The ester was distilled to give 1.31 g of water-white liquid: 87.5% yield, $n^{20.5}D$ 1.4450 (lit.[15] $n^{20}D$ 1.4430).

Mass Spectra.—The mass spectra of the six cyclobutanes are presented in Figure 1. In the spectrum of dimethyl 3-methylcyclobutane-1,2-dicarboxylate, peaks at *m/e* 172, 184, 185, and 186, were apparent only at low voltage. Similarly in the spectrum of dimethyl 1-cyanocyclobutane-1,2-dicarboxylate, peaks at *m/e* 172 and 182 were present only as traces, and the parent *m/e* 197 was not observed at 70 ev.

(15) G. J. Ostling, *J. Chem. Soc.*, **101**, 457 (1912).

Acknowledgment.—This work was supported by a grant (1324) from the Petroleum Research Fund. We gratefully acknowledge the support provided by the donors of this fund. We are indebted to Mr. D. L. Dugger and Drs. L. A. Shadoff and R. E. Winters who determined the spectra for us.

Heterocyclic Ring-Closure Reactions. I. A Novel Oxazole Synthesis from S,S'-Dialkyl or -Diaryl Dithiooxaldiimidates and Aromatic Aldehydes[1a]

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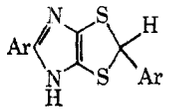
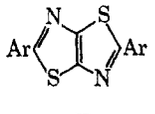
Received May 24, 1966

S,S'-Diaryl or -dialkyl dithiooxaldiimidates were found to react with aromatic aldehydes to give 5-benzylideneamino-4-aryl- or -alkylmercapto-2-aryloxazoles. In some cases *p*-nitrobenzaldehyde afforded the free amine. Mild acid hydrolysis converted the Schiff bases to α-alkylmercaptohippuronitriles. More vigorous conditions gave the α-alkylmercaptohippuramides. These were desulfurized to the known hippuronitriles and hippuramide.

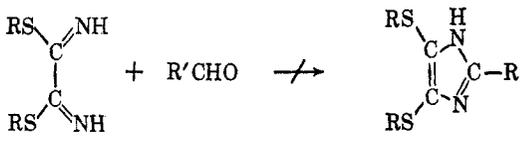
One possible *a priori* product of the thermal condensation of dithiooxamide and an aromatic aldehyde is the unsymmetrical structure I. The reaction, in fact, afforded symmetrical, fully aromatized diarylthiazolothiazoles[2] (II). As part of an investigation of possible methods for preparing structures of type I, we studied the condensations of S,S'-disubstituted dithiooxaldiimidates III with aldehydes. Elemental analyses of the yellow, crystalline substances obtained from aromatic aldehydes indicated that the expected products IV were not obtained. The sulfur:nitrogen ratio was 1:2 rather than the expected 1:1, thus indicating the loss of one sulfur function from III. It was further apparent that 2 moles of aldehyde had reacted with 1 mole of III, accompanied by loss of 1 mole each of mercaptan and water.



I



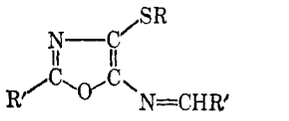
II



IIIa, R = CH_3
b, R = $C_6H_5CH_3$
c, R = C_6H_5

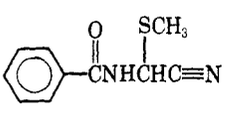
IV

These observations were best explained by structural formula V.[3] The nmr and ultraviolet spectra (the latter were very similar to the spectra of diphenylthiazolothiazoles II) are consistent with the proposed structures.

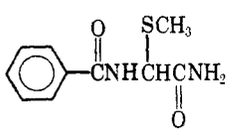


Va, R = CH_3; R' = C_6H_5
b, R = $C_6H_5CH_2$; R' = C_6H_5
c, R = C_6H_5; R' = C_6H_5
d, R = CH_3; R' = *p*-$MeOC_6H_4$
e, R = C_6H_5; R' = *p*-$O_2NC_6H_4$

The condensation product Va was rapidly and irreversibly destroyed by acid. The hydrolysis products were benzaldehyde and α-methylmercaptohippuronitrile (VI) or α-methylmercaptohippuramide (VII). These structures were converted by desulfurization to the known hippuric acid derivatives. The *nmr* spectrum of the nitrile VI is consistent with this structural assignment. These uniquely substituted glycine derivatives would appear to be unavailable by any direct route.

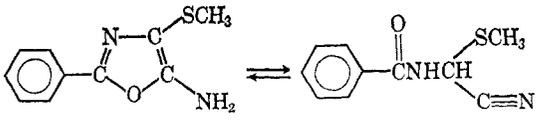


VI



VII

An effort was made to prepare the aminooxazole VIII, a suspected intermediate in the formation of Va. When benzaldehyde was added to a slight excess of S,S'-dimethyl dithiooxaldiimidate, a mixture of Va and the nitrile VI was isolated. The nitrile thus appears to be the more stable member of the ring–chain tautomeric system, VIII ↔ VI, if indeed, the free amine is ever formed.



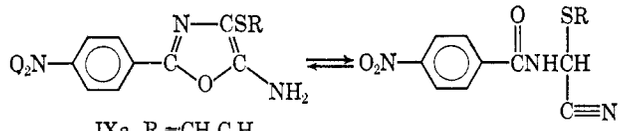
VIII VI

(1) (a) Supported by National Institutes of Health Training Grant 5 TI GM 728 and National Institutes of Mental Health Grant MH 08787. The nmr spectra were determined on an instrument purchased with funds supplied by the National Science Foundation (NSF-G-21268). (b) A portion of the Ph.D. thesis of A. R. M. (c) To whom inquiries should be sent.

(2) J. R. Johnson and R. Ketcham, *J. Am. Chem. Soc.*, **82**, 2719 (1960).

(3) This structure was first suggested by Dr. J. F. Oneto of this department.

The reaction of *p*-nitrobenzaldehyde with either S,S′-dibenzyl dithiooxaldiimidate or S,S′-dimethyl dithiooxaldiimidate afforded the aminooxazoles (IXa and b) in 84 and 76% yield, respectively. Neither the *p*-nitrobenzylidene derivatives of IX nor the open-chain tautomer X was isolated. Compound IXa shows an

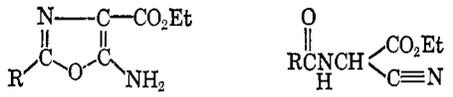


IXa, R = $CH_2C_6H_5$
b, R = CH_3

X

absorption maximum at 412 mμ (log ε 4.17) indicating extended conjugation. Such conjugation may account for the apparently greater stability of the ring tautomer IX over the chain tautomer X, in which the amide resonance would be opposed by the nitro group resonance. The S,S′-diphenyl dithiooxaldiimidate, however, gives Schiff base Ve with *p*-nitrobenzaldehyde.

The tautomeric equilibria between the chemically related aminooxazoles of type XI and the corresponding nitriles XII have been studied by Boon, *et al.*[4] When R is phenyl the ring tautomer XI predominates; when R is alkyl the chain tautomer XII is favored.



XI XII

The aminooxaxole IXa was hydrolyzed by dilute acid or dilute alkali to α-*p*-nitrobenzoylamino-α-benzylmercaptoacetamide rather than the nitrile X. This contrasts with the behavior of the benzylidene derivative Va which on mild acid hydrolysis gave primarily the nitrile VI. Under more vigorous conditions only the amide VII was obtained.

It was hoped that if the aminooxazole VIII were an intermediate in conversion of Va to VI, it would be possible to trap VIII as an acyl derivative. Acylations of Schiff bases are reported to fail if conditions are maintained rigidly anhydrous, implying that the first step is hydrolysis to the free amine.[5] Attempts to acylate the benzylidene derivatives Va and Vb under a variety of conditions[6] failed. In refluxing acetic anhydride and glacial acetic acid the nitrile VI was obtained. Attempts to benzoylate Va or b with benzoyl chloride in boiling pyridine[7] afforded only unreacted starting materials.

A possible explanation for the failure of Va to afford the acetamide is that opening of the oxazole ring may not involve prior hydrolysis of the Schiff base to the amine VIII, but proceed directly to the nitrile.[8] Furthermore, it is possible that in the formation of Va, two new carbon–nitrogen bonds are formed before ring closure occurs and that the aminooxazole is not an intermediate.[9] This suggestion may be reconciled with the observation that an aminooxazole IX is sometimes isolated when *p*-nitrobenzaldehyde is employed by assuming that in these cases the Schiff base is rapidly hydrolyzed to the more stable free amine.

The reaction between aromatic aldehydes and S,S′-disubstituted dithiooxaldiimidates seems to be general, the yields being directly related to the reactivity of the aldehyde: for instance with IIIa *p*-nitrobenzaldehyde (76% of IXb), benzaldehyde (63% of Va), and anisaldehyde (26% of Vd). However, no products have yet been obtained from anisaldehyde and either IIIb or c. Variation of the substituents (methyl, benzyl, or phenyl) of the dithiooxaldiimidate did not significantly affect the yields (with benzaldehyde 63, 68, and 58% of Va, b, and c, respectively) or the rates of the condensation.

Aliphatic aldehydes, such as chloral and butyraldehyde, and even the conjugated aldehydes, *trans*-cinnamaldehyde, and methyl glyoxylate, failed to give characteristic products. A possible explanation for the limitation to aromatic aldehydes is the resonance stabilization afforded by conjugation with the benzene ring. In this respect the reaction may be considered analogous to the Perkin reaction and to the reaction of aromatic aldehydes with dithiooxamide.[2] Further studies on the formation and reactions of these compounds are in progress.

Experimental Section[10]

Synthesis of Dialkyl Dithiooxaldiimidates.—The procedures used were those of Woodburn and Sroog[11] with minor modifications. The best results were obtained at low temperature (−80°), when an excess of cyanogen was avoided, and the product was worked up immediately on completion of the reaction.

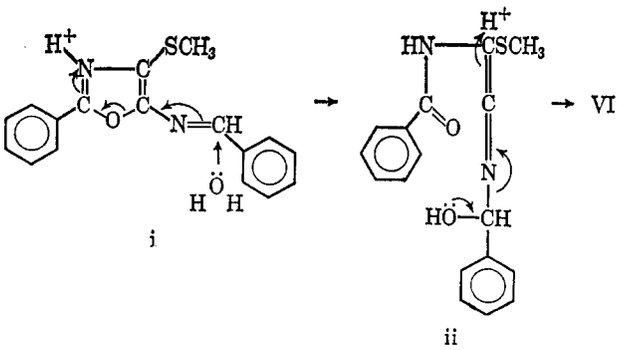
(4) W. R. Boon, H. C. Carrington, J. S. H. Davies, W. G. M. Jones, G. R. Ramage, and W. S. Waring in "The Chemistry of Penicillin," Princeton University Press, Princeton, N. J., 1949, p 700.

(5) G. Caronna, *Gazz. Chim. Ital.*, **78**, 38 (1948).

(6) (a) H. R. Snyder and J. C. Robinson, Jr., *J. Am. Chem. Soc.*, **63**, 3279 (1941); (b) A. Ludwig and R. I. Georgescu, *Bull. Chim. Soc. Romane Chim.*, **39**, 41 (1937); (c) G. La Parola, *Gazz. Chim. Ital.*, **64**, 919 (1934).

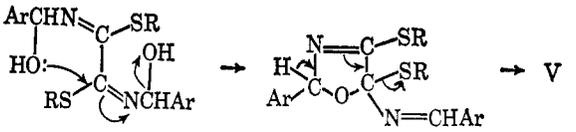
(7) H. Shechter, S. S. Rawalay, and M. Tubis, *J. Am. Chem. Soc.*, **86**, 1701 (1964).

(8) A more direct two-step hydrolysis (i → ii → VI) may occur



i ii

(9) For example, an intermediate such as iii might be formed which by dehydration and loss of mercaptan from iv would give V. It is equally



iii iv

plausible to suggest loss of mercaptan first followed by elimination of water.

(10) Melting points were measured using a Thomas–Hoover capillary melting point apparatus and are corrected. Elemental analyses were carried out by the microanalytical laboratory of the University of California at Berkeley. The ultraviolet spectra were determined in 95% ethanol using a Carey Model 11 spectrophotometer. The infrared spectra were determined using a Beckman IR-5 spectrophotometer. Potassium bromide was used for solids. Liquids were measured neat using two sodium chloride plates. The nuclear magnetic resonance spectra were measuring in deuteriochloroform (unless otherwise indicated), with tetramethylsilane (TMS) as the internal standard, using a Varian A-60 spectrometer.

(11) H. M. Woodburn and C. E. Sroog, *J. Org. Chem.*, **17**, 371 (1952).

The preparation of the previously undescribed dibenzyl dithiooxaldiimidate (IIIb, R = $CH_2C_6H_5$) illustrates the procedure. Into a stirred solution of 32 g (0.27 mole) of benzylmercaptan and 2 drops of *n*-butylamine, in 200 ml of hexane at −80°, was passed 6 g (0.125 mole) of previously weighed cyanogen gas (20 min). The cyanogen inlet tube was kept about 1 cm above the surface of the solution to avoid clogging. The reaction mixture was allowed to stand for 2 hr and to warm to room temperature. The diimidate was collected, washed with hexane, and crystallized twice from benzene to give 21.6 g (60%) of colorless needles, mp 147–149°. A portion of the material was crystallized to constant melting as colorless needles from ethanol, mp 148.5–150°. *Anal.* Calcd for $C_{16}H_{16}N_2S_2$: C, 63.96; H, 5.37; N, 9.32; S, 21.34. Found: C, 64.45; H, 5.66; N, 8.94; S, 20.48.

Diphenyl dithiooxaldiimidate (III, R = C_6H_5), mp 126–128° (lit.[12] 127–128°), was obtained in 76% yield and dimethyl dithiooxaldiimidate (III R = CH_3), mp 117–119° (lit.[12] 118–119°), was obtained in 52% yield by similar procedures.

5-Benzylideneamino-4-methylmercapto-2-phenyloxazole (Va).—Dimethyl dithiooxaldiimidate (4.32 g, 0.029 mole) and 8.5 g (0.08 mole) of benzaldehyde were heated under reflux in 50 ml of absolute ethanol for 3 hr. Cooling afforded a silky, yellow solid, mp 100–103°. A second drop brought the yield to 4.76 g (63%). An analytical sample obtained by further crystallization from ethanol gave mp 108–109°; λ_{max} 274 mμ (log ε 4.16) and 388 mμ (log ε 4.37); ν 3070 (aromatic CH), 2940 (CH_3), and 1590 cm^{-1} (aromatic C=C); singlet at δ = 8.73 (N=CH), complex multiplets centered at 8.17 and 7.58 (aromatic), and a singlet at 2.72 ppm (SCH_3). *Anal.* Calcd for $C_{17}H_{14}N_2OS$: C, 69.36; H, 4.79; N, 9.52; S, 10.89. Found: C, 69.11; H, 4.97; N, 9.34; S, 10.48.

When 1.06 g (10 mmoles) of benzaldehyde in ethanol was added over a 1-hr period to a refluxing solution of 1.63 g (11 mmoles) of the diimidate in ethanol followed by 6 hr more at reflux there was isolated 238 mg of Va, mp 101–103°, and 185 mg of VI, mp 128–132°, described below.

α-Benzoylamino-α-methylmercaptoacetonitrile (VI).—To 1.5 g (5.1 mmoles) of 5-benzylideneamino-4-methylmercapto-2-phenyloxazole in 50 ml of acetone was added 10 ml of 1 *N* hydrochloric acid. After standing at 25° for 5 min the solution was cooled, neutralized with solid sodium bicarbonate, diluted to 150 ml with water, saturated with sodium chloride, and extracted with ether. After washing and drying, the ether extract was evaporated to a tan, semisolid residue with the odor of benzaldehyde. This was extracted with hexane leaving a pale yellow solid, which crystallized from benzene in silky, white needles, mp 131–134° (0.905 g). The white solid was chromatographed on Florisil yielding 737 mg (70%) of the nitrile VI as colorless needles, mp 137–138°, eluted with chloroform, and recrystallized to analytical purity from ethanol: ν 3240 (amide NH), 2240 (nitrile), and 1645 cm^{-1} (amide C=O); = complex multiplet, integrating for six protons, centered at about δ = 8.9, decreases to five protons in D_2O (aromatic and NH), a doublet (J = 9 (cps) at 6.33 becomes a singlet in D_2O (tertiary CH), and a single at 2.44 ppm (SCH_3). *Anal.* Calcd for $C_{10}H_{10}N_2OS$: C, 58.23; H, 4.89; N, 13.58; S, 15.55. Found: C, 58.35; H, 4.88; N, 13.61; S, 15.56.

The hexane extract was concentrated to a brown oil which afforded 1.31 g (89%) of a 2,4-dinitrophenylhydrazone, melting point and mixture melting point with benzaldehyde 2,4-dinitrophenylhydrazone 238–239°.

Desulfurization of α-Benzoylamino-α-methylmercaptoacetonitrile.—α-Benzoylamino-α-methylmercaptoacetonitrile (206 mg, 1 mmole) and about 2 g of 1-year-old, W-2 Raney nickel were refluxed in 25 ml of absolute ethanol for 3 hr. Removal of the nickel and the solvent gave 128 mg of a pale yellow solid, mp 134–139°, which was chromatographed on Florisil. The major fraction, eluted with 5% ether in benzene, was 86 mg (54%) of benzoylaminoacetonitrile, mp 141–143° (lit.[12] 144°), confirmed by comparison of infrared spectra and mixture melting point with an authentic sample of benzoylaminoacetonitrile, obtained by reaction of aminoacetonitrile with benzoyl chloride in the presence of pyridine.

α-Benzoylamino-α-methylmercaptoacetamide (VII).—To 2 g (6.8 mmoles) of 5-benzylideneamino-4-methylmercapto-2-phenyloxazole, in 100 ml of acetone, was added 50 ml of 1 *N* hydrochloric acid. The reaction mixture was heated under reflux for 2 hr, neutralized with solid sodium bicarbonate, and concentrated to about 100 ml to give fine, white crystals, mp 168–169°. Crystallization of the amide VII from acetone gave 680 mg (91%) of colorless prisms: mp 171°; ν 3300 (NH), 1660, and 1615 cm^{-1} (C=O). *Anal.* Calcd for $C_{10}H_{12}N_2O_2S$: C, 53.55; H, 5.39; N, 12.45; S, 14.30. Found: C, 53.38; H, 5.38; N, 12.45; S, 14.17.

Desulfurization of α-Benzoylamino-α-methylmercaptoacetamide.—α-Benzoylamino-α-methylmercaptoacetamide (178 mg, 0.8 mmole) and about 2 g of 1-year-old W-2 Raney nickel were refluxed for 2 hr in absolute ethanol. Removal of the nickel and the solvent afforded 135 mg (95%) of a white solid, mp 179–182° (lit.[13] 183°) which when mixed with authentic benzoylaminoacetamide showed no depression. The infrared spectra of the two samples were identical.

5-Benzylideneamino-4-benzylmercapto-2-phenyloxazole (Vb).—Dibenzyl dithiooxaldiimidate (6 g, 0.02 mole) and 5.3 g (0.05 mole) of benzaldehyde were heated on a steam bath for 1.5 hr. The reaction mixture was cooled, and 50 ml of absolute ethanol was added causing precipitation of red-orange needles, mp 116–118°. More material was obtained by concentrating the mother liquor. Crystallization from absolute ethanol gave 5 g (68%) of yellow needles: mp 120°; ν 307 0(aromatic CH), 2940 (CH_2), and 1590 cm^{-1} (aromatic C=C); a singlet at δ = 8.73 (CH=N) two complex multiplets at 8.13 and 7.50 (aromatic), and a singlet at 4.48 ppm (SCH_2). *Anal.* Calcd for $C_{23}H_{18}N_2SO$: C, 74.51; H, 4.87; N, 7.57; S, 8.65. Found: C, 74.11; H, 4.61; N, 7.41; S, 8.59.

5-Benzylideneamino-2-phenyl-4-phenylmercaptooxazole (Vc).—Diphenyl dithiooxaldiimidate (2.52 g, 0.01 mole) and 3.2 g (0.03 mole) of benzaldehyde were refluxed in 25 ml of absolute ethanol for 2 hr. Yellow needles, mp 146–147°, crystallized when the reaction mixture cooled. More material was obtained from the mother liquor giving an over-all yield of 1.47 g (58%). Four crystallizations from ethanol gave yellow needles: mp 150–151°, ν 3030 (aromatic CH) and 1590 cm^{-1} (aromatic C=C), singlet at δ = 8.96 (N=CH) and two complex multiplets at 8.2 and 7.55 ppm (aromatic). *Anal.* Calcd for $C_{22}H_{16}N_2OS$: C, 74.13; H, 4.53; N, 7.86; S, 9.00. Found: C, 74.18; H, 4.20; N, 8.03; S, 9.22.

5-*p*-Methoxybenzylideneamino-2-*p*-methoxyphenyl-4-methylmercaptooxazole (Vd).—Dimethyl dithiooxaldiimidate (1.48 g, 0.01 mole) and 2.16 g (0.03 mole) of anisaldehyde were refluxed in benzene for 6 hr in a flask equipped with a Dean–Stark trap. The benzene was evaporated and the viscous, red oil was crystallized twice from ethanol to give 0.922 g (26%) of yellow needles: mp 118–119°; ν 2915 (CH_3), 1605 (aromatic C=C), and 1255 cm^{-1} (OCH_3); a singlet at δ = 8.70 (N=CH), two poorly resolved AB quartets at 8.10 and 7.18 (aromatics), a singlet at 3.98 (OCH_3), and a singlet of half the intensity of the methoxyl peak at 2.69 ppm (SCH_3). *Anal.* Calcd for $C_{19}H_{18}N_2O_3S$: C, 64.39; H, 5.12; N, 7.91; S, 9.05. Found: C, 64.65; H, 5.28; N, 8.05; S, 9.15.

5-Amino-4-benzylmercapto-2-*p*-nitrophenyloxazole (IXa).—Dibenzyl dithiooxaldiimidate (4.5 g, 0.015 mole) and 4.5 g (0.03 mole) of *p*-nitrobenzaldehyde were refluxed in 50 ml of benzene for 1 hr. The orange precipitate, which had begun to form after 10 min, was collected, washed with benzene, and crystallized from ethanol to give 4.08 g (83%) of orange needles: mp 180–181.5°; λ_{max} 412 mμ (log ε 4.17) and 247 mμ (log ε 4.06); ν 3365 (NH), 3235 (bonded NH), 3115 (aromatic CH), 1630 (aromatic C=C), and 1345 cm^{-1} (CNO_2); (dimethyl sulfoxide) an AB quartet (J = 9 cps) centered at δ = 8.28 (*p*-nitrophenyl), a singlet at 7.45 (benzyl aromatic), a wide peak at 6.87 which disappeared with D_2O (NH_2), and a singlet at 4.01 ppm (CH_2). *Anal.* Calcd for $C_{16}H_{13}N_3O_3S$: C, 58.70; H, 4.00; N, 12.84; S, 9.40. Found: C, 58.70; H, 3.91; N, 13.01; S, 9.52.

α-*p*-Nitrobenzoylamino-α-benzylmercaptoacetamide.—A solution of 1.09 g (3.3 mmoles) of 5-amino-4-benzylmercapto-2-*p*-nitrophenyloxazole, 75 ml of acetone, and 50 ml of 0.5 *N* hydrochloric acid, was refluxed for 2 hr. The red-orange solution gradually became pale yellow as the hydrolysis proceeded. The solution was neutralized with sodium carbonate and the acetone was distilled. The yellow precipitate was crystallized from acetone–hexane and to give 874 mg (96%) of silky white needles: mp 173–174°; ν 3350, 3225 (NH) and 1640, 1600 cm^{-1} (C=O). *Anal.* Calcd for $C_{16}H_{15}N_3O_4S$: C, 55.64; H, 4.37; N, 12.17; S, 9.28. Found: C, 55.78; H, 4.29; N, 12.21; S, 9.18.

(12) B. Johnson, *Am. Chem. J.*, **47**, 235 (1912).

(13) W. Bergell, *Z. Physiol. Chem.*, **64**, 362 (1910).

When 160 mg (0.5 mmole) of 5-amino-4-benzylmercapto-2-*p*-nitrophenyloxazole was hydrolyzed with 31 mg (0.5 mmole) of potassium hydroxide in ethanol at 25° for 12 hr, there was obtained 24 mg (14%) of silky, white needles, mp 172–173°, identical with the product of acid hydrolysis.

4-Benzylmercapto-5-diacetylamino-2-*p*-nitrophenyloxazole.—Compound IXa (1.09 g, 3.3 mmoles), in 15 ml of acetic anhydride, and 3 ml of acetic acid was heated on a steam bath for 20 hr. After addition of 20 ml of ethanol the volume was reduced to about 5 ml which gave yellow needles, mp 118–121°. Crystallization from acetone–hexane gave 0.863 g (62%) of pale yellow needles: mp 122–123.5°; ν 1720 and 1745 cm^{-1} (Ac_2N); an AB quartet at $\delta = 8.21$ ($J = 10$ cps, *p*-nitrophenyl), a singlet at 7.24 (benzyl aromatic), a singlet at 4.23 (CH_2), and a singlet integrating for six protons at 2.15 ppm (CH_3). *Anal.* Calcd for $C_{20}H_{17}N_3O_5S$: C, 58.57; H, 4.14; N, 10.16; S, 7.77. Found: C, 58.65; H, 4.11; N, 10.20; S, 7.57.

5-Acetylamino-4-benzylmercapto-2-*p*-nitrophenyloxazole.—When IXa (0.545 g, 1.7 mmoles) was treated with 10 ml of pyridine and 10 ml of acetic anhydride for 20 hr at 25° work-up afforded a viscous, brown oil. Chromatography on acid-washed alumina (pH 6), afforded 206 mg (29%) of diacetyl compound, mp 121–123°, and 188 mg (31%) of the monoacetyl compound, mp 181–186°, which gave ν 3270 (free NH), 3185 (bonded NH), and 1675 cm^{-1} (amide C=O). *Anal.* Calcd for $C_{18}H_{15}N_3O_4S$: C, 58.52; H, 4.09; N, 11.38; S, 8.68. Found: C, 58.39; H, 4.09; N, 11.61; S, 8.74.

Refluxing the diacetyl derivative (103 mg, 0.25 mmole) for 30 min in 5 ml of ethanol containing 2 drops of 1 *N* hydrochloric acid gave 78 mg (85%) of the monoacetyl derivative, mp 185–186°, after crystallization from ethanol–water.

5-Amino-4-methylmercapto-2-*p*-nitrophenyloxazole (IXb).—S,S'-Dimethyl dithiooxaldiimidate (1 g, 6.7 mmoles) and 2.1 g (14 mmoles) of *p*-nitrobenzaldehyde were heated for 45 min on a steam bath in 2 ml of benzene containing 1 drop of glacial acetic acid. The product was collected and washed with benzene to give red crystals, 1.3 g (76%), mp 164–169°. Further crystallization from benzene gave deep red crystals, mp 170–172°. *Anal.* Calcd for $C_{10}H_9N_3O_3S$: C, 47.81; H, 3.61; N, 16.73; S, 12.76. Found: C, 47.63; H, 3.42; N, 16.82; S, 12.92.

5-*p*-Nitrobenzylideneamino-4-phenylmercapto-2-*p*-nitrophenyloxazole (Ve).—S,S'-Diphenyl dithiooxaldiimidate (1.36 g, 5 mmoles), 1.66 g (11 mmoles) of *p*-nitrobenzaldehyde, and 2 ml of acetone were heated on a steam bath for 16 hr. After cooling, the crystalline product was separated and washed with acetone to give 1.35 g of dull, orange crystals. Recrystallization from acetone afforded 1.02 g (70%), mp 198–198.5°, of bright orange crystals. *Anal.* Calcd for $C_{22}H_{14}N_4O_5S$: C, 59.20; H, 3.16; N, 12.55; S, 7.18. Found: C, 58.99; H, 3.17; N, 12.64; S, 7.10.

Attempted Acylations of Va.—Compound Va (1 g, 3.3 mmoles) was refluxed for 2 hr in 10 ml of acetic anhydride and 3 ml of acetic acid. Addition of 20 ml of absolute ethanol, removal of volatile material, and dilution with 5 ml of absolute ethanol, gave yellow needles of Va, mp 100–103°. Addition of water to the mother liquor gave white crystals of α-benzoylamino-α-methylmercaptoacetonitrile (VI), mp 130–134°.

A similar experiment with refluxing acetic anhydride (10 ml) and pyridine (10 ml) gave only starting material after dilution with ethanol and evaporation of volatile material.

Compound Va (294 mg, 1 mmole), 0.4 g (3 mmoles) of benzoyl chloride, and 10 ml of pyridine were heated on a steam bath for 30 min. Neutralization with sodium bicarbonate at 5° gave, after crystallization from ethanol, 250 mg of the starting material Va. Repetition of the reaction for 12 hr under reflux also afforded only starting material.

Acknowledgment.—We wish to thank Miss Beth Bertram for technical assistance.

The Reaction of Diisopropyl Peroxydicarbonate with N,N-Dimethylaniline and N-Methyldiphenylamine

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Received March 28, 1966

Diisopropyl peroxydicarbonate (IPP) and N,N-dimethylaniline react at 8° in benzene to form carbon dioxide, isopropyl alcohol, and N-isopropoxymethyl-N-methylaniline as the major products. Carbon dioxide and isopropyl alcohol are also formed along with N-isopropoxymethyldiphenylamine in the reaction of IPP and N-methyldiphenylamine at 20°. A free-radical chain mechanism involving intermediate aminomethyl radicals is proposed for these reactions.

The reaction of diacyl peroxides, especially benzoyl peroxide, with N,N-dimethylaniline (DMA) has been studied rather extensively.[1-7] The present investigation was undertaken to study the reaction of diisopropyl peroxydicarbonate[8,9] (IPP) with tertiary amines. The initial studies have been carried out with DMA and N-methyldiphenylamine.

The reaction of IPP with DMA in benzene at 8° was much too rapid at reasonable concentrations for an accurate study of the kinetics by iodometric titration. For example, starting with initial concentrations of IPP and DMA of 0.0256 and 0.125 *M*, respectively, the half-life of the reaction was less than 30 sec. Significantly, running the reaction in a solvent containing 90 vol % benzene and 10% styrene led to an increase in the half-life by a factor of about 10.

The reaction of IPP with MDPA in benzene was much slower than that with DMA. It was studied at 10.0, 20.0, and 30.0° in all cases using a large excess of amine. Good pseudo-first-order rate plots were obtained during at least 1.5 half-lives in each case. The reaction is also first order in amine. Therefore, the kinetic expression describing the rate of reaction is as follows.

$$\text{rate} = k_2[\text{IPP}][\text{MDPA}]$$

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