Syntheses and Some Reactions of Allophanoyl Chlorides[1a]

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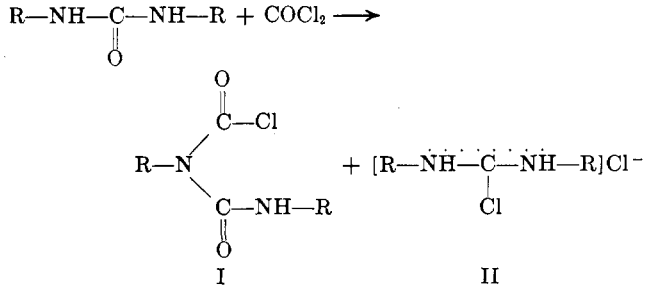
Cyclic and acyclic N,N′-Dialkylallophanoyl chlorides (I), a new class of intermediates, were synthesized from N,N′-disubstituted ureas and phosgene. The effect of substituent on the course of the reaction and some reactions of the allophanoyl chlorides are discussed.

Allophanic acid derivatives, especially the esters, the allophanates,[2] are known; however, the corresponding acid chlorides, the substituted allophanoyl chlorides, are not known. Allophanoyl chloride, although not characterized, was reported.[3]

The reaction of N,N′-dialkylureas with phosgene is reported[4] to give N,N′-dialkylchloroformamidine hydrochlorides (II). The formation of II suggests that phosgene is attacked by the oxygen rather than the nitrogen atom of the ureas. These results could have been expected in view of the facile reaction of N-alkylcarboxamides with phosgene which afforded high yields of the corresponding imide chlorides.[5]

Reinvestigation of the reaction of N,N′-dialkylureas with phosgene showed that in all cases studied, in addition to the reported N,N′-dialkylchloroformamidines (II), N,N′-dialkylallophanoyl chlorides (I) were formed. The distribution of I and II can be slightly controlled by the reaction conditions; however, structural features of the starting N,N′-dialkylureas seem to be the dominant factor (see Table I).



a, R = methyl
b, R = *n*-butyl
c, R = *n*-octadecyl
d, R = isopropyl
e, R = cyclohexyl

From Table I it appears evident that the steric factor mainly determines the course of the reaction. Thus, when the substituents are primary alkyls, the main product is allophanoyl chloride, arising from the nucleophilic attack of the urea nitrogen on phosgene, but, when the substituents are secondary alkyls, the main product is chloroformamidine hydrochloride.

The proportions of I and II could be determined by infrared spectroscopy, I showing a C=O band at 5.73–5.82 μ, II a C=N band at 5.95–6.02 μ.

The structure of the allophanoyl chlorides has been established by elemental analysis, infrared spectroscopy (NH, 2.94–3.02 μ; C=O, 5.73–5.82 μ), and conversion to the allophanates and biurets by means of sodium alkoxide and amines, respectively.

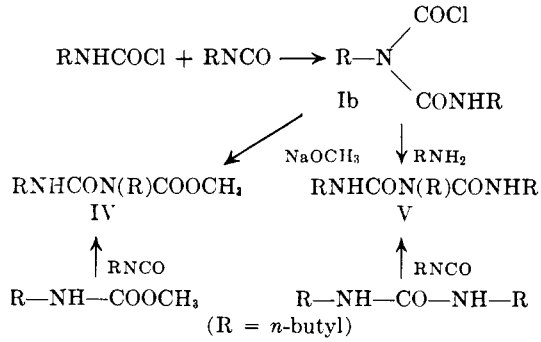
TABLE I

REACTION OF N,N′-DIALKYLUREAS WITH PHOSGENE[a]

Starting urea	N,N′-Dialkylallophanoyl chloride (I),[b] % yield	N,N′-Dialkylchloroformamidine·HCl (II), % yield
Dimethyl	71	28
Di-*n*-butyl	70.5	24
Di-*n*-octadecyl	69	28
Diisopropyl	6.7	75.6[c]
Dicyclohexyl	12.5	77.8

[a] Runs in ethylene dichloride at 2–5°. [b] The yields of I are not optimum yields. [c] Also 8.2% of N,N′-diisopropylchloroformamidine-N-carbonyl chloride was isolated. While phosgene does not react with I, with II it forms chloroformamidine-N-carbonyl chlorides.[6]

As a model compound, Ib was converted with sodium methoxide to methyl 2,4-di-*n*-butylallophanate (IV), which was found to be identical with a sample prepared from methyl N-*n*-butylcarbamate and *n*-butyl isocyanate. Similarly, Ib reacts with *n*-butylamine to give 1,3,5-tri-*n*-butylbiuret (V), which was synthesized independently from 1,3-di-*n*-butylurea and *n*-butyl isocyanate. Further evidence for the structure of Ib is its synthesis from *n*-butyl isocyanate and *n*-butylcarbamoyl chloride.



(R = *n*-butyl)

The structure of the chloroformamidine hydrochlorides (II) was confirmed by infrared spectroscopy, by conversion to guanidine hydrochlorides with primary amine, and by dehydrochlorination to carbodiimides with tertiary amine. Thus IIb was converted to di-*n*-butylcarbodiimide (III) using triethylamine, and IIb with *n*-butylamine afforded 1,2,3-tri-*n*-butylguanidine hydrochloride.

In the presence of triethylamine, N,N′-di-*n*-butylurea reacts with excess phosgene to give a mixture of Ib (31%) and N,N′-di-*n*-butylchloroformamidine-N-carbonyl chloride (VI, 69%). The latter is formed by addi-

(1) (a) Presented at the XIXth International Congress of Pure and Applied Chemistry, London, 1963; (b) To whom all inquiries should be directed.

(2) H. W. Blohm and E. I. Becker, *Chem. Rev.*, **51**, 471 (1952).

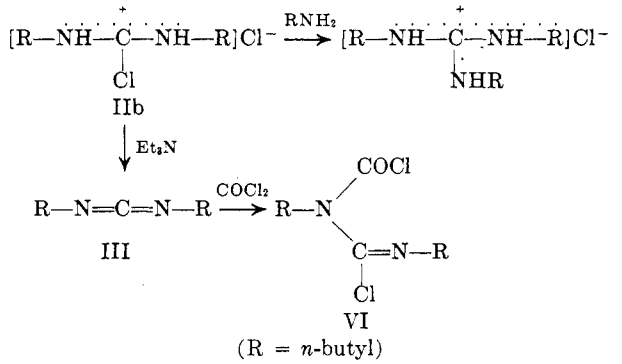
(3) C. Steigerwald, German Patent 238,961; *Chem. Zentr.*, **II**, 1285 (1911).

(4) H. Eilingsfeld, M. Seefelder, and H. Weidinger, *Angew. Chem.*, **72**, 836 (1960).

(5) I. Ugi, F. Beck, and U. Fetzer, *Ber.*, **95**, 126 (1962).

(6) H. Ulrich and A. A. R. Sayigh, *J. Org. Chem.*, **28**, 1427 (1963).

tion of phosgene to the intermediate di-*n*-butylcarbodiimide (III, R = *n*-butyl). Phosgene adds readily to carbodiimides at room temperature.[6]

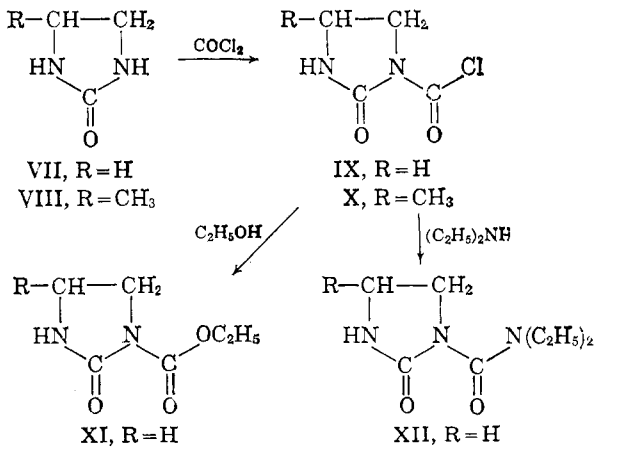


Cyclic alkylureas, such as ethyleneurea (VII) and propyleneurea (VIII), react similarly, apparently exclusively by N-attack, to form the corresponding cyclic allophanoyl chlorides (2-imidazolidinone-N-carbonyl chlorides, IX and X), since the yields of these are high and since the characteristic 6.0-μ[7] (C=N) absorption of the possible O-attack products (1-chloroimidazolines) was entirely absent. Similarly, ethyleneurea reacts with phosphorus pentachloride to give products arising only from N-attack.[8]

The assigned structure of X is based on the hypothesis that attack by the N-atom next to the primary carbon atom is more likely.

The infrared spectra of IX and X in chloroform show a characteristic triple band pattern in the carbonyl region (5.52, 5.67, and 5.77 μ) and two absorptions in the NH region, 2.93 and 3.1 μ, for the free and associated NH absorptions, respectively.

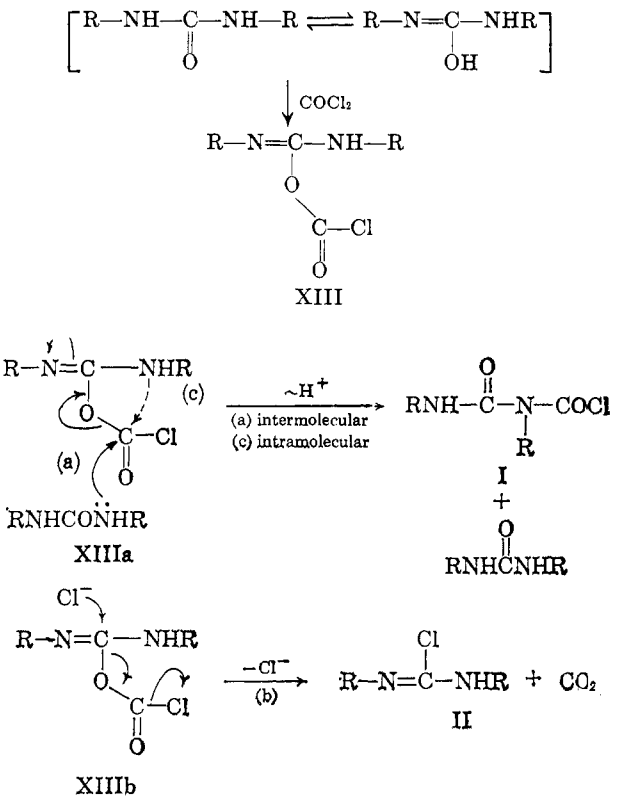
Further confirmation of the proposed structure is the reaction of IX with ethanol and with diethylamine to give XI and XII, respectively.



Perhaps one can accommodate the formation of the two major products I and II from a single intermediate XIII formed initially by a nucleophilic attack of the oxygen of the urea or pseudourea on phosgene. An intermolecular attack by the nucleophilic nitrogen of a second molecule of urea on this intermediate (process a) or even an intramolecular displacement (process c) can give I, while an attack by chloride ion (process b) would give II.

(7) P. T. Stoffel and A. T. Speciale, *J. Org. Chem.*, **27**, 3079 (1962).

(8) H. Najer, R. Giudicelli, and T. Sette, *Bull. soc. chim. France*, 2114 (1961).



This mechanism is consistent with our observation that the ratio of II:I is increased with higher chloride ion concentration. Thus, when a soluble quaternary ammonium chloride or a polar solvent is used in the reaction, the formation of II is favored over I.

Experimental

2,4-Di-*n*-butylallophanoyl Chloride (Ib). A. From 1,3-Di-*n*-butylurea and Phosgene in Ethylene Dichloride.—To 22.4 g. (0.13 mole) of 1,3-di-*n*-butylurea in 150 ml. of ethylene dichloride at 2° was added a solution of 13.8 g. (0.14 mole) of phosgene in 72 ml. of ethylene dichloride. After stirring for 1 hr. at room temperature and purging with nitrogen at 80°, the solvent was evaporated. The residue was extracted with four 200-ml. portions of dry ether, and evaporation of the ether afforded 21.5 g. (70.5%) of 2,4-di-*n*-butylallophanoyl chloride (Ib). Distillation of a 2-g. sample *in vacuo* afforded 1.8 g., b.p. 98° (0.5 mm.); $n^{23}D$ 1.4662; $\lambda_{max}^{CHCl_3}$ (infrared) 2.99, 3.42, 5.73, 6.55, 6.85, 7.25, 7.45, 8.47, 9.12, and 10.17 μ.

Anal. Calcd. for $C_{10}H_{19}ClN_2O_2$: C, 51.17; H, 8.15; N, 11.97. Found: C, 51.36; H, 8.32; N, 12.00.

The oily ether-insoluble material (7.1 g., 24%) was identified as N,N'-di-*n*-butylchloroformamidine hydrochloride (IIb) by its infrared spectrum (C=N, 6.0 μ), which was superimposable on that of N,N'-di-*n*-butylchloroformamidine hydrochloride prepared from di-*n*-butylcarbodiimide and hydrogen chloride, and by quantitative conversion to the known di-*n*-butylcarbodiimide, b.p. 33–34° (0.1 mm.), $n^{22}D$ 1.4482, upon addition of 2 equiv. of triethylamine to a benzene solution of IIb.

B. From 1,3-Di-*n*-butylurea and Phosgene in Benzene.—A solution of 51.6 g. (0.3 mole) of 1,3-di-*n*-butylurea in 216 ml. of benzene was added dropwise to a cold (8–10°), stirred solution of 73.7 g. (0.74 mole) of phosgene in 300 ml. of benzene while purging with nitrogen to remove the generated hydrogen chloride. After the addition was finished, the solution was heated to 80° to remove the excess phosgene. Evaporation of the benzene afforded 70.7 g. (calcd. 70.3 g.) of 2,4-di-*n*-butylallophanoyl chloride (Ib). The infrared spectrum of the obtained material was identical with that of distilled material obtained according to method A.

Anal. Calcd. for $C_{10}H_{19}ClN_2O_2$: Cl, 15.3. Found: Cl, 15.6.

C. From 1,3-Di-*n*-butylurea and Phosgene in Chloroform.—A solution of 13.9 g. (0.14 mole) of phosgene in 72 ml. of chloroform

was added dropwise to a stirred, cold (3–5°) solution of 22.4 g. (0.13 mole) of 1,3-di-*n*-butylurea in 150 ml. of chloroform. By the work-up procedure used in A, 14.7 g. (48.2%) of Ib and 14.1 g. (47.9%) of the ether-insoluble IIb was obtained.

D. From 1,3-Di-*n*-butylurea and Phosgene in the Presence of Triethylamine.—To 51.6 g. (0.3 mole) of 1,3-di-*n*-butylurea in 516 ml. of benzene, 60.6 g. (0.6 mole) of triethylamine was added. After cooling to 8–10°, about 0.5 mole of phosgene was added. The reaction mixture was purged with nitrogen at 80° for 30 min. After filtration of the triethylamine hydrochloride and evaporation of the benzene, 75.2 g. of a mixture of N,N′-di-*n*-butylchloroformamidine-N-carbonyl chloride (VI[6]) and Ib was obtained as shown by the infrared spectrum; VI is characterized by the C=N absorption at 5.98 μ, Ib by the NH band at 2.99 μ.

Since separation of VI and Ib was not possible by distillation, the yield of these substances was achieved by the following procedure. A 10-g. sample was refluxed in *o*-dichlorobenzene for 1 hr., thereby decomposing the 2,4-di-*n*-butylallophanoyl chloride to *n*-butyl isocyanate while leaving VI unchanged. According to quantitative infrared studies, the *n*-butyl isocyanate obtained corresponded to[4]31 ± 5% of Ib. Thus the yield of VI is 69 ± 5% (by difference and infrared analysis; *i.e.*, quantization of the C=N absorption at 5.98 μ compared with an authentic sample prepared from di-*n*-butyl carbodiimide and phosgene).

E. From *n*-Butyl Isocyanate and *n*-Butylcarbamoyl Chloride.—To 9.9 g. (0.1 mole) of *n*-butyl isocyanate was added 13.5 g. (0.1[4] mole) of *n*-butylcarbamoyl chloride. The mixture was slowly heated and finally refluxed (110–115°) for 15 min. Removal of the excess of starting materials *in vacuo* afforded 6.15 g. (51.5%) of slightly impure Ib as evidenced by its infrared spectrum. The C=O absorption at 5.73 μ was compared with that of a pure standard and a purity of 95 ± 5% was observed.

Reaction of Ib with Sodium Methoxide.—A solution of 0.6 g. of sodium methoxide in 10 ml. of methanol was added to 2.34 g. (0.01 mole) of Ib in 10 ml. of methanol. After standing for 20 hr., the methanol was evaporated and the residue was extracted with ether. Evaporation of the ether gave 1.8 g. (78%) of methyl 2,4-di-*n*-butylallophanate (IV), b.p. 95–97° (0.4 mm.). The infrared spectrum of IV was identical with that of IV synthesized from methyl N-*n*-butylcarbamate and *n*-butyl isocyanate.

Reaction of Ib with *n*-Butylamine.—Dropwise addition of a solution of 46.9 g. (0.2 mole) of Ib in 150 ml. of benzene to a stirred mixture of 32.12 g. (0.44 mole) of *n*-butylamine in 250 ml. of benzene, followed by removal of *n*-butylamine hydrochloride and evaporation of the solvent yielded 54.1 g. (99.8%) of crude 1,3,5-tri-*n*-butylbiuret (V). Distillation afforded 42.9 g. (79.3%) of pure V, b.p. 170° (0.1 mm.); $\lambda_{max}^{CHCl_3}$ (infrared) 2.9, 3.08, 3.43–3.5, 5.9, 6.08, 6.6, and 6.8 μ.

Anal. Calcd. for $C_{14}H_{29}N_3O$: N, 15.48. Found: N, 15.72.

Methyl 2,4-Di-*n*-butylallophanate (IV).—To 40 g. (0.3 mole) of methyl N-*n*-butylcarbamate in 100 ml. of xylene, 30 g. (0.3 mole) of *n*-butyl isocyanate was added. After reflux (140°) for 18 hr., the solvent was evaporated and the residue was distilled *in vacuo*. Thus 20 g. (50%) of methyl 2,4-di-*n*-butylallophanate, b.p. 95–97° (0.4 mm.), $n^{23}D$ 1.4510, was obtained; $\lambda_{max}^{CHCl_3}$ 3.03, 3.43–3.5, 5.84, 5.95 (weak), 6.5, 6.87, 7.3, 7.74, and 8.62 μ.

Anal. Calcd. for $C_{11}H_{22}N_2O_3$: N, 12.17. Found: N, 12.40.

1,3,5-Tri-*n*-butylbiuret (V).—To 17.2 g. (0.1 mole) of 1,3-di-*n*-butylurea in 100 ml. of toluene was added 9.9 g. (0.1 mole) of *n*-butyl isocyanate. After refluxing (110°) for 18 hr., the solvent was evaporated and the residue was distilled to give 26 g. (96%) of 1,3,5-tri-*n*-butylbiuret (V), b.p. 170° (0.1 mm.). The infrared spectrum of the distilled material was identical with that of V obtained from Ib and *n*-butylamine.

N,N′-Di-*n*-butylchloroformamidine Hydrochloride (IIb).—To 15.9 g. (0.1 mole) of di-*n*-butylcarbodiimide in 100 ml. of chloroform, hydrogen chloride was added until the exothermic reaction ceased. The excess of hydrogen chloride was removed with nitrogen, and evaporation of the solvent afforded 22.2 g. (97.7%) of N,N′-di-*n*-butylchloroformamidine hydrochloride (IIb); $\lambda_{max}^{CHCl_3}$ (infrared) 3.25, 3.42, 6.0, 6.42, 6.82, and 7.25 μ.

Reaction with *n*-Butylamine.—To 2.27 g. (0.01 mole) of IIb in 10 ml. of chloroform, 1.4 g. of *n*-butylamine was added dropwise with ice cooling. The chloroform was evaporated. Addition of water to the residue precipitated 1.2 g. (45.7%) of 1,2,3-tri-*n*-butylguanidine hydrochloride, m.p. 207–208°; $\lambda_{max}^{CHCl_3}$ (infrared): NH, 3.17 μ; C=N; 6.15 μ.

Anal. Calcd. for $C_{13}H_{30}ClN_3$: C, 59.25; H, 11.46; N, 15.93. Found: C, 59.25; H, 11.51; N, 16.24.

Reaction with Triethylamine.—To 2.27 g. (0.1 mole) of IIb in 20 ml. of dry benzene was added 2.02 g. (0.02 mole) of triethylamine. After stirring for 1 hr., 2.6 g. (94.5%) of triethylamine hydrochloride was filtered off. Evaporation of the benzene afforded 1.5 g. (97.2%) of di-*n*-butylcarbodiimide, b.p. 33–34° (0.1 mm.), $n^{22}D$ 1.4482; $\lambda_{max}^{CHCl_3}$ (infrared) 3.45–3.5, 4.73, 6.83, and 7.45 μ (lit.[9] b.p. 84–85° at 10 mm.).

2,4-Dimethylallophanoyl Chloride (Ia).—Procedure A afforded 28% of the ether-insoluble N,N′-dimethylchloroformamidine hydrochloride (IIa), m.p. 138–140°, lit.[4] m.p. 138–143°; $\lambda_{max}^{CHCl_3}$ (infrared) 3.15, 3.4, 5.95, 6.23, 6.8, 7.2, 8.75, and 9.62 μ. Upon evaporation of the ether, 70.9% of 2,4-dimethylallophanoyl chloride (Ia), m.p. 36°, was obtained; $\lambda_{max}^{CHCl_3}$ (infrared) 2.98, 3.4, 5.75, 6.53, 7.03, 7.68, 9.35, and 9.85 μ.

Anal. Calcd. for $C_4H_7ClN_2O_2$: N, 18.61. Found: N, 18.40.

2,4-Di-*n*-octadecylallophanoyl Chloride (Ic).—According to procedure A, 28.1% of N,N′-di-*n*-octadecylchloroformamidine hydrochloride (IId), m.p. 104° (ethyl acetate), was obtained; λ_{max}^{KBr} (infrared) 3.05, 3.45–3.52, 6.16, 6.32, 6.79, and 13.87 μ.

Anal. Calcd for $C_{37}H_{76}Cl_2N_2$: N, 4.53. Found: N, 4.62.

Evaporation of the ether gave 69% of 2,4-di-*n*-octadecylallophanoyl chloride (Ic), m.p. 68–69° (acetone); $\lambda_{max}^{CHCl_3}$ (infrared) 3.02, 3.48–3.53, 5.8, 6.6, 6.85, and 9.1 μ.

Anal. Calcd. for $C_{38}H_{75}ClN_2O_2$: N, 4.48. Found: N, 4.70.

2,4-Diisopropylallophanoyl Chloride (Id).—According to procedure A, 75.1% of the ether-insoluble N,N′-di sopropylchloroformamidine hydrochloride (IId) was obtained, m.p. 97–100°, lit.[4] m.p. 100–105°; $\lambda_{max}^{CHCl_3}$ (infrared) 3.24, 3.42, 6.02, 6.45, 6.8, 7.15, and 8.88 μ. Evaporation of the ether gave a mixture of products from which distillation afforded 8.2% of N,N′-di-isopropylchloroformamidine-N-carbonyl chloride,[6] b.p. 55–58° (0.3 mm.); $\lambda_{max}^{CHCl_3}$ (infrared) 5.75 (C=O) and 6.0 μ (C=N).

Recrystallization of the distillation residue from ligroin gave 6.7% of 2,4-diisopropylallophanoyl chloride (Id), m.p. 63°; $\lambda_{max}^{CHCl_3}$ (infrared) 3.02, 3.25, 3.43, 5.82, 6.67, 6.85, 7.18, 7.3, 7.85, 8.65, and 9.6 μ.

Anal. Calcd. for $C_8H_{15}ClN_2O_2$: C, 46.49; H, 7.31; N, 13.55. Found: C, 46.42; H, 7.50; N, 13.61.

2,4-Dicyclohexylallophanoyl Chloride (Ie).—Procedure A afforded 77.8% of N,N′-dicyclohexylchloroformamidine hydrochloride (IIe), m.p. 143–144°, lit.[10] m.p. 139–141°. On evaporation of the ethereal solution, 12.5% of 2,4-dicyclohexylallophanoyl chloride (Ie), m.p. 127–128° (*n*-hexane), was obtained; $\lambda_{max}^{CHCl_3}$ (infrared) 2.95, 3.25, 3.45, 5.82, 6.67, 6.87, 7.22, 7.45, 7.8, 8.75, and 9.3 μ.

Anal. Calcd. for $C_{14}H_{13}ClN_2O_2$: N, 9.77. Found: 9.55.

2-Imidazolidinone-N-carbonyl Chloride (IX).—Into 100 ml. of ethylene dichloride at 70–75° was admitted gaseous phosgene at a rate of *ca.* 127 ml./min. for 3 min. (0.02 mole of phosgene). Thereafter, simultaneous with the continued addition of phosgene, a hot solution (75–80°) of 17.2 g. (0.20 mole, recrystallized, m.p. 133–135°) of ethyleneurea dissolved in 220 ml. of ethylene dichloride was added at a rate of about 6.5-ml. increments/min., completing the addition in about 35 min. (0.2 mole of phosgene).

After the addition, phosgenation was continued 2 min., and then the hot mixture was purged for 0.5 hr. with nitrogen. The hot solution was filtered, and upon cooling to 15 to 20° deposited 25.6 g. (86%) of crystalline 2-imidazolidinone-N-carbonyl chloride, m.p. 155–157°. A second crop, 1.6 g., m.p. 150–153°, was obtainable from the mother liquors; $\lambda_{max}^{CHCl_3}$ (infrared) 2.93, 3.12, 5.52, 5.67, 5.80, 6.75, 7.25, 7.51, 7.76, and 8.67 μ; λ_{max}^{KBr} (infrared) 3.15, 5.55, 5.84, 6.78, 7.25, 7.55, 7.8, and 8.75 μ.

Anal. Calcd. for $C_4H_5ClN_2O_2$: C, 32.32; H, 3.39; Cl, 23.87; N, 18.86. Found: C, 32.06; H, 3.35; Cl, 23.84; N, 19.0.

Reaction with Ethanol.—A solution of 4.46 g. (0.03 mole) of IX in 50 ml. of ethanol was refluxed (80°) for 1 hr. Evaporation of the excess ethanol and trituration with small portions of benzene and chloroform with intermittent evaporation gave 4.5 g. (95%) of 1-carbethoxy-2-imidazolidinone (XI), m.p. 123.5–124.5° (chloroform).

Anal. Calcd. for $C_6H_{10}NO_3$: C, 45.58; H, 6.38; N, 17.72. Found: C, 45.54; H, 6.60; N, 17.90.

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(9) E. Schmidt, F. Hitzler, E. Lahde, R. Herbeck, and M. Pezzati, *Ber.* **71B**, 1933 (1938).

(10) M. Seefelder, German Patent 1,119,258 (Dec. 14, 1961).

Reaction with Diethylamine.—A solution of 1.5 g. (0.02 mole) of diethylamine in 10 ml. of benzene was added at once to a stirred suspension of 1.5 g. (0.01 mole) of IX in 20 ml. of benzene at room temperature. Filtration and evaporation afforded 1.39 g. (75%) of 1-(N,N-diethylcarbamoyl)-2-imidazolidinone (XII), b.p. 150° (0.5 mm.), m.p. 55–57°.

Anal. Calcd. for $C_8H_{15}N_3O_2$: C, 51.87; H, 8.16; N, 22.68. Found: C, 51.78; H, 8.19; N, 22.92.

Propyleneurea (3-Methyl-2-imidazolidinone, VIII).—To 39 g. (0.49 mole) of 1,2-diaminopropane (propylenediamine) and 80 g. (1.0 mole) of 50% sodium hydroxide in 100 ml. of water, 49.5 g. (0.5 mole) of phosgene was added at 10–20° while maintaining good agitation. The water was evaporated *in vacuo* and the residue was extracted with ethylene dichloride. Evaporation of the solvent gave 21.9 g. (43.7%) of methyl-2-imidazolidinone (VIII), m.p. 125–127°; $\lambda_{max}^{CHCl_3}$ (infrared) 2.93, 3.13, 3.40, 5.90, 6.7, 6.95, 7.25, and 7.95 μ.

Anal. Calcd. for $C_4H_8N_2O$: C, 48.00; H, 8.06; N, 28.00. Found: C, 47.92; H, 8.32; N, 27.91.

Methyl-2-imidazolidinone-N-carbonyl Chloride (X).—A solution of 10 g. (0.1 mole) of VIII in 100 ml. of ethylene dichloride was added from a heated (60°) addition funnel simultaneously with 10 g. (0.1 mole) of phosgene to 100 ml. of ethylene dichloride at 72–77°. After purging with nitrogen fo 30 min., the reaction mixture was filtered while hot. On cooling, 9.5 g. (58.6%) of methyl-2-imidazolidinone-N-carbonyl chloride (X), m.p. 145–146°, separated.

Anal. Calcd. for $C_5H_7ClN_2O_2$: C, 36.92; H, 4.34; N, 17.23. Found: C, 36.90; H, 4.44; N, 16.42.

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Allene Chemistry. II.[1] Free-Radical Addition of Hydrogen Bromide to Allene

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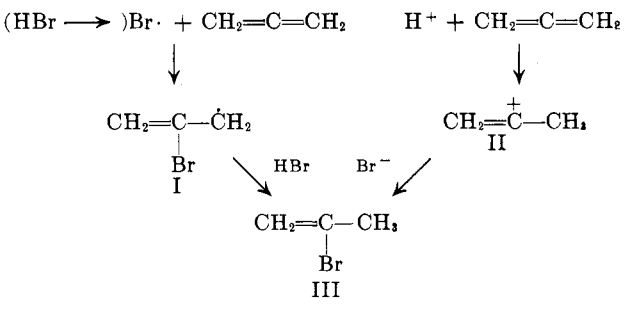
The free-radical addition of hydrogen bromide to allene was examined under different reaction conditions and the product mixtures were analyzed by capillary gas–liquid chromatography and n.m.r. spectroscopy. The ultraviolet light catalyzed gas phase reaction of equimolar amounts of the reactants at ambient temperatures yielded 2-bromopropene as the major product, along with minor amounts of 1,2-dibromopropane and 2,2-dibromopropane. No measurable terminal attack was observed. Equimolar amounts of the reactants in the liquid phase produced 2-bromopropene, 3-bromopropene, 1,2-dibromopropane, and in some cases also 1,3-dibromopropane in varying relative amounts, depending on the reaction conditions. Attack of the bromine atoms at the terminal positions of allene increased from 7% at ambient temperatures to 24% at −40° and 36% at −70°. Up to 48% of terminal attack was observed when a propane solution containing 1 mole of each of the reactants was irradiated at −70°. Reaction of excess allene with hydrogen bromide at −70° yielded mainly the monoadducts 2-bromopropene and 3-bromopropene, but none of the isomeric 1-bromopropenes, thus excluding any significant amount of isomerization of allene to methylacetylene. The amount of terminal attack decreased drastically with an increasing excess of allene. Reactions of excess hydrogen bromide with allene were complicated by competing ionic addition reactions leading to considerable amounts of 2,2-dibromopropane.

The problem of terminal *vs.* center attack in free-radical addition reactions to allene was outlined in our previous paper dealing with thiol addition reactions.[1] We proposed there that the observed preference of thiyl radicals for the terminal positions of allene may be a consequence of the particular geometry of the allene molecule. It was pointed out that, owing to perpendicular arrangement of its π-orbitals, the incipient radical derived from a center attack will not be resonance stabilized and its formation may, therefore, require a higher activation energy than does the formation of the vinylic radical derived from a terminal attack. A similar idea was advanced independently by Jacobs and Illingworth.[2] The exclusive terminal attack of CF_3 radicals, reported by Haszeldine and co-workers[3] in the photoaddition of trifluoroiodomethane to allene, seems also to agree with this concept.

Kovachic and Leitch[4] arrived at the opposite conclusion in interpreting the homolytic addition of hydrogen bromide to allene. They isolated 2-bromopropene (III) as the major reaction product and reasoned that the reaction should proceed *via* the resonance-stabilized 2-bromopropenyl radical (I). However, the homolytic conditions claimed were not supported by control experiments. Thus, an ionic reaction path *via* the carbonium ion intermediate II was not ruled out. Such a path would be analogous to the addition of hydrogen chloride[5] and hydrogen fluoride[6] to allene, both of which occur in the usual Markownikoff manner to yield the corresponding 2-halopropenes and/or 2,2-dihalopropanes. Furthermore, Kovachic and Leitch's experiments were apparently carried out in the gas phase and, therefore, cannot be directly related to the previously reported radical additions to allene which were generally carried out in the liquid phase.



In view of our continued interest in allene chemistry, we investigated the free-radical addition of hydrogen bromide to allene in detail.

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