[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. XXXVI. The Reaction of Dimethylamine with α-Methylallyl Chloride

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The bimolecular displacement reaction between dimethylamine and α-methylallyl chloride in benzene solution has been investigated. *trans*-N,N-Dimethyl-γ-methylallylamine, resulting from an SN2′ displacement, was the sole product. Reaction rates and thermodynamic functions of activation for this reaction are presented.

Introduction

Bimolecular nucleophilic displacement upon an allylic system may proceed by two mechanisms: normal displacement, SN2, and abnormal displacement, SN2′.

A detailed review on the chemistry of allylic systems has been published recently.[1] In this Laboratory interest in allylic systems has been concerned, in part, with their displacement reactions with amines. Young, *et al.*,[2] demonstrated that the reaction of diethylamine with α-methylallyl chloride proceeds exclusively by unambiguous SN2′ displacement. The authors pointed out that, with secondary amines, an important factor in promoting SN2′ displacement might be specific hydrogen-bond interaction between the entering and leaving groups, as

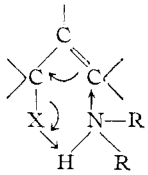


Fig. 1

However, it has been proved that a tertiary amine, such as trimethylamine, is capable of undergoing an SN2′ type attack. Furthermore, it was demonstrated that in the reaction of this amine with α-methylallyl chloride the major product isolated was that resulting from an abnormal bimolecular displacement, SN2′.

The present work endeavors to examine the size of the nucleophile as a factor in the direction of a nucleophilic attack on an allylic system, as well as the influence of the possibility of hydrogen bonding.

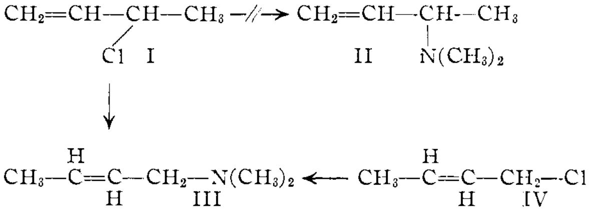
Results

Two of the compounds that could result reasonably from the reaction of dimethylamine with α-methylallyl chloride (I) have been unambiguously synthesized. The normal product, resulting from SN2 displacement, would be N,N-dimethyl-α-methylallylamine (II) and has been reported previously.[3] The abnormal product, due to SN2′ displacement, would be *trans*-N,N-dimethyl-γ-methylallylamine (III). This has now been prepared by the reaction of dimethylamine with *trans*-γ-methylallyl chloride (IV) which is known to undergo only SN2 displacement with amines in non-ionizing media.

When α-methylallyl chloride (I) was allowed to react with dimethylamine in benzene solution, III was obtained in 82% yield, based on the amount of dimethylamine hydrochloride formed. With cyclohexane as solvent the yield of amine was 95%. The constants of this material, and its picrate derivative, were in good agreement with those of the authentic material above. However, in the fractionation of the reaction mixture, the small first cut gave an amine picrate containing impurities, probably due to traces of the picrate of dimethylamine or of isomeric allylic amine II. This latter amine was not present in excess of 2% in this cut; otherwise its detection by infrared spectrum would have been possible.

The infrared spectrum of III exhibited a band at 10.28 μ associated with the *trans* configuration. There was no band at 13.8 μ, generally attributed to a *cis* configuration.

The possibility of rearrangement of α-methylallyl chloride (I) to γ-methylallyl chloride prior to reaction, or formation of the normal product II with subsequent rearrangement to the abnormal product III, was discarded in view of previously reported observations.[3]



In the study[3] of the reaction between trimethylamine and α-methylallyl chloride (I), acetone was employed as solvent. Inert solvents were used in the present work as the reaction conditions caused condensation of acetone, forming mesityl oxide and water. Since this change in solvent might have influenced the ratio of products resulting from SN2 and SN2′ attack, the reaction of the chloride I with trimethylamine was investigated in benzene solution. No significant change in the proportion of the abnormal product was observed. Although slightly more abnormal product was formed, the difference probably is within the experimental variation to be expected from two different operators.

The kinetics of the reaction of dimethylamine and α-methylallyl chloride (I) in benzene were shown to be first order with respect to each of the reactants, second order over-all. The reaction was followed by analysis for chloride ion formed in the reaction, using the Volhard method,[3] and by acid titration of the amines present.[2] Rate con-

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[1] R. H. Dewolfe and W. G. Young, *Chem. Revs.*, **56**, 753–901 (1956).

[2] W. G. Young, I. D. Webb and H. L. Goering, THIS JOURNAL, **73**, 1076 (1951).

[3] W. G. Young, R. A. Clement and Chin-Hua Shih, *ibid.*, **77**, 3061 (1955).

stants were calculated from the integrated form of the usual second-order rate expression, modified to account for the fact that one mole of amine will react with the tertiary amine hydrochloride formed during the reaction to give dimethylamine hydrochloride.[2] The rate expression is given in equation 1.

$$k_2 = \frac{2.303}{t(b-2a)} \log \frac{(b-2x)}{(a-x)} \frac{a}{b} \qquad (1)$$

where x is the amount reacted in moles/l., b is the initial concentration of dimethylamine in moles/l., a is the initial concentration of α-methylallyl chloride in moles/l. and t is the time elapsed from zero time, in hours. Rate constants are listed in Table I and a typical rate run is given in Table II.

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF DIMETHYLAMINE WITH α-METHYLALLYL CHLORIDE IN BENZENE

Run	RCl, mole/l.	Me_2NH, mole/l.	Temp., °C.	k_2, mole/l.$^{-1}$ hr.$^{-1}$
1	0.186	0.529	49.6	0.054 ± 0.003
2	.186	.497	60.3	.135 ± .008
3	.151	.566	60.3	.144 ± .001

TABLE II

THE REACTION OF DIMETHYLAMINE WITH α-METHYLALLYL CHLORIDE IN BENZENE AT 69.6°

Time, hr.	Equivalent reacted	Reacted, %	k_2
9.75	0.044	23.8	0.059
19.0	.070	37.3	.056
29.5	.092	49.2	.056
46.0	.114	60.9	.056
71.0	.135	72.4	.052
121.0	.153	81.8	.046

Average $k_2 = 0.054 \pm 0.003$

The thermodynamic functions of activation for the reaction now may be calculated from the data in Table I. The transition state theory[4] proposes an equation for the experimental energy of activation, E^{ss}

$$E^{ss} = \frac{2.303\,RT_1T_2}{T_2 - T_1} \log \frac{k_2}{k_1} \qquad (2)$$

where k_1 and k_2 are the second-order rate constants at temperatures T_1 and T_2. The heat of activation, ΔH^{ss}, and the entropy of activation were derived by use of equations 3 and 4

$$\Delta H^{ss} = E^{ss}/RT \qquad (3)$$

$$\Delta S^{ss} = (\Delta H^{ss}/T) + 2.303R \log (k_2h/T_2k_\beta) \qquad (4)$$

Where h is Planck's constant and k_β is Boltzmann's constant. Table III includes the thermodynamic values for the S_N2' displacements of α-methylallyl chloride with dimethylamine and trimethylamine.[3]

TABLE III

Amine	E^{ss}	ΔH^{ss}, kcal./mole	ΔS^{ss}, cal./mole/°A.	Solvent
Dimethyl-	18.3	17.6	−26.2	Benzene
Trimethyl-	14.5	13.9	−38	Acetone

Discussion

Whereas dimethylamine on reacting with α-methylallyl chloride attacks the γ-carbon atom only trimethylamine yields products due to attack on both the α- and γ-carbon atoms.

There are at least three factors, all pertaining to the nucleophile, that demand consideration in an attempt to explain these results. First, trimethylamine carries an additional methyl group and its larger size makes nucleophilic attack hindered and less effective than with dimethylamine. Second, there exists a difference in base strength; K_b is 5.4×10^{-4} for dimethylamine and 5.9×10^{-5} for trimethylamine. A study of the effect of base strength of the nucleophile on S_N2 and S_N2' displacements is in progress and will be reported in the near future. Third, consideration must be given to the possibility of hydrogen bonding between the amine hydrogen atom and the chlorine atom. Such an interaction would exercise a directional effect on the attacking nucleophile, making approach to the γ-carbon atom of the allylic chloride more probable, as depicted in Fig. 1. However, with trimethylamine no such interaction is possible as is indicated by the smaller amount of abnormal product formed. Direct comparison of entropy values grouped in Table III is not possible, because of the different solvent used and because the fact that both *cis* and *trans* abnormal product was formed in the trimethylamine reaction, but the *trans* isomer only was isolated in the dimethylamine reaction.

Experimental

Commercial Materials.—Braun C.P. acetone was dried over Drierite and distilled from Drierite, b.p. 56.6°. J. T. Baker C.P. benzene was redistilled and the center fraction used, b.p. 80.0°. Philips Petroleum Co. cyclohexane was run through a silica column and redistilled, b.p. 80.0°. Mathieson Chemical Co. dimethylamine and trimethylamine were dried by passage through a potassium hydroxide filled drying tower. *trans*-γ-Methylallyl chloride and α-methylallyl chloride were prepared according to the procedure of Young, *et al.*[3]

(A) *trans*-N,N-Dimethyl-γ-methylallylamine (III).—Dimethylamine (0.153 mole) in benzene (200 ml.) was placed in a 500-ml. pressure bottle and *trans*-γ-methylallyl chloride (7.24 g., 0.08 mole) was added. The bottle was placed in a bath at 50°. A precipitate formed during 10 minutes. After three days, the bottle was removed, cooled, and the precipitate was collected by filtration and washed with benzene and dry pentane. Hydrogen chloride gas was passed into the combined filtrate and washings and almost instantaneously a gel was formed. Addition of the gas was continued until all the gel had disappeared. The benzene was evaporated on a steam-bath, the residual precipitate was dissolved in ethylene glycol (20 ml.), and sodium (2.3 g., 0.1 mole) in ethylene glycol (20 ml.) was added to it with cooling. After addition of ethylcyclohexane (10 ml.), the resulting solution was fractionated through a Podbielniak column: fraction 1, b.p. 96°, 2.38 g., $n^{25}D$ 1.4198; fraction 2, b.p. 97–98°, 2.00 g., $n^{25}D$ 1.4138. The picrate of fraction 2 was prepared, m.p. 78.5–79.5°.

Anal. Calcd. for $C_{12}H_{16}N_4O_7$: C, 43.90; H, 4.88. Found: C, 43.68; H, 4.67.

(B) *trans*-N,N-Dimethyl-γ-methylallylamine (III).—Dimethylamine (0.153 mole) in benzene (200 ml.) was placed in a 500-ml. pressure bottle and α-methylallyl chloride (3.6 g., 0.04 mole) was added. The mixture was kept at room temperature for one day and then in a 50° bath for seven days. It was then cooled and the precipitate was collected and washed with benzene. Hydrogen chloride gas was passed into the combined filtrate and washings until the solution turned clear and gave a positive acid test. The benzene

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(4) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

was evaporated on the steam-bath and the residual precipitate was dissolved in ethylene glycol and treated with sodium in ethylene glycol as above. Addition of ethylcyclohexane as "pusher" and distillation through a Podbielniak column afforded the following cuts: fraction 1, b.p. 94–97°, 0.23 g., $n^{25}D$ 1.4120, picrate m.p. 120–140°; fraction 2, b.p. 97–99°, 1.70 g., $n^{25}D$ 1.4129, picrate m.p. 79–79.5°; fraction 3, b.p. 99–110°, 0.30 g., $n^{25}D$ 1.4139.

Using the above procedure, but substituting cyclohexane for benzene as solvent, yielded the amine in 95% yield.

Kinetic Methods.—To about 49 ml. of a solution of dimethylamine in benzene, in a 50-ml. volumetric flask, was added a certain weight of α-methylallyl chloride. The volume was brought up to the mark with benzene and thorough mixing was achieved by vigorous shaking. Equal aliquots (5.00 ml.) were placed in ampoules, which were cooled in a Dry Ice-bath and sealed and placed in a constant temperature bath. Zero time was taken as the time of immersion. The ampoules were removed at intervals and the contents titrated for ionic halogen using the modified Volhard method.[3] The initial concentration of dimethylamine in the rate runs was determined by titrating the amine solution with standard hydrochloric acid. In an alternate method, the ampoules were broken under 50 ml. of ice-cold water and the amines titrated with dilute hydrochloric acid, using methyl red as indicator.

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Allylic Rearrangements. XXXVII. The Ultraviolet Absorption Spectra of Cinnamylmagnesium Bromide and Dicinnamylmagnesium[1]

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The ultraviolet absorption spectra of the Grignard solution prepared from cinnamyl bromide and of dicinnamylmagnesium have been determined. These spectra are quite similar to those of model compounds having an olefinic linkage conjugated with a benzene ring, and it is concluded that the cinnamyl Grignard reagent is formed without rearrangement. The fact that cinnamyl Grignard reagents give rearranged products in reactions with carbonyl compounds is supporting evidence for the cyclic reaction mechanism proposed by Young and Roberts.

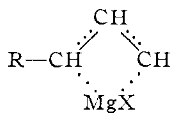
Several structures have been considered for Grignard reagents prepared from primary allylic halides. Different reactions of these reagents can best be explained by assuming that the reagent has the primary (I) or the secondary configuration (II) or that it is a cyclic hybrid of I and II (III) or a mixture of I and II.[4]

$RCH{=}CHCH_2MgX$

I

$RCH(MgX)CH{=}CH_2$

II



III

For example, the butenyl[5] and cinnamyl[6] Grignard reagents react with all but the most sterically hindered carbonyl compounds to give products derived from II, while reaction of cinnamylmagnesium chloride with chloramine gives only the primary amine derived from I ($R = C_6H_5$).[7] Reactions with proton donors and coupling reactions with organic halides usually give mixtures of hydrocarbons indicating that a hybrid structure or a mixture of I and II is involved.[8-10]

Due to the fact that rearrangements can occur both during the preparation and subsequent reactions of allylic Grignard reagents, it is doubtful that their chemical properties can furnish reliable evidence concerning their structure. It is only through examination of some physical property such as absorption spectrum that information regarding the structure of these reagents can be obtained. The Grignard reagent prepared from cinnamyl chloride or bromide lends itself particularly well to a study of configuration based on absorption spectra. In the primary form (I, $R = C_6H_5$), this reagent has a double bond conjugated with the aromatic ring. This type of conjugation is reflected in a large molar extinction coefficient at about 250 mμ.[11] In the secondary form (II, $R = C_6H_5$), the double bond is not conjugated with the ring, and the molar extinction coefficient at 250 mμ should be much smaller.

Experimental

Materials.—Anhydrous Baker and Adams or Mallinckrodt ether was used. For preparing cinnamyl Grignard solutions it was distilled into the reaction flask from an ether solution of n-butylmagnesium bromide. For a spectrophotometric solvent, it was dried over sodium ribbon and then stored over a generous quantity of fresh sodium ribbon in a bottle with a foil-lined screw cap.

Commercial dioxane was purified by the method of Fieser[12] and redistilled from over molten sodium shortly before use.

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[1] Presented at the Regional Meeting of the American Chemical Society, Los Angeles, Calif., May 8, 1954. Taken in part from the Ph.D. thesis of David L. Hagmann, 1950.

[2] Standard Oil Co. Fellow in Chemistry, 1946–1950.

[3] To whom inquiries concerning this paper should be addressed.

[4] (a) W. G. Young and J. D. Roberts, THIS JOURNAL, **68**, 1472 (1946); (b) R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 872 (1956).

[5] See K. W. Wilson, J. D. Roberts and W. G. Young, THIS JOURNAL, **72**, 218 (1950), and earlier papers by these authors.

[6] (a) H. Gilman and S. A. Harris, *ibid.*, **49**, 1825 (1927); **53**, 3541 (1931); (b) O. Kuin-Houo, *Ann. chim.*, [11] **13**, 175 (1940); (c) R. H. DeWolfe, D. E. Johnson, R. I. Wagner and W. G. Young, THIS JOURNAL, **79**, 4798 (1957).

[7] G. H. Coleman and R. A. Forrester, *ibid.*, **58**, 27 (1936).

[8] K. W. Wilson, J. D. Roberts and W. G. Young, *ibid.*, **72**, 215 (1950).

[9] (a) W. G. Young, G. Ballou and K. Nozaki, *ibid.*, **61**, 12 (1939); (b) W. G. Young, J. D. Roberts and H. Wax, *ibid.*, **67**, 841 (1945); (c) H. Koch, *J. Chem. Soc.*, 1111 (1948).

[10] For other references to the literature on reactions of allylic Grignard reagents, see ref. 4b.

[11] (a) T. W. Campbell, S. Linden, S. Godshalk and W. G. Young, THIS JOURNAL, **69**, 880 (1947); (b) H. P. Koch, *J. Chem. Soc.*, 1123 (1948).

[12] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 368.