spectively. The intermediate, (4-hydroxybenzal)-aniline, was synthesized by an adaptation of a known method.[5] All of the monoalkoxyhydroquinones used were prepared by a modification of the method of Klarmann,[6] and the *m*-hydroxydiphenylamine and *o*-hydroxydiphenylamine intermediates by modification of a known method.[7]

Acknowledgments.—We are indebted to Dr. R. K. Richards and Dr. J. L. Schmidt for pharmacologic studies, to M. Freifelder and G. R. Stone for hydrogenation and pressure reactions and to E. F. Shelberg, Chief Microanalyst, and his staff for analytical data.

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[5] H. Herzfeld, *Ber.*, **10**, 1271 (1877).

[6] E. Klarmann and L. Gatyas, U. S. Patent 1,883,952 (October 25, 1932).

[7] To be reported later by M. Freifelder and G. R. Stone.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF WAYNE UNIVERSITY]

Nitrogen Analogs of Ketenes. II. Dehydrochlorination of Imino Chlorides[1,2]

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A method for the preparation of nitrogen analogs of ketenes (*cf.* Table III) has been developed which involved dehydrochlorination of the corresponding imino chlorides.

The purpose of this investigation was the preparation of representative examples of nitrogen analogs of ketenes as a prelude to the study of the chemical and physical properties of these compounds.

The results indicated that certain ketenimines could not be conveniently prepared by the recently discovered method of dechlorination of α-chloroimino chlorides[2] using sodium iodide. Subsequently, another new method for the preparation of nitrogen analogs of ketenes was developed which involved the facile dehydrochlorination of imino chlorides bearing a single α-hydrogen atom.[4] Although previous work with imino chlorides which contained an α-hydrogen indicated that these compounds were unstable,[5] useful imino chloride intermediates of this type were prepared in this work. Each α-hydrogen imino chloride could be dehydrochlorinated with triethylamine to give the corresponding ketenimine.

A preliminary survey of the scope of the recently discovered method for the preparation of ketenimines[2] indicated that the method failed for the preparation of examples such as dimethylketene *p*-tolylimine (II). The corresponding α-chloroimino chloride VIII was readily prepared in 87% yield from the *p*-toluidide of isobutyric acid (VI) and the structure was shown by hydrolysis to the *p*-toluidide of α-chloroisobutyric acid (X). Treatment of VIII with excess sodium iodide in acetone for three hours at room temperature caused the precipitation of 86% of one equivalent of sodium chloride, accompanied by only a small evolution of iodine. That the intermediate product was the α-chloroimino iodide IX was shown by hydrolysis of the reaction mixture at this stage to give an 86% yield of the α-chloroamide X. After nine days at room temperature, 89% of the iodine had been liberated; the presence of a ketenimine was indicated by hydrolysis at this stage to afford a 60% yield of α-hydrogen amide VI. However, using the isolation procedure previously described,[2] no ketenimine could be obtained.

In contrast to the above procedure, dimethylketene *p*-tolylimine (II) could be prepared conveniently and rapidly in 66% yield by dehydrochlorination of the corresponding imino chloride VII. This imino chloride was prepared from the known amide and phosphorus pentachloride in 87% yield. In contrast to the report of v. Braun[5] which indicated that imino chlorides of the type $R_2CH—CCl{=}NR$ were unstable and could not, as a rule, be isolated, VII could be obtained analytically pure by distillation. The structure of VII was proved by hydrolysis to the amide VI in 94% yield.

The ketenimine II was a yellow liquid which was stable for several weeks at $-80°$ but which was converted to a deep yellow, viscous oil when stored for two days at room temperature. The ketenimine structure was confirmed by rapid hydrolysis to the corresponding α-hydrogen amide VI and by the characteristic infrared absorption band at 4.95 μ.

The preparation of ethylbutylketene *n*-butylimine (I) in 57% over-all yield from the N-butyl amide XI of α-ethylcaproic acid represented a rapid and convenient synthesis of a ketenimine completely substituted with aliphatic groups. The structures of the intermediate imino chloride XII and the ketenimine I were both confirmed by hydrolysis to the starting amide. The ketenimine and the imino chloride in this series proved to be unusually stable. Whereas the ketenimines which have aromatic substituents on the carbon or nitrogen are yellow in color, I is colorless. The infrared absorption band corresponding to the twinned double bond appeared at 4.89 μ and the ultraviolet spectrum showed a maximum at 294 mμ (log ϵ 2.06). This ketenimine, as well as the others, had a distinctive odor.

Initially, the preparation of diphenylketene

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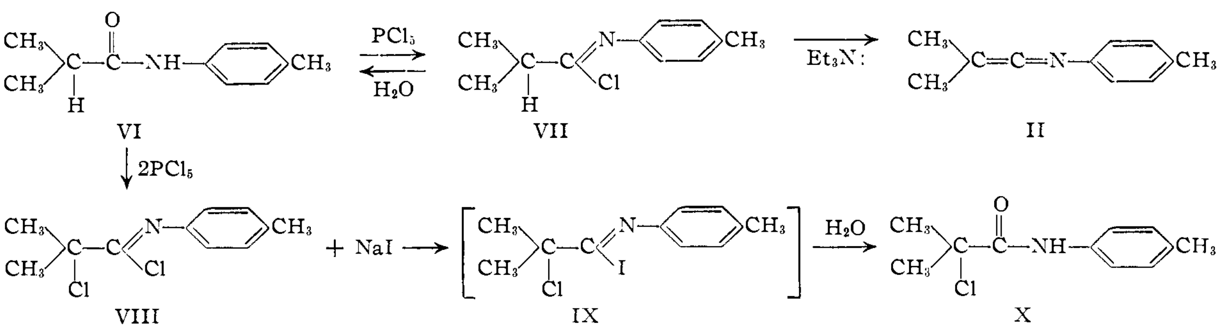
[1] Presented before the Organic Division at the 125th meeting of the American Chemical Society in Kansas City, March, 1954.

[2] The previous paper in this series was: C. L. Stevens and J. C. French, THIS JOURNAL, **75**, 657 (1953).

[3] Public Health Service Research Fellow of the National Institutes of Health, 1952–1953.

[4] *Cf.* the dehydrochlorination of acid chlorides with the formation of ketenes as summarized by W. E. Hanford and J. C. Sauer in "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 124.

[5] For leading references, see J. v. Braun and W. Rudolph, *Ber.*, **67**, 1762 (1934).



methylimine (III) by dehydrohalogenation failed because the required imino chloride XIII was not stable toward isolation by distillation. Distillation of XIII gave a 25% yield of crude diphenylacetonitrile[6] and a 40% yield of a dimer. Prior to the distillation, the imino chloride was present as indicated by hydrolysis of the crude oil in 60% yield to the starting amide. When the crude imino chloride was treated with triethylamine, the main product upon distillation was the dimer (60%) and only a very small amount of impure ketenimine (2.4%) could be obtained by the isolation procedure used. Since the dimer could not be hydrolyzed and since an aliquot of the reaction mixture before distillation could be hydrolyzed to the α-hydrogen amide in 34% yield, the ketenimine III must have been present before distillation in at least this amount. The catalytic effect of organic amine hydrochlorides on the dimerization of ketenes is well known[7] and the formation of the large amount of dimer in this particular reaction is probably due to a similar catalytic effect.

That the two new methods for the preparation of ketenimines complement each other well was further shown by the fact that III could be prepared in 46% yield from the corresponding α-chloroimino chloride XIV using sodium iodide and acetone. III and XIV were hydrolyzed to N-methyldiphenylacetamide and N-methyl-α-hydroxydiphenylacetamide, respectively, as a confirmation of structure. The ketenimine slowly changed to a viscous liquid at room temperature and a sizable residue always remained after distillation.

The structures of the ketenimines have been assigned on the basis of their physical properties and chemical reactions. Finally, in this work, the ketenimine IV (diphenylketene *n*-butylimine) was synthesized by both newly developed methods to complete the proof of structure. Attempted distillation of the corresponding imino chloride XVI gave a unique result; hydrogen chloride was liberated under reduced pressure and a significant amount of the ketenimine IV was formed directly.[8]

Treatment of the crude imino chloride with triethylamine prior to distillation gave the ketenimine in 69% over-all yield from the amide XV.

The α-chloroimino chloride XVII could be readily prepared, and when treated with sodium iodide in acetone gave IV in 70% over-all yield from the amide. In this particular instance, the yields by the two methods were comparable and the two products were identical as indicated by a comparison of the physical properties and the infrared spectra.

The N-butylketenimine IV was much more stable toward dimerization than the corresponding N-methylketenimine III, although a small amount of a dimer could be obtained. The chemical and physical properties of these dimers are presently being studied.

The ketenimine V which has previously been prepared[2] by the dehalogenation of the corresponding α-chloroimino chloride in 56% over-all yield from the amide was also prepared by the dehydrohalogenation of the corresponding imino chloride in 65% over-all yield.[9]

For the preparation of large amounts of ketenimines, the dehydrochlorination method appears to be the method of choice. However, for those ketenimines which are easily dimerized, the dehalogenation of the α-chloroimino chlorides appears to be the better method.

Experimental

Starting Materials.—The amides XI and XV were prepared from the corresponding acid chloride and 2.2 equivalents of *n*-butylamine in ether solution. The imino chlorides VII and XII were isolated *via* distillation of the reaction mixture of one equivalent of phosphorus pentachloride and one equivalent of the corresponding amide in dry benzene solution after a one-hour reflux period. The α-chloroimino chlorides VIII, XIV and XVII were obtained *via* distillation of the reaction mixture of two equivalents of phosphorus pentachloride and one equivalent of the corresponding amide in dry benzene solution after a three hour reflux period. The physical properties, yields and analyses of these compounds are listed in Table I.

Ethyl-*n*-butylketene *n*-Butylimine (I).—The reaction mixture consisting of 31.8 g. of N-(*n*-butyl)-α-ethylcaproimino chloride, 45 ml. of redistilled triethylamine and 175 ml. of dry benzene was heated under reflux for 32 hours. The triethylamine hydrochloride (19.0 g., 94%) was filtered and washed with dry ether. The filtrate and ether washings were combined and concentrated under reduced pressure. Distillation of the residual oil in a Claisen flask with a 12-cm. Vigreux column gave two fractions: (1) b.p. 53–56° (0.2 mm.), n^{25}_{D} 1.4538, 16.5 g. (62%); and (2) b.p. 57–61° (0.2 mm.), n^{25}_{D} 1.4525, 5.2 g. A portion of the first faction which was nearly pure ketenimine was distilled through a 300 × 6 mm. tubular column to give the colorless analytically pure ketenimine; b.p. 46° (0.1 mm.), n^{25}_{D} 1.4540, d^{25} 0.812.

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(6) The formation of diphenylacetonitrile upon pyrolysis of N-methyldiphenylacetimino chloride is similar to the formation of benzonitrile upon the attempted distillation of N-methylbenzimino chloride as observed by H. v. Pechmann (*Ber.*, **33**, 611 (1900)). For other examples of the formation of nitriles and alkyl halides from imino chlorides, see J. v. Braun, *Ber.*, **38**, 2340 (1905).

(7) U. S. Patents 2,238,826 (*C. A.*, **35**, 4970 (1941); 2,268,169 (*C. A.*, **36**, 2737 (1942)), see also H. Staudinger and H. Klever, *Ber.*, **41**, 594 (1908).

(8) This thermal elimination of hydrogen chloride is analogous to the work of R. C. Fuson, *et al.* (THIS JOURNAL, **66**, 1464 (1944)) who prepared mesitylphenylketene by heating mesitylphenylacetyl chloride with a catalytic amount of pyridine.

(9) Experimental results of Mr. Robert Gasser of this Laboratory.

TABLE I

PROPERTIES OF STARTING MATERIALS

No.	Compound	M.p., °C.	B.p. °C.	B.p. Mm.	$n^{25}D$	d^{25}	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found
XI	N-(*n*-Butyl)-α-ethylcaproamide[a]	...	110–114	0.3	1.4470	...	93	$C_{12}H_{25}NO$	72.30	72.21	12.64	12.23	...	...
XV	N-(*n*-Butyl)-diphenylacetamide	96–97	.....	..	....	...	97	$C_{18}H_{21}NO$	81.04	80.94	7.92	8.23	...	...
VII	N-(*p*-Tolyl)-isobutyrimino chloride	...	80–85	0.8	1.5299	...	82.5	$C_{11}H_{14}ClN$	67.51	67.12	7.21	7.44	18.12	17.86
XII	N-(*n*-Butyl)-α-ethylcaproimino chloride	...	72–76	0.7	1.4485	0.893	92.5	$C_{12}H_{24}ClN$	66.18	66.07	11.11	11.10	16.28	16.54
VIII	N-(*p*-Tolyl)-α-chloroisobutyrimino chloride	...	93–45	0.5	1.5429	1.141	87	$C_{11}H_{13}Cl_2N$	57.41	57.77	5.69	5.88	...	...
XIV	N-Methyl α-chlorodiphenylacetimino chloride	70–72	147–152	0.4	....	...	92	$C_{15}H_{13}Cl_2N$	64.76	65.03	4.71	5.04	25.49	25.20
XVII	N-(*n*-Butyl)-α-chlorodiphenylacetimino chloride	...	160–163	0.2	1.5749	...	88.5	$C_{18}H_{19}Cl_2N$	67.50	67.54	5.98	5.87	22.15	21.92

[a] F. F. Blicke and A. P. Centolella, THIS JOURNAL, **60**, 2924 (1938), reported b.p. 177–178° (5 mm.).

Anal. Calcd. for $C_{12}H_{23}N$: C, 79.49; H, 12.79. Found: C, 79.64; H, 12.98.

The infrared spectrum of this substance showed a strong absorption at 4.89 μ and no absorption in the 6.0 μ region. The ultraviolet spectrum taken in cyclohexane showed λ_{max} 294 mμ (log ε 2.06).

Dimethylketene *p*-Tolylimine (II).—This ketenimine was prepared by a procedure similar to that used for I. From 4.77 g. of freshly distilled N-*p*-tolylisobutyrimino chloride, 30 ml. of dry triethylamine and 110 ml. of dry toluene was obtained 3.1 g. (92.4%) of triethylamine hydrochloride after nine hours at 95–100°. The yellow-green ketenimine, b.p. 85–89° (0.2 mm.), was isolated by distillation and amounted to 2.57 g. (66.3%). The analytical sample was obtained upon redistillation, b.p. 65–66° (0.05 mm.), $n^{25}D$ 1.5540, d^{25} 0.935.

Anal. Calcd. for $C_{11}H_{13}N$: C, 82.98; H, 8.23. Found: C, 83.08; H, 8.62.

Dimethylketene *p*-tolylimine is stable for several weeks at −80° but is converted into a deep yellow, viscous oil when stored for two days at room temperature. The infrared spectrum of the freshly distilled ketenimine showed a strong absorption at 4.95 μ.

Diphenylketene Methylimine (III).—To a solution of 60 g. of sodium iodide dissolved in 300 ml. of dry acetone was added 10 g. of N-methyl-α-chlorodiphenylacetimino chloride. The reaction mixture, which rapidly liberated iodine, was heated under reflux for 75 minutes. The acetone was then removed under reduced pressure. The residual green solid mass was digested well with 200 ml. of dry petroleum ether and then transferred to a filter and washed with additional petroleum ether until no more yellow color passed into the filtrate. The filtrate was concentrated under reduced pressure and the residual yellow oil transferred to a small Claisen flask. Distillation afforded 3.45 g. (46%) of the golden yellow, liquid ketenimine, b.p. 120–123° (0.2 mm.).[10] A considerable amount of dark red residue remained in the distillation pot. A portion of the ketenimine was distilled through a 30-cm. tubular column to give the analytical sample; b.p. 121–122° (0.05 mm.), $n^{25}D$ 1.6362, d^{25} 1.056.

Anal. Calcd. for $C_{15}H_{13}N$: C, 86.92; H, 6.32. Found: C, 86.85; H, 6.49.

Diphenylketene methylimine changed to a viscous oil when stored at room temperature for several days; the infrared spectrum of the freshly distilled material showed strong absorption at 4.98 μ.

Diphenylketene N-Butylimine (IV). A. From the Dechlorination of N-(*n*-Butyl)-α-chlorodiphenylacetimino Chloride.—The reaction mixture resulting from the interaction of 5.79 g. of this α-chloroimino chloride and 150 ml. of a saturated solution of sodium iodide in dry acetone was heated under reflux for three hours. Most of the acetone was removed under reduced pressure and the dark green residue was thoroughly digested with dry petroleum ether. The same isolation procedure as described for the preparation of III was used to obtain 3.21 g. (71%) of a golden yellow liquid; b.p. 143–147° (0.12 mm.), $n^{25}D$ 1.6026, d^{25} 1.029. A repeated distillation yielded the analytical sample of the ketenimine; b.p. 137–138° (0.1 mm.), $n^{25}D$ 1.6025.

Anal. Calcd. for $C_{18}H_{19}N$: C, 86.70; H, 7.68. Found: C, 86.98; H, 7.50.

The infrared spectrum of this ketenimine possessed a strong band at 4.97 μ.

B. From the Dehydrohalogenation of N-(*n*-Butyl)-diphenylacetimino Chloride.—The reaction mixture of 4.0 g. (0.015 mole) of N-(*n*-butyl)-diphenylacetamide, 3.12 g. (0.0149 mole) of phosphorus pentachloride and 25 ml. of dry benzene was heated under reflux for 90 minutes. The volatile components were then removed *in vacuo*. The residual oil was redissolved in 20 ml. of dry benzene and the solution was evaporated to dryness under reduced pressure. This co-distillation, to remove the remaining phosphorus oxychloride, was repeated two more times and the remaining oil was left one hour at 0.2 mm. The amber oil was dissolved in 15 ml. of dry ether and then 10 ml. of freshly distilled triethylamine was added. The reaction mixture which rapidly precipitated a voluminous solid was allowed to stand for six hours and then filtered. The triethylamine hydrochloride was washed with dry ether and weighed 1.86 g. (90.5%). The yellow filtrate was concentrated *in vacuo* and the residual oil was transferred to a small Claisen flask. Distillation afforded 2.58 g. (69.2%) of the yellow ketenimine; b.p. 154–158° (0.15 mm.), $n^{25}D$ 1.6002. The small amount of pot residue was further heated and *ca.* 0.2 g. of a very viscous liquid was collected; b.p. 210–225° (0.12 mm.). This oil only partially crystallized. Two recrystallizations from acetone afforded a small amount of the dimer, m.p. 109–110°.

Anal. Calcd. for $(C_{18}H_{19}N)_2$: C, 86.70; H, 7.68. Found: C, 86.57; H, 7.77.

The infrared spectrum of this material showed absorption bands at 5.8 and 6.1 μ.

This material readily formed a picrate in ether solution which was recrystallized from 95% ethanol, m.p. 228–229°.

Anal. Calcd. for $(C_{18}H_{19}N)_2 \cdot C_6H_3N_3O_7$: C, 69.32; H, 5.68. Found: C, 69.17; H, 5.77.

Redistillation of the ketenimine isolated above afforded an analytical sample; b.p. 148–149° (0.15 mm.), $n^{25}D$ 1.6024.

Anal. Calcd. for $C_{18}H_{19}N$: C, 86.70; H, 7.68. Found: C, 86.92; H, 8.00.

The infrared spectrum of this sample of diphenylketene N-butylimine indicated that the product was identical with the ketenimine prepared by the dehalogenation of N-(*n*-butyl)-α-chlorodiphenylacetimino chloride.

Action of Sodium Iodide on N-(*p*-Tolyl)-α-chloroisobutyrimino Chloride (VIII).—To a solution of 1.28 g. of this freshly distilled α-chloroimino chloride dissolved in 5 ml. of dry acetone was added 12 ml. of a saturated solution of sodium iodide in dry acetone. An instantaneous white precipitate formed and no evolution of iodine occurred. The

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[10] H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 892 (1921), obtained this ketenimine in impure state in unspecified yield from diphenylketene and triphenylphosphine methylimine.

TABLE II

HYDROLYSIS PRODUCTS OF IMINO CHLORIDES AND KETENIMINES

Starting material a. Imino chlorides	Product	M.p., °C.	Yield, %	Note
VII	N-(*p*-Tolyl)-isobutyramide	105–106	94	*a*
XII	N-(*p*-Butyl)-α-ethylcaproamide	.....	82	*b*
VIII	N(-*p*-Tolyl)-α-chloroisobutyramide	66–67[d]	98	*a*
XIV	N-Methyl-α-hydroxydiphenylacetamide	147–148[e]	87	*a*
XVII	N-(*n*-Butyl)-α-hydroxydiphenylacetamide	73–74	94	*c*
b. Ketenimines				
I	N-(*n*-Butyl)-α-ethylcaproamide	......	75	*b*
II	N-(*p*-Tolyl)-isobutyramide	104–106	65	*a*
III	N-Methyldiphenylacetamide	160–162[f]	92	*a*
IV	N-(*n*-Butyl)-diphenylacetamide	93–94	97	*a*

[a] A mixed melting point with an authentic sample was undepressed. [b] n^{25}D 1.4471; the infrared spectra of the product and a known sample of XI were indistinguishable. [c] *Anal.* Calcd. for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.47. Found: C, 76.56; H, 7.56. [d] C. A. Bischoff and P. Walden, *Ann.*, 279, 117 (1894), reported a m.p. of 70°. [e] J. H. Billman, *et al.*, THIS JOURNAL, **67**, 130 (1945), reported a m.p. of 146–147°. [f] H. Staudinger and E. Hauser, ref. 10, reported a m.p. of 163–164°.

reaction mixture was allowed to stand three hours at room temperature and the sodium chloride that precipitated was filtered and washed with 30 ml. of dry acetone. The sodium chloride was dried and weighed 0.28 g. which corresponded to 86% of one equivalent precipitated. The filtrate[11] which possessed only a slight coloration of iodine was diluted with 300 ml. of water containing a small amount of sodium sulfite. A white solid began to precipitate immediately. The mixture was allowed to stand overnight in the refrigerator and the crystalline solid which was then filtered and dried weighed 0.96 g. (85.7%), m.p. 66.5–69°. A mixed melting point of this material with N-(*p*-tolyl)-α-chloroisobutyramide was 66–67°.

In another experiment, 2.70 g. of N-(*p*-tolyl)-α-chloroisobutyrimino chloride was treated with 54 ml. of a saturated solution of sodium iodide in dry acetone and the reaction mixture which only very slowly liberated iodine was allowed to stand at 24°. After 60 hours only 60% of the theoretical amount of iodine was liberated; however, after nine days, a titration of an aliquot showed that 89% of the iodine had been liberated. The reaction mixture was treated with a large amount of water containing a sufficient amount of sodium sulfite to completely reduce the iodine. The solid that precipitated was filtered and after drying weighed 1.51 g. (61%), m.p. 85–90°. This crude material was easily recrystallized from ether–petroleum ether to give needles, m.p. 103–105°. A mixed melting point with authentic N-(*p*-tolyl)-isobutyramide was 104–106°. In similar experiments, attempts to isolate the corresponding ketenimine were unsuccessful.

Attempted Isolation of N-(*n*-Butyl)-diphenylacetimino Chloride (XVI).—A solution of 4.08 g. (0.0153 mole) of N-(*n*-butyl)-diphenylacetamide and 3.19 g. (0.0153 mole) of phosphorus pentachloride dissolved in 25 ml. of dry benzene was heated under reflux for 90 minutes. The volatile components were removed *in vacuo* and the residual amber oil transferred to a 10-ml. distilling flask. At a bath temperature of 130° the pressure increased from an initial 0.4 to 2.5 mm. At a bath temperature of 180–190°, the pressure began to decrease slowly and a colorless liquid began to distil. About 3 g. of a yellow liquid was collected between 150–160° over a pressure range of 1.1 to 0.2 mm. This crude material consisted of both the imino chloride and the ketenimine since the infrared spectrum showed the characteristic strong absorption band at 4.9 μ (ketenimine) and also a considerable band at 6.0 μ (imino chloride).

Pyrolysis of N-Methyldiphenylacetimino Chloride (XIII).—Hydrogen chloride was smoothly evolved when a solution of 5.1 g. (0.0227 mole) of N-methyldiphenylacetamide and 4.8 g. (0.023 mole) of phosphorus pentachloride dissolved in 25 ml. of dry benzene was heated under reflux for one hour. The reaction mixture was evaporated under reduced pressure and the residual amber oil was transferred to a 10-ml. distilling flask and heated at an initial pressure of 0.2 mm. At a bath temperature of 110°, the contents of the flask became dark and the pressure increased steadily to 2.5 mm. At a bath temperature of 190°, the pressure was *ca.* 6 mm. and a colorless liquid began to condense in the upper part of the flask. The duration of heating to this point was 12 minutes, after which time the pressure steadily decreased and 1.05 g. of a pale yellow liquid was collected, b.p. 140–145° (2.5–2.0 mm.) at a bath temperature of 195–200°. Continued heating (bath temperature, 220°) resulted in the slow distillation of a small amount of additional yellow liquid, b.p. 130–135° (1 mm.). After several minutes, no further distillation occurred and the pressure dropped to 0.2 mm. However, at a bath temperature of 250–265°, 1.94 g. of a deep amber, very viscous liquid was collected, b.p. 220–227° (0.1 mm.).

TABLE III

	Ketenimine	Yield, % *a*	*b*	Infrared, μ
I	$\genfrac{}{}{0pt}{}{n\text{-}C_4H_9}{C_2H_5}{>}C{=}C{=}N{-}(CH_2)_3CH_3$	57	..	4.89
II	$\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C{=}C{=}N{-}C_6H_4{-}CH_3\text{-}p$	58	0	4.95
III	$\genfrac{}{}{0pt}{}{C_6H_5}{C_6H_5}{>}C{=}C{=}N{-}CH_3$	2.4	42	4.98
IV	$\genfrac{}{}{0pt}{}{C_6H_5}{C_6H_5}{>}C{=}C{=}N{-}(CH_3)_3CH_3$	69	63	4.97
V	$\genfrac{}{}{0pt}{}{C_6H_5}{C_6H_5}{>}C{=}C{=}N{-}C_8H_4{-}CH_3\text{-}p$	65	56	5.00

[a] Based on the starting amide *via* the dehydrochlorination of the intermediary imino chloride. [b] Based on the starting amide *via* the dechlorination of the α-chloroimino chloride.

The lower boiling fraction (1.13 g., which represents a 25.8% yield of diphenylacetonitrile) rapidly crystallized when stirred with a glass rod and the resulting solid melted at 65–67° with previous softening. When this material was recrystallized from hexane–acetone, a colorless solid was obtained, m.p. 70–73°, which did not depress the melting point (71–73°) of an authentic sample of diphenylacetonitrile prepared in the usual way from thionyl chloride and diphenylacetamide.

The higher boiling fraction (1.94 g., which represents a 41% yield of diphenylketene methylimine dimer) crystallized overnight. When this crude solid was recrystallized from hexane–acetone, colorless prisms were obtained, m.p. 165–167°. The analytical sample of the dimer of diphenylketene methylimine was obtained after one more crystallization from hexane–acetone, m.p. 166–167.5°.

Anal. Calcd. for $(C_{15}H_{13}N)_2$: C, 86.92; H, 6.32; N, 6.76. Found: C, 87.14; H, 6.39; N, 6.94.

The infrared spectrum of this material showed an absorption band at 5.8 μ and a strong band at 6.1 μ.

A monohydrochloride was obtained by heating the dimer with a 1:1 mixture of ethanol and concentrated hydrochloric acid. The yellow reaction mixture was concentrated to a small volume and the residual solution diluted with water.

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[11] In a similar experiment, the filtrate was evaporated to dryness *in vacuo* and the residual solids were digested with petroleum ether. After the petroleum ether solution was concentrated, attempted isolation of N-(*p*-tolyl)-α-chloroisobutyrimino iodide (IX) from the remaining yellow oil, *via* distillation, resulted in extensive decomposition, evidenced by the evolution of iodine. However, a very low yield of a dark brown (iodine contaminated) liquid was obtained, b.p. 45–51° (0.2 mm.) which was not further investigated.

The oil that initially precipitated completely crystallized after several hours. Stout rods of the colorless hydrochloride were obtained after one recrystallization from ethyl acetate, m.p. 216–219°.

Anal. Calcd. for $(C_{15}H_{13}N)_2 \cdot HCl$: C, 79.89; H, 6.04. Found: C, 80.27; H, 6.42.

When an ethanolic solution of this hydrochloride was treated with dilute ammonium hydroxide, a white solid precipitated, m.p. 163–166°. A mixed melting point with the original dimer was undepressed.

A monopicrate was prepared when a saturated solution of picric acid in ether was added to an ether–chloroform solution of the dimer. One crystallization from hexane–acetone gave a yellow solid, m.p. 237–238°.

Anal. Calcd. for $(C_{15}H_{13}N)_2 \cdot C_6H_3N_3O_7$: C, 67.18; H, 4.54; N, 10.88; mol. wt., 643.6. Found: C, 67.39; H, 4.66; N, 10.86; mol. wt., 630.[12]

Action of Triethylamine on Crude N-Methyldiphenylacetimino Chloride.—This crude imino chloride was prepared by heating under reflux a solution of 5.01 g. (0.0223 mole) of N-methyldiphenylacetamide and 4.63 g. (0.0222 mole) of phosphorus pentachloride in 35 ml. of dry benzene for 90 minutes. The reaction mixture was concentrated *in vacuo* and the residual oil co-distilled three times, *in vacuo*, with 20-ml. portions of dry benzene. The pale yellow imino chloride[13] was dissolved in 35 ml. of dry toluene and then 30 ml. of freshly distilled triethylamine was added. The reaction mixture, which soon precipitated triethylamine hydrochloride, was maintained at 100–110° in an atmosphere of dry nitrogen for six hours. The white precipitate was filtered, washed with dry ether and dried to a constant weight (2.68 g.). The filtrate was evaporated nearly to dryness and the residual mixture was treated with 30 ml. of dry ether and an additional 0.23 g. of white solid was filtered. The total weight of triethylamine hydrochloride was 2.91 g. (95%). The filtrate was again concentrated and the residual amber oil transferred to a 10-ml. distilling flask. Distillation afforded two distinct fractions: (1) 0.77 g. (17%), b.p. 120–140° (0.2 mm.); (2) 2.80 g. (61%), b.p. 215–225° (0.1 mm.). The first fraction was redistilled through a 30-cm. tubular column to give 0.11 g. (2.4%) of somewhat impure diphenylketene methylimine, b.p. 124–125° (0.15 mm.); $n^{25}\text{D}$ 1.6141. The infrared spectrum showed the characteristic strong band at 4.98 μ in addition to weak absorption bands at 5.8 and 6.1 μ, which are associated with the dimer impurity.

The second fraction readily crystallized. One recrystallization from hexane–acetone afforded a solid, m.p. 165–167°, which did not depress the melting point of the above-described dimer of diphenylketene methylimine obtained from the pyrolysis of N-methyldiphenylacetimino chloride.

Hydrolysis of Ketenimines and Imino Chlorides.—In each case hydrolysis was effected in aqueous acetone at room temperature. The addition of dilute hydrochloric acid greatly accelerated the hydrolysis of the ketenimines as indicated by the discharge of the yellow color. The properties and yields of the various hydrolysis products are listed in Table II.

Acknowledgment.—The authors wish to thank Miss Phylis Tocco and Mr. Robert French for the microanalyses.

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[12] We are indebted to Dr. J. M. Vandenbelt, Parke, Davis and Co., for the spectrophotometric molecular weight determination of this material as well as for the ultraviolet spectrum reported in this paper.

[13] To more definitely establish the nature of this material, in an identical experiment an aliquot of this oil was readily hydrolyzed in aqueous acetone solution to afford a 98% yield of crude N-methyldiphenylacetamide. One crystallization from aqueous acetone gave a 45% yield of pure N-methyldiphenylacetamide, m.p. 162–163°

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF WAYNE UNIVERSITY]

Epoxyethers. IX. Acid-catalyzed Rearrangements[1]

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A wide variety of epoxyethers were cleanly rearranged to give a good yield of the corresponding methoxy ketones using magnesium bromide as a catalyst (*cf.* Table I). The structures of the new epoxyethers were proved by degradation reactions and the methoxy ketones were prepared independently or the structures proved by a second order Beckmann degradation of the corresponding oxime.

The acid-catalyzed rearrangement of ethylene oxides to carbonyl compounds has been widely studied and has found much use.[3] The utility of the rearrangement is based upon the ability to predict the direction in which the oxide ring is opened as well as the choice of which of the two groups migrates during the rearrangement.

The oxide rearrangement has been recognized for some time as one of the group of pinacol-type rearrangements.[4] From the examples reported of the pinacol-type rearrangement, the course of the rearrangement of an individual compound must depend upon the nature of the group that is leaving,[4,5] the stability of the transition states,[5,6] the nature of the migrating group and the reaction media.

The ionization of the carbon–oxygen bond in oxides corresponds to the steps in which a group leaves in the pinacol rearrangement, and the relative ease of ionization of the two carbon–oxygen bonds in oxides generally determines the direction of ring opening in acid-catalyzed rearrangements.

In this work, examples of epoxyethers were chosen which demonstrate that the scope of the rearrangement is broad and that the reaction may be used for the preparation of methoxy ketones. In every example the direction of ring opening is predictable on the basis of the relative ease of ionization of the carbon–oxygen bonds since the methoxy ketone was the only product that could be isolated. Although the ability of one group to migrate in preference to another is dependent upon

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[2] Abstracted in part from the Ph.D. thesis of Mr. Stanley J. Dykstra, Wayne University, June, 1953.

[3] A review of acid-catalyzed rearrangements of ethylene oxides has been written recently by S. Winstein and R. B. Henderson in R. C. Elderfield's "Heterocyclic Compounds," John Wiley and Sons, Inc., New York, N. Y., Vol. 1, 1950, p. 48.

[4] *Cf.* G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 494–519.

[5] E. R. Alexander and D. C. Dittmer, THIS JOURNAL, **73**, 1665 (1951).

[6] D. Curtin, *et al.*, *ibid.*, **72**, 961 (1950); **73**, 992, 3453 (1951).