[CONTRIBUTION FROM THE ORGANIC CHEMISTRY LABORATORIES OF THE UNIVERSITY OF FLORIDA]

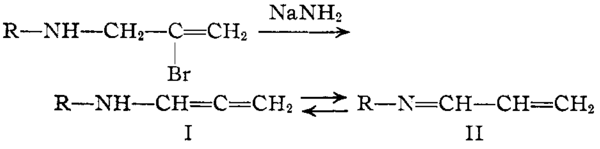
Synthesis of N-Allylidene-alkylamines

BY C. B. POLLARD AND R. F. PARCELL

Whereas the dehydrohalogenation of N-(2-bromoallyl)-dialkylamines, using sodium amide in liquid ammonia, leads to the formation of tertiary acetylenic amines, it has been found that the similar dehydrohalogenation of N-(2-bromoallyl)-alkylamines results in the formation of N-allylidene-alkylamines. The structure of these compounds has been established. Four members of the series have been prepared and their physical constants determined.

In two previous papers[1,2] the authors have described the synthesis of tertiary acetylenic amines by the dehydrohalogenation of tertiary haloalkenylamines, using sodium amide in liquid ammonia. When this reaction was extended to secondary haloalkenylamines, it was found that N-allylidene-alkylamines resulted in each case. These compounds are those which would result if acrolein reacted with primary amines to form a normal Schiff base. The reaction of acrolein with primary amines, however, leads to various products other than the simple imine.[3-6]

The dehydrohalogenation reaction by which these compounds were obtained probably proceeds through the intermediate formation of the allene (I), with subsequent rearrangement to the conjugated system (II)



$$R—NH—CH_2—\underset{\displaystyle Br}{\overset{|}{C}}{=}CH_2 \xrightarrow{NaNH_2}$$

$$\underset{\text{I}}{R—NH—CH{=}C{=}CH_2} \rightleftarrows \underset{\text{II}}{R—N{=}CH—CH{=}CH_2}$$

Compounds of the type represented by Formula I are α,β-unsaturated amines and as such should be in equilibrium with II; but this equilibrium would be expected to favor greatly the existence of the compound as the imine, rather than the allene, due to the enhanced stability of the conjugated system.

The ultraviolet absorption spectra of three members of the series are shown in Fig. 1. Although the compounds were examined spectroscopically up to a wave length of 350 mμ, the longer wave lengths have been omitted from Fig. 1 for convenience since no absorption maxima occur in this region. The single maximum observed corresponds closely to that obtained with conjugated systems such as acrolein and butadiene, both in wave length and in intensity.

The infrared spectra of these compounds are shown in Figs. 2, 3 and 4. They show a fairly

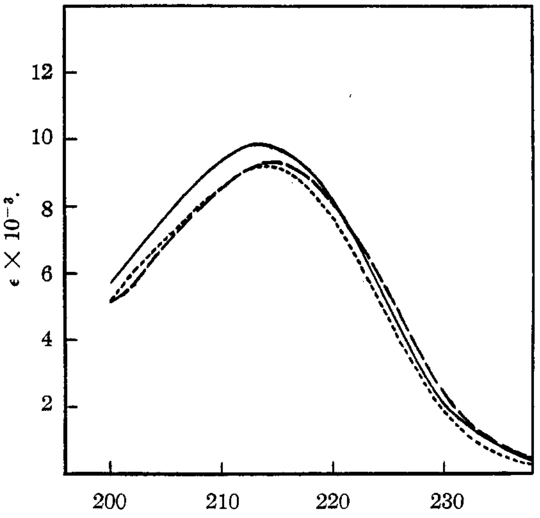


Fig. 1.—Ultraviolet absorption spectra of N-allylidene-alkylamines in cyclohexane; $R—N{=}CH—CH{=}CH_2$: —, R = ethyl; — — —, R = isopropyl; - - - - - - - -, R = 3,5,5-trimethylhexyl.

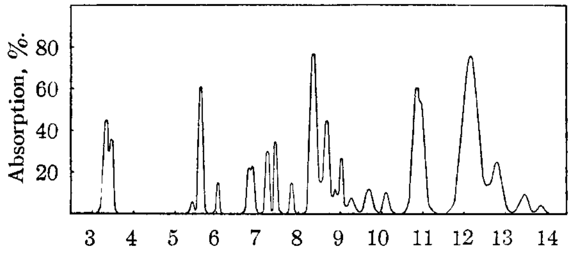


Fig. 2.—Infrared absorption spectrum of N-allylidene-ethylamine.

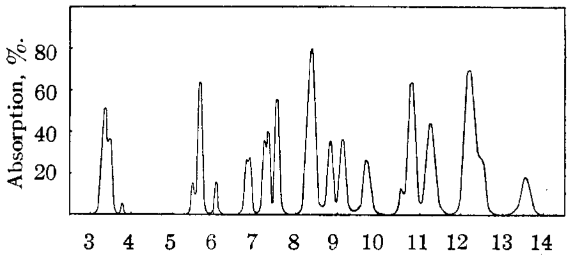


Fig. 3.—Infrared absorption spectrum of N-allylidene-isopropylamine.

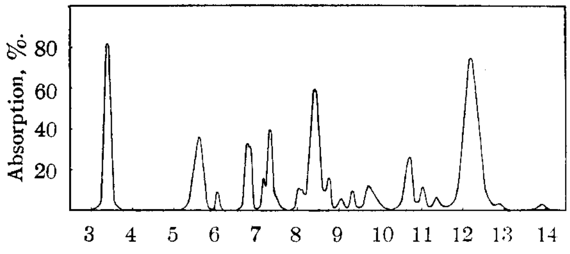


Fig. 4.—Infrared absorption spectrum of N-allylidene-3,5,5-trimethylhexylamine.

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(1) R. F. Parcell and C. B. Pollard, THIS JOURNAL, **72**, 2385 (1950).

(2) R. F. Parcell and C. B. Pollard, *ibid.*, **72**, 3312 (1950).

(3) F. L. Carnahan and C. D. Hurd, *ibid.*, **52**, 4586 (1930).

(4) F. G. Mann, *J. Chem. Soc.*, **121**, 2178 (1922).

(5) L. Schmidt and B. Becker, *Monatsh.*, **46**, 675 (1926).

(6) M. Kh. Gluzman, *Trudy Inst. Khim. Khar'kov. Gosudarst. Univ.*, **5**, 93 (1940).

strong band near 5.65 μ which is the most unusual feature of the spectra; a weak absorption at 6.06 μ; a close pair of bands near 6.85 μ; a strong band near 8.4 μ; and another strong band at 12.2 μ. The absence of an allenic isomer is indicated by the absence of an N–H stretching absorption in the region around 3.10 μ. That no terminal acetylenic group is present is shown by the absence of an absorption band near 5.75 μ. The strong band near 5.65 μ, already mentioned as being an unusual feature of the spectra, is of too high frequency to be considered as a fundamental stretching vibration of either the carbon–carbon or the carbon–nitrogen double bond, and is therefore probably a harmonic or combination frequency. The infrared spectra were run on a Beckman IR-2 spectrophotometer, using sodium chloride optics and a capillary-film cell.

Both the infrared and the ultraviolet spectra indicate clearly the fundamental similarity of the various members of the series.

The N-allylidene-alkylamines are quite stable when pure, their physical constants remaining approximately the same over periods of several months. They are severe lachrymators and are extremely reactive. They are easily hydrolyzed by dilute acids. The alkylamine resulting from this hydrolysis may be recovered, but the aldehyde undergoes decomposition.

A sample of N-allylidene-ethylamine was hydrolyzed with dilute mineral acid in the cold, yielding ethylamine and an aldehyde. The ethylamine was identified by boiling point and by the melting point of its derivative with α-naphthyl isocyanate. A sample of N-allylidene-*n*-butylamine similarly hydrolyzed yielded *n*-butylamine and an aldehyde. The *n*-butylamine was identified by boiling point and refractive index.

The aldehydes which resulted from the above hydrolyses were not isolated in pure form, due to the decomposition accompanying each effort. This instability of the aldehyde might be expected, since acrolein is the aldehyde which would normally be formed. The compounds were shown to be aldehydes by the formation of a 2,4-dinitrophenylhydrazine, formation of a silver mirror with Tollens reagent and by reduction of Fehling solution. The aldehydes resulting from each of the above hydrolyses were shown to be identical by the melting points (124–125°) and mixed melting point (124–125°) of their 2,4-dinitrophenylhydrazones.

The same 2,4-dinitrophenylhydrazone resulted when the imine was added directly to a mineral acid solution of 2,4-dinitrophenylhydrazine in the cold and allowed to stand as was obtained when the imine was first hydrolyzed and then 2,4-dinitrophenylhydrazine reagent added to the acid solution. A purer product was obtained by the first method. When the imine was added to a solution of 2,4-dinitrophenylhydrazine in dilute hydrochloric acid the resulting derivative contained organic chlorine and melted at 124–125°. This is the derivative used to prove that the aldehydes obtained by hydrolysis of the various members of the series were identical. When the derivative was prepared in dilute sulfuric acid solution the compound contained organic sulfur and melted above 200°. Clearly, the mineral acid used in hydrolysis enters into the reaction. Analysis of the derivative containing chlorine indicated definitely that it was not the 2,4-dinitrophenylhydrazone of a chloropropionaldehyde, as might be expected if hydrogen chloride had added across the carbon–carbon double bond during the reaction. The constitution of this derivative is unknown.

Anal. Calcd. for $C_9H_9N_4O_4Cl$: C, 39.65; H, 3.33; Cl, 13.01. Found: C, 50.89, H, 3.85; Cl, 12.03.[7]

Low pressure hydrogenation of a sample of N-allylidene-ethylamine was carried out using a platinum catalyst. The theoretical amount of hydrogen (two moles per mole of imine) was absorbed in 25 minutes; a sharp rise in temperature occurred. There was no further absorption. The resulting compound was compared with the ethyl-*n*-propylamine reported by Campbell, Sommers and Campbell[8] with respect to boiling point, refractive index and melting point of the hydrochloride and was found to be identical. The yield was almost quantitative.

Analysis of ethyl-*n*-propylamine hydrochloride obtained by reduction of N-allylidene-ethylamine and subsequent formation of hydrochloride. *Anal.* Calcd. for $C_5H_{14}NCl$: C, 48.57; H, 11.41. Found: C, 48.49; H, 11.25.[7]

Unlike the synthesis of tertiary acetylenic amines by this method, the yield obtained in these reactions was greatly decreased by use of large excesses of sodium amide.

Experimental

N-(2-Bromoallyl)-ethylamine.—To 900 ml. (about 10 moles) of a commercial aqueous 70% ethylamine solution was added 600 g. (3 moles) of 2,3-dibromopropene over a period of two hours, cooling whenever necessary to prevent boiling. When the addition was complete, the mixture was heated gently on a steam-bath for 20 minutes. Solid sodium hydroxide was cautiously added until separation into layers occurred. The upper layer was removed, dried over solid sodium hydroxide and distilled rapidly through a Vigreux column, collecting the portion boiling from 148–153°. The yield was 350 g., corresponding to 71% of the theoretical amount, based upon the 2,3-dibromopropene used.

Anal. Calcd. for $C_5H_{19}NBr$: N, 8.54. Found: N, 8.43.

Other N-(2-Bromoallyl)-alkylamines.—The 2,3-dibromopropene was slowly added to an ethereal solution containing an excess of the appropriate primary amine. The reaction mass was cooled whenever necessary to prevent too vigorous reaction. The mixture was allowed to stand for about 12 hours after the addition, and the precipitated amine hydrobromide was filtered off.[9] The N-(2-bromo-allyl)-alkylamine was obtained by drying and distilling the ethereal filtrate. Pertinent data concerning these preparations are given in Table I.

N-Allylidene-alkylamines.—One mole of the appropriate N-(2-bromoallyl)-alkylamine reacted with 1.15 moles of sodium amide in 2 liters of liquid ammonia for a period of 12 hours. When the reaction period was complete and the liquid ammonia had evaporated until a total volume of about 500 ml. remained in the flask, 600 ml. of water and

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(7) Analyses through courtesy of Mr. C. E. Childs of Parke, Davis & Co., Detroit, Mich.

(8) K. N. Campbell, A. H. Sommers and Barbara K. Campbell, THIS JOURNAL, **66**, 82 (1944).

(9) In the preparation of N-(2-bromoallyl)-*n*-butylamine the butylamine hydrobromide did not precipitate in crystalline form and was extracted with water.

TABLE I

DATA CONCERNING PREPARATION OF N-(2-BROMOALLYL)-ALKYLAMINES

Primary amine reacted	Mole of: Amine	Mole of: 2,3-Dibromopropene	Characterization of product: Yield, %	B.p. °C.	B.p. Mm.	Nitrogen, % Calcd.	Nitrogen, % Found
Isopropylamine	6.8	2.0	68	64–67	27	7.87	7.66
n-Butylamine	10.3	5.0	74.5	71–73 cor.	10	7.29	7.12
3,5,5-Trimethylhexylamine	3.14	1.5	45	91–93 cor.	1.4	5.34	5.20

TABLE II

PHYSICAL CONSTANTS AND PERCENTAGE YIELDS OF FOUR N-ALLYLIDENE-ALKYLAMINES

Compound	B.p.,[a] °C.	Yield,[b] %	n^{25}_D	d^{25}_4	Molar refraction Calcd.	Molar refraction Found	Nitrogen, % Calcd.	Nitrogen, % Found
N-Allylidene-ethylamine	77.2–77.5	55	1.4284	0.7795	27.50	27.46	16.85	16.76
N-Allylidene-isopropylamine	93–94	57	1.4269	.7759	32.12	32.14	14.42	14.44
N-Allylidene-*n*-butylamine	129.5–130.5	77	1.4375	.7941	36.73	36.72	12.60	12.58
N-Allylidene-3,5,5-trimethylhexylamine	86.5–87.5 (10 mm.)	72	1.4489	.8113	59.83	59.93	7.73	7.83

[a] Corrected; atmospheric pressure unless otherwise indicated. [b] Based upon the N-(2-bromoallyl)-alkylamine used.

600 ml. of ether were cautiously added into the flask. The mixture was filtered, and the ethereal layer was removed and dried over solid sodium hydroxide. The product was isolated by fractional distillation of this solution.

The physical constants and percentage yields of those prepared may be found in Table II.

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The Reactivities of Benzaldehydes with Perbenzoate Radicals

BY CHEVES WALLING[1] AND ELIZABETH A. MCELHILL

By carrying out competitive oxidations of benzaldehydes in acetic anhydride, so that the intermediate peracids are converted to stable acetyl benzoyl peroxides, it has been found possible to develop kinetic expressions and study the relative rates of reaction of a series of benzaldehydes with various perbenzoate radicals. Relative rates have been found to increase with increasing electron donating properties of the substituents, and the results have been interpreted in terms of polar interaction between radical and aldehyde in the transition state, with contributions suggested for structures involving electron donation from the aldehyde to the perbenzoate radical. Interestingly, *n*-butyraldehyde has been found to be several times as reactive as benzaldehyde toward attack by perbenzoate radicals.

Copolymerization studies in this Laboratory and elsewhere have established that the relative reactivities of organic molecules toward free radical attack are determined both by the structure of the organic molecule and the nature of the attacking radical.[2] In particular, they have led to the recognition of the important role of the polar properties of radical and substrate in determining reaction rates in radical addition reactions, and investigations have recently been extended to include both the addition[3] and displacement[4] steps in the radical addition of mercaptans to double bonds. This paper describes a similar study of the competitive autoxidation of *m*- and *p*-substituted benzaldehydes, undertaken to determine the relation between structure and reactivity toward the peroxy radicals involved in such a process. The reaction of autoxidation was chosen because of its widespread importance and because its study yields information on the effects of substitution on both substrate and radical in a radical displacement reaction. Benzaldehydes were selected because their mechanism of autoxidation is well established, because quantitative techniques are available for analysis of the products, and because interpretation of the effects of nuclear substitution on the side chain reactions of benzene is free of complications arising from steric effects and changes in entropy of activation.[2,5]

Experimental Method.—The autoxidation of benzaldehyde possesses all the established features of a radical chain reaction—sensitivity to trace catalysis and inhibition and photocatalysis with high quantum yield.[6]

The first product of sufficient stability to permit isolation is perbenzoic acid, and the chain reaction involved in its formation presumably involves the alternating propagation steps

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[1] Lever Brothers Co., 164 Broadway, Cambridge, Massachusetts.

[2] F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).

[3] C. Walling, D. C. Seymour and K. B. Wolfstirn, THIS JOURNAL, **70**, 2559 (1948).

[4] C. Walling, *ibid.*, **70**, 2561 (1948).

[5] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Ch. VII.

[6] For a general description and additional references, see W. A. Waters, "The Chemistry of Free Radicals," Clarendon Press, Oxford, 1946, Ch. XI.