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

Allylic Rearrangements. XL. The Reaction of Allylic Diazonium Ions in Acetic Acid[1]

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RECEIVED FEBRUARY 19, 1958

The silver ion-catalyzed acetolyses of α- and γ-methylallyl and α,α- and γ,γ-dimethylallyl chlorides seem to proceed through resonating carbonium ion intermediates or S$_N$1 mechanisms. However, the deaminations of the corresponding amines in acetic acid involve not only the S$_N$1 intermediates but also as much as 40–50% of non-resonating or "hot" carbonium ion intermediates in which the positive charge is never delocalized from the α-carbon due to the spatial orientation of the p-orbital on the α-carbon. Such a "hot" ion yields only non-rearranged allylic acetate.

Introduction

The silver ion-catalyzed acetolyses of α-methylallyl, γ-methylallyl, α,α-dimethylallyl and γ,γ-dimethylallyl chlorides and the nitrite–acetic acid deaminations of the corresponding primary amines have been studied in an effort to determine the mechanisms of these reactions. The investigations involved determinations of the product compositions obtained under various conditions and included stereochemical studies of the deaminations of optically active α-methylallylamine in acetic acid.

Preparations and Reactions of Chlorides and Amines.—The butenyl and pentenyl chlorides were prepared by the 1,2- and 1,4-additions of the elements of hydrogen chloride to butadiene and isoprene, respectively, as previously described.[3,4]

The acetolyses of α,α-dimethylallyl and γ,γ-dimethylallyl chlorides in the presence of silver acetate were essentially as previously described for the butenyl chlorides.[5] The product compositions were determined by measurements of refractive indices. The failure of the workup procedure to produce rearrangements of the product acetates was established by a blank run on an acetate mixture of known composition.

The α- and γ-methylallyl[6] and γ,γ-dimethylallylamines[7] were synthesized from the corresponding chlorides by the phthalimide synthesis as previously described for the butenylamines.[6] This method was unsatisfactory for the preparation of α,α-dimethylallylamine as were the reactions of α,α-dimethylallyl chloride with liquid ammonia at −60° and with ammonia at 30° under 70 p.s.i. and of excess pentenylmagnesium bromide with α-methylhydroxylamine. The α,α-dimethylallylamine was prepared satisfactorily in 80% yield by the Hofmann rearrangement of dimethylvinylacetamide prepared in 86% yield from dimethylvinylacetic acid as previously described.[8] The amine was characterized by analysis of the pure amine and its picrate and phenylthiourea derivatives as well as by hydrogenation to *t*-amylamine and analysis of the picrate and phenylthiourea derivatives of the saturated amine.

The optically active α-methylallylamine used in the stereochemical studies was obtained by the partial resolution of the *d*-tartrate salt. The configuration and degree of optical purity of the unsaturated amine was determined by the Raney nickel catalyzed hydrogenation to *sec*-butylamine which had previously been completely resolved[9] and its configuration established.[10] A control run established that neither the unsaturated nor saturated amine racemized on the catalyst or under the workup conditions.

The relationship of sign of rotation to optical configuration for the α-methylallyl acetate product of the deamination reaction in acetic acid was established by conversion of optically active α-methylallyl alcohol (resolved as the brucine salt of the acid phthalate ester) of known sign and configuration[10] to the acetate with retention of configuration by the use of acetic anhydride in pyridine. It was found that (+)α-methylallylamine and (−)α-methylallyl acetate have corresponding configurations.

All deamination reactions were carried out at about 30° with stirring and with an excess of nitrite salt relative to amine. The completion of the reaction was indicated by the evolution of approximately the theoretical quantity of nitrogen gas. All product mixtures were analyzed qualitatively by infrared spectral measurements and quantitatively by refractive index measurements.

Sodium nitrite was used as the source of nitrous acid in the pentenylamine deaminations. For the butenylamine reactions both sodium and silver nitrites were used. The maximum acetate ion concentration in solution was reached when the sodium salt employed was about 350 times that for the silver salt; also the maximum value for the ratio of acetate ion concentration to nitrite ion concentration was roughly 10 times greater for the sodium salt than for the silver salt.

Deuterated acetic acid (CH_3CO_2D) as well as ordinary acetic acid were used in the butenylamine deaminations. Infrared and nuclear magnetic resonance spectra were used to analyze for deuterium in the product acetates.

The stereochemical studies on α-methylallylamine were accompanied by controls that established that the starting amine did not racemize in the presence of acetic acid and acetate ion and that

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(1) This work was supported in part by a grant from the National Science Foundation.

(2) National Science Foundation Post-doctorate Fellow, 1955–1957.

(3) W. C. Percival and F. C. Whitmore, THIS JOURNAL, **72**, 4163 (1950).

(4) A. J. Ultee, *J. Chem. Soc.*, 530 (1948).

(5) J. D. Roberts, W. G. Young and S. Winstein, *ibid.*, **64**, 2157 (1942).

(6) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951).

(7) E. Späth and S. Prokopp, *Ber.*, **57**, 479 (1924).

(8) J. D. Roberts, W. T. Moreland, Jr., and W. Fraser, THIS JOURNAL, **75**, 637 (1953).

(9) L. G. Thome, *Ber.*, **36**, 582 (1903).

(10) (a) P. Brewster, *et al.*, *Nature*, **166**, 179 (1950); (b) K. Wiberg, Ph.D. Thesis, Columbia University, 1950; (c) F. Caserio, Ph.D. Thesis, Univ. of Calif at Los Angeles, 1955.

the product α-methylallyl acetate did not racemize under the reaction or workup conditions.

Results and Discussion

The results of the silver ion-catalyzed acetolyses of the butenyl and pentenyl chlorides are summarized in Table I.

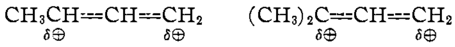
TABLE I

COMPOSITIONS OF ACETATE PRODUCT MIXTURES FROM THE REACTIONS OF ALLYLIC CHLORIDES WITH ACETIC ACID AT ROOM TEMPERATURE IN THE PRESENCE OF SILVER ACETATE

Halide	Acetates % t. or s. ± 4%	% p. ± 4%[b]
1° $CH_3CH{=}CHCH_2Cl$[a]	40[a]	60[a]
2° $CH_3CHClCH{=}CH_2$[a]	44[a]	56[a]
1° $(CH_3)_2C{=}CHCH_2Cl$	46	54
3° $(CH_3)_2CClCH{=}CH_2$	45	55

[a] See ref. 5. [b] 4% error figure is estimate of the precision of the refractive index method of product analysis.

Both members of the butenyl and pentenyl chloride pairs give the same distribution of products within the limits of experimental error. This result is to be expected if a common resonating allylic carbonium ion intermediate (I for butenyl and II for pentenyl) is involved for the two members of a given pair. For the purposes of these mechanistic studies *it is assumed* that the product compositions obtained from these chloride acetolyses represent the compositions of acetates arising from reactions of resonating carbonium ion intermediates I and II, respectively, with the acetate-producing moiety.



$$\underset{\delta\oplus}{CH_3CH}{=\!=}CH{=\!=}\underset{\delta\oplus}{CH_2} \qquad (CH_3)_2\underset{\delta\oplus}{C}{=\!=}CH{=\!=}\underset{\delta\oplus}{CH_2}$$

I II

The results of the deamination reactions in acetic acid are summarized in Table II.

TABLE II

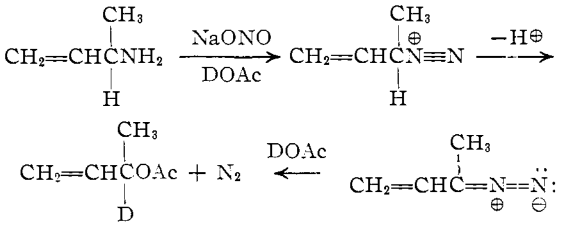
COMPOSITIONS OF THE ACETATE PRODUCT MIXTURES FROM THE REACTIONS OF ALLYLIC AMINES WITH SODIUM NITRITE AT ROOM TEMPERATURES[a]

Amine	Acetates % t. or s. ± 4%	% p. ± 4%	Product from unknown path U, %
$CH_3CH{=}CH{-}CH_2NH_2$	20	80	52
$CH_3CH(NH_2)CH{=}CH_2$	67	33	43
$(CH_3)_2C{=}CHCH_2NH_2$	22	78	52
$(CH_3)_2C(NH_2)CH{=}CH_2$	40	60	..

[a] All runs were performed at least twice and the results agreed to ±1%. The 4% error figure is an estimation of the precision of the refractive index method of analysis.

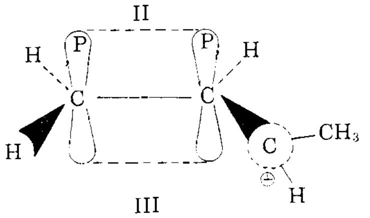
These results show that more unrearranged acetate is usually formed than is expected from the resonating carbonium ions I and II based on the chloride acetolyses discussed above. If it is assumed that all of the rearranged product arises from the resonating carbonium ion, then the percentage of unrearranged product arising from some other mechanism(s) designated unknown path U may be calculated (see Table II). It was hoped that a single mechanism accounted for all of the unrearranged product resulting from path U in any given case, and experiments were devised to elucidate the nature of path U.

It was known that 1-diazo-2-butene and 3-diazo-1-butene reacted with 3,5-dinitrobenzoic acid in ethyl ether to give the unrearranged dinitrobenzoate ester in each case.[11] If such diazo compounds were involved in the present case, reaction in deuterated solvent would necessitate incorporation of deuterium in the product.



The use of deuterated solvent in the deaminations of both α- and γ-methylallylamine produced acetates free from excess deuterium as indicated by the absence of any C–D stretching frequencies in the infrared spectra (spectra were identical with those of non-deuterated material) and by no decrease in intensities of the nuclear magnetic resonance proton bands as compared to the products from runs with ordinary acetic acid. On this evidence the diazo intermediate was eliminated as a mechanistic possibility.

The remaining mechanisms which occurred as possibilities for path U were: (1) S_N2 attack on the diazonium ion by acetate ion or acetic acid molecule leading to complete (100%) inversion of optical configuration; (2) S_Ni here *defined* as *any* cyclic process which leads to complete (100%) retention of optical configuration; (3) a "hot" or non-resonating carbonium ion (III) in which the p-orbital at the α-carbon atom forms an angle of much greater than 0° (perhaps 90°) with the p-orbitals of the double bond carbon atoms; thus no overlap involving the α-carbon orbital is possible, hence no charge delocalization occurs and only unrearranged product is formed. Since this mechanism *by definition* involves a carbonium ion intermediate in which the bond to nitrogen has been broken, the stereochemical result expected from an optically active amine would be extensive racemization with possibly some net inversion due to shielding by departing nitrogen. The idea that a non-resonating carbonium ion might be possible was suggested by Professor S. Winstein.



III

Variations of acetate ion concentrations as described in the preceding section produced no change in the product composition and S_N2 attack by acetate ion was eliminated on this basis.

The stereochemical consequences for the deamination of optically active α-methylallylamine predicted for each of the remaining mechanistic pos-

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[11] D. Y. Curtin and S. M. Gerber, THIS JOURNAL, **74**, 4052 (1952).

sibilities as well as the experimentally observed results are given in Table III. The calculated predicted values are based on the assumption that 57% of the product is formed through the SN1 mechanism (see Table II).

TABLE III

PREDICTED AND OBSERVED STEREOCHEMICAL RESULTS FOR THE DEAMINATION OF OPTICALLY ACTIVE α-METHYLALLYLAMINE IN ACETIC ACID[a]

	Predicted			
	If SN1 → 50% inv.		If SN1 → 60% inv.	
Over-all result	Inv.,[b] %	Ret.,[b] %	Inv.,[b] %	Ret.,[b] %
SN2 (by HOAc)	72	28	77	23
SNi	28	72	34	66
Hot carbonium ion				
a. If hot ion → 50% inv.	50	50	56	44
b. If hot ion → 60% inv.	54	46	60	40
c. If hot ion → 70% inv.	58	42	64	36
	Observed			
	Inv., %		Ret., %	
Run 1	58.3		41.7	
Run 2 (AgOAc)	57.9		42.1	

[a] All runs are with NaONa unless otherwise stated. [b] All values in table are for over-all results.

The reliability of the conclusions drawn from these results may be assessed from the fact that the lowest rotation possible for the SN2 mechanism (*i. e.*, 72% inversion) would be $-0.90°$ and for the SNi mechanism (*i. e.*, 66% retention) $+0.78°$. whereas the experimentally measured rotation was $-0.32 \pm 0.01°$.

The experimental results are in best accord with a Path U which involves a "hot" carbonium ion intermediate such as III. The common occurrence of complete racemization (*i. e.*, 50% inversion) in SN1 reactions at optically active allylic centers along with the over-all experimental results suggests that a short-lived "hot" carbonium ion which leads to 70% inversion (for path U only) is involved. This less extensive racemization for the "hot" as compared to the resonating ion seems reasonable upon consideration of the exceedingly rapid reaction of the hot ion to form acetate (even before its α-carbon can rotate into alignment with the other unsaturated carbon atoms) and hence a greater stereospecific shielding effect by the departing nitrogen.

Experimental

α- **and** γ-**Methylallyl Chlorides.**—The procedure was as previously described. In a typical run 459 g. (8.5 moles) of butadiene, 24 moles of concentrated hydrochloric acid and 6 moles of zinc chloride gave after fractionation 155 g. (20%) of α-methylallyl chloride, b.p. 63.0–63.5°, $n^{25}\text{D}$ 1.4140, and 396 g. (52%) of γ-methylallyl chloride, b.p. 46–47° (200 mm.), $n^{25}\text{D}$ 1.4330–1.4342.

α,α- **and** γ,γ-**Dimethylallyl Chlorides.**—The procedure was as previously described.[4] In a typical run 11.4 moles of isoprene and 474 g. (13 moles) of hydrogen chloride gave after fractionation through a 40″ glass helices packed column 180 g. (15%) of α,α-dimethylallyl chloride, b.p. 34° (153 mm.), $n^{25}\text{D}$ 1.4177 (lit.[12] b.p. 41° (200 mm.), $n^{20}\text{D}$ 1.4188) and 487 g. (39%) of γ,γ-dimethylallyl chloride, b.p. 65.5° (153 mm.), $n^{25}\text{D}$ 1.4472 (lit.[12] b.p. 67.2° (167 mm.) $n^{20}\text{D}$ 1.4495).

α-**Methylallylamine.**—The procedure was as previously described.[6] In a typical run 2.77 moles of α-methylallyl chloride and 3 moles of potassium phthalimide gave 372 g. (67%) of crude N-α-methylallylphthalimide. From the phthalimide, 2 moles of hydrazine hydrate and 2.9 moles of concd. hydrochloric acid and then treatment with excess sodium hydroxide was obtained after purification 61% of α-methylallylamine, b.p. 64°, $n^{25}\text{D}$ 1.4104 (lit.[6] b.p. 62–64°, $n^{25}\text{D}$ 1.4090).

Anal. Calcd. for C_4H_9N: C, 67.55; H, 12.75. Found: C, 67.75; H, 12.87.

γ-**Methylallylamine.**—The method was as previously described.[6] In a typical run 2.69 moles of γ-methylallyl chloride and 3 moles of potassium phthalimide gave 453 g. (84%) of crude N-γ-methylallylphthalimide which upon treatment with 2.4 moles of hydrazine hydrate and 2.9 moles of concd. hydrochloric acid followed by excess potassium carbonate gave after purification 57% of γ-methylallylamine, b.p. 85–86°, $n^{25}\text{D}$ 1.4292 (lit.[6] b.p. 81–82°, $n^{25}\text{D}$ 1.4303).

Anal. Calcd. for C_4H_9N: C, 67.55; H, 12.76. Found: C, 67.74; H, 13.02.

γ,γ-**Dimethylallylamine.**—The procedure was similar to that described previously.[6] In a typical run 1.82 moles of γ,γ-dimethylallyl chloride and 2 moles of potassium phthalimide gave after precipitation by pouring into water a quantitative yield of N-γ,γ-dimethylallylphthalimide which upon treatment with 1.92 moles of hydrazine hydrate and 200 ml. of concd. hydrochloric acid and then an excess of sodium hydroxide gave after purification 65% of γ,γ-dimethylallylamine, b.p. 110.5° (lit.[13] b.p. 105–108°), $n^{25}\text{D}$ 1.4420.

N-γ,γ-**Dimethylallyl-N′-phenylthiourea** was prepared by the standard method and after four recrystallizations from ethanol–water melted at 105.0–105.5°.

Anal. Calcd. for $C_{12}H_{16}N_2S$: C, 65.41; H, 7.32. Found: C, 65.17; H, 7.42.

γ,γ-**Dimethylallylamine picrate** was prepared by the standard method and after repeated recrystallizations from ethyl acetate–benzene melted at 138.6–139.2 (lit.[7] m.p. 138.5–139.5°).

Anal. Calcd. for $C_{11}H_{14}N_4O_7$: C, 42.04; H, 4.48. Found: C, 42.12; H, 4.58.

α,α-**Dimethylallylamine. A. Pentenyl Bromides.**—The procedure was as for the preparation of the pentenyl chlorides. From 30 moles of isoprene and 20 moles of hydrogen bromide was obtained 15 moles (75%) of pentenyl bromides, a mixture of α,α- and γ,γ-dimethylallyl bromides, b.p. 29–55° (51 mm.).

B. Pentenylmagnesium Bromide.—The procedure was as previously described.[14] Magnesium covered with a saturated dry ethereal solution of mercuric chloride was allowed to stand in the tube of a cyclic reactor for 12 hours. The mercuric and magnesium chlorides were then removed by a refluxing dry ether current to give activated dull grey magnesium. A small quantity of ethyl iodide and iodine was added to the reactor through a side arm and the reactor heated to initiate the Grignard reaction. Then freshly distilled pentenyl bromide mixture prepared above diluted with three times its volume of dry ether was added very slowly from a dropping funnel at the top of a reflux condenser and further diluted by a rapidly refluxing column of pure dry ether from the reactor pot. Titration of aliquots of the Grignard reagent so prepared showed yields of 62–92%.

C. Dimethylvinylacetic Acid.—Pentenylmagnesium bromide was poured onto powdered Dry Ice covered with dry ether. Hydrochloric acid was added, the ether layer separated and the aqueous layer washed with ether. The ethereal portions were combined and extracted with aqueous sodium hydroxide. The aqueous portion was acidified, the organic layer separated and the aqueous layer extracted with ether. The organic portions were dried over magnesium sulfate and distilled to give 79% of pure dimethylvinylacetic acid, b.p. 121° (78 mm.), $n^{25}\text{D}$ 1.4272.

D. Dimethylvinylacetamide.—The method was as previously described.[8] From 1.57 moles of dimethylvinylacetic acid, 1.57 moles of triethylamine, 1.57 moles of ethyl chlorocarbonate and an excess of ammonia gas was

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(12) W. G. Young, S. Winstein and H. L. Goering, THIS JOURNAL, **73**, 1958 (1951).

(13) E. Späth and W. Spitzy, *Ber.*, **58**, 2275 (1925).

(14) (a) B. L. Garner, unpublished experiments, Univ. of Calif. at Los Angeles; (b) K. W. Greenlee, private communication; (c) R. C. Rowlands, K. W. Greenlee and C. E. Boord, Absts. of Papers, 117th Am. Chem. Soc. Meeting, April, 1950.

obtained 86% of dimethylvinylacetamide, m.p. 97° (lit.[15] m.p. 93°).

E. α,α-**Dimethylallylamine.**—The amine was obtained from the Hofmann reaction rearrangement of the amide essentially as previously described.[16] From 0.55 mole of dimethylvinylacetamide, 550 ml. of 10% aqueous sodium hydroxide and 1.65 l. of 0.33 *N* alkaline sodium hypochlorite solution was obtained 80% of α,α-dimethylallylamine, b.p. 75°, $n^{25}\text{D}$ 1.4108.

Anal. Calcd. for $C_5H_{11}N$: C, 70.53; H, 13.05; N, 16.45. Found: C, 70.32; H, 12.95; N, 16.39.

N-α,α-Dimethylallyl-N′-phenylthiourea, prepared as for the γ,γ-amine, melted 88.0–88.5°.

Anal. Calcd. for $C_{12}H_{16}N_2S$: C, 65.41; H, 7.32. Found: C, 65.54; H, 7.41.

α,α-**Dimethylallylamine picrate**, prepared as for the γ,γ-amine, melted 179.8–180.4°.

Anal. Calcd. for $C_{11}H_{14}N_4O_7$: C, 42.04; H, 4.48. Found: C, 42.12; H, 4.54.

t-**Amylamine.**—α,α-Dimethylallylamine (6.02 g., 0.706 mole) was shaken with Adams catalyst until the theoretical quantity of hydrogen was absorbed. The catalyst was removed by filtration and the product distilled to give impure *t*-amylamine, b.p. 68–73°, $n^{25}\text{D}$ 1.3954, which was used in the preparation of derivatives described below.

N-*t*-Amyl-N′-phenylthiourea, prepared as for the unsaturated amines, melted at 116–117° and gave a depression (m.p. 88–102°) upon admixture with a sample of N-α,α-dimethylallyl-N′-phenylthiourea.

Anal. Calcd. for $C_{12}H_{18}N_2S$: C, 64.81; H, 8.16. Found: C, 64.72; H, 8.02.

t-**Amylamine picrate**, prepared as for the unsaturated amines, melted at 179° (lit.[17] m.p. 182–183°) and gave only a small depression (m.p. 177.2–177.6°) upon admixture with α,α-dimethylallylamine picrate.

Anal. Calcd. for $C_{11}H_{16}N_4O_7$: C, 41.77; H, 5.10. Found: C, 42.01; H, 4.91.

Resolution of α-Methylallylamine. A. (+)-α-Methylallylamine *d*-Tartrate.—In a typical run 2.04 moles of α-methylallylamine and 2.04 moles of *d*-tartaric acid were placed in 900 ml. of water, heated to boiling and concentrated to 600 ml., cooled and allowed to stand for 10 hours at 4° to give 187 g. of α-methylallylamine *d*-tartrate salt which after two recrystallizations from 95% ethanol amounted to 166 g. The specific rotation in water was $[\alpha]^{25}\text{D}$ 19.07°, *c* 2.684 g./100 ml. Subsequent recrystallizations from water or 94% ethanol did not increase the optical purity although subsequent experiments indicated that the salt was only about one-fourth (or 23%) optically pure.

B. **(+)-α-Methylallylamine.**—In a typical run the α-methylallylamine *d*-tartrate prepared above was dissolved in a small quantity of water and excess solid potassium hydroxide added. The organic layer was removed and repeatedly treated with excess solid potassium hydroxide until no aqueous layer formed. The amine was then further dried over barium oxide and fractionated to give (+)-α-methylallylamine, b.p. 63.0–63.8°, $n^{25}\text{D}$ 1.4103, $\alpha^{25}\text{D}$ neat +5.94°. A control run showed that the amine did not racemize during this procedure.

Anal. Calcd. for C_4H_9N: C, 67.55; H, 12.76. Found: C, 67.20; H, 12.67.

C. **Hydrogenation of (+)-α-Methylallylamine.**—In a typical run 0.06 mole of (+)-α-methylallylamine prepared above was dissolved in 25 ml. of water and shaken over Raney nickel until the theoretical quantity of hydrogen was absorbed. The workup was as for (+)-α-methylallylamine in part B above and gave (+)-*sec*-butylamine, b.p. 62.0–62.5°, $n^{25}\text{D}$ 1.3920, $\alpha^{25}\text{D}$ neat +1.22°, 23% optically pure, since for optically pure (+)-*sec*-butylamine, $\alpha^{20}\text{D}$ neat 5°23′.[9] It was shown by a control run that (+)-*sec*-butylamine did not racemize on the catalyst surface or during the workup procedure.

Optical Configuration of (−)-α-Methylallyl Acetate. A. (+) α-Methylallyl Alcohol.—Partially resolved (+) α-methylallyl alcohol was prepared by the procedure previously described,[10c,18] b.p. 97–98°, $n^{25}\text{D}$ 1.4115, $\alpha^{25}\text{D}$ neat +11.637°.

B. **(−)-α-Methylallyl Acetate.**—(+)-α-Methylallyl alcohol (0.068 mole), prepared above, acetic anhydride (0.070 mole) and 12 ml. of pyridine were mixed together and allowed to stand in a stoppered flask for 3 hours. Water (30 ml.) and pentane (25 ml.) were added, the pentane layer separated and washed successively with water, 0.5% hydrochloric acid, then water and dried over magnesium sulfate. Distillation of the product gave 4.9 g. of α-methylallyl acetate, b.p. 110°, $n^{25}\text{D}$ 1.4011, $\alpha^{25}\text{D}$ neat −10.97°. Thus optically pure (−)-α-methylallyl acetate was calculated to have $\alpha^{25}\text{D}$ neat −26.29°.

Acetolyses of α,α- and γ,γ-Dimethylallyl Chlorides.—Typically 200 ml. of anhydrous acetic acid and 0.21 mole of silver acetate were placed in a 500-ml. 3-necked round-bottomed flask fitted with a mechanical stirrer, reflux condenser bearing a drying tube and a dropping funnel containing 0.2 mole of freshly distilled α,α-dimethylallyl chloride. The chloride was added with stirring during five minutes and the mixture was stirred at room temperature for an additional two hours. Ice-water (800 ml.) was added, the silver chloride removed, triturated, and washed several times with pentane. The aqueous filtrate was extracted with pentane and the pentane portions combined and washed with cold 5% aqueous sodium bicarbonate, then water, and dried over magnesium sulfate. The crude product mixture was flash distilled at reduced pressure and the distillate fractionated to give 7.06 g. of α,α-dimethylallyl acetate and 8.71 g. of γ,γ-dimethylallyl acetate (61% total yield) as analyzed by refractive index measurements which were shown by standard curves to be linear with composition. A control run on an acetate mixture of known composition established that the acetates did not rearrange under the reaction or work-up conditions.

Deaminations in Acetic Acid.—Typically the apparatus consisted of a 2-necked Erlenmeyer flask containing a magnetic stirring bar and thermometer and filled with a solids addition funnel and a gas outlet tube which connected through an empty trap and three potassium permanganate traps to a large water filled graduated bottle for the collection of nitrogen. Sodium nitrite (1 mole) was added to a stirred solution of 0.2 mole of α-methylallylamine in 200 ml. of anhydrous acetic acid over 7 hours at room temperature and stirred for an additional 3.5 hours at the end of which time approximately the theoretical amount of nitrogen had been collected. The mixture was poured onto 600 ml. of ice-water containing 100 g. of dissolved potassium bicarbonate and then extracted with five 100-ml. portions of pentane. The pentane extracts were combined and washed successively with 20 ml. of cold 0.5 *N* hydrochloric acid, 20 ml. of cold 20% aqueous potassium bicarbonate and three 20-ml. portions of cold water, then dried over magnesium sulfate. The pentane was removed by distillation at atmospheric pressure. The product was distilled at reduced pressure to give 15 g. (70%) of an acetate mixture, b.p. 54–72° (90 mm.), which was analyzed by refractive index measurements. A control run showed that the acetates did not rearrange under the reaction or workup conditions.

Acknowledgments.—We are indebted to Dr. K. Olivier for some specially purified reagents and to Dr. J. D. Roberts for measurements and interpretations of nuclear magnetic resonance spectra.

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