Notes

Reactions of Some Derivatives of 1-Methyl-2-imidazolidinone[1]

ANTHONY M. FUSCO, GUY J. DEL FRANCO, AND ELI J. ARONOFF

Central Research Laboratories, Interchemical Corporation, Clifton, New Jersey 07015

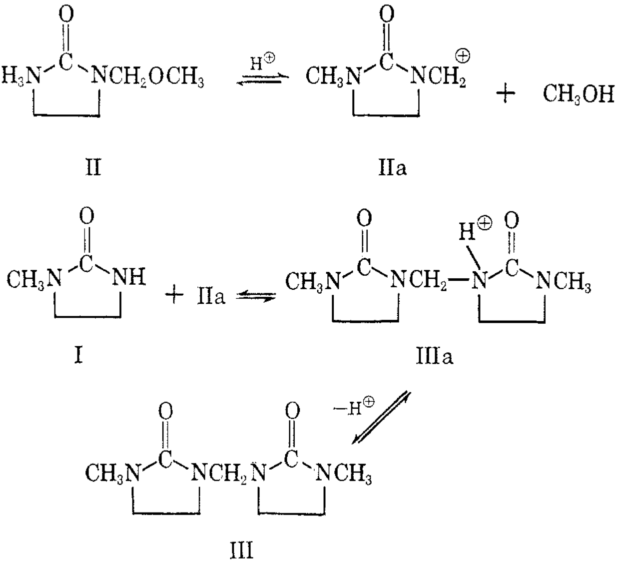
Received February 11, 1965

The technically important reaction between urea and formaldehyde to give hydroxymethylureas and subsequently methylenebisureas has been the subject of much investigation.[2–8] Unfortunately, the systems employed in these studies were polyfunctional and the data in aqueous solution suffers from the fact that a complex set of simultaneous equilibria and reactions due in part to solvent participation are under observation.

The assignment of individual rate and equilibrium constants is therefore difficult, and it seemed desirable to study the reactions of monofunctional urea derivatives, namely those of 1-methyl-2-imidazolidinone (I), in aprotic solvents.

I reacts with 1-methoxymethyl-3-methyl-2-imidazolidinone (II) in 1,2-dimethoxyethane with *p*-toluenesulfonic acid as the catalyst very rapidly at 25° to give 1,1′-methylenebis(3-methyl-2-imidazolidinone) (III) and methanol. The reaction was subsequently found to be a facile equilibrium which took *ca.* 15 min. to achieve under those conditions. Catalysis by weaker acids such as acetic and chloroacetic acid gave a very slow reaction at this temperature. However, it was possible to obtain an equilibrium constant at 40° in both directions by using trifluoroacetic acid as the catalyst. (See Chart I.)

CHART I

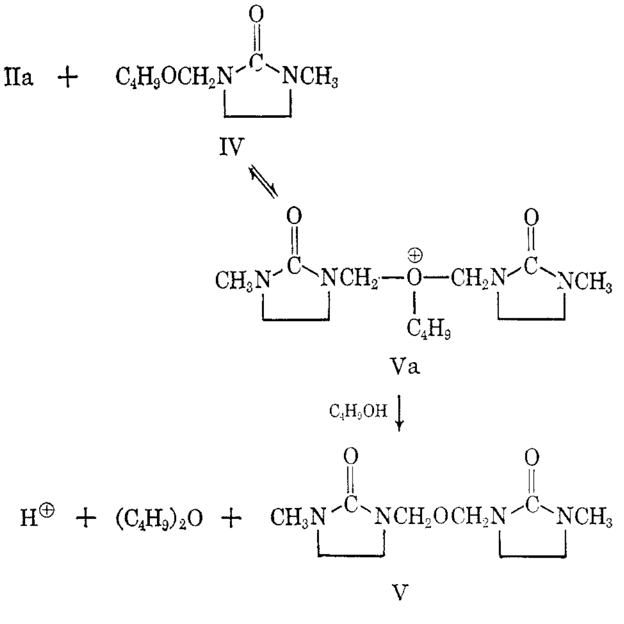


No attempts were made to obtain rate constants by a kinetic study over the first few per cent of reaction. However, a qualitative idea of the concentration dependence was obtained by experiments in which the concentrations of I and II were varied at constant temperature and trifluoroacetic acid concentration (Figure 1). A comparison of the plots shows that over the initial part of the reaction the rate is dependent on the concentration of II only.

This result, the facile acid-catalyzed alcohol interchange reaction of II to give other alkoxymethyl derivatives of I and the dependence of the rate of equilibration on the acid strength, suggests that these reactions proceed through the common carbonium ion IIa and furthermore that the rate-determining step is the formation of IIa.

The possibility that III can result by attack of IIa on the nitrogen atom of II to displace the methoxymethyl group[6] was discounted since this would lead to the formation of methylal. This was not observed when II was treated with *p*-toluenesulfonic acid in 1,2-dimethoxyethane for 24 hr. at 25°. At the end of the period, II was recovered almost quantitatively. In earlier work, however, it was found that II underwent methanolysis under acid catalysis in methanol solution to give I and methylal. The rate of this reaction was very slow at 25°. III, which was obtained as the product, undoubtedly arose from the reaction between I and unreacted II rather than by reaction between I and methylal. These latter reactants did not give III under identical reaction conditions.

CHART II



---

[1] Presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1963.

[2] J. de Jonge and J. de Jonge, *Rec. trav. chim.*, **71**, 643, 661, 890 (1952); **72**, 139, 653 (1953).

[3] N. Landqvist, *Acta Chem. Scand.*, **9**, 1127, 1459, 1466, 1477 (1955); **11**, 776, 780, 786, 792 (1957).

[4] G. Smets and A. Borzee, *J. Polymer Sci.*, **8**, 371 (1952).

[5] A. S. Dunn, *J. Chem. Soc.*, 1446, 4687 (1957).

[6] R. Saxon and F. Listienne, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1962, p. 3R; *J. Appl. Polymer Sci.*, **8**, 475 (1964).

[7] H. P. Wohnsiedler, *Ind. Eng. Chem.*, **44**, 2679 (1952).

[8] G. Widmer, *Schweiz. Arch. angew. Wiss. Tech.*, **11**, 1 (1954).

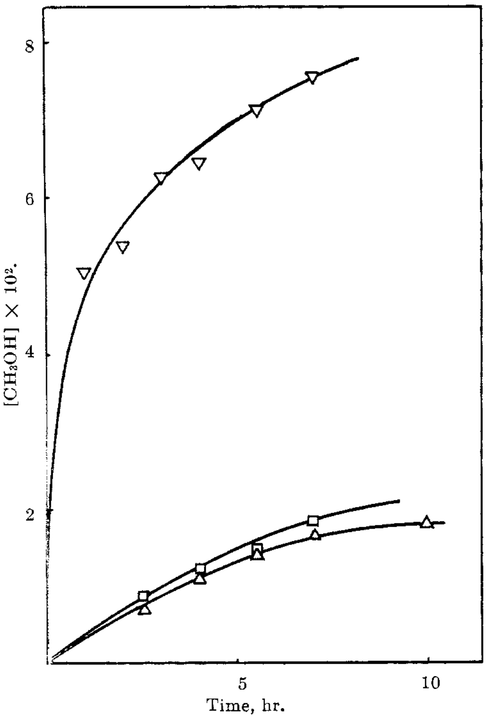


Figure 1.—The condensation of 1-methyl-2-imidazolidinone (I) and 1-methoxymethyl-3-methyl-2-imidazolidinone (II) at low conversion at 25° and $[CF_3COOH] = 0.001$ *M*: □, [I] = 0.0803 *M*, [II] = 0.0802 *M*; △, [I] = 0.1606 *M*, [II] = 0.0802 *M*; and ▽, [I] = 0.0803 *M*, [II] = 0.1604 *M*.

Infrared analysis of urea–formaldehyde films and microanalysis of low molecular weight condensation products of urea and formaldehyde indicate that "methylene ether" cross links as well as methylene cross links can occur in this class of resins.[7,9–12] A possible reaction path leading to the formation of this type of cross link could involve an "oxonium ion" intermediate such as Va. In order to form the "methylene ether" derivative V, a solvent molecule would have to displace the butyl group of Va to form dibutyl ether.[13] However, the formation of dibutyl ether was not observed on treating 1-butoxymethyl-3-methyl-2-imidazolidinone (IV)[14] with *p*-toluenesulfonic acid in butanol at 25° to reflux temperature. (See Chart II.)

Experimental Section[15]

1-Methyl-2-imidazolidinone (I) was prepared after the method of Frick, *et al.*[16] The crude product was distilled at 125–130° (0.7 mm.) and crystallized from toluene. Further purification was achieved by vacuum sublimation at 2 mm.: m.p. 116–116.5°, 59% yield.

Anal. Calcd. for $C_4H_8N_2O$: C, 48.00; H, 8.00; N, 28.00. Found: C, 47.74; H, 8.09; N, 28.16.

1-Methoxymethyl-3-methyl-2-imidazolidinone (II).—In a 5-l. flask fitted with a mechanical stirrer, dropping funnel, thermometer, and a calcium chloride drying tube were placed 110 g. (27.6 g., 1.15 moles) of 25% sodium hydride dispersion in mineral oil and 2000 ml. of dry toluene.[17] The flask and contents were cooled to 5–10° and 120 g. (1.20 moles) of I was added in small portions at a rate that the reaction temperature did not rise above 15°. The resulting slurry was stirred for 3 hr. at 5–10° and 100 g. (1.24 moles) of chloromethyl methyl ether in 100 ml. of dry toluene was added dropwise while the reaction temperature was maintained below 15°. After stirring for an additional 3 hr. at 5–10°, the reaction was allowed to warm to room temperature and filtered. The filtrate was evaporated at reduced pressure, whereupon separation into two phases occurred. The upper phase (the mineral oil from the sodium hydride dispersion) was discarded. The lower phase was washed with three 25-ml. portions of petroleum ether (b.p. 30–60°) and added to 500 ml. of ether. The ether solution was maintained at 0° for 4 hr. and unreacted I, which precipitated, was removed by filtration. The ether solution was evaporated under reduced pressure and the residue was distilled under nitrogen through a 30 × 1 cm. column packed with glass helices. A water-white liquid,[18] b.p. 92–93° (0.7 mm.), was obtained in 73% yield.

Anal. Calcd. for $C_6H_{12}N_2O_2$: C, 50.00; H, 8.33; N, 19.44. Found: C, 50.21; H, 8.28; N, 19.18.

1,1′-Methylenebis(3-methyl-2-imidazolidinone) (III).—I (4.86 g., 0.0486 mole) and 7.0 g. (0.0486 mole) of II were dissolved in dry 1,2-dimethoxyethane[19] in a 50-ml. erlenmeyer flask with a ground-glass stopper. A few crystals of *p*-toluenesulfonic acid were added and, after shaking for a few minutes, III crystallized out. The product was recrystallized from 1,2-dimethoxyethane: m.p. 127–128°, lit.[16] m.p. 129–130. It was obtained in 99% yield.

Anal. Calcd. for $C_9H_{16}N_4O_2$: C, 50.94; H, 7.54; N, 26.41. Found: C, 50.50; H, 7.57; N, 26.31.

1-Butoxymethyl-3-methyl-2-imidazolidinone (IV).—In a 125-ml. erlenmeyer flask with a ground-glass stopper were placed 5 g. (0.0347 mole) of II, 50 ml. of *n*-butyl alcohol,[20] and a few crystals of *p*-toluenesulfonic acid. The flask was stoppered and allowed to stand at room temperature for 3 days after which 5 g. of powdered sodium bicarbonate was added. The flask was again stoppered and the contents were stirred overnight at room temperature. After filtering, the butanol solution was evaporated under reduced pressure and the residue was distilled under nitrogen through a 10 × 1 cm. Vigreux column: b.p. 86° (0.2 mm.), 5.46 g. (85% yield).

Anal. Calcd. for $C_9H_{18}N_2O_2$: C, 58.06; H, 9.67; N, 15.05. Found: C, 58.53; H, 9.30; N, 14.82.

The Methanolysis of II.—A solution, 12.5×10^{-3} *M* in II and 1.87×10^{-4} *M* in *p*-toluenesulfonic acid, was prepared in dry methanol.[21] The solution was thermostated at 25° and from time to time samples were withdrawn and analyzed for methylal by gas–liquid partition chromatography (g.l.p.c.).[22] After 48 hr., less than 1% methanolysis of II had occurred.

The Butanolysis of IV.—In a 10-ml. micro distilling flask fitted with a reflux condenser and a calcium chloride drying tube were placed 2 g. (0.0107 mole) of IV, 2 g. of dry *n*-butyl alcohol, and a few crystals of *p*-toluenesulfonic acid. The reaction mixture was heated at reflux for 2.5 hr. and, after cooling to room temperature, transferred to a 25-ml. erlenmeyer flask with a ground-glass stopper. Approximately 0.25 g. of powdered sodium bicarbonate was added, the flask was stoppered, and the contents was stirred for 2 hr. After filtering, the neutral reaction mixture was analyzed by g.l.p.c.[22] Dibutylformal was present in the reaction mixture. There was no dibutyl ether present.

---

(9) H. J. Becker and F. Griffet, *Chem. Ber.*, **91**, 2032 (1955).

(10) G. Zigeuner and H. Fritz, *Monatsh.*, **90**, 211 (1959).

(11) G. Zigeuner and R. Pitter, *ibid.*, **86**, 57 (1955).

(12) G. Zigeuner, K. Vogler, and R. Pitter, *ibid.*, **85**, 1196 (1954).

(13) Oxonium ion salts have been used as alkylating agents. See, H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, *J. prakt. Chem.*, **154**, 83 (1939).

(14) IV in butanol was used instead of II in methanol in these experiments because should this reaction occur then the product would be volatile dimethyl ether.

(15) The microanalyses cited in this work were performed by Mrs. B. Artman, Mrs. C. Morris, Miss R. De Angelo, and Mr. R. Mangravite. All melting points were determined in soft-glass capillaries using a Vanderkamp block and calibrated thermometers.

(16) J. G. Frick, Jr., B. A. Kottis, and J. D. Reid, *Textile Res. J.*, **29**, 314 (1959).

(17) Toluene was distilled over calcium hydride and stored over sodium wire.

(18) The preparation of this compound as a solid product has been reported. No experimental procedure or physical properties were given. See D. D. Gagliardi, *Textile Res. J.*, **30**, 524 (1960).

(19) 1,2-Dimethoxyethane was given a preliminary drying over calcium hydride followed by distillation over lithium aluminum hydride.

(20) *n*-Butyl alcohol was heated at reflux overnight over calcium hydride and then distilled over calcium hydride.

(21) Methanol was dried after the method of Lund and Bjerrum. See L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1957, p. 289.

(22) G.l.p.c. analyses were carried out on an Aerograph A-90S using a 6 ft. × 0.25 in. column packed with G. E. Silicone SF-96 on 60–80 mesh Chromosorb W (regular).

Unlike II in methanol, IV in *n*-butyl alcohol did not undergo alcoholysis under acid catalysis in the temperature range 25–60°.

Equilibrium Measurements. 1.—A reaction solution 0.080 *M* in I, 0.100 *M* in II, and 0.001 *M* in trifluoroacetic acid in dry 1,2-dimethoxyethane was prepared from stock solutions. Aliquots of 3 ml. of this solution were sealed in 5-ml. glass ampoules and the ampoules were thermostated at 40°. From time to time, ampoules were removed from the bath and the contents were quantitatively analyzed for methanol by g.l.p.c.[23] From the equilibrium plot of the data, the equilibrium constant was calculated at 45.1.

2.—Using the same technique, a reaction solution 0.085 *M* in III, 0.095 *M* in methanol, and 0.001 *M* in trifluoroacetic acid in dry 1,2-dimethoxyethane gave an equilibrium constant of 0.0198.

3.—In a similar experiment, a reaction solution 0.205 *M* in III, 0.125 *M* in methanol, and 0.001 *M* in trifluoroacetic acid in dry 1,2-dimethoxyethane gave an equilibrium constant of 0.0219.

Reactions at Low Conversions and Different Reactant Concentrations.—Reaction solutions of I, II, and trifluoroacetic acid were prepared in dry 1,2-dimethoxyethane. The solutions were thermostated at 25° and from time to time samples were withdrawn and analyzed for methanol.[23] The experiments were carried out with the following reactant concentrations at a constant concentration of 0.001 *M* trifluoroacetic acid. The results are plotted in Figure 1.

Expt.	Concn. of I, *M*	Concn. of II, *M*
1	0.0803	0.0802
2	0.1606	0.0802
3	0.0803	0.1604

Acknowledgment.—The authors wish to express their appreciation to Professor Nathan Kornblum of Purdue University for many stimulating discussions during the course of this work.

[23] G.l.p.c. analyses were carried out on an Aerograph A-600 Hy Fy using a 5 ft. × 1/8 in. column packed with G. E. Silicone SF-96 on 60–80 mesh Chromosorb W (regular). The injector and oven temperature were maintained at the reaction temperature. Methanol concentrations were computed from an area *vs.* concentration calibration curve at constant sample volume.

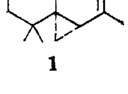
Constituents of Hiba Wood Oil. The Isolation and Synthesis of Two Isomeric Cuprenenes[1]

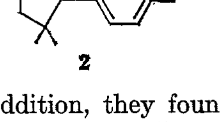
WILLIAM G. DAUBEN AND PETER OBERHÄNSLI[2]

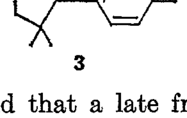
Department of Chemistry, University of California, Berkeley, California 94720

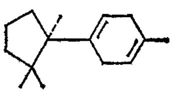
Received July 1, 1965

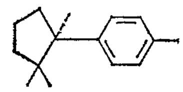
In 1960, Nozoe and Takeshita[3] reported that the sesquiterpene thujopsene (1) was the major constituent of the essential oil of the Japanese Hiba tree (*Thujopsis dolabrata*). In addition, they found that a late fraction in the sesquiterpene distillation range was a mixture of other sesquiterpenes. From chemical and spectral studies of this fraction it was suggested that, among other things, the two isomeric cuprenenes 2 and 3 were present, but the materials were never isolated in pure form. This oil has been re-examined and two isomeric cuprenenes (2 and 4) as well as cuparene (5), terpinen-4-ol (6), and widdrol (7) have been isolated in pure form.

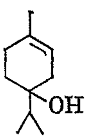

1


2

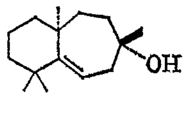

3


4


5



6



7

Hiba wood oil[4] was chromatographed on neutral alumina. The petroleum ether eluate (~90%) consisted mainly of hydrocarbons (plus a small amount of alcohols) and the methanol eluate (~5%) consisted of alcohols. The remainder of the oil (~5%) remained on the column and presumably contained acids; this material was not investigated.

A v.p.c. analysis of the total hydrocarbon fraction (DEGS column, 130°) indicated the presence of approximately 60% thujopsene (1), 7% of cuprenene 2, 3% of cuprenene 4, 2.5% of cuparene (5), and 1.5% of monoterpenes [including terpinen-4-ol (6)]. The remainder of the fraction consisted of a large number of minor constituents. In order to isolate the five major components, the hydrocarbon fraction was fractionated by distillation using a spinning-band column followed by preparative v.p.c. The details of the complicated fractionation are given in the Experimental Section.

Cuparene could not be obtained completely free of olefinic impurities by the above separation scheme, and so the mixture was subjected to oxidation with performic acid and the oxidation products were separated from the unchanged cuparene by alumina chromatography. The infrared spectrum of the purified material was identical with the published spectrum of cuparene.[5]

The gross carbon skeleton of the two cuprenenes 2 and 4 was established by their conversion to cuparene upon prolonged standing in air. The presence of a conjugated diene in cuprenene 2 was indicated by its ultraviolet spectrum [$\lambda_{\max}^{\mathrm{EtOH}}$ 271 mμ (ϵ 6300)]. The n.m.r. spectrum showed absorption for two vinyl hydrogens (τ 4.49), a methyl group on an olefinic double bond (τ 8.29), and three methyl groups on saturated centers (τ 9.01 and 9.20). These spectral data permit the specific placement of the diene system as shown in 2. Cuprenene 4 was isomeric with cuprenene 2, but the two double bonds were not conjugated. Again the placement of the unsaturated centers was possible on the basis of the n.m.r. spectrum which showed the presence of two vinyl hydrogens (τ 4.56 and 4.68), four diallylic hydrogens (τ 7.40), one methyl group on an olefinic linkage (τ 8.37), and three methyl groups on saturated centers (τ 8.98, 9.00, and 9.20).

These structures of the compounds were proved by synthesis from cuparene. Reduction of the aromatic

[1] This work was supported in part by Grant GP-3890, National Science Foundation.

[2] Roche Anniversary Foundation Postdoctoral Fellow, 1963–1965.

[3] T. Nozoe and H. Takeshita, *Tetrahedron Letters*, **No. 23**, 14 (1960).

[4] Kindly supplied by Fritzsche Brothers, New York, N. Y., and the Saisei Camphor Co., Ltd., Japan.

[5] C. Enzell and H. Erdtman, *Tetrahedron*, **4**, 361 (1958).