benzal chloride with small amounts of stilbene and diphenylethane and only traces of the $C_{13}H_{16}$ hydrocarbons.

n-**Butyllithium and Benzyl Chloride.**—The procedure used was based on the method outlined by Closs and Closs.[1] A butyllithium solution was prepared from 3.6 g. (0.54 g.-atom) of lithium, 34.25 g. (0.25 mole) of butyl bromide, and 150 ml of dry ether as described by Jones and Gilman.[18] The *n*-butyllithium solution was added slowly to a mixture of benzyl chloride (50.6 g., 0.4 mole) and cyclohexene (50 g., 0.6 mole) maintained at 10°. The reaction mixture was then hydrolyzed and the ether layer was separated and dried over sodium sulfate. The solvent was removed by distillation before evaluation of the product by v.p.c. In addition to the products reported by Closs and Closs[1] (14% 1,2-diphenylethane, 14% 7-phenylnorcarane, 19% 3-benzylcyclohexene, and 30% amylbenzene), a small amount of stilbene was detected.

Acknowledgment.—Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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[18] R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 352 (1951).

Dithiolium Derivatives. VI. Reactions of Primary Amines and Ammonia with 2-Methylthio-1,3-dithiolium Perchlorate[1]

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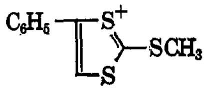
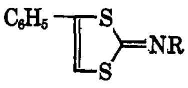
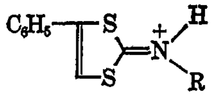
We have recently reported the facile nucleophilic attack on 2-methylthio-1,3-dithiolium salts by active methylene carbanions[3,4] and secondary amines.[5] Secondary amines have also been shown to react with 3-methylthio-5-phenyl-1,2-dithiolium perchlorate to form N,N-disubstituted 3-amino-5-phenyl-1,2-dithiolium perchlorates.[5] However, Olofson[6] has reported an excellent yield of 4-phenylisothiazole when a 4-phenyl-1,2-dithiolium salt was treated with ammonia in alcohol. While we have shown that aminodithiolium derivatives result from the reaction of dialkyl or alkylarylamines with 2-methylthio-1,3-dithiolium perchlorates, it is possible that reaction with primary amines or ammonia might lead to the more stable thiazole derivatives. Therefore the reaction of 4-phenyl-2-methylthio-1,3-dithiolium perchlorate (**1**) with several primary amines and with ammonia was investigated.



1



2a, R=C_6H_5
b, R=C_6H_4Br-*p*
c, R=C_6H_{11}



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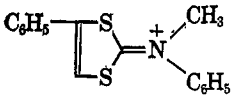

4

The reaction of **1** with aniline, *p*-bromoaniline, or cyclohexylamine in glacial acetic acid produced the neutral imino derivatives, **2**, in good yield. In trifluoroacetic acid these compounds are evidently protonated to the immonium derivatives **3**, since in this solvent they showed the characteristic aminodithiolium ultraviolet absorption band in the 315–345-mμ region,[7] as well as n.m.r. signals for the C-5 proton at τ 2.60–2.72, and a proton on nitrogen at 7.62–7.63. The n.m.r. spectrum of the neutral N-cyclohexyl-2-imino-4-phenyl-1,3-dithiole (**2c**), taken in carbon tetrachloride, shows the C-5 proton at τ 3.50, an upfield shift for this proton characteristic of such dithioles,[4] but no proton on nitrogen. The identity of the aniline derivative **2a** was further confirmed by methylation of the nitrogen atom to form the same methylanilinium salt (**4**) previously obtained from **1** and methylaniline.[5]

The reaction of ammonia with **1** under a variety of conditions was investigated, but only intractable tars were obtained. These conditions included ammonium acetate in acetic acid, ammonia in ethanol, acetonitrile, tetrahydrofuran, or water, and addition of **1** to liquid ammonia. Since 4-phenyl-2-methylthiothiazole is a stable derivative which forms high-melting salts,[8] one must conclude that little, if any, of this is present in the mixture produced by decomposition of **1** with ammonia.

Experimental[9]

N,4-Diphenyl-2-imino-1,3-dithiole (2a).—The procedure employed was that described by Schmidt, Lüttringhaus, and Hübinger.[10] To 3.24 g. (0.01 mole) of 2-methylthio-4-phenyl-1,3-dithiolium perchlorate (**1**) dissolved in 25 ml. of hot glacial acetic acid was added 1.86 g. (0.02 mole) of aniline. The solution was refluxed an additional 5 min., and then poured into 400 ml. of ice–water. This mixture was stirred several hours and the solid material which separated was collected and dried, yielding 2.25 g. (84%) of **2a**. Recrystallization twice from acetonitrile (Norit) afforded colorless needles which melted at 93–95°: $\lambda_{\max}^{CF_3CO_2H}$ 343 mμ (log ε 4.07); $\tau_{CF_3CO_2H}$ 2.38 (m, 5H), 2.47 (m, 5H), 2.63 (1H), and 7.63 (1H).

Anal. Calcd. for $C_{15}H_{11}NS_2$: C, 66.88; H, 4.12; S, 23.81. Found: C, 66.71; H, 4.35; S, 23.75.

A similar procedure was employed with *p*-bromoaniline to afford **N-*p*-bromophenyl-2-imino-4-phenyl-1,3-dithiole (2b)** in 95% yield. After two recrystallizations from acetonitrile, **2b** melted at 149–151°: $\tau_{CF_3CO_2H}$ 2.20 (d, 2H), 2.45 (m, 5H), 2.57 (d, 2H), 2.60 (1H), and 7.62 (1H).

Anal. Calcd. for $C_{15}H_{10}BrNS_2$: C, 51.73; H, 2.89; S, 18.41. Found: C, 51.69; H, 2.91; S, 18.19.

The dithiolium perchlorate **1** and cyclohexylamine treated similarly afforded **N-cyclohexyl-2-imino-4-phenyl-1,3-dithiole (2c)** in 71% yield. In this case, it was necessary to extract the aqueous solution with benzene and recover **2c** by evaporation. Two recrystallizations from hexane gave colorless plates which

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[1] Contribution No. 1277. This research was supported by a grant from the Mead-Johnson Corp. of Evansville, Ind., which we gratefully acknowledge.

[2] Taken in part from the Ph.D. Thesis of R. D. Hamilton, submitted to Indiana University, June 1964.

[3] E. Campaigne and R. D. Hamilton, *J. Org. Chem.*, **29**, 1711 (1964).

[4] E. Campaigne and F. Haaf, *ibid.*, **30**, 732 (1965).

[5] E. Campaigne and R. D. Hamilton, *ibid.*, **29**, 2877 (1964).

[6] R. A. Olofson, J. M. Landesberg, and R. O. Berry, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963, p. 45M.

[7] E. Campaigne and N. W. Jacobsen, *J. Org. Chem.*, **29**, 1703 (1964).

[8] E. B. Knott, *J. Chem. Soc.*, 1656 (1947).

[9] All melting points were determined in soft glass capillaries using a Mel-Temp heated block and are corrected. Analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind. Ultraviolet measurements were made with a Cary 14 spectrophotometer. Infrared spectra were recorded by a Perkins-Elmer Model 137 Infracord in potassium bromide mulls. All n.m.r. measurements were at concentrations between 6–10% w./v. at approximately 31°, using a Varian A-60 spectrometer operating at 60 Mc./sec. Chemical shifts are recorded on the frequency independent τ-scale relative to an internal TMS reference. For multiple signals the following abbreviations are used: d = doublet, m = multiplet.

[10] U. Schmidt, A. Lüttringhaus, and F. Hübinger, *Ann.*, **631**, 138 (1960).

melted at 80–81°: $\lambda_{\max}^{CF_3CO_2H}$ 314 mμ (log ε 4.21); $\tau_{CF_3CO_2H}$ 2.48 (m, 5H), 2.72 (1H), 7.65 (d, 1H), and 7.50–8.83 (m, 11H); τ_{CCl_4} 2.72 (m, 5H), 3.50 (1H), and 7.92–8.90 (m, 11H).

Anal. Calcd. for $C_{15}H_{17}NS_2$: C, 65.41; H, 6.22; S, 23.28. Found: C, 65.65; H, 6.35; S, 23.65.

Methylation of N,4-Diphenyl-2-imino-1,3-dithiole.—To 2 ml. of dimethyl sulfate was added 0.4 g. of **2a**, and the mixture was heated gradually to 140°, then allowed to cool slowly to room temperature. Glacial acetic acid (6 ml.) followed by 0.5 ml. of 70% perchloric acid was added. Dilution of the resulting solution with *ca.* 100 ml. of ether afforded 0.55 g. of a solid, which was collected, dried, and recrystallized once from 95% ethanol. It melted at 213–215°, and the mixture melting point with an authentic sample of N-methyl-N,4-diphenyl-2-imino-1,3-dithiolium perchlorate (**4**) was undepressed. The infrared and n.m.r. spectra of these compounds were identical.

Reaction of 2-Methylthio-4-phenyl-1,3-dithiolium Perchlorate with Ammonia in Acetonitrile.—**1** (2.5 g., 7.65 mmoles) was dissolved in 75 ml. of acetonitrile and ammonia was allowed to bubble into the solution for 5 min. at room temperature. During the addition of ammonia the solution progressively changed color from yellow to black, with the appearance of some fine black solid. The solution was then heated gently for 20 min. and filtered to remove the insoluble black solid. An infrared spectrum of this solid indicated it to be ammonium perchlorate. The acetonitrile was stripped from the reaction mixture, leaving a black solid which was washed with ethyl acetate, dissolved in 10 ml. of 70% perchloric acid, heated for 5 min., and cooled; 40 ml. of ethyl acetate was added and the solution was filtered. The solid isolated was shown to be ammonium perchlorate. Similar experiments using ethanol, tetrahydrofuran, or aqueous ammonium hydroxide gave only tarry residues from which no crystalline solids could be isolated.

When 2.0 g. of **1** was stirred into 20 ml. of liquid ammonia, and the ammonia was allowed to evaporate slowly, the residue was a black tar containing crystals of ammonium perchlorate.

Terpenes. XVI. Optical Rotatory Dispersion Studies of Some Diterpenoid Derivatives Possessing a Bicyclo[2.2.2]octanone Ring System[1]

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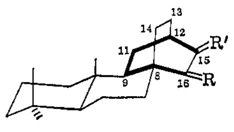
Received November 3, 1964

During the course of another investigation,[2] we had occasion to prepare a number of bicyclo[2.2.2]octanones derived from maleopimaric acid (the Diels–Alder adduct of abietic acid and maleic anhydride). Since the literature contains little information[3] on optical rotatory dispersion curves of optically active bicyclo[2.2.2]-octanones, we wish to record here our preliminary observations. An attempt to apply the octant rule[4] to these substances is described.

As in cyclopentanones,[5] in some cyclohexanones under the boat form the Cotton effect would be expected to arise mainly from the asymmetry of the cyclohexanone carbon atoms ("first-order effect"[5]) and only secondarily from the substituents ("second-order effect"[5]) attached to the cyclohexanone ring. The experimentally observed Cotton effects shown in Table I and Table II may therefore be interpreted as follows. If in compounds I and II the octant rule is applied to the cyclohexanone ring formed by C-8, C-9, C-11, C-12, C-15, and C-16, one finds that, in ketone I, C-11 is severely skewed in the positive upper left octant, and this effect is only partly counterbalanced by the negative contribution of substituent C-13 in the lower left octant, resulting in a positive Cotton effect. In ketone II, C-9 is strongly skewed in the negative upper right octant. Moreover, the negative contribution made by C-9 is enhanced by ring A, also in a negative octant, and this is only partly counterbalanced by the positive contribution of substituent C-14 in the lower right octant, resulting in a negative Cotton effect. Because of the "quasi-enantiomeric" relationship presented by ketones I and II, one would predict opposite Cotton effects for the two, and they exhibit similar intensities.

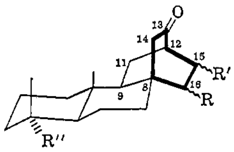
TABLE I



Compd.	R	R′	Cotton effect,[a] deg.
I	H_2	O	$[\Phi]_{308} = +3023$
II	O	H_2	$[\Phi]_{312} = -3445$

[a] The experimental molecular rotations of the peaks or troughs of the highest wave length are shown. In most cases both peaks and troughs were not obtained for a given compound since rotations could not be measured below ~300 mμ with the instrument used in this study.

TABLE II



Compd.	R	R′	R″	Cotton effect,[a] deg.
III	H	H	CH_3	$[\Phi]_{310} = +1713$
IV	H	H	CO_2CH_3	$[\Phi]_{310} = +1608$
V	β-CO_2CH_3	α-CO_2CH_3	CO_2CH_3	$[\Phi]_{319} = +941$
VI	β-CO_2CH_3	β-CO_2CH_3	CO_2CH_3	$[\Phi]_{303} = -4664$
VII	Double bond at C-15–C-16		CO_2CH_3	$[\Phi]_{315} = +24327$

[a] The experimental molecular rotations of the peaks or troughs of the highest wave length are shown. In most cases both peaks and troughs were not obtained for a given compound since rotations could not be measured below ~300 mμ with the instrument used in this study.

In compounds III–VI of Table II the octant rule is applied to the cyclohexanone ring formed by C-8, C-14, C-13, C-12, C-15, and C-16. In ketones III–V, C-15 is strongly skewed into the positive upper left octant, and the positive Cotton effect is still enhanced by the fused decalin moeity, also falling into a positive octant. Since the C-11 carbon atom in the lower left

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[1] Paper XVI in the series from Oklahoma State University. The work at Oklahoma State University was supported by the National Science Foundation (GP-233).

[2] L. H. Zalkow and N. N. Girotra, *J. Org. Chem.*, **29**, 1299 (1964), and references therein.

[3] (a) A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962); (b) K. Mislow and J. G. Berger, *ibid.*, **84**, 1956 (1962); (c) E. Bunnenberg, C. Djerassi, K. Mislow, and A. Moscowitz, *ibid.*, **84**, 2823 (1962); (d) K. Mislow, *Ann. N. Y. Acad. Sci.*, **93**, 459 (1962).

[4] W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 4013 (1961).

[5] W. Klyne, *Tetrahedron*, **13**, 29 (1961).