to be proportionality between the deshielding of the hydroxyl proton and the lowering of the intramolecularly bound hydroxyl frequency.[19,20] Dilution causes only secondary effects in the chemical shifts.[21]

Kuhn[2b] derived an expression in which $\Delta\nu$ is inversely related to the distance between the hydroxyl proton and the bonding oxygen. Using the modified expression,[3c] the respective calculated bond distances for diols and ol–ethers with a $\Delta\nu$ of 160–170, 100, 67, and 42–46 cm.$^{-1}$ are 1.6, 1.8, 2.0, and 2.3 Å. This compares favorably with the distances measured on Drieding models of 1.3, 1.6, 2.4, and 2.4 Å., respectively. The largest $\Delta\nu$ (160–170) is caused by the bonding of a 12β-hydroxyl with a C-20 ethylene ketal oxygen and represents an extremely small bonding distance.

The respective $\Delta\nu$ for the 11,12-ketols VII and V is 140–150 and 180–217 for the 12β-hydroxy-20-keto derivatives. No general equation for the dependence of ketol frequencies and bonding distances has yet been derived. However, if the dependence of $\Delta\nu$ with bonding distance also holds in ketols, the bonding distance in 12β-hydroxy 20-ketones should be less than in the 11,12-ketols VII and V (2.2 Å.).

[19] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 15.

[20] In ref. 19, p. 406, the authors suggest similar correlation of infrared and n.m.r. data.

[21] See ref. 19, p. 413.

Formation and Identification of *cis*- and *trans*-Dihydroxyimidazolidinones from Ureas and Glyoxal

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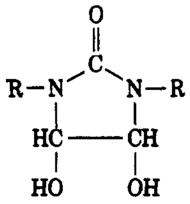
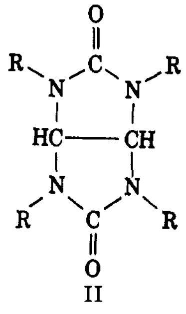
The additions of N,N′-dimethylurea and urea to glyoxal under both acidic and basic conditions to form 4,5-dihydroxy-2-imidazolidinones have been studied. Rates for the formation of *cis*- and *trans*-4,5-dihydroxy-1,3-dimethyl-2-imidazolidinone and for conversion of the pure isomers to an equilibrium mixture at various pH values were examined by n.m.r. It is probable that equimolar amounts of the *cis* and *trans* isomers are formed initially by a nonstereospecific addition, but the less stable *cis* isomer is rapidly converted to *trans* under the conditions of the reaction. The resulting equilibrium mixture of products is predominantly the *trans* isomer.

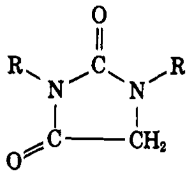
The addition of ureas to glyoxal produces several different heterocyclic compounds. 4,5-Dihydroxy-2-imidazolidinones (I) generally are isolated from base-catalyzed additions, synthesis of both Ia[3] and Ib[4] having been reported. Separation of the geometric isomers was indicated[4a] for the latter compound (Ib); however, the isomers were not assigned a configuration, nor was there described an adequate procedure by which they could be isolated. Several 1-alkyl and 1-aryl derivatives of I have been reported in the patent literature,[5] but characterization of the products was incomplete. In acid-catalyzed additions glycolurils (II) and/or hydantoins (III) are the reported products[6]; however, formation of III ($R = CH_3$) has not been found[7] in acid-catalyzed additions using N,N′-dimethylurea.



Ia, R=H
b, R=CH₃



II



III

The base-catalyzed addition of ureas to glyoxal is thought to be preceded by the abstraction of a proton from the urea. The resulting nucleophile attacks the glyoxal to produce the linear intermediate IV. Cycliza-

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[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Inquiries should be directed to this laboratory to the attention of S. L. V. or R. H. B.

[2] The mention of trade names and firms does not imply their endorsement by the Department of Agriculture over similar products or firms not mentioned.

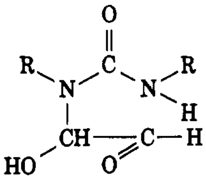
[3] See, for example, (a) H. Pauly and H. Sauter, *Ber.*, **63B**, 2063 (1930); (b) Badische Anilin- and Soda-Fabrik Akt., British Patent 717,287 (Oct. 27, 1954); (c) E. Torke and J. König (to Phrix-Werke A. G.), U. S. Patent 2,876,062 (March 3, 1959); (d) H. B. Goldstein and M. A. Silvestri (to Sun Chemical Corp.), U. S. Patent 3,049,446 (Aug. 14, 1962); (e) D. D. Gagliardi, W. J. Jutras, Jr., and E. Stern (to Gagliardi Research Corp.), Belgian Patent 616,785 (May 15, 1962); *Chem. Abstr.*, **58**, 1467c (1963). In general, these patents agree that Ia is isolated under neutral or basic conditions; however, there is not general agreement on the results when the addition is acid catalyzed.

[4] (a) S. L. Vail, P. J. Murphy, Jr., J. G. Frick, Jr., and J. D. Reid, *Am. Dyestuff Reptr.*, **50**, 550 (1961); (b) S. L. Vail and P. J. Murphy, Jr. (to U. S. Department of Agriculture), U. S. Patent 3,112,156 (Nov. 26, 1963); (c) M. T. Beachem and W. K. Van Loo, Jr. (to American Cyanamid Co.), Belgian Patent 614,586 (Sept. 3, 1962); *Chem. Abstr.*, **58**, 10348c (1963); (d) W. A. Burris (to American Cyanamid Co.), U. S. Patent 3,091,617 (May 28, 1963); the dimethyl ether of Ib is reported in this reference.

[5] Badische Anilin- and Soda-Fabrik Akt., British Patent 783,051 (Sept. 18, 1957).

[6] (a) F. B. Slezak, H. Bluestone, T. A. Magee, and J. H. Wotiz, *J. Org. Chem.*, **27**, 2181 (1962); (b) J. Nematollahi and R. Ketcham, *J. Org. Chem.*, **28**, 2378 (1963); (c) E. Ware, *Chem. Rev.*, **46**, 403 (1950).

[7] Our attempts to prepare III ($R = CH_3$) from N,N′-dimethylurea and glyoxal yielded only II ($R = CH_3$). A literature search indicated that formation of III ($R = CH_3$) from these reactants has not been reported.



IV

tion to a 4,5-dihydroxy-2-imidazolidinone (I) follows by a similar addition involving the second nitrogen of the urea residue and the remaining aldehyde moiety. A very similar reaction path would be expected for the acid-catalyzed reaction involving nucleophilic attack by the neutral amido nitrogen on the previously protonated carbonyl function. In either acid- or base-catalyzed reactions the conformation of IV before ring closure determines which geometric isomer is formed. However, in acidic solutions I would be subject to protonation and subsequent formation of products other than I.

In this work the configurations of the urea or dimethylurea and glyoxal adducts (I) were assigned from periodate oxidations and n.m.r. studies of the adducts. It is well established[8] that *cis* 1,2-diols in five-membered ring systems are more rapidly oxidized with a suitable oxidizing agent, *e.g.*, periodic acid or sodium metaperiodate, than the corresponding *trans* diols. The lower melting isomer which was designated *cis*-Ib was oxidized quantitatively by sodium metaperiodate in the 5–10 min. required to mix the reagents and perform the titration. On the other hand, the isomer designated *trans*-Ib was oxidized very slowly, *i.e.*, about 62% oxidized in 24 hr. The only product (Ia) isolated from the addition of urea to glyoxal was assigned a *trans* configuration because its rate of peroidate oxidation was even slower than that found for *trans*-Ib.

The n.m.r. spectra of Ia, *cis*-Ib, *trans*-Ib, II (R = CH_3), and 2-imidazolidinone in D_2O and assignment of bands are shown in Table I. The spectra definitely detect and differentiate between the *cis* and *trans* isomers of Ib. Single lines are observed for the ring protons and for the methyl protons. The single signals for the methyl protons of *cis*- and *trans*-Ib are between the signals of the methyl protons of N,N′-dimethylurea and II (R = CH_3). Thus, the signals of the starting material and expected products are easily distinguishable. Since these signals were not complicated by the water present in the sample, the formation of these isomers in aqueous reaction mixtures could be studied by n.m.r.

TABLE I

N.M.R. SPECTRA OF 2-IMIDAZOLIDINONES IN DEUTERIUM OXIDE

Compd.	Signals, p.p.m. Ring protons	Signals, p.p.m. Methyl protons
2-Imidazolidinone	3.51	...
Ia	5.08	...
cis-Ib	5.05	2.78
trans-Ib	4.87	2.83
II (R = CH_3)	5.22	2.94

N.m.r. studies established that the formation of the isomers at about 22° was very rapid. Formation of Ib was essentially complete in 7.5 hr. at pH 4 (obtained by mixing 40% aqueous glyoxal and N,N′-dimethylurea). At a pH of 8.3 (sodium bicarbonate added) or 2.0 (6 *N* hydrochloric acid added) the formation of Ib was essentially complete in 3.3 and 2 hr., respectively. After 20 hr. at pH 2 products other than Ib were slowly forming. Under basic conditions the concentrations of *cis*- and *trans*-Ib were equal in the early stages of the reaction, but, as the reaction proceeded, the relative concentration of the *cis* component decreased. Under acidic conditions the concentration of *cis* isomer reached a maximum very rapidly and remained at this low level as the concentration of the *trans* isomer increased rapidly.

In order to establish the stereochemistry of this addition, conversions of the pure isomers to the equilibrium mixture were followed by n.m.r. The conversion of the *cis* isomer was catalyzed by acid. At a pH of 2.0 the equilibrium was reached in 4–5 min., whereas about 4 hr. was required to attain equilibrium at pH 3.9. In distilled water or at pH values of 8.6 and 10.0 the conversion to the equilibrium mixture was essentially complete in 24 hr. The conversion of the *trans* isomer was similarly catalyzed by acid. At pH values of 2.4 and 3.0 equilibrium was attained in about 5 min. At a pH of 8.3 this state was reached in about 2 hr. (Thus, it is probable that much of the oxidation of *trans*-Ib by periodate was preceded by isomerization to the *cis* configuration.)

Therefore, it appears probable that under acidic or basic conditions IV cyclizes to Ib to form equimolar amounts of the *cis* and *trans* isomers followed by isomerization to an equilibrium mixture which is predominantly (>95%) *trans.*

Since the cyclization of IV to I appears to be nonstereospecific, the ring opening under basic conditions must occur more slowly in the case of the *trans* isomer. This is consistent with a mechanism in which the transition states leading to IV from both *cis* and *trans* isomers are similar. Thus, the activation energy for the opening of the more stable ring in the *trans* compound would be larger and the opening considerably slower. Under acidic conditions, opening of the ring is not required and several mechanisms are possible. The most plausible of these would seem to be one involving a resonating carbonium–immonium ion.[9] Since the intermediate from the dehydration would be the same from both isomers, it would seem logical that the less stable *cis* isomer should react faster. A similar argument would apply if the intermediate were a protonated epoxide, except that in this case the hydration step would be expected to lead stereospecifically to the *trans* isomer.

To confirm the results from the n.m.r. studies, formation and conversions of the isomers were achieved with isolation and identification of the products.[10] Isolation of *cis*- and *trans*-Ib was complicated by their slow

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(8) (a) C. C. Price and M. Knell, *J. Am. Chem. Soc.*, **64**, 552 (1942); (b) G. J. Buist, C. A. Bunton, and J. H. Miles, *J. Chem. Soc.*, 743 (1959).

(9) H. Hellman, "Newer Methods of Preparative Organic Chemistry," Vol. II, W. Foerst, Ed., Academic Press, Inc., New York, N. Y., 1963, p. 277.

(10) Once the isomers of Ib were separated and identified, infrared spectra of these isomers were used to determine the composition of unknown solid samples. Contamination of one isomer by another was easily discerned by the appearance of strong bands at 8.82 and 11.35 μ due to the *cis* isomer or at 9.60 and 12.38 μ due to *trans* isomer. Also, in the hydroxyl stretching region the *cis* hydroxyls appear to be H-bonded, whereas the *trans* hydroxyls do not. A dilution study was attempted; however, the solubility of the isomers in nonpolar solvents was too low to assign configurations from the spectra.

rates of crystallization. However, if the alkaline, aqueous solutions of the products were stored at low temperatures to delay the conversion of the *cis* isomer to *trans*, the isomers crystallized separately with no by-products encountered. The *trans* isomer was the only product isolated if the alkaline, aqueous products were kept at room temperature for several days or if the addition was acid catalyzed and isolation of Ib was rapid.

The addition of unsubstituted urea to glyoxal in aqueous solutions was not studied by n.m.r. because the resonance signal of the ring protons of Ia (Table I) and the adjacent region of the spectrum were not free of interference from water and glyoxal. Addition of urea to glyoxal under alkaline conditions similar to those used to isolate the geometric isomers of Ib produced only the *trans* isomer. The same isomer was isolated from a reaction mixture adjusted to pH 2.

Experimental[11]

Geometric Isomers of 4,5-Dihydroxyl-1,3-dimethyl-2-imidazolidinone (Ib).—This synthesis may be carried out equally well with equimolar quantities of glyoxal and N,N′-dimethylurea or as described below. To 132 g. (1.5 moles) of N,N′-dimethylurea was added 200 g. (1.0 mole) of 30% glyoxal which had been made alkaline with 20% sodium hydroxide. The solution (pH 9) was stirred, cooled after a slight temperature rise was noticed, and then divided into four equal parts. Two of these four parts were marked A and B. The third part, C, was adjusted to pH 8 with 1 *N* HCl. The fourth part, D, was adjusted to pH 10 with 20% NaOH. After standing at room temperature (RT) for 4 hr., the A, C, and D portions were stored at −12 to −20° and the fourth portion, B, was stored at RT. After a 1-week storage, solution A contained a slight precipitate. At this point solution B was stored at −12 to −20°. On the eighth day A and C contained considerable precipitate and were filtered. On the ninth day B and D contained considerable precipitate and these were filtered. The solids were pressed dry with filter paper and dried *in vacuo* at 40°. The pH values of the filtrates were essentially unchanged from the original adjusted pH values. Glyoxal adjusted to a pH of 9 became acidic on storage at RT in just a day or two. After filtration the filtrates were returned to storage as before. The second precipitation was quite slow in occurring, almost a month after the first. B was seeded with material from the first fraction of B crystals and placed in −12 to −20° storage for crystallization. After this filtration *all* mother liquors were stored at −12 to −20°. Third and fourth fractions of crystals were obtained.

The isomers as isolated from the reaction mixture in the first crystallization were essentially pure as determined from their infrared spectra. However, improved melting points were obtained by recrystallization from ethanol. Essentially pure *cis* isomer in about 10% yield with a trace of *trans* isomer was obtained from A, C, and D in the first fractions. Essentially pure *trans* isomer with a trace of *cis* was the only product isolated from B. The second fractions of crystals contained little or no *cis* isomer. No *cis* isomer was found in the third and fourth fractions except in the third fraction from D. The pH of the filtrates from the fourth fraction was essentially the same as the starting pH for all samples; yield of Ib was 60–70%. The *cis* isomer has been prepared in yields up to 25% by chilling equimolar amounts of the reactants to 0–5° before mixing and then storing the mixed reactants at −12 to −20°. The *cis* isomer had m.p. 135–136°; the *trans* isomer had m.p. 145–146°. Mixture melting point of isomers was 122–130°

Anal. Calcd. for $C_5H_{10}N_2O_3$: C, 41.09; H, 6.90; N, 19.17; mol. wt., 146. Found for the *cis* isomer: C, 41.35; H, 6.90; N, 19.16; mol. wt. (by osmometer), 147. Found for the *trans* isomer: C, 41.24; H, 6.86; N, 19.16; mol. wt. (by osmometer), 144.

Infrared data (μ) for *cis*-Ib: 2.97, 3.15, 3.37, 3.43, 3.62, 6.00, 6.70, 7.07, 7.33, 7.44, 7.90, 8.23, 8.82, 9.20, 9.78, 10.22, 11.35, 12.43, 12.66, 12.80, and 13.21; *trans*-Ib: 3.04, 3.40, 6.05, 6.63, 6.84, 7.13, 7.82, 8.20, 8.86, 9.24, 9.60, 10.12, 10.30, 12.38, and 13.13. The 8.86 band is the weakest of those recorded and may originate from a trace quantity of the *cis* isomer.

Attempted Interconversions of the *cis–trans* Isomers of Ib in Solution. *trans* **to** *cis*.—*trans*-Ib (second fraction, sample B, 1.8 g.) was dissolved in 30 g. of distilled water, and 18 ml. of methanol was added to depress the freezing point of the solution. The pH of the solution was 7.5. Three equal portions were obtained from the solution and were labeled E, F, and G. F and G were adjusted to pH 10.0 and 10.7, respectively, with 20% NaOH and all three samples were stored at −12 to −20°. These samples were stored under these conditions for 21 months with aliquots being removed to check for formation of the *cis* isomer. At no time during this period was any additional *cis* isomer formed as determined by examination of the infrared spectra of the residues from the aliquots.

cis **to** *trans*.—*cis*-Ib (first fraction, sample C, 1.8 g.) was dissolved in 30 g. of distilled water. The pH of this solution was 7.5. Three equal portions were obtained from this solution and were labeled H, J, and K. J and K were adjusted to pH 9.9 and 10.7, respectively, with 20% NaOH and all three samples were stored for 2 days at RT. After an unsuccessful attempt to obtain crystals by chilling the solutions, the solutions were evaporated *in vacuo;* the infrared spectra were obtained as before. The spectra obtained from H, J, and K were all similar and indicated that the *cis* isomer had been converted to the *trans* with only a trace of *cis* isomer remaining. In a second experiment solution H was prepared again and divided into two portions. The second portion, labeled L, was adjusted to a pH of 6.5 with dilute HCl and treated in a similar fashion. The infrared spectrum of the residue from L was identical with those previously obtained from H, J, and K.

Interconversion of *cis–trans* Isomers of Ib in the Solid State.—The infrared spectra of the solid isomers were examined after a 6-month storage at RT and changes in the spectra were noted. The *cis* isomer of Ib (first fraction, sample C, isolated as described previously and not recrystallized) contained several per cent of the *trans* isomer. Samples of *cis* isomer which were recrystallized from ethanol were stable and no *trans* isomer had formed. The *trans* isomer was stable during storage, recrystallized or not.

4,5-Dihydroxy-2-imidazolidinone (Ia).—To 90 g. (1.5 moles) of urea was added 150 g. (1.0 mole) of 40% glyoxal, which had been made alkaline with 20% sodium hydroxide, and 50 ml. of ethanol. The solution was divided into four parts and treated as described previously for Ib. The ethanol was added in this case to prevent freezing of the solution at the reduced storage temperature. D contained crystals after a 24-hr. storage, at which point B was stored at −12 to −20°. Within 3 days all samples, except C, contained solids. These solids were filtered, dried as before, and found to melt at 133–135°, lit.[3a] m.p. 146° from methanol. From the infrared spectra and mixture melting points these reaction products were found to be identical.

Periodate Oxidations and Titrations.—Weighed portions (100–200 mg.) of *cis*-Ib, *trans*-Ib, and Ia were added to 100 ml. (pipet) of a 0.6–0.7% sodium metaperiodate ($NaIO_4$) solution. The solution was kept at RT and 25-ml. aliquots were removed by pipet (a) immediately after mixing, (b) after 1 hr., and (c) after 7 hr. for titration. After 24 hr. a 20-ml. aliquot was removed by pipet from the residue. To each aliquot was added 30 ml. of saturated $NaHCO_3$ and 20 ml. of 20% KI. The iodine released was immediately titrated with a standard 0.100 *N* sodium arsenite solution using starch for the end point. A blank was run prior to a series of titrations. Milligrams of the dihydroxy compound oxidized were calculated from the following equation.

$$\text{mg.} = (\text{blank} - \text{titration})(0.100)\,\frac{\text{mol. wt.}}{2}$$

The lower melting isomer (*cis*) was oxidized quantitatively on mixing, allowing for 5–10 min. to complete the analytical procedures. In comparison, the oxidation of the higher melting isomer (*trans*) was negligible for the immediate and 1-hr. determina-

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(11) All melting points are uncorrected and were determined on a Thomas-Hoover melting point apparatus. Room temperature was 20–25°. Glyoxal used in this work was the 30 and 40% "pure" grades supplied by these commercial firms: BASF Colors and Chemicals, Inc., Dr. F. Jonas Co., and Union Carbide Corp. A Varian A-60 n.m.r. spectrometer was calibrated with an external standard, tetramethylsilane, at 0 p.p.m. The infrared spectral data were obtained with a Perkin-Elmer 21 spectrophotometer using KBr. RT stands for room temperature.

tions. For 7 and 24 hr., respectively, about 16 and 62% of the sample was oxidized by the periodate.

Oxidation of Ia proceeded at an even slower rate than did *trans*-Ib. For 7 and 24 hr., respectively, about 10 and 42% of the sample was oxidized by the periodate.

Acid-Catalyzed Additions. **A.**—Equimolar quantities of N,N′-dimethylurea and aqueous 40% glyoxal at pH 2 and 4 were allowed to stand 30–60 hr. at RT. Crystals were obtained by chilling or samples were withdrawn and evaporated to dryness using vacuum only, and the infrared spectra were obtained. In both cases the spectra of the residue or the crystalline product indicated that *trans*-Ib was the major or only product. This procedure was repeated using urea and glyoxal. Again, spectra indicated that the desired dihydroxy derivative, Ia, was the major product. Some higher melting products were also isolated in both cases, especially if delays occurred in the isolation of the products.

B.—From glyoxal and N,N′-dimethylurea using the conditions of Nematollahi and Ketcham[6b] for the synthesis of II (R = CH_3) and III (R = C_6H_5), the glycoluril (II, R = CH_3), m.p. 224–226°, lit.[6b] m.p. 225–227°, was the sole product isolated (lit.[12] m.p. 44–45° for N,N′-dimethylhydantoin).

N.m.r. Spectral Data.—Once isolation of products (including isomers) was completed, these compounds, in addition to 2-imidazolidinone, were dissolved in D_2O and their proton n.m.r. spectra were obtained (see Table I). Spectra were obtained of the reactants in aqueous solution before and after addition of the products (Ia and the Ib isomers) to determine which, if any, of the protons of Ia and Ib were free of interference from the other materials. These preliminary experiments suggested that the methyl protons of N,N′-dimethylurea and Ib could be used to follow the addition reaction to glyoxal. The similar reaction with urea was not followed because the signal from the ring protons of Ia and the adjacent region of the spectrum were not free of interference from signals from water and glyoxal.

Under basic conditions the methyl peak of N,N′-dimethylurea was a doublet separated by a distance of 0.07 p.p.m. Proceeding downfield from these peaks, the methyl peak of *cis*-Ib was a distance of 0.05 p.p.m. and the similar peak of *trans*-Ib was a distance of another 0.05 p.p.m., all peaks being in a 0.17-p.p.m. range. Under acidic conditions the methyl peak of N,N′-dimethylurea was a singlet. Proceeding downfield the methyl peak of *cis*-Ib was a distance of about 0.08 p.p.m. and the similar peak of *trans*-Ib was a distance of another 0.05 p.p.m., all peaks being in a 0.13-p.p.m. range. From these preliminary experiments it was possible to follow the reaction of N,N′-dimethylurea and glyoxal in aqueous solutions at various pH values and to follow the rates of conversion of the pure geometric isomers into an equilibrium mixture of more than 95% *trans*.

The addition reactions were carried out by altering the pH of the 40% glyoxal with either 6 *N* HCl or solid $NaHCO_3$. An equimolar amount of N,N′-dimethylurea was added to the glyoxal. The stirred solution was maintained at room temperature. A final, slight adjustment of the pH was then made. An aliquot was withdrawn and placed in the instrument as rapidly as possible. A sweep of 0.7–0.8 p.p.m. was obtained over the region of the spectrum of the methyl protons. Reactions were considered to be essentially complete when an estimated 5% or less of the urea remained. Using these procedures the following results were obtained.

pH 2.0.—The reaction was 50% completed in 35–50 min., essentially complete in 2 hr. All of the N,N′-dimethylurea reacted in 20 hr., but other products were forming at this time. The contribution to the spectra from the *cis* isomer was very small except at the beginning of the reaction.

pH 4.0.—The reaction was 50% completed in about 3.3 hr., essentially complete in 7.5 hr. All of the N,N′-dimethylurea reacted in 27 hr. Very little *cis* isomer was noted and no other products were observed forming.

pH 8.3.—The reaction was 50% completed after 35–45 min., essentially complete in about 3 hr. The *cis–trans* ratio was about 1:1 at the start of the reaction, but decreased as the reaction proceeded. No other products were observed forming.

Similar procedures were used to determine the rates at which the pure isomers were converted at various pH values to the equilibrium mixture. The conversion was considered to be essentially completed after three partial spectra appeared equivalent.

pH 2.0.—Pure *cis* was converted to the equilibrium mixture in 4–5 min.

pH 3.9.—Pure *cis* was converted 50% in 35 min. and was converted to the equilibrium mixture in 4 hr.

pH 8.6, 10.0, and in Distilled Water.—Pure *cis* was converted to the equilibrium mixture in 24 hr. (20% NaOH was used to obtain pH 10).

pH 2.4.—Pure *trans* was converted to the equilibrium mixture in 5 min.

pH 8.3.—Pure *trans* was converted to the equilibrium mixture in 2 hr.

Acknowledgment.—The authors wish to express their appreciation to P. J. Murphy, Jr., and G. Bremenstul for assistance in laboratory procedures and to S. A. Miles and E. R. McCall for assistance in obtaining the spectral data.

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[12] H. Biltz and R. Lemberg, *Ann.*, **432**, 137 (1923).

The Photolysis of Polyfluoroacyl Fluorides, Chlorides, and Bromides

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Contribution No. 914 from the Central Research Department, Experimental Station,
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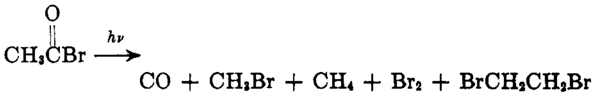
The photolysis of polyfluoroacyl fluorides yields largely fluoroalkanes resulting from the combination of two fluoroalkyl radicals together with ethers formed by addition of two fluoroalkyl radicals to the carbonyl group of the acyl fluoride. Photolysis of polyfluoroacyl chlorides and bromides leads to the formation of decarbonylation products, *i.e.*, polyfluoroalkyl chlorides and bromides, as the major products. When they are irradiated in the presence of terminal fluoro olefins, a variety of products, including oxetanes, fluoroalkyl bromides or chlorides, and polyfluoroalkanes, are formed.

Although photolyses of aliphatic aldehydes and ketones, including fluorinated ones,[1,2] have been studied extensively, there have been relatively few studies of the effects of ultraviolet radiation upon the related acyl halides. From the vapor phase photolysis of acetyl bromide, Etzler and Rollefson[3] obtained carbon monoxide and methyl bromide as major products and small quantities of ethylene bromide, methane, and bromine by what appeared to be a nonchain process (eq. 1). Similarly, the major products from the photolysis of acetyl iodide or acetyl chloride were the methyl



$$CH_3\overset{\overset{O}{\|}}{C}Br \xrightarrow{h\nu} CO + CH_3Br + CH_4 + Br_2 + BrCH_2CH_2Br \quad (1)$$

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[1] R. E. Dodd and J. W. Smith, *J. Chem. Soc.*, 1465 (1957).

[2] P. B. Ayscough and E. W. R. Steacie, *Can. J. Chem.*, **34**, 103 (1956).

[3] (a) D. H. Etzler and G. K. Rollefson, *J. Am. Chem. Soc.*, **61**, 800 (1939); (b) D. H. Etzler and G. K. Rollefson, *J. Chem. Phys.*, **6**, 653 (1938).