

Lithium-Methylamine Reduction. I. Reduction of Furan, 2-Methylfuran, and Furfuryl Alcohol¹

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Received December 30, 1968

Rosenblum⁴ has reported the reduction of the furan ring of 2-furoic acid using sodium and ammonia as well as sodium, alcohol, and ammonia, but he was unable to reduce furan (**1**) by the same methods. 2-Methylfuran (**2**) also is not reducible using sodium in ammonia.⁵ Furfuryl alcohol (**3**) has been converted (about 40%) into **2** with sodium in liquid ammonia, but no further reduction was observed.⁶

It has been shown that there are only slight differences between sodium-alcohol-ammonia reductions and those employing lithium-alcohol-methylamine.⁷ However, in previous work Benkeser and coworkers⁸ demonstrated that lithium-amine is a more powerful if less selective reducing system than sodium-ammonia.

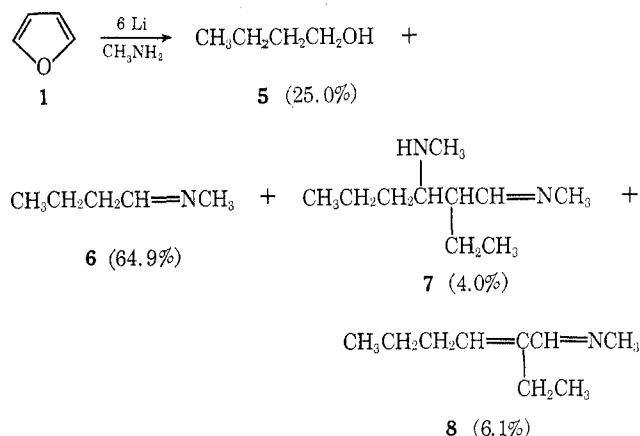
On the basis of the aforementioned facts, it seemed worthwhile to attempt the reduction of **1-3** using lithium in methylamine.

Results

The reduction of 2-methylfuran (**2**) with lithium in methylamine produces six products (see Table I), some of which indicate that extensive ring opening has occurred. The relative amounts of these products is dependent on the amount of lithium employed. One of the products of this reaction, N-1-methylbutylidene-methylamine (**4**), was characterized by matching its infrared spectrum with that of an authentic sample prepared⁹ from 2-pentanone and methylamine. The fact that **4** (very sensitive to moisture) could be reduced either catalytically or by lithium in methylamine to the known N-1-dimethylbutylamine contributed to its identification. The ethanol isolated in the reduction of **2** is unexpected and seemingly results from the rupture at -6° of a carbon-carbon as well as a carbon-oxygen bond.¹⁰

The reduction of **1** (*vide infra*) yielded four products, two of which (**7** and **8**) were probably the result of

an aldol-type condensation of N-butylidenemethylamine (**6**). N-(2-Ethyl-2-hexenylidene)methylamine (**8**) was identified by independent synthesis,¹¹ comparison of ir spectra, and an nmr spectrum. Glpc collection and reinjection of the other product (**7**), probably N-(2-ethyl-3-methylaminohexylidene)methylamine, showed considerable conversion of this compound into **6** and **8**. Further substantiation of this identification was obtained from an nmr spectrum (see Experimental Section). Attempts to isolate **7** again for further study failed.



The reductions of furfuryl alcohol with lithium and methylamine are summarized in Table II.

Discussion

The present conception of the reduction of the furan ring is shown in Scheme I. No attempt was made to postulate the role of lithium in the reaction or the reducing species involved (*i.e.*, e^- , e_2^{2-} , $e^-\text{Li}^+$).¹²

The reduction of **2** (Table I) with 2 equiv of lithium apparently results from the reduction of half of **2** with 4 equiv of lithium, and half of **2** remains unreacted. The inability to account for all the starting material appears to be characteristic of this type of reduction.^{4,6}

A carbinolamine species is an obvious intermediate in the conversion of 2-pentanone into **4**,¹³ and by analogy with aliphatic ketals¹⁴ one would not expect an aliphatic carbinolamine to be reduced. Thus it is believed that a carbinolamine or some ionic form thereof is an intermediate in this reduction.

The products previously discussed are predictable on the basis of metal-ammonia reduction of benzofurans,^{15,16} but the isolation of ethanol is quite unexpected. Although carbon-carbon bond cleavage in metal-ammonia reductions is not unknown, those compounds in which it has been observed have one or more phenyl groups on each carbon involved in the bond cleavage¹⁷ or contain a cyclopropyl system.¹⁸ It is

(1) (a) This work was supported in part by funds given to the University of Southern Mississippi by the Mississippi Board of Trustees of Institutions of Higher Education for the support of basic research. (b) Portions of this work were presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, and the 20th Southeastern Regional Meeting of the American Chemical Society, Tallahassee, Fla., Dec 1968.

(2) University of Southern Mississippi Graduate Fellow.

(3) National Science Foundation Graduate Fellow.

(4) L. Rosenblum, Ph.D. Dissertation, The Ohio State University, 1952.

(5) A. P. Dunlop and F. N. Peters, "The Furans," Reinhold Publishing Corp., New York, N. Y., 1953, p 52.

(6) A. J. Birch, *J. Chem. Soc.*, 809 (1945).

(7) R. A. Benkeser, M. L. Burrous, J. J. Hazdra, and E. M. Kaiser, *J. Org. Chem.*, **28**, 1094 (1963).

(8) R. A. Benkeser in "Metal-Organic Compounds," Advances in Chemistry Series, No. 23, American Chemical Society, Washington, D. C., 1959, pp 58-62.

(9) R. Tiollais, *Bull. Soc. Chim. Fr.*, 708 (1947).

(10) To eliminate the possibility that the ethanol was a contaminant of the ether used for extraction, methyl *n*-propyl ether was used as the extracting solvent on one occasion with the same results.

(11) R. Tiollais and H. Guillermin, *Compt. Rend.*, **236**, 1798 (1953).

(12) J. L. Dye, *Accounts Chem. Res.*, **1**, 306 (1968).

(13) M. M. Sprung, *Chem. Rev.*, **26**, 297 (1940).

(14) R. A. Benkeser, C. Arnold, Jr., R. F. Lambert, and O. H. Thomas, *J. Amer. Chem. Soc.*, **77**, 6042 (1955).

(15) S. D. Darling and K. D. Wills, *J. Org. Chem.*, **32**, 2794 (1967).

(16) D. P. Brust and D. S. Tarbell, *ibid.*, **31**, 1251 (1966).

(17) (a) C. B. Wooster and J. F. Ryan, *J. Amer. Chem. Soc.*, **56**, 1133 (1934); (b) C. B. Wooster and D. S. Latham, *ibid.*, **55**, 76 (1936).

(18) (a) R. van Volkenburg, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *ibid.*, **71**, 3595 (1949); (b) W. G. Dauben and E. J. Deviny, *J. Org. Chem.*, **31**, 3794 (1966); (c) H. M. Walborsky, F. P. Johnson, and J. B. Pierce, *J. Amer. Chem. Soc.*, **90**, 5222 (1968).

TABLE I
 REDUCTION OF 2-METHYLFURAN^a

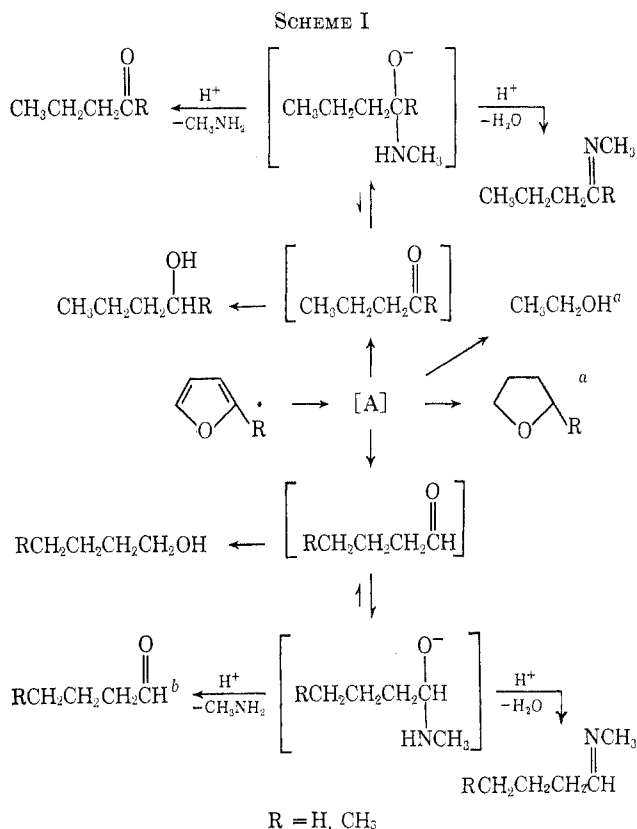
Products from reduction with	2 Li	4 Li	6 Li	8 Li
Tetrahydro-2-methylfuran, % ^b	4.8	14.4	13.4	10.5
2-Pentanone, %	5.6	10.3	...	...
N-1-Methylbutyldenemethylamine, % ^c	80.0	47.1	33.6	37.4
2-Pentanol, %	1.0	7.2	28.6	28.6
1-Pentanol, %	3.8	16.6	12.7	15.6
Ethanol, %	4.8	4.5	13.4	8.1
Amount of reduced material recovered, g	10.6	16.3	19.1	19.7

^a In all the reactions 20.5 g (0.250 mol) of 2-methylfuran and 500 ml of methylamine were used. ^b This is per cent of reduced material recovered. It was determined from glpc curve areas. No attempt was made to correct the peak areas for differences in thermal conductivity of the components. ^c See Experimental Section for the preparation of the authentic sample.

 TABLE II
 REDUCTION OF FURFURYL ALCOHOL^a

Products from reduction with	2 Li	4 Li	6 Li	8 Li
Tetrahydrofurfuryl alcohol, % ^b	...	...	8.4	...
2-Methylfuran, %	51.5	12.3	...	...
Tetrahydro-2-methylfuran, %	...	...	...	2.6
2-Pentanone, %	...	26.9	9.8	3.8
N-1-Methylbutyldenemethylamine, % ^c	24.2	39.8	41.2	17.4
N-Pentyldenemethylamine, %	...	...	...	15.5
2-Pentanol, %	...	...	7.3	41.9
1-Pentanol, %	...	12.8	19.3	18.7
Ethanol, %	4.8	2.7	13.7	...
Furfuryl alcohol, %	19.9	5.4	...	...
Amount of reduced material recovered, g	15.0	19.1	17.3	14.8

^a In each reaction 24.5 g (0.250 mol) of furfuryl alcohol and 500 ml of methylamine were used. ^b This is per cent of reduced material recovered. The percentages were determined from glpc curve areas uncorrected for differences in thermal conductivity of the components. ^c See Experimental Section for the preparation of the authentic sample.



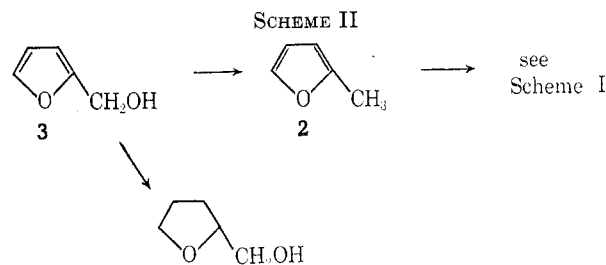
^a These products were not observed in the reduction of furan.
^b This product was observed in the reduction of furfuryl alcohol but not in the reduction of 2-methylfuran.

presently thought that ethanol produced in the reduction arises from C₂-C₃ cleavage of a ring-intact intermediate followed by a base-catalyzed ether cleav-

age of the ion produced (possibly a concerted process). A study of variables in the production of ethanol is currently in progress. Initial investigations show that the amount of ethanol formed is dependent on solution conditions and ring substituents. Up to 48% ethanol can be obtained.¹⁹

The reduction of furan was differentiated from that of 2 by the aldol-type imine condensation, absence of ethanol, and absence of cyclic products.

The reduction of furfuryl alcohol (Scheme II) involved extensive hydrogenolysis of 3 to 2, as Birch observed using sodium-ammonia.⁶ Tetrahydrofurfuryl alcohol



and N-pentyldenemethylamine were isolated in addition to the products found from the reduction of 2. The absence of N-pentyldenemethylamine among the products of reduction of 2 and its occurrence in reduction of 3 is attributed to the more acidic conditions existing during the reduction of 3 owing to the ionizable hydroxyl hydrogen.

Experimental Section

Ir spectra were recorded on a Perkin-Elmer Model 257 grating spectrophotometer. Nmr spectra were determined on a Varian

(19) Unpublished results from this laboratory.

Model A-60D spectrometer with tetramethylsilane as an internal reference. Glpc analyses were carried out on a Microtek Model GC-2000R linear temperature programmed gas chromatograph using 0.25 in. $\times$ 10 ft coiled stainless steel tubes packed with 20% Carbowax 20M on 60-80 mesh nonacid-washed Chromosorb W. The carrier gas in these determinations was helium, and the temperature program was 50-225° at a rate of 10 deg/min.

General Procedure.—After a three-necked Pyrex flask equipped with Dry Ice condenser and mercury trap, mechanical stirrer, and gas-inlet tube was flushed with dry nitrogen, 2-methylfuran (2) or furfuryl alcohol (3) was added. The desired amount of methylamine was then condensed in the flask, and the calculated amount of 1/8-in. lithium wire was added to the stirred mixture. The solution was decomposed with ammonium chloride in water, and the product was extracted with ether and dried (Na₂SO₄). The solvent was distilled off under vacuum without heat, the products were analyzed by glpc, and the compounds were identified by comparison of their ir and, where noted, nmr spectra with those of authentic compounds.²⁰ The results of the reduction of 2-methylfuran and furfuryl alcohol are summarized in Tables I and II, respectively.

Reduction of 2-Methylfuran (2).—Following the general procedure above, 20.5 g (0.250 mol) of 2 and 10.35 g (1.50 g-atoms of lithium in 500 ml of methylamine were allowed to react for 8 hr. After extraction (methyl *n*-propyl ether), 23.3 g of reduced material was recovered. The major products, in order of their elution from glpc, were tetrahydro-2-methylfuran²¹ (7.1%) ethanol²¹ (7.7%), 2-pentanone²¹ (31.6%), N-1-methylbutylenemethylamine²¹ (29.1%), 2-pentanol²¹ (17.7%), and 1-pentanol²¹ (6.8%). Their relative retention times were 1:2.26:2.64:2.93:3.89:5.14.

N-1-Methylbutylenemethylamine (4).—Using a modification of Tiollais' method⁹ for preparation of N-alkylaldimines, 40.5 g (0.472 mol) of 2-pentanone was added dropwise to 150 ml of methylamine and stirred for 1.5 hr. The excess methylamine was removed by heating to 50°. Addition of potassium carbonate caused foaming and separation into two layers. The organic layer was decanted, diluted with an equal volume of ether, and dried (Na₂SO₄). A 45-50% yield of 4, bp 108-110°, was realized:²² ir $\nu_{\text{max}}^{\text{CCl}_4}$ 2962, 2879, 1451, 1358 (CH), and 1659 cm⁻¹ (C=N); nmr (CCl₄, max) τ 6.90 (s, 3, C=NCH₃), 7.39-8.80 (complex m, 7, CH₂ and CH₃), and 9.06 (t, 3, CH₃).

Reduction of N-1-Methylbutylenemethylamine (4). **A. Catalytic Hydrogenation of Authentic 4.**—An 8.80-g mixture of 4 and 2-pentanone was allowed to react in a Parr hydrogenation apparatus²³ until detectable reaction ceased (5.5-psi decrease). The final product mixture, analyzed by glpc, was composed of 2-pentanone (18.2%), 2-pentanol (23.2%), and N,1-dimethylbutylamine (58.6%).

The spectral data for N,1-dimethylbutylamine follow: ir $\nu_{\text{max}}^{\text{CCl}_4}$ 2966, 2935, 2875, 2791, 1467, 1372 (CH), 3263 (NH, very weak), and 1161 cm⁻¹ (CN); nmr (CDCl₃, max) τ 7.58 (s, 3, NCH₃) and 8.33-9.30 (complex m, 11, CH, CH₂, and CH₃).

Anal. Calcd for C₆H₁₅N: C, 71.21; H, 14.94. Found: C, 70.95; H, 14.77.

B. Catalytic Hydrogenation of 4 from the Reduction of 2-Methylfuran (2).—In a Brown² Micro Hydro-Analyzer²⁴ was placed 4.0 mg (0.0403 mmol) of 4. The reduction, which consumed 0.0400 mmol of the theoretical 0.0403 mmol of hydrogen, produced N,1-dimethylbutylamine identical with that obtained from reduction of the authentic 4.

C. Reduction of 4 with Lithium in Methylamine.—Using the general procedure (*vide supra*), an 18.5-g mixture of 0.1 mol of 2-pentanone, 0.1 mol of 4, 2.76 g (0.400 g-atom) of lithium, and 400 ml of methylamine were stirred together for 5 hr and 10 min. The 17.0-g product mixture, analyzed by glpc, was composed of N,1-dimethylbutylamine (54.7%), 2-pentanol (7.9%), 2-pentanone (13.3%), and 4 (24.2%).

Reduction of Furan (1).—After 8 hr, the reaction of 34.0 g (0.500 mol) of freshly distilled furan and 20.7 g (3.00 g-atoms) of lithium in 1000 ml of methylamine yielded 21.9 g of reduced material. This was composed of N-butylenemethylamine²¹ (64.9%), 1-butanol²¹ (25.0%), N-(2-ethyl-2-hexenyldene)-

methylamine²¹ (6.1%), and N-(2-ethyl-3-methylaminohexyldene)methylamine (4.0%).

N-Butylenemethylamine (6)⁹ gave the following spectral data: ir $\nu_{\text{max}}^{\text{CCl}_4}$ 2969, 2878, 2846, 1457 (CH), and 1672 cm⁻¹ (C=N); nmr (CDCl₃, max) τ 2.35 (perturbed s, 1, CH=N), 6.73 (perturbed s, 3, C=NCH₃), and 7.66-9.31 (complex m, 7, CH₂ and CH₃).

N-(2-Ethyl-2-hexenyldene)methylamine (8)¹¹ gave the following spectral data: ir $\nu_{\text{max}}^{\text{CCl}_4}$ 2972, 2945, 2882, 2849, 2777, 1463, 1456, 1402 (CH), 1644 (C=N), and 1633 cm⁻¹ (C=C); nmr (CDCl₃, max) τ 2.28 (perturbed s, 1, CH=N), 4.25 (t, 1, CH=C), 6.64 (s, 3, C=NCH₃), 7.69 (perturbed quintet, 4, C=CCH₂), and 8.28-9.28 (complex m, 8, CH₂ and CH₃).

N-(2-Ethyl-3-methylaminohexyldene)methylamine (7) gave the following spectral data: nmr (CD₃COCD₃, max) τ 4.38 (perturbed s, 1, CH=N), 6.47-6.77 (complex m, 1, CHC=N), 7.52 (s, 3, C=NCH₃), 7.85 (s, 3, NDCH₃), and 8.00-9.32 (complex m, CH, CH₂, and CH₃).

N-Pentylenemethylamine was prepared using the procedure for the preparation of N-1-methylbutylenemethylamine, and gave the following spectral data: ir $\nu_{\text{max}}^{\text{CCl}_4}$ 2958, 2880, 2863, 2846, 2781, 1459 (CH), and 1671 cm⁻¹ (C=N); nmr (CCl₄, max) τ 2.43 (br s, 1, CH=N), 6.83 (perturbed s, 3, C=NCH₃), and 7.37-9.31 (complex m, 9, CH₂ and CH₃).

Registry No.—1, 110-00-9; 2, 534-22-5; 3, 98-00-0; 4, 22431-09-0; 7, 22431-11-4; N-1-dimethylbutylamine, 22431-10-3; N-pentylenemethylamine, 10599-75-4.

Acknowledgment.—The authors wish to thank the Perkin-Elmer Corp. for mass spectra of the components of some of the reduction mixtures.

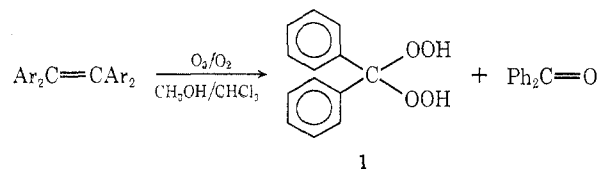
Diphenylmethyl Bishydroperoxide. An Anomalous Product from the Ozonolysis of Tetraphenylethylene

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Received March 6, 1969

The ozonolysis of an olefin in a hydroxylic solvent is one method of synthesizing alkoxy hydroperoxides.²⁻⁴ Tetraphenylethylene has been ozonized in the presence of methanol,^{5,6} but the resultant methoxy hydroperoxide from the interception of the Criegee zwitterion (2) has never actually been isolated. We have made numerous attempts to prepare the expected methoxy hydroperoxide at temperatures ranging from -78 to 0° and have isolated only the expected benzophenone and the completely unexpected diphenylmethyl bishydroperoxide (1). A bishydroperoxide during ozonation in a hydroxylic solvent has not been previously observed.



(1) National Science Foundation Graduate Teaching Assistant Fellow, summers of 1968, 1969.

(2) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

(3) R. Criegee and G. Lohaus, *Ann. Chem.*, **583**, 6 (1953).

(4) R. Criegee in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p 34.

(5) S. Fliszar, D. Gravel, and E. Cavalleri, *Can. J. Chem.*, **44**, 67 (1966).

(6) S. Fliszar and M. Granger, *J. Amer. Chem. Soc.*, **91**, 3330 (1969).

(20) Unless otherwise noted, the authentic samples were obtained from commercial sources.

(21) Nmr spectra were used for identification.

(22) This yield is based on glpc analysis of the product mixture.

(23) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1957, p 867.

(24) C. A. Brown, *Anal. Chem.*, **39**, 1882 (1967).