mol; the per cent yield from 211.7 g of salt (1.00 mol if pure) and 190 g of acid (2.0 mol) was 32%. The product, a colorless liquid, was stable indefinitely; stored at 0–5°, it did not etch the glass vessel or develop an acid odor, but retained an odor milder than that of nitromethane. It was sparingly soluble in water and CCl_4: infrared (CH_2Cl_2) 6.27 (s), 7.27, 7.37 (doublet, m), 8.8 μ (s); nmr ($CHCl_3$) δ 5.68 ppm (doublet, J = 46.0 cps).

The spectra of nitromethane follow: infrared (CH_2Cl_2) 6.40, 7.20, 7.30 μ (doublet), *inter alia* [These are shifted in IV in the expected directions;[13] nmr ($CHCl_3$) δ 4.32 ppm (singlet)].

The nmr spectrum of bromonitromethane ($CHCl_3$) had δ 5.60 ppm (singlet).

Anal. Calcd for CH_2NO_2F: C, 15.20; H, 2.55; N, 17.72; mol wt, 79.03. Found (MIT Microanalytical Laboratory): C, 15.17; H, 2.76; N, 17.71. Found (Schwarzkopf Microanalytical Laboratory): C, 14.54; H, 3.05; N, 16.85.

Titration of IV with Standard Base.—Solutions of IV, 0.100 *N*, 5-ml aliquots, were titrated with standardized 0.100 *N* sodium hydroxide using a Beckman Zeromatic SS-3 pH meter standardized with fresh 0.1 *N* Borax solution (pH 9.18). Addition of 0.5-ml aliquots of base to the rapidly stirred solution caused a rapid rise of pH to a maximum followed by a rapid drop for about 3 sec, then a slow decline. In runs 1 and 2, Table I, the maximum was read; in runs 3 and 4, the value after cessation of the rapid drop. In run 5, at the suggestion of a referee, given amounts of base were added all at once to fresh 5-ml aliquots of IV solution; the meter was read as in runs 3 and 4. Solutions developed both a yellow color and a characteristic sweet odor unlike that of IV, oxides of nitrogen, or formaldehyde. The odor disappeared after 24-hr exposure to air.

A solution resulting from a slower titration was acidified to pH 2.8 with chloroacetic acid and extracted with sufficient dichloromethane to make a 2% solution of IV if recovery were complete. The infrared spectrum showed a trace of IV.

Another titration was carried only to pH 8.70, then treated as above. The infrared spectrum of the extract showed that some 50% of IV had been recovered.

Spectrophotometry of IV in Basic Buffers.—Solutions of IV in pure water and in buffers were examined using quartz cells in a Cary 14 UV-Vis spectrophotometer. Solution in pure water showed only end absorption. In 0.125–0.16 *M* phosphate and borate buffers of pH 6.6–9.45, a broad absorption with λ_{max} 380 mμ appeared, reaching a maximum absorbance at pH 8.24 and remaining constant for at least 1 hr. This is attributed to an impurity.

Recovery of IV from Aqueous Solutions.—IV, 0.079 g (1.0 mol), was dissolved in 50 ml of 0.1 *M* Borax, pH 9.18; after 2 min the solution was acidified to pH 4 with chloroacetic acid and extracted with 4 ml and 3 ml portions of dichloromethane. The infrared spectrum of the extract showed IV; by comparison with a standard, the recovery was found to be 50%. Similar experiments using buffers initially of pH 8.7 allowed recovery of more than 50% of IV.

A solution of 79 mg of IV in 20 ml of 0.1 *N* HCl was allowed to stand 5 min and then shaken with 5 ml of CH_2Cl_2. The infrared spectrum showed a nearly complete recovery of IV by comparison with a standard.

Nmr Spectra of Basic Solutions of IV.—To 1 ml of a 3 *N* buffer of tris(hydroxymethyl)aminomethane and sulfuric acid at pH 9.0 was added 79 mg of IV; the solution was shaken and its nmr spectrum immediately recorded. The doublet characteristic of IV was evident and decreased 50% in intensity in a few minutes. A solution of IV in 3 *N* sodium hydroxide showed no absorption at all for IV.

Base-Catalyzed Hydrogen–Deuterium Exchange of IV and Nitromethane.—Approximately 2-g samples of IV and nitromethane were added to 20–25 ml of buffers prepared in D_2O, which were stirred for specified times and then acidified to pH 5 with chloroacetic acid. The solutions were extracted with 20 ml of dichloromethane and the extracts washed twice with H_2O; most of the solvent was distilled through a Snyder column. Traces of water were thus removed as the dichloromethane azeotrope. The residue was analyzed by glpc using known mixtures of dichloromethane and nitro compound as standards. Aliquots of the residues were sealed into dried glass tubes and submitted to Mr. Josef Nemeth for total deuterium analysis by the combustion and falling drop method. The per cent exchange by the nitro compound could easily be calculated. The buffer used consisted typically of 3.04 g, 25.0 mmol, of tris(hydroxymethyl)aminomethane in 14 ml of D_2O and enough of a solution of 1.26 g of 96% H_2SO_4 in 14 ml of D_2O to bring the pH to the desired value (8.5 or 8.0) before addition of nitro compound. Typical raw data appear in Table III.

TABLE III

TYPICAL ANALYSIS OF MIXTURES OF CH_3NO_2 AND FCH_2NO_2 WITH CH_2Cl_2

Compound	Wt % from glpc	Total atom % excess *d*
CH_3NO_2	41.0	4.95
CH_2FNO_2	54.5	8.30

Approximate second-order rate constants for exchange were calculated assuming that the reactions were pseudo first order and specific base catalyzed. For nitromethane in both runs and for IV in run 2, the concentration of OH^- was assumed constant at $0.9 \times 10^{-6}\ M$. For IV in run 1, the pH was treated as a step function, decreasing 0.1 unit each minute; the reported rate constant reproduces the observed extent of exchange.

Registry No.—I, 603-67-8; II, 680-42-2; III, 21824-09-9; IV, 21824-10-2.

Acknowledgments.—We are grateful to the Petroleum Research Fund, administered by the American Chemical Society, for support *via* Grant No. PRF-592-Gl, and to the Fisher Scientific Co. for the loan of an Orion specific ion meter and fluoride electrode.

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[13] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley & Sons, Inc., New York, N. Y., 1962, pp 299–300.

Stereochemistry of Acid-Catalyzed Hydride Transfer to Cyclic Alkenes

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Though electrophilic additions to alkenes usually proceed with *trans* stereochemistry,[2] a number of exceptions to this generalization have been noted. Hammond and his students first observed that, though hydrogen bromide added exclusively *trans* to 1,2-dimethylcyclohexene, acid-catalyzed hydration gave approximately equal amounts of *cis* and *trans* alcohols.[3] Dewar and Fahey have shown that addition of deuterium bromide to alkenes which afford benzylic carbonium ions (acenaphthylene, indene, 1-phenylpropene) occurs predominantly *cis*,[4] and addition of DBr even to cyclohexene has been reported to yield significant amounts of *cis* adduct.[5] Some *cis* addition of chlorine results with aryl-substituted alkenes,[6] and *cis* addition of

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(1) (a) Department of Chemistry, University of Minnesota, Duluth, Minn. 55812; (b) Department of Chemistry, University of Georgia, Athens, Ga. 30601.

(2) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier Publishing Co., New York, N. Y., 1966.

(3) (a) G. S. Hammond and T. D. Nevitt, *J. Amer. Chem. Soc.*, **76**, 4121 (1954); (b) C. H. Collins and G. S. Hammond, *J. Org. Chem.*, **25**, 911 (1960).

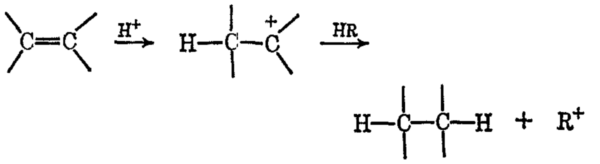
(4) (a) M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, **85**, 2245 (1963); (b) **85**, 2248 (1963); (c) **85**, 3645 (1963).

(5) I. V. Smirnov-Zamkov and G. A. Piskovitina, *Ukr. Khim. Zh.*, **28**, 531 (1962); *Chem. Abstr.*, **58**, 2335 (1963).

(6) (a) S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *J. Amer. Chem. Soc.*, **78**, 4939 (1956); (b) S. J. Cristol and R. S. Bly, *ibid.*, **82**, 142 (1960); (c) R. C. Fahey and C. Schubert, *ibid.*, **87**, 5172 (1965).

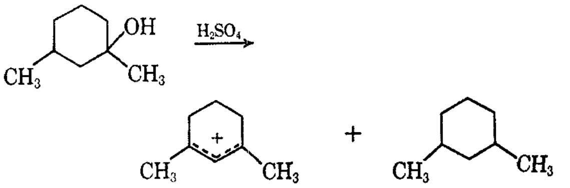
mercuric acetate and other electrophiles to norbornenes has been reported.[7]

The stereochemistry of acid-catalyzed hydride transfer[8] to alkenes would be of considerable interest in this connection,[9] since this reaction may be viewed as a two-step electrophilic addition in which the nucleophile (H^-) is delivered from a neutral molecule (eq 1). Involvement of ion-pair intermediates, which play a crucial role in the explanations[4b,7a] offered for the stereochemistry of ionic addition, could not be a factor in this case.

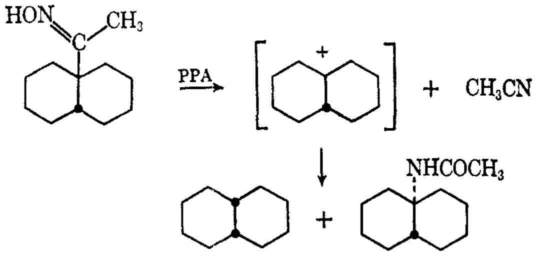


(1)

Two previous reports bear on this question of stereochemistry of intermolecular hydride transfer to carbonium ions. Deno and Pittman[10] found that the 1,3-dimethylcyclohexane formed upon treatment of 1,3-dimethylcyclohexan-1-ol with sulfuric acid (eq 2) had a *cis/trans* ratio of 65:1. This may not necessarily reflect the kinetic preference, since the *cis* is the thermodynamically more stable isomer. In another study,[11] the decalin formed in the acid-catalyzed fragmentation of 9-acetyldecalin oxime (eq 3), presumably by hydride transfer to the 9-decalyl cation, was found to be predominantly *cis;* the identity of the hydride donor was not determined.



(2)



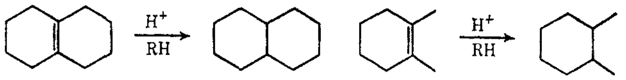
(3)

In the present study, carbonium ions were generated from $\Delta^{9,10}$-octalin (I) and 1,2-dimethylcyclohexene (II) in polyphosphoric acid in the presence of a hydride donor and the stereochemistry of the reduction products was examined. The results are listed in Table I. They show a consistent preference for *cis* product, with *cis/trans* ratios ranging from 4.5–6.5 in the decalins and 1.8–2.5 in the dimethylcyclohexanes.

Minor trends within Table I which might have been attributed to the bulk of the hydride donor must be viewed with skepticism, since tetralin and *o*-xylene were invariably identified by vpc analysis among the products. The presence of these aromatized products indicates that, not surprisingly, the alkenes themselves are effective hydride donors. The remarkable efficiency of this latter process was demonstrated when triphenyldeuteromethane was used as the hydride donor for the decalyl cation. Mass spectral analysis of the decalins produced showed only about 3% deuterium incorporation.

Table I

Stereochemistry of Intramolecular Hydride Transfer



Alkene	Hydride donor	Mol ratio of RH/alkene	Temp, °C	Conversion, %	Product *cis/trans* ratio
I	Tropilidene	1.0	95–100	26	5.65
I	Tropilidene	2.0	95–100	22	4.54
I	Tropilidene	1.0	75–80	25	5.33
I	$(C_6H_5)_3CH$	1.0	100–110	27	6.55
I	$(C_6H_5)_3CH$	1.0	75–80	25	6.50
I	None	. . .	75–80	28	6.38
II	Tropilidene	1.0	95–100	90	1.85
II	None	. . .	75–80	60	2.48

The predominance of the less stable *cis* isomers from both alkenes shows clearly that they are the products of kinetic control. These results as well as those cited above are consistent with preferential delivery of hydride from the less hindered face of the carbonium ion. A similar preference for formation of *cis*-decalin has been observed in hydrogen atom transfer to the 9-decalyl radical.[12] It is amusing that the proportion of *cis* product from hydride transfer is higher than from many reported catalytic hydrogenations of the same olefins.[13]

Experimental Section

$\Delta^{9,10}$-Octalin was prepared by dehydration of *trans*-β-decalol and purified through the nitrosochloride derivative.[14] 1,2-Dimethylcyclohexene was prepared by the method of Signaigo and Cramer.[15] Triphenyldeuteromethane was prepared by hydrolysis of triphenylmethyllithium[16] with D_2O; mass spectroscopic analysis showed a deuterium content of 90%. Polyphosphoric acid was freshly prepared by heating 6 ml of 85% phosphoric acid with 5.1 g of phosphorus pentoxide on the steam bath for 1 hr. Product mixtures were analyzed by vpc, using an Aerograph A-90-P instrument with 0.25-in. columns of 15% Carbowax on 45–60 mesh firebrick and authentic samples of the decalins and dimethylcyclohexanes as standards. Two typical runs are described.

Hydride Transfer to 9,10-Octalin.—A solution of 9,10-octalin (1.36 g, 0.010 mol) and tropilidene (0.92 g, 0.010 mol) was added to polyphosphoric acid (6.0 ml of phosphoric acid, 5.1 g of phosphorus pentoxide) at 75°. The reaction mixture was kept at this temperature for 0.5 hr, cooled, poured over ice, and neutralized with solid sodium carbonate, and the aqueous solution was extracted with pentane (two 25-ml portions). The combined pentane extracts were washed with brine and dried over anhydrous sodium carbonate. The pentane solution was concentrated and

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[7] (a) A. Factor and T. G. Traylor, *J. Org. Chem.*, **33**, 2607 (1968), and references cited therein; (b) T. T. Tidwell and T. G. Traylor, *ibid.*, **33**, 2614 (1968).

[8] N. C. Deno, H. J. Peterson, and G. S. Saines, *Chem. Rev.*, **60**, 7 (1960).

[9] For a study of the stereochemistry of an *intramolecular* acid-catalyzed hydride transfer, see R. K. Hill and R. M. Carlson, *J. Amer. Chem. Soc.*, **87**, 2772 (1965).

[10] N. C. Deno and C. U. Pittman, Jr., *ibid.*, **86**, 1744 (1964).

[11] R. K. Hill, R. T. Conley, and O. T. Chortyk, *ibid.*, **87**, 5646 (1965).

[12] P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel, and L. A. Singer, *ibid.*, **87**, 2590 (1965).

[13] (a) M. Cardew and R. L. Burwell, Jr., *ibid.*, **82**, 6289 (1960); (b) S. Siegel and G. V. Smith, *ibid.*, **82**, 6087 (1960); (c) J. F. Sauvage, R. H. Baker, and A. S. Hussey, *ibid.*, **82**, 6090 (1960); **83**, 3874 (1961); (d) G. V. Smith and R. L. Burwell, Jr., *ibid.*, **84**, 925 (1962).

[14] (a) W. Hückel, R. Danneel, A. Schwartz, and A. Gercke, *Ann.*, **474**, 121 (1929); (b) A. S. Hussey, J. F. Sauvage, and R. H. Baker, *J. Org. Chem.*, **26**, 256 (1961).

[15] F. K. Signaigo and P. L. Cramer, *J. Amer. Chem. Soc.*, **55**, 3326 (1933).

[16] H. Gilman and B. J. Gaj, *J. Org. Chem.*, **28**, 1725 (1963).

the remaining oil was distilled to give a small amount of colorless oil (*ca.* 0.3 g) and a large pot residue.

Hydride Transfer to 1,2-Dimethylcyclohexene.—To the same amount of polyphosphoric acid was slowly added a solution of 1,2-dimethylcyclohexene (1.10 g, 0.010 mol, 78% 1,2-dimethylcyclohexene) and tropilidene (0.92 g, 0.010 mol). The reaction mixture was heated on the steam bath for an additional 15 min, cooled, poured over ice, neutralized with solid sodium carbonate, and extracted with pentane (two 25-ml portions). The combined pentane extracts were washed with brine and dried over anhydrous sodium sulfate. The majority of the pentane was removed and the residual oil was distilled (0.15 g, bp 50–170°). Analysis of the distillate by vpc indicated a 1.85:1 *cis*/*trans* ratio of dimethylcyclohexanes.

Registry No.—I, 493-03-8; II, 1674-10-8.

The Reaction of Primary Amides with Phosgene in the Presence of Hydrogen Chloride

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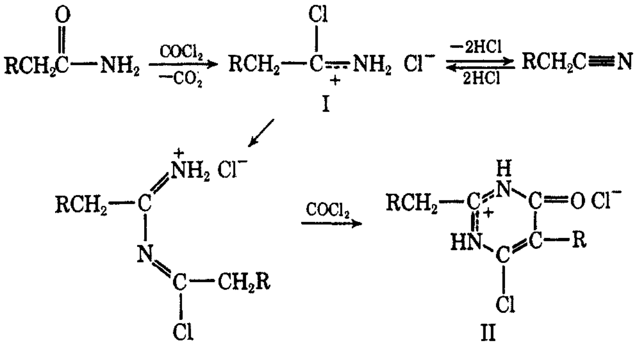
It has previously been reported[1] that the reaction of primary amides with phosgene, especially in the presence of bases, gives nitriles through the formation of imidoyl chloride hydrochloride (I) (Scheme I). In the preceding papers,[2,3] we have reported that nitriles react with phosgene in the presence of hydrogen chloride to give 6-chloro-2,5-dialkyl-4(3H)-pyrimidone hydrochlorides (II), and that this reaction proceeds *via* I and a N-(1-chloroalkylidene)alkylamidine hydrochloride (Scheme I).

Scheme I



Noting these observations, we carried out the reaction of primary amides with phosgene in the presence of hydrogen chloride and found a satisfactory one-step synthesis of the pyrimidone hydrochlorides (II). The results are summarized in Table I.

Acetamide is basic enough to react violently with phosgene to give acetamide hydrochloride, but, when acetamide hydrochloride which had been prepared previously was allowed to react with excess phosgene in nitrobenzene at 60–65° using a sealed glass tube, 6-chloro-2-methyl-4(3H)-pyrimidone hydrochloride was isolated by filtration of the reaction mixture as the only pure product. We examined the yields of the reaction with varying molar ratios of the reactants, and found that more than 2 mol of phosgene to 1 mol of acetamide hydrochloride is essential for pyrimidone formation.

Table I

The Reaction of Fatty Amides with Phosgene in the Presence of Hydrogen Chloride[a]

Fatty amides	Reaction time, hr	Yield of products, %	
		Pyrimidones (II)	Nitriles[b]
Acetamide[c]	200	83	
Propionamide[d]	115	54	22
Butyramide[d]	191	34	28
Caproamide[d]	197	44	32
Lauroamide[d]	206	22	78

[a] Conditions: 60–65°; solvent, nitrobenzene. [b] Determined by glpc. [c] Molar ratio of acetamide hydrochloride/$COCl_2$, 1:8. [d] Molar ratio of amide/$COCl_2$/HCl, 1:3:1.

A solvent effect was also observed in this reaction. Table II gives the yield of product and the dielectric constant of the solvent. Taking into account the ionic mechanism proposed for the reaction yielding the pyrimidones (II) from nitriles and phosgene,[3] it is expected that a high dielectric constant should give a high yield of the pyrimidone hydrochloride. However, the lack of reaction in nitromethane suggests that solubility also plays an important part. Acetamide hydrochloride did not dissolve in nitromethane during the reaction and was recovered unchanged. Analogous results were obtained on the reactions in benzene and toluene, and without solvent. In dioxane, acetonitrile was detected by glpc but the pyrimidone hydrochloride was not obtained.[4] In acetonitrile [ϵ 37.5 (20°)], acetamide hydrochloride readily disappeared as the reaction proceeded and the pyrimidone hydrochloride was formed in a shorter time. It is clear that some product is formed from acetonitrile used as solvent. Thus it is of interest to compare the reactivity of acetamide hydrochloride with that of acetonitrile under comparable conditions. The molar ratios of the reactants were determined as shown in Figure 1 in order to maintain, during the reaction, identical concentrations of hydrogen chloride and phosgene, for each experiment. Figure 1 shows that they have

Table II

Effect of Solvent on the Yield[a]

Solvent	Yield, %	Dielectric constant,[b] ϵ (temp, °C)
Nitrobenzene	83	34.8 (25)
Benzonitrile	53[c]	25.2 (25)
Chlorobenzene	28	5.6 (25)
Nitromethane	0	35.9 (30)
Toluene	0	2.4 (25)
Benzene	0	2.3 (25)
Dioxane	0	2.2 (25)
None	0	

[a] Conditions: 60–65°; 200 hr; concentration, see Experimental Section; molar ratio of acetamide hydrochloride/phosgene 1:8. [b] H. A. Lange, "Handbook of Chemistry", 10th ed, McGraw-Hill Book Co., New York, N. Y., 1967, p 1233. [c] 72 hr; with longer reaction time, another reaction occurred, which is now under investigation.

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[1] A. J. Speziale and L. R. Smith, *J. Org. Chem.*, **28**, 1805 (1968).

[2] S. Yanagida, M. Ohoka, M. Okahara, and S. Komori, *Tetrahedron Lett.*, 2351 (1968).

[3] S. Yanagida, M. Ohoka, M. Okahara, and S. Komori, *J. Org. Chem.* **34**, 2972 (1969).

[4] It has recently been reported that phosgene in dioxane is an easy and convenient agent for the dehydration of amides, and that this dehydration is free of side reaction [M. Wilchek, S. Ariely, and A. Patchornik, *ibid.*, **33**, 1258 (1968)].