S, 26.60.

Under similar conditions 4,5-benzodithiol-3-one (IX[8]) gave 4,5-benzo-1,2-dithiole-$\Delta^{3,\alpha}$-malonitrile (XI), mp 250–254° dec (AcOH).

Anal. Calcd for $C_{10}H_4N_2S_2$: C, 55.53; H, 1.86; N, 12.96; S, 29.65. Found: C, 55.21; H, 1.95; N, 12.92; S, 29.85.

α-Cyano-5-phenyl-1,2-dithiole-$\Delta^{3,\alpha}$-acetamide (XII).—A mixture of 10.0 g (0.041 mole) of 5-phenyl-1,2-dithiole-$\Delta^{3,\alpha}$-malononitrile (X) and 10 g of sodium hydroxide in 750 ml of water was stirred and refluxed for 5.5 hr, cooled, and filtered. Acidification of the filtrate gave 8.8 g (82%) of product, mp 246–258°. Acetic acid gave golden brown needles, mp 254–257°.

Anal. Calcd for $C_{12}H_8N_2OS_2$: C, 55.39; H, 3.10; N, 10.77; S, 24.60. Found: C, 55.33; H, 3.11; N, 10.62; S, 24.74.

This compound was recovered unchanged after being dissolved in dilute aqueous sodium hydroxide and refluxed for 48 hr. It is also resistant to dilute sulfuric acid.

α-Cyano-5-phenyl-1,2-dithiole-$\Delta^{3,\alpha}$-thioacetamide (XIII).—One gram (3.8 mmoles) of XII and 0.85 g (3.8 mmoles) of phosphorus pentasulfide were stirred and refluxed for 25 min in 50 ml of pyridine. Careful dilution followed by filtration gave 0.72 g (68%) of brown product, which decomposed at approximately 245–250°. Crystallization from acetic acid raised the decomposition point to about 255°. It can also be crystallized from butyl acetate or nitromethane.

Anal. Calcd for $C_{12}H_8N_2S_3$: C, 52.18; H, 2.92; N, 10.14; S, 34.76. Found: C, 51.60; H, 2.90; N, 10.00; S, 34.71.

One-half gram of this compound was refluxed for 5 hr in 200 ml of water containing 2.0 g of sodium hydroxide. Acidification of the solution gave 0.40 g of unchanged starting material.

Both XII and XIII show nitrile stretching frequencies at about 2190 cm^{-1}, NH_2 stretching frequencies near 3400 and 3500 cm^{-1}, and NH_2 deformation at about 1620 cm^{-1} (Nujol). A carbonyl stretching frequency at about 1660 cm^{-1} is present in XII but absent in XIII.

Acknowledgment.—The author is greatly indebted to Miss Vera Jordan and Miss Jessie L. Gove for spectral data, and to John J. Kobliska and his staff for microanalyses.

(8) E. W. McClelland, L. A. Warren, and J. H. Jackson, *J. Chem. Soc.*, 1582 (1929).

The 2,3-Diazabicyclo[2.2.1]heptyl Ring System. I. Synthesis and Characterization of Some 5-Substituted Derivatives[1]

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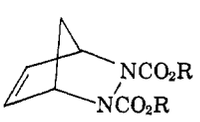
A survey of the feasibility of the synthesis of 5-substituted 2,3-diazabicyclo[2.2.1]heptyl derivatives by addition to the carbon–carbon double bond of 2,3-dicarboalkoxy-2,3-diazabicyclo[2.2.1]hept-5-enes is reported. Attempted additions of water (H^+) and formic acid were unsuccessful. Hydroboration–oxidation of Ia was successful giving 2,3-dicarbomethoxy-*exo*-2,3-diazabicyclo[2.2.1]heptan-5-ol along with two partially fragmented products. The latter were identified as 4-(N,N′-dicarbomethoxyhydrazino)cyclopentene and 3-(N,N′-dicarbomethoxyhydrazino)cyclopentanol. The synthesis and characterization of 2,3-dicarbomethoxy-2,3-diazabicyclo[2.2.1]heptan-5-one and 2,3-dicarbomethoxy-*endo*-2,3-diazabicyclo[2.2.1]heptan-5-ol also are described. Epoxidation of Ia afforded 2,3-dicarbomethoxy-*exo*-2,3-diazabicyclo[2.2.1]-5,6-epoxyheptane.

Although the 2,3-diazabicyclo[2.2.1]heptyl ring system has been known for 41 years,[2] it appears that C-substituted derivatives are almost entirely unknown. This system with appropriate substituents is of considerable theoretical interest, and also offers a potential synthetic route to some very interesting substituted bicyclo[2.1.0]pentanes.[3] From the original work of Diels and co-workers[2] and from subsequent work,[4] the 2,3-dicarboalkoxy-2,3-diazabicyclo[2.2.1]hept-5-enes Ia and Ib appeared to be attractive starting materials for the synthesis of 5- and 5,6-substituted 2,3-diazabicyclo[2.2.1]-heptyl derivatives. These materials are obtained in essentially quantitative yield *via* the facile Diels–Alder reaction between dialkyl azodicarboxylates and cyclopentadiene.[2,4] According to published reports, bromination of the carbon–carbon double bond of Ib proceeds in a normal manner to give the 5,6-dibromide in high yield.[2,4] In this paper we report an investigation of some other additions to the carbon–carbon double bond of I. We also describe the preparation and characterization of four substituted 2,3-diazabicyclo[2.2.1]heptyl derivatives.



Ia, R = CH_3
b, R = CH_2CH_3

Attempted Addition of Water (H^+) and Formic Acid.—Recently Stille and Anyos[5] reported on the treatment of Ib with 10% hydrochloric acid under conditions of continuous reflux. The isolated products, diethyl hydrazodicarboxylate, carbon dioxide, nitrogen, and cyclopentadiene, were accounted for on the basis

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(5) J. K. Stille and T. Anyos, *ibid.*, **27**, 3352 (1962).