Experimental Section

Infrared spectra were taken on a Perkin-Elmer Model 137 spectrophotometer and ultraviolet spectra were taken on a Perkin-Elmer Model 202 spectrophotometer. Nmr spectra were obtained on a Varian Associates A-60 spectrometer, and mass spectra on a Perkin-Elmer Hitachi RMU-6E spectrometer. Melting points were taken on a Fisher-Johns melting point apparatus. The analysis for elements was done by Galbraith Laboratories, Inc., Knoxville, Tenn., and by the Scandinavian Micro-Analytical Laboratory, Herlev, Denmark. Desyl thiocyanate was prepared from desyl chloride and potassium thiocyanate.[2]

2,4,5-Triphenyl-2H-1,3-oxathiole (1).—Sodium hydride (13.4 g, 0.312 mol, 56% dispersion in mineral oil) was added to 100 ml of dry dimethoxyethane. A solution of desyl thiocyanate (48.7 g, 0.192 mol) in 200 ml of dimethoxyethane was cooled to −10° and added in three portions over a 20-min period to the sodium hydride which also was cooled to −10°. The temperature quickly rose to room temperature. Stirring was continued for 90 min. Water (3 ml) was added to destroy any remaining sodium hydride, and the inorganic salts were removed by filtration and washed with two 30-ml portions of ether. The solvents were then removed on a rotary evaporator, the residue was dissolved in 350 ml of ether and washed with two 25-ml portions of water, and the ether solution was dried over anhydrous magnesium sulfate overnight. Evaporation of the solvent to about 200 ml precipitated *cis*-dibenzoylstilbene (3.10 g, 0.00795 mol, 8.3%) after several hours. Recrystallization from glacial acetic acid gave white crystals, mp 211–212° and mmp 209.5–211° (lit.[11] mp 210.0–210.8°). The olefin was further identified by thin layer chromatography (tlc) and its infrared and ultraviolet spectra which were the same as those reported.[11,12] The material remaining in the ether solution was chromatographed on a silicic acid column with benzene as eluent. A light yellow band, which preceded the band of *cis*-dibenzoylstilbene episulfide, was collected. A total of 11.1 g of crude 2,4,5-triphenyl-2H-1,3-oxathiole (0.0352 mol, 55%) and episulfide (13.1 g, 0.0311 mol, 32%) was collected. The oxathiole was recrystallized from petroleum ether (66–78°) several times and purified on a silicic acid column using a 4:1 pentane–benzene mixture as the eluent. Yellow crystals, mp 77–78°, were obtained which gave only one spot (R_f 0.67) on a tlc plate (Merck silica gel GF_{254}, benzene eluent). *Anal.* Calcd for $C_{21}H_{16}OS$: C, 79.71; H, 5.10; S, 10.13; mol wt, 316. Found: C, 79.57; H, 5.16; S, 10.19; mol wt, 328 (osmometry in acetone). The infrared spectrum of the oxathiole (KBr disk) exhibited bands at 3030 (w), 2880 (w), 1620 (m), 1600 (m), 1570 (m), 1495 (m), 1440 (m), 1350 (w), 1315 (w), 1245 (s), 1210 (m), 1175 (w), 1155 (w), 1080 (m), 1070 (m), 1060 (s), 1020 (m), 990 (m), 955 (m), 920 (w), 910 (w), 875 (m), 827 (w), 781 (w), 765 (m), 750 (s), 710 (s), and 691 (s) cm^{-1}. The ultraviolet spectrum was obtained in two solvents: $\lambda_{max}^{CH_3CN}$ 226, 342 mμ; $\lambda_{max}^{95\%C_2H_5OH}$ 225 mμ (ε 18,600), 342 mμ (ε 6760).

Mass spectrometry also was used to establish the empirical formula of the oxathiole using the isotope abundances of the molecular ion *m/e* 316 (P) at *m/e* 317 (P + 1) and *m/e* 318 (P + 2). *Anal.* Calcd[13] for $C_{21}H_{16}OS$: 100[(P + 1)/P], 23.8; 100[(P + 2)/P], 7.1. Found: 100[(P + 1)/P], 22.6; 100[(P + 2)/P], 7.3. The mass spectrum of the oxathiole was obtained at 110° using the direct inlet at 20-ev ionizing potential:[14] *m/e* 318 (7.62), 317 (26.3), 316 (100), 284 (15.5), 283 (5.50), 239 (5.47), 212 (6.58), 211 (38.8), 210 (20.4), 179 (6.66), 178 (28.4), 167 (23.4), 166 (5.28), 165 (26.0), 121 (7.86), 106 (7.95), 105 (9.54).

The proton nmr spectrum (60 MHz in $CDCl_3$) of the oxathiole had a complex multiplet centered at 433 Hz and a sharp resonance absorption at 418 Hz relative to tetramethylsilane. The ratio of the high-field absorbance to the low-field absorbance was 1:14.4 (calcd 1:15).

When the oxathiole (0.051 g, 0.00016 mol) was refluxed in 20 ml of 95% ethanol and 1 ml of concentrated hydrochloric acid, hydrogen sulfide was evolved as detected by lead acetate paper. Thin layer chromatography indicated also the presence of benzaldehyde, benzoin, and possibly monothiobenzoin. The solution from hydrolysis of the oxathiole was treated with an amount of 2,4-dinitrophenylhydrazine reagent[15] sufficient only to react with the benzaldehyde. The orange precipitate was filtered and recrystallized from a commercial mixture of xylenes to give benzaldehyde 2,4-dinitrophenylhydrazone, mp 240–241° (lit.[16] mp 239–240°). The infrared spectrum of the derivative was identical with that of authentic benzaldehyde 2,4-dinitrophenylhydrazone.[17]

Registry No.—**1**, 19206-52-1; desyl thiocyanate, 19203-00-0.

(11) N. M. Bikales and E. I. Becker, *J. Org. Chem.*, **21**, 1405 (1956).
(12) R. E. Lutz, W. J. Welstead, Jr., R. G. Bass, and J. I. Dale, *ibid.*, **27**, 1111 (1962).
(13) J. H. Beynon and A. E. Williams, "Mass Abundance Tables for Use in Mass Spectroscopy," Elsevier Publishing Co., New York, N. Y., 1963.
(14) Percentage of base peak is given in parenthesis. Only fragments which were 5% or greater of the base peak and above *m/e* 104 are tabulated.
(15) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1956, p 219.
(16) G. D. Johnson, *J. Amer. Chem. Soc.*, **75**, 2720 (1953).
(17) "Sadtler Standard Spectra," Midget ed, The Sadtler Research Laboratories, Philadelphia, Pa., 1962, No. 4156.

Hydrolysis and Decarboxylation of Diethyl 1-Methyl-4-nitro-5-imidazolylmalonate

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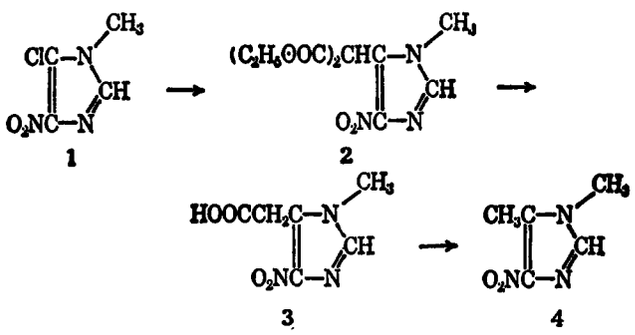
During a study of certain imidazole derivatives, 1-methyl-4-nitro-5-imidazolylacetic acid (**3**) was desired. A convenient route appeared to be the conversion of 5-chloro-1-methyl-4-nitroimidazole (**1**)[2] into its corresponding diethyl 5-imidazolylmalonate (**2**) followed by hydrolysis and decarboxylation. Starting



compound **1** was prepared by nitration of 5-chloro-1-methylimidazole.[3–5]

The formation of the substituted malonic ester **2** was achieved in good yield by a malonic ester condensation reaction. However, when acid hydrolysis (1.2 *N* aqueous HCl) of **2** was attempted, 1,5-dimethyl-4-nitroimidazole (**4**)[6] was isolated as the sole product in high yield.[7]

(1) Deceased.
(2) J. Sarasin and E. Wegmann, *Helv. Chim. Acta*, **7**, 713 (1924).
(3) O. Wallach and A. Boehringer, *Ann.*, **184**, 50 (1877).
(4) O. Wallach, *ibid.*, **214**, 257 (1882).
(5) F. F. Blicke and H. C. Godt, Jr., *J. Amer. Chem. Soc.*, **76**, 3653 (1954).
(6) A. Windaus [*Ber.*, **42**, 758 (1909)] prepared this compound by nitrating 1,5-dimethylimidazole with fuming nitric acid.

If **3** is formed but decarboxylates rapidly to **4** through its carbanion,[7] carrying out the reaction in stronger acid concentration should inhibit the conversion of **3** into **4** and permit the isolation of **3**. Nmr studies of the reaction in various acid concentrations aided in establishing the best conditions for obtaining **3**. When the reaction was performed in 6 *N* aqueous HCl, **3** was isolated in high yield.

Experimental Section

The nmr spectral data were obtained on a Varian A-60 nmr spectrophotometer using dimethyl sulfoxide-d_6 as solvent. Chemical shifts are reported in parts per million downfield from tetramethylsilane (TMS).

5-Chloro-1-methylimidazole[5] had the following nmr analysis: δ 3.60 ppm (CH_3, 1 position, 3 H, doublet, J = 0.9 Hz), 7.76 ppm (H, 2 position, 1 H), 7.00 ppm (H, 4 position, 1 H, doublet, J = 1.0 Hz).

5-Chloro-1-methyl-4-nitroimidazole (1)[2] had the following nmr analysis: δ 3.76 ppm (CH_3, 1 position, 3 H, doublet, J = 0.4 Hz), 8.02 ppm (H, 2 position, 1 H, unresolved multiplet).

Diethyl 1-Methyl-4-nitro-5-imidazolylmalonate (2).—Diethyl malonate (144 g, 0.9 mol) was added dropwise with stirring to a solution of sodium metal (17.4 g, 0.75 g-atom) in 750 ml of absolute ethanol. A Soxhlet extractor, containing 48.3 g (0.3 mol) of **1** in its thimble, was attached to the reaction flask, and the reaction mixture was refluxed for 12 hr after all of **1** had dissolved. The ethanol was removed under reduced pressure (steam bath). The residue was dissolved in 750 ml of water extracted with ether, and acidified with dilute hydrochloric acid. The aqueous layer was separated from the orange oil, and extracted with chloroform. The oil and chloroform extract were combined and filtered. After stripping of the chloroform, the oil solidified on cooling. The product was recrystallized from diisopropyl ether–ethanol (3:1): yield, 70.5 g (82.4%); mp 67°.

Anal. Calcd for $C_{11}H_{15}N_3O_6$: C, 46.31; H, 5.30; N, 14.73. Found: C, 46.60; H, 5.19; N, 14.65.

Nmr analysis showed δ 3.84 ppm (CH_3, 1 position, 3 H, doublet, J = 0.3 Hz), 7.93 ppm (H, 2 position, 1 H, unresolved multiplet), 5.94 ppm (CH, 5 position, 1 H, singlet), 4.28 ppm (CH_2, ester, 4 H, quartet), 1.22 ppm (CH_3, ester, 6 H, triplet).

1,5-Dimethyl-4-nitroimidazole (4).—Compound **2** (17.1 g, 0.06 mol) and 250 ml of 1.2 *N* aqueous HCl were refluxed (100°) for 12 hr. The solution was cooled to 25° and made basic with solid sodium carbonate. The precipitated product was filtered, and the aqueous filtrate extracted with chloroform. The solid obtained by evaporation of the chloroform extract was combined with the rest of the product, and recrystallized from water: yield, 6.8 g (80%); mp 162° (lit.[6] mp 160–161°).

Anal. Calcd for $C_5H_7N_3O_2$: C, 42.55; H, 5.00; N, 29.78. Found: C, 42.92; H, 5.18; N, 29.60.

Nmr analysis showed δ 3.68 ppm (CH_3, 1 position, 3 H, doublet, J = ~0.3 Hz), 7.74 ppm (H, 2 position, 1 H, unresolved multiplet), 2.57 ppm (CH_3, 5 position, 3 H, singlet).

Following the course of the above reaction in refluxing 1.2 *N* aqueous HCl by nmr,[8] **3** had formed in large amounts within 30 min. Also **4** was present in significant amounts by this time. After 12 hr, essentially complete conversion into **4** had occurred.

1-Methyl-4-nitro-5-imidazolylacetic Acid (3).—A solution of **2** (8.5 g, 0.03 mol) in 85 ml of 6 *N* aqueous HCl was refluxed (104°) for 25 min. The reaction mixture was cooled to 0° and neutralized to pH of 2.5 (pH meter) using solid sodium carbonate. The product **3** precipitated and was filtered. Purification was achieved by dissolving in 10% sodium carbonate solution at 10°, filtering, and precipitating the product with 6 *N* aqueous HCl. The product was filtered, washed with water, and dried: yield, 4.8 g (87.3%); mp 144° dec.

Anal. Calcd for $C_6H_7N_3O_4$: C, 38.92; H, 3.81; N, 22.70; neut equiv, 185.1. Found: C, 38.65; H, 3.87; N, 22.73; neut equiv, 185.3.

Nmr analysis showed δ 3.70 ppm (CH_3, 1 position, 3 H), 4.13 ppm (CH_2, 5 position, 2 H), 7.69 ppm (H, 2 position, 1 H). Neither spin coupling nor carboxyl hydrogen was observed.

The course of the above reaction in refluxing 6 *N* aqueous HCl was followed by nmr. Compound **3** was present in greatest amount within 30 min after reflux had begun with no **2** or **4** evident. Only after 5 hr at reflux did **4** become apparent. By this time, the nmr spectrum showed evidence of competing reactions taking place with only a small buildup of **4**. After 12 hr at reflux, only 5.9% **4** was isolated from the reaction mixture. The nmr spectrum still indicated the presence of a significant amount of **3**.

Registry No.—II, 7464-80-4.

Acknowledgment.—The authors thank Drs. M. W. Dietrich and M. D. Wolfinger for assistance with the nmr spectral data.

(7) Several other nitrogen-containing heterocyclic-substituted carboxylic and acetic acids are known to undergo decarboxylations with relative ease. For a review with references and mechanistic considerations, see E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp 348–351.

(8) Aqueous HCl (6 *N*) was added to the initial aliquots, after cooling, to clarify the solutions.

Oxidation of Some Cyclic Benzylic Hydrazines Derived from Naphthalene, Acenaphthene, and Diphenylmethane

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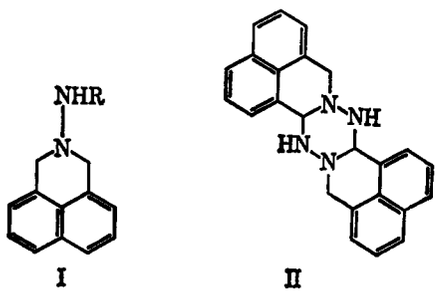
Although the oxidation of 1,1-dibenzylhydrazines with the formation of hydrocarbon products appears to be a general reaction, oxidation of cyclic benzylic hydrazine I (R = H) by means of mercuric oxide or other oxidants gave none of the expected acenaphthene.[1] Instead only the corresponding tetrazene was isolated.



I II

It has now been found that treatment of the *p*-toluenesulfonyl derivative (I, R = $SO_2C_6H_4CH_3$-*p*) with sodium ethoxide in ethanol, or simply by warming in ethanol alone, yields neither acenaphthene nor the tetrazene but rather the high melting compound II.[2] Structure II was established by an alternate synthesis involving treatment of tribromide III with hydrazine according to the method used by Schmitz[3] to obtain the analogous hexahydro-*s*-tetrazine IV from 2-(2-bromo-

(1) L. A. Carpino, *J. Amer. Chem. Soc.*, **85**, 2144 (1963).

(2) Depending on the specific case there may or may not be a correspondence between the products obtained by direct oxidation of a 1,1-disubstituted hydrazine and those obtained by alkaline degradation of the *p*-toluenesulfonyl derivative. See also D. M. Lemal, T. W. Rave, and S. D. McGregor, *J. Amer. Chem. Soc.*, **85**, 1944 (1963).

(3) E. Schmitz, Ber., **91**, 1495 (1958). Several attempts to obtain an 8-halomethyl-1-naphthaldehyde having been unsuccessful, tribromodimethylnaphthalene was used as a convenient substitute.