urethanes is reported[12] to be in the range 1736–1700 cm.$^{-1}$, and carbonyl absorption for an O-acylated hydroxamic acid is reported[13] to be at 1520, 1588, 1610, and 1653 cm.$^{-1}$.

Amidoximes A. Reaction of *p*-Toluic Acid with Nitroethane.—A mixture of 11.5 g. (0.084 mole) of *p*-toluic acid, 10 g. (0.134 mole) of nitroethane and 35 g. of PPA was heated at 115–125° for 2 hr., poured into 100 g. of crushed ice, stirred, and filtered. *p*-Toluic acid, 1.0 g., was recovered. The filtrate was basified with KOH, cooled for 2 hr. at 5°, and filtered. N-(*p*-Tolyl)acetamidoxime, m.p. 127°, 7.0 g. (63% yield), was obtained. The material required recrystallization from water to give a pure product.

B. Reaction of *p*-Chloroaniline with Acethydroxamic Acid.—A mixture of 12.75 g. (0.1 mole) of *p*-chloroaniline, 7.5 g. (0.1 mole), of acethydroxamic acid, and 70 g. of PPA was heated for 90 min. at 110–115°, poured into crushed ice, basified with KOH, and filtered. N-(*p*-Chlorophenyl)acetamidoxime, m.p. 130° (from water), 10.1 g. (54% yield), was obtained. The infrared spectrum was superimposable on the product from the reaction of *p*-chlorobenzoic acid and nitroethane.

An attempt to react aniline with *p*-nitrobenzhydroxamic acid gave none of the expected N-phenyl-*p*-nitrobenzamidoxime. Instead, rearrangement of the starting acid to *p*-nitroaniline (12% yield) and hydrolysis to *p*-nitrobenzoic acid (63% yield) occurred.

C. Reaction of Aniline with Nitroethane.—A mixture of 9.3 g. (0.1 mole) of aniline, 7.5 g. (0.1 mole) of nitroethane, and 100 g. of PPA was heated for 10 hr. at 120–130°, poured into 100 g. of crushed ice, basified with KOH, cooled at −10° overnight, and filtered. N-Phenylacetamidoxime, 6.1 g. (41% yield), m.p. 121° (from water), was obtained; lit.[14] m.p. 120–121°.

A similar experiment with *p*-nitroaniline instead of aniline gave no amidoxime. Similarly, *p*-cresol and *p*-thiocresol failed to give the corresponding O-aryl and S-aryl hydroxamic acids. These three compounds are probably too weakly nucleophilic to react with hydroxamic acids.

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[12] L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 221.

[13] E. M. Usova and E. M. Voroshin, *Dokl. Akad. Nauk SSSR*, **113**, 1306 (1957).

[14] E. Nordmann, *Ber.*, **17**, 2746 (1884).

Enamine Chemistry. VIII.[1] Reactions with Miscellaneous Carbonyl and Active Hydrogen Compounds[2]

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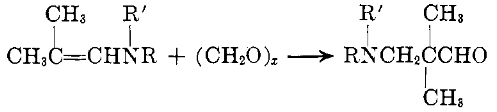
Received February 24, 1964

The reactions of enamines with a number of carbonyl and active hydrogen compounds are reported. Enamines derived from isobutyraldehyde react with paraformaldehyde to give Mannich-type products, with 2 moles of chloral to give 2,6-bis(trichloromethyl)-4-(dialkylamino)-5,5-dimethyl-*m*-dioxanes, with diethyl malonate to give a mixture of diethyl isobutylidenemalonate and diethyl isobutenylmalonate, and with acetamide to give N-[1-(dimethylamino)-2-methylpropyl]acetamide. Enamines derived from isobutyraldehyde and butyraldehyde react with *p*-benzoquinone to give substituted dihydrobenzofuranols.

Enamines have been shown to behave as nucleophilic reagents in many of their reactions. Since there is a large segment of organic chemistry which involves interactions of carbonyl compounds with nucleophiles, we have undertaken a survey of the reactions of enamines (most of which are derived from isobutyraldehyde) with several reactive carbonyl compounds. A logical starting point was the reaction with formaldehyde, the simplest carbonyl compound, at least in the structure of its monomer.

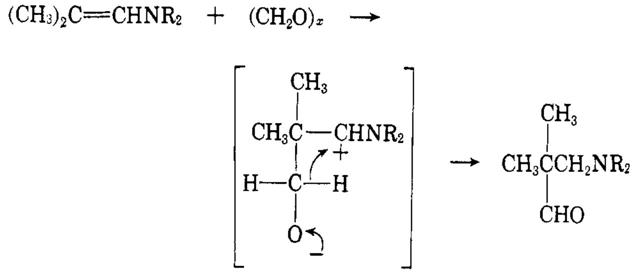
Reaction with Formaldehyde.—We found that heating N,N-dimethylisobutenylamine or 1-isobutenylpiperidine with paraformaldehyde produced substituted aminopivalaldehydes which have also been obtained by the Mannich reaction of isobutyraldehyde, formaldehyde, and the appropriate amine.[3]



$$CH_3C(CH_3){=}CHNRR' + (CH_2O)_x \longrightarrow RR'NCH_2C(CH_3)_2CHO$$

1, R = CH_3; R′ = CH_3
2, R = R′ = $—CH_2(CH_2)_3CH_2—$

One possible course of the reaction is that the small amount of water present in paraformaldehyde hydrolyzes a part of the enamine and the reaction then proceeds as a simple Mannich reaction with recycling of the water. Another reaction path considered involved intermediate **3**, which could form the observed product by a 1,3-hydride transfer.



$$(CH_3)_2C{=}CHNR_2 + (CH_2O)_x \longrightarrow \left[CH_3C(CH_3)(CHNR_2^{+})CH_2O^{-} \right] \longrightarrow CH_3C(CH_3)(CHO)CH_2NR_2$$

3

If the reaction were carried out using formaldehyde-d_2 as a reactant, the distribution of deuterium atoms in the products would show whether the latter route is feasible.

As a check, a Mannich reaction of isobutyraldehyde, dimethylamine, and formaldehyde was carried out using a large molar excess of deuterium oxide as solvent. The product, as expected, showed no detectable amount of deuterium present when checked by n.m.r. and infrared spectroscopy. Thus, no "scrambling" of deuterium should occur in a Mannich reaction using formaldehyde-d_2. A reaction of N,N-dimethylisobutenylamine with formaldehyde-d_2 was carried out, and in the n.m.r. spectrum of the product no peak assignable to N-methylene hydrogens was present, but a peak of

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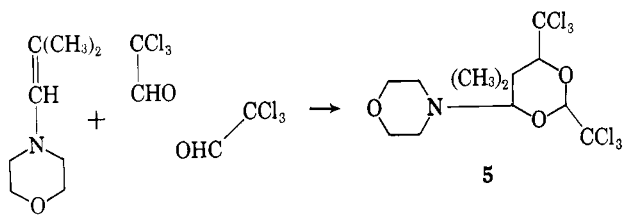
[1] Paper VII of this series: K. C. Brannock, R. D. Burpitt, and J. G. Thweatt, *J. Org. Chem.*, **29**, 940 (1964).

[2] A portion of the material in this paper was presented at the Southeast Regional Meeting of the American Chemical Society, Gatlinburg, Tenn., Nov. 1–3, 1962.

[3] C. Mannich, *Ber.*, **65**, 378 (1932).

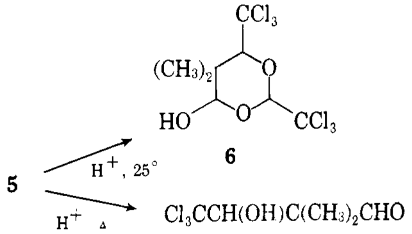
normal intensity for the aldehyde proton was present. As a result of these experiments, we concluded that the enamine–formaldehyde reaction is simply a modification of the Mannich reaction.

Reaction with Chloral.—When chloral was substituted for formaldehyde, an entirely different type of product was obtained. Two moles of chloral reacted with 1 mole of 4-isobutenylmorpholine (**4**), regardless of the ratio of reactants or order of addition, to form 2,6-bis(trichloromethyl)-5,5-dimethyl-4-morpholino-*m*-dioxane (**5**) in good yield.



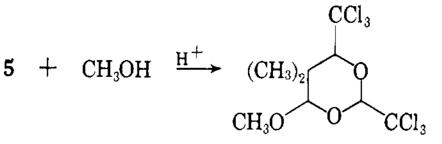
4 **5**

Hydrolysis of **5** at room temperature with excess acid gave the hemiacetal **6** but, when **5** was heated with an equivalent amount of acid, the aldol **7** was obtained.



6 **7**

Methanolic hydrogen chloride reacted with **5** to give the methoxy derivative **8** in good yield.



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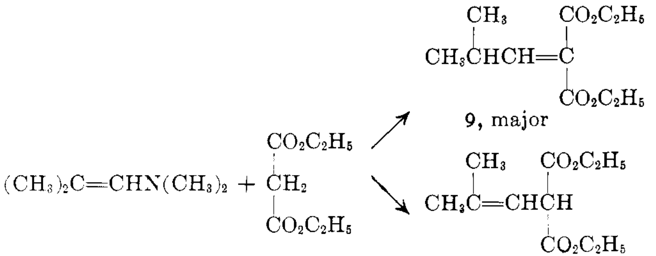
Reaction with Diethyl Malonate.—Diethyl malonate is reactive at the methylene position rather than at a carbonyl group. When this ester was heated with N,N-dimethylisobutenylamine, dimethylamine was evolved and the product obtained on distillation appeared to be mainly diethyl isobutylidenemalonate (**9**). A second component, shown to be present by vapor phase chromatography, was apparently diethyl isobutenylmalonate (**10**) since hydrogenation of the mixture yielded a single component which was identical with authentic diethyl isobutylmalonate.

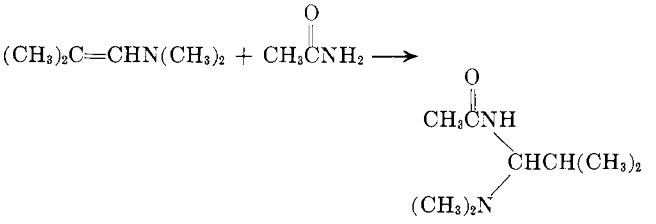


9, major

10, minor

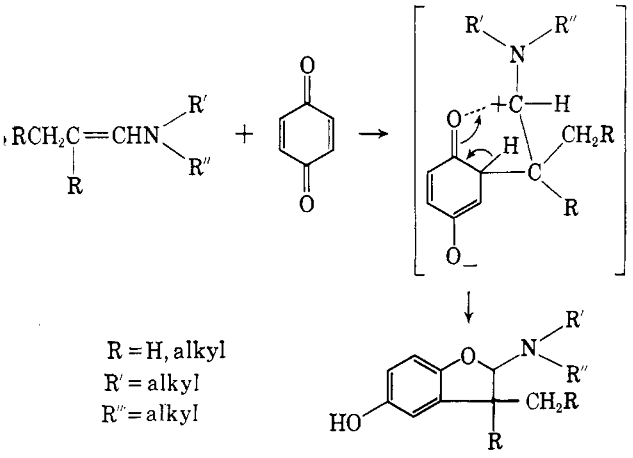
The success of this reaction suggests the possible intermediacy of enamines in some amine-catalyzed reactions of aldehydes with dimethyl malonate.

Reaction with Acetamide.—When N,N-dimethylisobutenylamine was allowed to react with acetamide, N-[1-(dimethylamino)-2-methylpropyl]acetamide (**11**) was formed. The scope of this novel reaction has not been determined.



11

Reaction with *p*-Benzoquinones.—Enamines derived from isobutyraldehyde and butyraldehyde react exothermally with *p*-benzoquinones to give substituted dihydrobenzofuranols 12.[4]

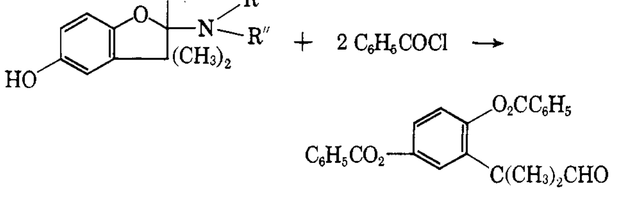


R = H, alkyl
R' = alkyl
R'' = alkyl

12

This is similar to the reaction recently reported[5] between N,N'-(2,5-cyclohexadiene-1,4-diylidene)dibenzenesulfonamide and alicyclic enamines such as 1-(1-cyclohexen-1-yl)pyrrolidine which gives 6-(phenylsulfonylamino)-9-(phenylsulfonyl)-1,2,3,4-tetrahydrocarbazole.

When the benzofuranol from an isobutyraldehyde enamine was treated with benzoyl chloride in pyridine, the hydroquinone dibenzoate **13** was formed. Other attempts to open the furan ring with aqueous acids were unsuccessful.



13

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[4] See G. Domschke, *Z. Chem.*, **4**, 29 (1964). This author erroneously regards the adducts as hydroquinones rather than benzofuranols. We are indebted to a referee for calling this reference to our attention.

[5] M. E. Kuehne, *J. Am. Chem. Soc.*, **84**, 837 (1962).

Experimental[6,7]

(Dimethylamino)pivalaldehyde (1).—N,N-Dimethylisobutenylamine[8] (33 g., 0.33 mole) and paraformaldehyde (10 g., 0.33 mole) were combined and heated in an autoclave for 2 hr. at 160°. Distillation of the reaction product gave, after removal of a 6 g. forerun, 25 g. (54%) of (dimethylamino)pivalaldehyde,[3] b.p. 144–146°, $n^{20}{}_{\mathrm{D}}$ 1.4241.

Piperidinopivalaldehyde (2).—1-Isobutenylpiperidine[9] (41.7 g., 0.3 mole) and paraformaldehyde (9.0 g., 0.3 mole) were combined and heated in an autoclave for 2 hr. at 150°. Distillation of the liquid product gave 42.0 g. (83%) of piperidinopivalaldehyde, b.p. 55–60° (*ca.* 1 mm.), $n^{20}{}_{\mathrm{D}}$ 1.4637. The product was characterized as its semicarbazone, m.p. 181° (lit.[3] m.p. 175°), and its hydrochloride, m.p. 166° (lit.[3] m.p. 164°).

(Dimethylamino)pivalaldehyde Prepared in Water and in Deuterium Oxide.—To a mixture of 25% aqueous dimethylamine (36 g., 0.2 mole) and isobutyraldehyde (14.4 g., 0.2 mole) paraformaldehyde (6.0 g., 0.2 mole) was added. The stirrer was started and the temperature rose rapidly to 40°, then slowly to 47°. The mixture was stirred until it had cooled to room temperature and then for 1 hr. longer. The organic layer was separated and the aqueous phase was extracted with ether (20 ml.). Distillation of the combined organic layers gave 13.5 g. (52%) of (dimethylamino)pivaldehyde, b.p. 57–59° (26 mm.), $n^{20}{}_{\mathrm{D}}$ 1.4250.

This experiment was repeated using, in place of the aqueous dimethylamine, a solution of dimethylamine (9.5 g., 0.21 mole) in deuterium oxide (30 g.). Seven grams (28%) of product, b.p. 58–60° (26 mm.), was obtained. The infrared, n.m.r., and mass spectra of this material and the material prepared in water were identical, indicating that no deuterium exchange had occurred.

(Dimethylamino)pivalaldehyde Prepared from Formaldehyde-d_2.—Formaldehyde-d_2[10] (1.0 g., 0.033 mole) and N,N-dimethylisobutenylamine (10 g., 0.1 mole) were combined and heated in an autoclave for 2 hr. at 160° under 1000 p.s.i. of nitrogen. Distillation of the mixture gave 1.5 g. (35%) of product, b.p. 56° (26 mm.). The n.m.r. spectrum of the product did not show the peak at 2.42 p.p.m. (N-methylene hydrogens), but did show the aldehyde proton peak at 9.45 p.p.m. of normal intensity.

2,6-Bis(trichloromethyl)-5,5-dimethyl-4-morpholino-*m*-dioxane (5).—Chloral (294 g., 2 moles) was added dropwise to a stirred solution of 4-isobutenylmorpholine[11] (141 g., 1 mole) in acetonitrile (200 ml.). The rate of addition was adjusted to keep the temperature at 35 ± 3°. After being allowed to stand 1 hr., the mixture was chilled and the crystalline solid was washed with cold acetonitrile and dried to give 360 g. (83%) of 2,6-bis(trichloromethyl)-5,5-dimethyl-4-morpholino-*m*-dioxane, m.p. 154–155° with sintering and development of opaqueness at about 132–136°. A sample for elemental analysis was recrystallized from acetone. The infrared spectrum showed no absorption bands in the carbonyl or double bond region, from 5.5 to 6.2 μ. The n.m.r. spectrum exhibited a single peak at 5.13 p.p.m. for the $-OCH(CCl_3)O-$ proton, peaks at 1.27 and 1.37 p.p.m. for the two methyl groups, multiplets centered at 3.00 and 3.67 p.p.m. for the methylene protons of morpholine, and single peaks at 3.85 and 4.02 p.p.m. for the remaining two tertiary protons.

Anal. Calcd. for $C_{12}H_{17}Cl_6NO_3$: C, 33.1; H, 3.9; Cl, 48.8; N, 3.2. Found: C, 33.2; H, 3.5; Cl, 48.1; N, 3.5.

An additional experiment was carried out using ether as the solvent with essentially the same results. In another experiment, 1 mole of chloral was added to 1 mole of 4-isobutenylmorpholine, and the 2:1 adduct was the only product isolated. When the mode of addition was reversed and the 1:1 ratio of reactants used, the 2:1 adduct was still the only product isolated.

2,6-Bis(trichloromethyl)-5,5-dimethyl-*m*-dioxan-4-ol (6).—2,6-Bis(trichloromethyl)-5,5-dimethyl-4-morpholino-*m*-dioxane (43.6 g., 0.1 mole) was added to a solution of water (200 ml.) and concentrated hydrochloric acid (80 ml.), and the resulting mixture was stirred overnight at room temperature. The solid was removed by filtration and dried in a vacuum desiccator to give 33 g. (90%) of 2,6-bis(trichloromethyl)-5,5-dimethyl-*m*-dioxan-4-ol, m.p. 133–137°. A sample recrystallized from hexane melted at 138–139.5°. The infrared spectrum showed no absorption in the carbonyl region. The n.m.r. spectrum showed peaks at 1.00 and 1.25 p.p.m. for the two methyl groups, a single peak at 5.40 p.p.m. for the $-OCH(CCl_3)O-$ proton, a single peak at 2.10 p.p.m. for the hydroxy proton, and single peaks at 4.12 and 4.48 p.p.m. for the two remaining tertiary protons.

Anal. Calcd. for $C_8H_{10}Cl_6O_3$: C, 26.2; H, 2.7. Found: C, 26.3; H, 2.7.

When chloral was allowed to react with N,N-dimethylisobutenylamine, an undistillable oil was obtained. This oil, on treatment with acid as previously described, gave 2,6-bis(trichloromethyl)-5,5-dimethyl-*m*-dioxan-4-ol.

2,6-Bis(trichloromethyl)-4-methoxy-5,5-dimethyl-*m*-dioxane (8).—A solution of 2,6-bis(trichloromethyl)-5,5-dimethyl-4-morpholino-*m*-dioxane (87 g., 0.2 mole) in methanol (800 ml.) was added rapidly to a solution of anhydrous hydrogen chloride (14 g., 0.38 mole) in methanol (100 ml.). The resulting clear solution was allowed to stand for 72 hr., during which time a white solid crystallized. This was removed by filtration to give 40 g. of 2,6-bis(trichloromethyl)-4-methoxy-5,5-dimethyl-*m*-dioxane, m.p. 162–165°. Concentration of the filtrate gave an additional 16.5 g. which, combined with the original material, gave a yield of 74%. The n.m.r. spectrum showed peaks at 1.29 and 1.38 p.p.m. for the two methyl groups, a peak at 3.48 p.p.m. for the methoxy group, a single peak at 5.45 p.p.m. for the $-OCH(CCl_3)O-$ proton, and single peaks at 4.33 and 4.65 p.p.m. for the two remaining tertiary protons.

Anal. Calcd. for $C_9H_{12}Cl_3O_3$: C, 28.4; H, 3.2. Found: C, 28.5; H, 3.4.

4,4,4-Trichloro-3-hydroxy-2,2-dimethylbutyraldehyde (7).—2,6-Bis(trichloromethyl)-5,5-dimethyl-4-morpholino-*m*-dioxane (62 g., 0.14 mole), concentrated hydrochloric acid (60 ml.), and water (250 ml.) were combined and the mixture was heated on the steam bath for 0.5 hr. The mixture was cooled and the oil removed by extraction with ether. Distillation gave, after removal of ether and a small forerun, 11.5 g. (37%) of 4,4,4-trichloro-3-hydroxy-2,2-dimethylbutyraldehyde, b.p. 98–102° (1.8 mm.), $n^{20}{}_{\mathrm{D}}$ 1.5052. The infrared spectrum showed the presence of carbonyl, hydroxyl, and aldehyde functions.

Anal. Calcd. for $C_6H_9Cl_3O_2$: C, 32.8; H, 4.1. Found: C, 32.7; H, 4.1.

The **2,4-dinitrophenylhydrazone** was recrystallized from ethyl alcohol and melted at 171–172°.

Anal. Calcd. for $C_{12}H_{12}Cl_3N_4O_5$: C, 36.1; H, 3.3. Found: C, 36.0; H, 3.6.

On standing, the aldol dimerized to give a white, crystalline solid which melted at 180–181° on recrystallization from benzene.

Anal. Calcd. for $C_{12}H_{18}Cl_6O_4$: mol. wt., 438. Found: mol. wt., 444.

Diethyl Isobutylidenemalonate (9).—N,N-Dimethylisobutenylamine (50 g., 0.5 mole) was refluxed and diethyl malonate (80 g., 0.5 mole) was added dropwise with stirring over a 1-hr. period. The mixture was stirred and heated for 3 hr. longer, while the temperature rose to a maximum of 144°. Dimethylamine was evolved during the reaction. Distillation through a 6-in. Vigreux column gave, after removal of a 2-g. forerun, 75 g. (73%) of diethyl isobutylidenemalonate, b.p. 63–65° (1 mm.), $n^{20}{}_{\mathrm{D}}$ 1.4410.

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.5; H, 8.4. Found: C, 61.7; H, 8.8.

Gas chromatographic analysis (Carbowax column at 150°, preheated at 200°) of the product showed it to be mostly one component with a small amount of a second component, which was probably the isomer, diethyl isobutenylmalonate (10).

Diethyl Isobutylmalonate.—Diethyl isobutylidenemalonate (75 g., 0.35 mole) was subjected to hydrogenation over 5 g. of Raney nickel at 100° and 2000 p.s.i. The reaction mixture was filtered and distilled to give 58 g. (77%) of diethyl isobutylmalonate, b.p. 85–89° (3 mm.), $n^{20}{}_{\mathrm{D}}$ 1.4207 [lit.[12] b.p. 112–114° (12 mm.), $n^{15.9}{}_{\alpha}$ 1.4219]. Gas chromatographic analysis showed this product to contain only one component, and the infrared spectrum was identical with that of an authentic sample.

N-[1-(Dimethylamino)-2-methylpropyl]acetamide (11).—Acetamide (29.5 g., 0.5 mole), N,N-dimethylisobutenylamine (49.5 g., 0.5 mole), and acetonitrile (200 ml.) were combined

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(6) Melting points were determined using a calibrated Fisher-Johns melting point apparatus.

(7) N.m.r. spectra were recorded either on a Varian Model A-60 or Model V4300-B 40-Mc. spectrometer. Peak positions are in parts per million relative to internal tetramethylsilane.

(8) K. C. Brannock and R. D. Burpitt, *J. Org. Chem.*, **26**, 3576 (1961).

(9) C. Mannich and H. Davidsen, *Ber.*, **69**, 2106 (1936).

(10) Merck Sharp and Dohme of Canada Limited.

(11) E. Benzing, *Angew. Chem.*, **71**, 521 (1959).

(12) E. Fischer, *Ber.*, **39**, 351 (1906).

and refluxed for 4 hr. The mixture was then chilled to give 34 g. (43%) of N-[1-(dimethylamino)-2-methylpropyl]acetamide. A sample recrystallized from hexane melted at 63–65°. The n.m.r. spectrum showed a doublet centered at 0.90 p.p.m. for the two methyls of the isopropyl group, a broad absorption from 1.5 to *ca.* 2.0 p.p.m. for the tertiary proton of the isopropyl group, a single peak at 2.00 p.p.m. for the acetyl group, a single peak at 2.20 p.p.m. for the dimethylamino group, a doublet at 7.95 p.p.m. for the NH proton, and a triplet at 4.18 p.p.m. for the remaining tertiary proton.

Anal. Calcd. for $C_8H_{18}N_2O$: C, 60.7; H, 11.5. Found: C, 60.3; H, 11.4.

2-(Dimethylamino)-2,3-dihydro-3,3-dimethyl-5-benzofuranol.—N,N-Dimethylisobutenylamine (5 g., 0.5 mole) was added to a slurry of *p*-benzoquinone (5.4 g., 0.05 mole) in benzene (50 ml.) over a 0.5-hr. period at such a rate as to maintain the temperature at 40–50°. The mixture stood overnight and the solid was removed by filtration and recrystallized three times from benzene to give 5 g. (48%) of 2-(dimethylamino)-2,3-dihydro-3,3-dimethyl-5-benzofuranol, m.p. 155–157°. The n.m.r. spectrum (in acetone) showed peaks at 1.17 and 1.23 p.p.m. for the *gem*-dimethyl group, a single peak at 2.23 p.p.m. for the dimethylamino group, a single peak at 4.83 p.p.m. for the -OCHN< proton, and peaks centered at 6.55 p.p.m. corresponding to three aromatic protons. In addition, the single phenolic proton appeared as a broad peak at 5.25 p.p.m. at room temperature and was shifted to a sharper peak at 4.9 p.p.m. at 50°.

Anal. Calcd. for $C_{12}H_{17}NO_2$: C, 69.5; H, 8.3; N, 6.8. Found: C, 69.7; H, 8.0; N, 6.7.

2,3-Dihydro-3,3-dimethyl-2-piperidino-5-benzofuranol.—To a slurry of benzoquinone (108 g., 1 mole) in xylene (500 ml.), 1-isobutenylpiperidine (142 g., 1 mole) was added in portions over a 0.5-hr. period with cooling to maintain the temperature at 50–60°. After the addition was complete, the mixture was allowed to stand 0.5 hr. and 200 ml. of xylene was added along with some Super Cel. The mixture was heated to 115° and filtered while hot. On cooling, the filtrate gave 2,3-dihydro-3,3-dimethyl-2-piperidino-5-benzofuranol, which was removed by filtration and washed with xylene and hexane. The product weighed 122 g. (49%), m.p. 158°. A sample for analysis was recrystallized from benzene to a constant melting point of 164–165°. The n.m.r. spectrum of this compound, and of the benzofuranols described subsequently, showed only three aromatic protons and one phenolic proton.

Anal. Calcd. for $C_{15}H_{21}NO_2$: C, 72.8; H, 5.7; N, 8.6. Found: C, 72.6; H, 5.6; N, 8.6.

(1-Formyl-1-methylethyl)hydroquinone Dibenzoate.—Benzoyl chloride (3 g., 0.021 mole) was added to 2,3-dihydro-3,3-dimethyl-2-piperidino-5-benzofuranol (2.5 g., 0.01 mole) in pyridine (10 ml.) and the mixture was heated on the steam bath for 20 min. Saturated sodium bicarbonate solution (50 ml.) was added to the mixture which was then filtered. The solid was recrystallized from aqueous ethyl alcohol to give 1.5 g. of (1-formyl-1-methylethyl)hydroquinone dibenzoate, m.p. 146–147°.

Anal. Calcd. for $C_{24}H_{20}O_5$: C, 74.2; H, 5.2. Found: C, 74.2; H, 5.5.

The **2,4-dinitrophenylhydrazone** melted at 261–262°.

Anal. Calcd. for $C_{30}H_{24}N_4O_8$: C, 63.4; H, 4.3. Found: C, 63.3; H, 4.6.

3-Ethyl-2,3-dihydro-2-piperidino-5-benzofuranol.—To a slurry of *p*-benzoquinone (21.6 g., 0.2 mole) in benzene, 1-(1-butenyl)-piperidine[13] was added in portions over a 10-min. period with cooling to maintain the temperature at 25–30°. The mixture was filtered, and the filter cake was washed with cold pentane to give, after drying, 42.8 g. (87%) of 3-ethyl-2,3-dihydro-2-piperidino-5-benzofuranol. A sample for analysis, recrystallized from benzene, melted at 173–175°.

Anal. Calcd. for $C_{15}H_{21}NO_2$: C, 72.8; H, 8.5. Found: C, 72.8; H, 8.4.

2-(Dimethylamino)-3-ethyl-2,3-dihydro-5-benzofuranol.—In a manner similar to that described previously, N,N-diethyl-1-butenylamine[14] (63.5 g., 0.5 mole) and *p*-benzoquinone (54 g., 0.5 mole) gave 141 g. (60%) of 2-(dimethylamino)-3-ethyl-2,3-dihydro-5-benzofuranol, b.p. 143–146° (*ca.* 1.5 mm.), n^{20}_D 1.5380.

Anal. Calcd. for $C_{14}H_{21}NO_2$: C, 71.5; H, 9.0. Found: C, 70.8; H, 9.2.

2,3-Dihydro-2-morpholino-3-pentyl-5-benzofuranol.—In a similar manner, 4-(1-heptenyl)-morpholine[15] (46 g., 0.25 mole) and *p*-benzoquinone (27 g., 0.25 mole) gave 70 g. (96%) of 2,3-dihydro-2-morpholino-3-pentyl-5-benzofuranol, m.p. 83–84.5°.

Anal. Calcd. for $C_{17}H_{25}NO_3$: C, 70.2; H, 8.7. Found: C, 70.1; H, 8.8.

Acknowledgment.—The authors wish to acknowledge the assistance of V. W. Goodlett of these laboratories for the n.m.r. spectra and for aid in their interpretation.

[13] C. Mannich and H. Davidsen, *Ber.*, **69**, 2106 (1963).

[14] Prepared in 61% yield by the method described by Mannich and Davidsen[13]; b.p. 39–41° (12 mm.), n^{20}_D 1.4470. *Anal.* Calcd. for $C_8H_{17}N$: N, 11.0. Found: N, 10.9.

[15] P. L. de Benneville and J. H. Macartney, *J. Am. Chem. Soc.*, **72**, 3073 (1950).

The Transformation of 3-Amino-2-iminooxazolidines to Semicarbazone Derivatives[1]

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Received April 24, 1964

Heating 2-imino-3-(5-nitrofurfurylideneamino)oxazolidine hydrochloride or 3-(benzylideneamino)-2-iminooxazolidine hydrochloride in xylene affords the corresponding 2-(2-chloroethyl)semicarbazones, which have been aminated with various secondary amines. The reaction of benzaldehyde 2-(2-chloroethyl)semicarbazone with ammonia results in the formation of 1-benzylideneamino-1-(2-hydroxyethyl)guanidine. Proposed mechanisms are discussed.

As reported previously,[2] the action of thionyl chloride on 5-nitro-2-furaldehyde 2-(2-hydroxyethyl)semicarbazone (Ib) produced a quantitative yield of 2-imino-3-(5-nitrofurfurylideneamino)oxazolidine hydrochloride (IIb) rather than the chloroethylsemicarbazone IIIb. When IIb was recrystallized repeatedly from 95% ethanol or from ethanolic hydrogen chloride, a partial transformation to IIIb was effected.

To investigate this transformation further, heated suspensions of IIb in toluene and xylene were examined. After 30 min. in boiling xylene, a 96% yield of IIIb was obtained, while 2 hr. in boiling toluene resulted in a 73% yield of IIIb. The benzaldehyde analog Ia underwent the same reaction with thionyl chloride and subsequent ring opening of the iminooxazolidine hydrochloride in boiling xylene.

The mechanism of ring cleavage of the iminooxazolidines probably involves chloride ion attack at the C-5 position. This is supported by the observation

[1] Presented at the 19th International Congress of Pure and Applied Chemistry, London, July 10–17, 1963.

[2] K. Hayes, F. Ebetino, and G. Gever, *J. Am. Chem. Soc.*, **77**, 2282 (1955).