

**N-Nitroso-4-chlorodibutylamine.**—N-Chlorodibutylamine prepared from dibutylamine (64.5 g.) by the usual procedure was irradiated in 85% sulfuric acid (200 ml.) for 36 hours at 25°. The resulting brown solution was diluted to 500 ml. with ice and water and extracted with ether to remove the color. A concentrated solution of potassium bicarbonate (500 g.) was added slowly followed by a concentrated solution of sodium nitrite (70 g.). The resulting mixture was heated at 100° for 30 minutes, cooled, and extracted with ether. The yellow oil (60.0 g.) obtained distilled at 88° (0.017 mm.) with some decomposition;  $n_D^{20}$  1.4733,  $d_4^{20}$  1.042.

**N-Nitroso-N-methyl-4-chlorobutylamine.**—N-Chloro-N-methylbutylamine was prepared in the usual way from methylbutylamine (43.6 g.) and irradiated in 85% sulfuric acid (150 ml.) at 10° for 42 hours. The solution when treated as above for the N-nitroso-4-chlorodibutylamine gave 7.52 g. of a yellow liquid boiling at 78° (1.5 mm.). Considerable tar was formed during the distillation.

*Anal.* Calcd. for  $C_8H_{11}ON_2Cl$ : C, 39.87; H, 7.36. Found: C, 39.65; H, 6.91.

**Lithium Aluminum Hydride Reduction of N-Nitroso-4-chlorodibutylamine.**—A solution of freshly distilled N-nitroso-4-chlorodibutylamine (58 g.) in absolute ether (100 ml.) was treated slowly with a slurry of lithium aluminum hydride (12.5 g.) in absolute ether (200 ml.) over a period of 2.5 hours. The resulting mixture was allowed to stand overnight and decomposed with water. Removal of the ether gave an oil which on distillation gave three fractions.

The first fraction (5.1 g.) distilled at 68–94° (29 mm.) and on refractionation gave a product (3.00 g.) boiling at 68–76° (29 mm.). This product, N-butylpiperidazine, gave a positive Fehling test, contained no chlorine and gave an acid oxalate, when mixed with an equimolar amount of oxalic acid dihydrate in absolute ethanol, which melted at 220–220.5°.

*Anal.* Calcd. for  $C_{10}H_{20}O_4N_2$ : C, 51.71; H, 8.68. Found: C, 50.63; H, 8.68.

The second fraction distilled at 94–106° (29 mm.). Redistillation gave a liquid (5 g.) boiling at 62–65° (10 mm.),  $d_4^{20}$  0.808. 1,1-Dibutylhydrazine is reported to boil at 60–62° (11 mm.),  $d_4^{20}$  0.8029.<sup>10</sup> The oxalate had a melting point of 166–168° after several recrystallizations from ethanol. This compound did not depress the melting point (168–169°) of an authentic sample of 1,1-dibutylhydrazine hydrogen oxalate.<sup>11</sup>

The third fraction, b.p. 110–142° (29 mm.), gave on redistillation a liquid (17.46 g.) boiling at 124–126° (21 mm.),  $n_D^{20}$  1.4485,  $d_4^{20}$  0.900. Similar properties are reported for N-nitrosodibutylamine.<sup>12</sup>

(10) A. I. Vogel, W. T. Cressell, G. H. Jeffrey and J. Leichster, *J. Chem. Soc.*, 514 (1952).

(11) R. A. Rowe and L. F. Audrieth, *THIS JOURNAL*, **78**, 563 (1956).

(12) A. I. Vogel, *J. Chem. Soc.*, 1849 (1948).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, TULANE UNIVERSITY]

### Acid-catalyzed Reactions between Carbonyl Compounds and Organic Azides. III. Aromatic Ketones<sup>1</sup>

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Aromatic ketones of the type  $C_6H_5COCH_2R$  in an inert solvent containing concentrated sulfuric acid are transformed by certain alkyl azides into benzaldehyde and an aldehyde corresponding to the alkyl group ( $RCH_2$ ). The best yields (70–85%) of benzaldehyde are obtained from acetophenone. Alkyl azides are reduced to corresponding primary amines in 50–65% yields. A probable explanation requires (1) a Lewis acid–base reaction between the ketone conjugate acid and an alkyl azide, (2) dehydration and elimination of nitrogen and (3) recombination with water followed by proton elimination and breakdown of a proposed intermediate adduct of an  $\alpha$ -ketoalcohol and a primary amine. The last step (3) apparently occurs only after dilution with water and is supported by the acid-catalyzed breakdown of phenacyl alcohol into benzaldehyde and formaldehyde.

The first acid-catalyzed reaction between organic azides and the carbonyl function was realized in the transformation of aromatic aldehydes into amides or their derivatives.<sup>2–4</sup> In a recent communication a one-step transformation of acetophenone into benzaldehyde using alkyl azides in the presence of sulfuric acid was announced.<sup>5</sup> A study of this new transformation as well as similar investigations on propiophenone, isobutyrophenone, benzophenone, desoxybenzoin *p*-nitrobenzyl phenyl ketone, *m*-nitroacetophenone, *p*-hydroxyacetophenone and *o*-acetylbenzoic acid is described here.

Benzaldehyde, in 70–85% yield, is obtained from acetophenone in combination with each of four alkyl azides but not with phenyl, benzyl,  $\beta$ -

phenylethyl or  $\gamma$ -phenylpropyl azides. With the latter four, other acid-catalyzed transformations occur. The reaction may be carried out using sulfuric acid as a catalyst in either benzene or nitrobenzene at 70–75°. The methyl group of acetophenone is transformed into formaldehyde, isolated in 80–86% yield as its bis-methone condensation, and the alkyl azide is reduced to the corresponding primary amine in 50–65% yield. These data describe an acid-catalyzed oxidation–reduction reaction with no over-all molecular rearrangement.

In a similar manner propiophenone is transformed into benzaldehyde (62%) and acetaldehyde (50%). The higher and very critical temperature of 90–91° is required. Below and above this temperature propiophenone has been quantitatively recovered. Tar formation increases with temperature and apparently results from azide decomposition. Isobutyrophenone is not transformed into benzaldehyde using *n*-butyl azide and sulfuric acid in either benzene or nitrobenzene at temperatures ranging from 75 to 115°. In all cases isobutyrophenone may be recovered, and at the higher temperatures there is considerable tar formation. Similar results are obtained from the combination

(1) Financial assistance under a National Institutes of Health Grant No. H-2295 and contracts Nos. DA-01-009-ORD-428 and DA-01-009-ORD-699 with Office of Ordnance Research is gratefully acknowledged.

(2) J. H. Boyer and J. Hamer, *THIS JOURNAL*, **77**, 951 (1955), Part I.

(3) J. H. Boyer and L. R. Morgan, Jr., *J. Org. Chem.*, **24**, in press (1959), Part II.

(4) Earlier attempts to realize a similar reaction between methyl azide and either benzoic acid (L. H. Briggs, G. G. De Ath and S. R. Ellis, *J. Chem. Soc.*, **61**, (1942)) or acetophenone (P. A. S. Smith, *THIS JOURNAL*, **70**, 320 (1948)) were unsuccessful.

(5) J. H. Boyer and L. R. Morgan, Jr., *ibid.*, **80**, 2020 (1958).



TABLE I  
 ALDEHYDES AND AMINES FROM KETONES AND AZIDES

Ketone	Azide	Reaction temp., °C.	Solvent	Aldehydes (yield, %)	Amine (yield, %)	B.p., °C.	Derivatives, m.p., °C.
Acetophenone	<i>n</i> -Butyl	70-75	Benzene	Benzaldehyde <sup>a</sup> (70) Formaldehyde <sup>c</sup> (86.1)	<i>n</i> -Butyl (60.7)	78 <sup>b</sup>	Hydrochloride, 195 dec. <sup>b</sup> Picrate, 145 <sup>b</sup>
Acetophenone	<i>n</i> -Hexyl	70-75	Benzene	Benzaldehyde <sup>a</sup> (79.9) Formaldehyde <sup>c</sup> (80.2)	<i>n</i> -Hexyl (65.1)	130 <sup>d</sup>	Hydrochloride, 219 <sup>d</sup> Chloroplatinate, 238 dec. <sup>d</sup>
Acetophenone	Cyclohexyl	70-75	Benzene	Benzaldehyde <sup>a</sup> (85)	Cyclohexyl <sup>e</sup> (50.1)	134 <sup>f</sup>	Hydrochloride, 206-207 <sup>f</sup>
Acetophenone	<i>n</i> -Octyl	70-75	Benzene	Benzaldehyde <sup>a</sup> (70)	<i>n</i> -Octyl (52)	175 <sup>g</sup>	Picrate, 111.5-112.5 <sup>g</sup>
Propiophenone	<i>n</i> -Butyl	90-91 <sup>h</sup>	Toluene	Benzaldehyde <sup>a</sup> (62.1) Acetaldehyde <sup>i</sup> (50)			
Desoxybenzoin	<i>n</i> -Butyl	135-138	Nitrobenzene	Benzaldehyde <sup>a</sup> (19) <sup>j</sup>			

<sup>a</sup> Identification based on b.p. 35° (2 mm.),  $n_D^{25}$  1.5427, phenylhydrazone m.p. and mixture m.p. 156° (S. R. Pound, *J. Phys. Chem.*, **31**, 1496 (1931), reports b.p. 34° (2 mm.),  $n_D^{25}$  1.5420, phenylhydrazone m.p. 157°). <sup>b</sup> R. Brown and W. E. Jones, *J. Chem. Soc.*, 781 (1946). <sup>c</sup> Identification based on m.p. and mixture m.p. 191-192° for the dimethone derivative (W. Weinberger, *Ind. Eng. Chem., Anal. Ed.*, **3**, 365 (1931), reports m.p. 191.4°). <sup>d</sup> A. Nyssens, *Ingenieur Chimiste*, **18**, 40 (1930). <sup>e</sup>  $n_D^{20}$  1.4370. <sup>f</sup> A. Guyot, *Bull. soc. chim. France*, **47**, 205 (1930). <sup>g</sup> D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 838 (1934). <sup>h</sup> At temperatures above or below 90-91°, propiophenone is quantitatively recovered. <sup>i</sup> Identification based on 2,4-dinitrophenylhydrazone, m.p. and mixture m.p. 146°. <sup>j</sup> Yield based on recovered desoxybenzoin (62%).

reaction mixtures, including those from experiments with two moles of azide per mole of acetophenone or of propiophenone, gives no indication of the presence of a secondary amine.

Formaldehyde also cannot be detected prior to dilution. Upon passing as stream of nitrogen gas through the reaction mixture, obtained from acetophenone with an alkyl azide and concentrated sulfuric acid in benzene, and then into a methone solution there was no detection of the formation of the formaldehyde bis-methone condensation product; however, this technique successfully allowed the formation in good yield of this derivative of formaldehyde after the reaction mixture was diluted with water as well as from a prepared solution of formalin in concentrated sulfuric acid.

### Experimental<sup>8</sup>

**Preparation of the Azides.**—*n*-Butyl,<sup>5</sup> *n*-hexyl,<sup>5</sup> *n*-octyl,<sup>5</sup> cyclohexyl,<sup>5</sup> phenyl,<sup>9</sup>  $\beta$ -phenylethyl<sup>2</sup> and benzyl<sup>2</sup> azides were previously prepared.

To a solution of 32.2 g. (0.2 mole) of  $\gamma$ -phenylpropyl bromide in 60 ml. of 95% ethanol is added a slurry of 34.2 g. (0.43 mole) of sodium azide in 42 ml. of water. Upon completion of solution a small amount of sodium azide is added until a solid phase persists. The mixture is refluxed for 24 hours, cooled, diluted with an equal volume of water and extracted with ether. Upon removal of ether from the combined dried extracts,  $\gamma$ -phenylpropyl azide is obtained, 22.5 g. (70%), b.p. 55° (0.25 mm.),  $n_D^{25}$  1.5268.

*Anal.* Calcd. for C<sub>9</sub>H<sub>11</sub>N<sub>3</sub>: C, 67.21; H, 6.84; N, 26.11. Found: C, 67.18; H, 6.85; N, 26.19.

**General Procedure for the Ketone-Aldehyde Transformation (Table I).**—To a mixture of 0.05 mole of ketone in 50 ml. of solvent and 6 ml. of concentrated sulfuric acid heated to within ten degrees below reaction temperature, 0.05 mole of an azide is added dropwise at a rate which keeps the well-stirred mixture at a specified temperature. Upon completion of nitrogen gas evolution, 50 ml. of ice and water is added. The aqueous layer is neutralized with sodium hydroxide and extracted with ether. Amines are distilled from the oil residue obtained upon removal of ether. The in-

tractable tar obtained at this stage from reactions with propiophenone and with desoxybenzoin does not allow isolation of expected amines.

Benzaldehyde is obtained upon distillation of the organic layer of the reaction mixture.

To the aqueous acid layer after ether extraction, a solution of 20 g. of methone, 36 ml. of 50% methanol and 13 drops of piperidine is added and heated on the water-bath for 10 minutes. Upon cooling, the bis-methone condensation product of formaldehyde separates. It is recrystallized from methanol from which it separates as colorless plates.

**Acid-catalyzed Breakdown of Phenacyl Alcohol.**—A 50-ml. round-bottomed flask containing 4.0 g. (0.029 mole) of phenacyl alcohol,<sup>10</sup> m.p. 85-86°, 3 ml. of concentrated sulfuric acid and 25 ml. of water is attached to a gas trap containing 20 g. of methone in 36 ml. of 50% methanol and 13 drops of piperidine and is heated on a water-bath at 45-50° with constant shaking for 15 minutes during which time no gas evolution is observed. An oil residue, obtained after removal of benzene from combined benzene extractions of the mixture, gives upon distillation 2.6 g. (68.5%) of benzaldehyde, b.p. 42-43° (6 mm.),  $n_D^{25}$  1.5329, phenylhydrazone m.p. and mixed m.p. 156°. As previously described formaldehyde is isolated as its bis-methone condensation product, 2.89 g. (30.2%), m.p. and mixture m.p. 191-192°.

**An Acid-catalyzed Reaction of  $\beta$ -Phenylethyl Azide.**—To 50 ml. of benzene and 6 ml. of concentrated sulfuric acid heated to 45°, 7.35 g. (0.05 mole) of  $\beta$ -phenylethyl azide is added dropwise at a rate which keeps the temperature between 45 and 60°. After nitrogen gas evolution has ceased, 50 ml. of ice and water is added. The aqueous layer is neutralized with sodium carbonate and extracted with ether. Upon removal of ether an unidentified yellow solid is isolated, 1.1 g., m.p. 93° after recrystallization from methanol.

*Anal.* Calcd. for C<sub>10</sub>H<sub>11</sub>N<sub>3</sub>O: C, 87.04-86.25; H, 6.16-7.01; N, 3.17-3.14; O, 3.62-3.59. Found: C, 86.28; H, 6.34; N, 3.55; O, 3.83.

This product, no depression in mixture m.p., is also obtained in the presence of acetophenone. The ketone is quantitatively recorded.

In a similar manner benzyl azide in the presence or absence of acetophenone is transformed into an unidentified yellow solid which, upon exposure to air, becomes a tar.

**An Acid-catalyzed Reaction between *o*-Acetylbenzoic Acid and Alkyl Azides.**—To a solution of 4.12 g. (0.05 mole)

(8) Semi-micro analyses by Alfred Bernhardt, Microanalytisches Laboratorium, Mülheim (Ruhr), Germany.

(9) R. O. Lindsay and C. F. H. Allen, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 710.

(10) W. L. Evans, *Am. Chem. J.*, **35**, 119 (1906).

of *o*-acetylbenzoic acid<sup>11</sup> in 25 ml. of benzene and 3 ml. of concentrated sulfuric acid at 60–70°, 4.02 g. (0.025 mole) of  $\gamma$ -phenylpropyl azide is added dropwise with stirring. The reaction mixture upon dilution with 25 ml. of water is separated. From the benzene layer a colorless amorphous solid, 3.9 g., m.p. 221–223° after recrystallization from ethanol, is obtained.

*Anal.* Calcd. for (C<sub>9</sub>H<sub>6</sub>O<sub>2</sub>)<sub>n</sub>: C, 73.95; H, 4.11; O, 21.91. Found: C, 73.82; H, 4.28; O, 21.90.

(11) H. L. Vale, *THIS JOURNAL*, **69**, 1547 (1947).

This product, no depression in mixture m.p., is obtained when *n*-butyl azide is substituted for  $\gamma$ -phenylpropyl azide. Under similar experimental conditions in which no azide is present *o*-acetylbenzoic acid is nearly quantitatively recovered.<sup>12</sup>

(12) S. Gabriel, *Ber.*, **17**, 2665 (1884), reports that concentrated sulfuric acid transforms *o*-acetylbenzoic acid into an unidentified compound, C<sub>15</sub>H<sub>12</sub>O<sub>4</sub>, m.p. 213–215°.

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## Reduction with Lithium Aluminum Hydride. II. Lithium Aluminum Hydride Reduction of Aryloxyalkylketene Monomers and Dimers

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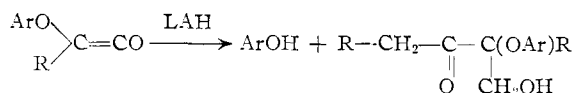
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Lithium aluminum hydride reduction of aryloxyalkylketene monomers and dimers of the type, Ar—C=C=O, where Ar

is *p*-*t*-butylphenoxy and 2,4-dichlorophenoxy, and R is H, C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>3</sub>H<sub>7</sub> and *n*-C<sub>4</sub>H<sub>9</sub>, has been investigated. Lithium aluminum hydride converted the *p*-*t*-butylphenoxyalkylketene monomers to  $\beta$ -ketocarbinols and *t*-butylphenol; the dimers to glycols. 2,4-Dichlorophenoxyketene monomer was reduced to 2,4-dichlorophenoxyethanol and 2,4-dichlorophenoxyethylketene dimer to the corresponding glycol. The infrared spectra of the ketenes and their reduction products have been studied.

An earlier investigation in this Laboratory established that lithium aluminum hydride reduces ( $\omega$ -cyclohexylalkyl)-ketene dimers to  $\beta$ -ketocarbinols. We have shown also that high pressure catalytic reduction of monomeric and dimeric aryloxyketenes produces glycols and the corresponding phenol.<sup>2</sup> The present investigation was undertaken with the object of exploring the reductive action of lithium aluminum hydride on aryloxyalkylketene monomers and dimers.

An ethereal solution of lithium aluminum hydride reacted with the *p*-*t*-butylphenoxyalkylketene monomers to give substituted  $\beta$ -ketocarbinols and the corresponding phenol. The constitution of the  $\beta$ -ketocarbinols indicated that lithium aluminum hydride cleaved the ketene monomers at the ether bond.<sup>3</sup> We have observed that lithium



aluminum hydride reacts with *p*-*t*-butylphenoxyethyl-, *p*-*t*-butylphenoxypropyl- and *p*-*t*-butylphenoxybutylketene monomers to give 2-ethyl-2-(*p*-*t*-butylphenoxy)-3-keto-1-hexanol (67%), 2-*n*-propyl-2-(*p*-*t*-butylphenoxy)-3-keto-1-heptanol (30%) and 2-*n*-butyl-2-(*p*-*t*-butylphenoxy)-3-keto-1-octanol (32%), respectively. *t*-Butylphenol was isolated from each experiment. These reduction products were similar to those isolated in our study of lithium aluminum hydride reduction of  $\omega$ -cyclohexylalkyl-ketene dimers.<sup>1</sup> However, catalytic hydrogenation of aryloxyalkylketene monomers gave substituted 1,3-glycols.<sup>2</sup>

(1) A. S. Spriggs, C. M. Hill and G. W. Senter, *THIS JOURNAL*, **74**, 1555 (1952).

(2) C. M. Hill, M. E. Hill, A. O. Williams and E. M. Shelton, *ibid.*, **75**, 1084 (1953).

(3) V. L. Tweedie and M. Cuscurida, *ibid.*, **79**, 5463 (1957).

Lithium aluminum hydride reduced 2,4-dichlorophenoxyketene monomer to 2,4-dichlorophenoxyethanol (85%).

Glycols were formed when lithium aluminum hydride reacted with *p*-*t*-butylphenoxyalkylketene and 2,4-dichlorophenoxyethylketene dimers. In these experiments, lithium aluminum hydride reduced *p*-*t*-butylphenoxy-, *p*-*t*-butylphenoxyethyl-, *p*-*t*-butylphenoxy-*n*-propyl-, *p*-*t*-butylphenoxy-*n*-butyl- and 2,4-dichlorophenoxyethylketene dimers to 2,4-di-(*p*-*t*-butylphenoxy)-, (72%), 2,4-(*p*-*t*-butylphenoxy)-2,4-diethyl-(30%), 2,4-di-(*p*-*t*-butylphenoxy)-2,4-di-*n*-propyl-(25%), 2,4-di-(*p*-*t*-butylphenoxy)-2,4-di-*n*-butyl-(31%) and 2,4-di-(2,4-dichlorophenoxy)-2,4-diethyl-1,3-cyclobutanediol (77%), respectively.<sup>2</sup>

The ketene monomers were characterized by molecular weight determinations, infrared spectra, comparison of observed physical constants with those reported (in some cases) and preparation of solid derivatives. The monomers formed substituted hydrazides when treated with 2,4-dinitrophenylhydrazine. The infrared spectra of the ketene monomers showed four bands in the double bond region, 5.7, 5.8, 5.9 and 6.02  $\mu$ ; the band at 6.02  $\mu$  is characteristic of the C=C bond. Infrared spectra of the ketene monomers were analogous.

The ketene dimers reacted with 2,4-dinitrophenylhydrazine to produce the dihydrazones. The infrared spectra of the dimers were similar, showing two bands in the double bond region at 5.7 and 5.8  $\mu$ .

Reduction products of *p*-*t*-butylphenoxyethyl- and *p*-*t*-butylphenoxy-*n*-butylketene monomers formed substituted pyrazolines when treated with 2,4-dinitrophenylhydrazine; the reduction product from 2,4-dichlorophenoxyketene monomer gave the 3,5-dinitrobenzoate. Attempts were made to pre-