

C. From the reaction with acenaphthenequinone hydrazone oxime (VII, 756 mg., 3.6 mmoles), 210 mg. of acenaphthene oxime (VIII) was isolated from the weakly acidic fraction; m.p. 175–180° dec. (reported²⁴ m.p. 175°).

D. From the reaction with camphorquinone 2-hydrazone 3-oxime (IX, 1.29 g., 6.6 mmoles), a weakly acidic product (403 mg.) was obtained which was sublimed, giving 369 mg. of crystals (2.1 mmoles, 32%). Crystallization from benzene-hexane and resublimation yielded camphano[2,3-d]-*v*-triazole (XI), m.p. 124–137°.

Anal. Calcd. for C₁₀H₁₅N₃: C, 67.8; H, 8.5; N, 23.7. Found: C, 67.6; H, 8.5; N, 23.6.

The neutral product (790 mg.) was chromatographed on 25 g. of acid-washed alumina. The bulk of the material was eluted by methylene chloride, and this material was sublimed to yield 640 mg. (3.8 mmoles, 58%) of epicamphor oxime X, m.p. 104–105° and $[\alpha]_D^{25}$ 98.5° (c 4.0, benzene) after recrystallization from aqueous methanol (reported²⁵ m.p. 103–104°, $[\alpha]_D$ 100.5°).

Anal. Calcd. for C₁₀H₁₇NO: C, 71.8; H, 10.3; N, 8.4. Found: C, 71.5; H, 10.5; N, 8.7.

D. From the reaction with 2,3-octanedione-2-hydrazone-3-oxime (XVI, 3.14 g., 18.3 mmoles), the neutral fraction (1.86 g.) obtained was chromatographed on acid-washed alumina (40 g.) and was separated into 3-octanone (507 mg., 4.0 mmoles, 21%) and 3-octanone oxime (1.33 g., 9.3 mmoles, 50%). Both products had identical infrared spectra and retention times on vapor phase chromatography with authentic samples and differed significantly from the corresponding 2-isomers. The 3-octanone oxime was prepared in the usual manner from 3-octanone and had b.p. 89° (6 mm.), n_D^{25} 1.4546 (reported²⁶ b.p. 92° (5 mm.), n_D^{25} 1.4517).

Anal. Calcd. for C₈H₁₇NO: C, 67.1; H, 12.0; N, 9.8. Found: C, 67.0; H, 12.0; N, 9.8.

E. From the reaction with biacetyl hydrazone oxime (XVII, 2.20 g., 19.1 mmoles), a weakly acidic fraction (700 mg.) and a neutral fraction (175 mg.) were obtained.

(24) C. Graebe and E. Gfeller, *Ann.*, **276**, 1 (1893).

(25) J. Bredt and W. H. Perkin, *J. Chem. Soc.*, **103**, 2182 (1913).

(26) F. Asinger, G. Geiseler and P. Laue, *Ber.*, **90**, 485 (1957).

Both were shown to be methyl ethyl ketoxime (52% yield) by direct comparison with an authentic sample.

F. From the reaction with α -oximinopropiophenone hydrazone (XIV, 4.7 g.), the only identifiable product was about a 5% yield of benzoic acid in the strongly acidic fraction. Exactly the same result was obtained with phenylacetone oxime. In both cases, the majority of the material remained as polymeric material in the neutral fraction.

G. From the reaction with α -oximinoacetophenone hydrazone²⁷ (XIII, 1.16 g., 7.1 mmoles), a strongly acidic fraction (758 mg., 5.6 mmoles, 78%) was obtained and was identified as phenylacetic acid.

Phenylacetaldoxime²⁸ (1.17 g., 8.6 mmoles) and potassium hydroxide (2.4 g., 43 mmoles) in 80 ml. of diethylene glycol gave as the only significant product a strongly acidic fraction (945 mg., 6.9 mmoles, 80%), also identified as phenylacetic acid.

2-Methylindano[1,2-d]-*v*-triazole.—1,2-Indandione 1-methylhydrazone 2-oxime in acetic anhydride was heated at reflux for 1 hour. Water was then added, the solution was made alkaline with 3 *N* sodium hydroxide, and 1% potassium permanganate solution was added until the purple color persisted. The mixture was extracted with an equal volume of methylene chloride (in two portions), and the residue after evaporating the methylene chloride was chromatographed on alumina. Benzene eluted the 2-methylindano[1,2-d]-*v*-triazole, m.p. 58–59°; ultraviolet absorption: λ_{max} 261 m μ (ϵ 19,000), 268 (18,500), 285 (10,500), 293 (11,700).

Anal. Calcd. for C₁₀H₉N₃: C, 70.2; H, 5.3; N, 24.5. Found: C, 70.3; H, 5.3; N, 24.2.

2-Phenylindano[1,2-d]-*v*-triazole was prepared from 1,2-indandione 1-phenylhydrazone 2-oxime and acetic anhydride by the procedure described above for the 2-methyl analog. On recrystallization from benzene-hexane, it melted at 129–130° (reported²⁹ m.p. 125°); ultraviolet absorption: λ_{max} 223 m μ (ϵ 10,600), 287 (18,000), 311 (36,900).

Anal. Calcd. for C₁₅H₁₁N₃: C, 77.2; H, 4.8; N, 18.0. Found: C, 77.3; H, 4.7; N, 18.1.

(27) B. B. Dey, *J. Chem. Soc.*, **105**, 1039 (1914).

(28) R. A. Weerman, *Ann.*, **401**, 1 (1913).

(29) G. Charrier, *Gazz. chim. ital.*, **58**, 254 (1928).

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENN., AND THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF FLORIDA, GAINESVILLE, FLA.]

Molecular Rearrangements. XIX. The Thermal Decomposition of N-Acetyl-N-nitroso-1,2,2-triphenylethylamine¹

BY CLAIR J. COLLINS, JOAN B. CHRISTIE^{2,3} AND VERNON F. RAAEN

RECEIVED MAY 11, 1961

Several isotope position isomers of N-acetyl-N-nitroso-1,2,2-triphenylethylamine (III) have been prepared in optically active form. The thermal decompositions of these in *p*-cymene and in glacial acetic acid at several temperatures have been followed kinetically. The product, partially racemic 1,2,2-triphenylethyl acetate (IV), has been resolved, and the carbon-14 distributions in each enantiomer have been determined. The nitrosoamide IIIa, labeled in the 1-position with carbon-14, has been subjected to thermal decomposition also in propionic acid, and the yields of acetate IV and propionate VI have been determined. Both exhibit scrambling of their chain labels. The identification of labeled acetoxyl with D-(+)-1,2,2-triphenylethyl acetate (IVc) in the thermal decomposition of (-)-IIIc in glacial acetic acid establishes the D-configurations of (+)-I, (+)-II and (-)-III. Optically active 1,2,2-triphenylethyl-1-C¹⁴-amine (Ia) has been deaminated in glacial acetic acid containing sodium acetate, the partially racemic product IVab has been resolved and the carbon-14 distribution in each enantiomer has been determined. The extent of inversion during each reaction was measured. All results are explained in terms of a mechanism involving ion pairs of the acetoxyl anion with equilibrating, classical triphenylethyl carbonium ions.

Introduction

The stereochemistry of the deamination of 1,2,2-triphenylethylamine in aqueous solution con-

taining a small concentration of acetic acid has been reported.⁴ Thus D-(+)-1,2,2-triphenylethyl-

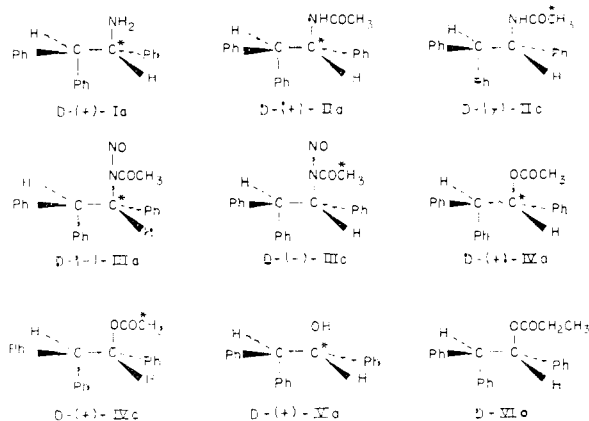
(1) This paper is based upon work performed at Oak Ridge National Laboratory, which is operated by Union Carbide Corporation for the Atomic Energy Commission. Previous paper, B. M. Benjamin and C. J. Collins, *J. Am. Chem. Soc.*, **83**, 3682 (1961).

(2) Predoctoral Fellow of the Oak Ridge Institute of Nuclear Studies from the University of Florida, Gainesville.

(3) Portions of this paper are from the Ph.D. thesis of Joan B. Christie, whose advisor at the University of Florida was the late Professor C. B. Pollard. The authors are indebted to Professor Pollard for his interest in and support of the work herein presented, parts of which were published in preliminary form: *J. Am. Chem. Soc.*, **82**, 1255 (1960).

(4) C. J. Collins, W. A. Bonner and C. T. Lester, *ibid.*, **81**, 466 (1959).

amine (I), for example, yielded, in addition to small amounts of olefin and acetate, partially racemic 1,2,2-triphenylethanol (V) consisting of approximately 70% of the D-(+)-enantiomer and 30% of the L-(-)-enantiomer. Resolution of the carbinol produced from labeled reactant, followed by determinations of the carbon-14 distributions in these resolved products, served as evidence that rearranging, open, unbridged carbonium ions were responsible for the net retention of configuration. Presumptive but inconclusive evidence for like configuration of amine I and carbinol V of like sign of rotation was based upon optical rotatory dispersion data,^{4,5} upon comparison with the results of solvolyses of labeled, optically active 1,2,2-triphenylethyl tosylate and upon melting-point-composition diagrams.^{6,7} The thermal decomposition of D-(-)-N-nitroso-N-acetyl-1,2,2-triphenylethylamine (III) to produce acetate containing 70% (+)-1,2,2-triphenylethyl acetate (IV) and



30% of the (-)-isomer, however, was the chemical evidence upon which the configurational assignment was made. The work of Huisgen⁸ and of White⁹ has established that the thermal decompositions of N-nitrosoamides ordinarily proceed with partial retention of configuration. Although solvent competition^{8,9} can in some cases produce inversion, that portion of the decomposition which proceeds intramolecularly yields ester of predominantly retained configuration. The N-nitroso derivative III is sufficiently different¹⁰ from the compounds studied by Huisgen⁸ and by White,⁹ however, that we sought additional evidence of its mode of decomposition. Such evidence has now been obtained through data which leave no doubt concerning the configuration of the D-(+)-amine I, and which, in addition, shed some light upon the

(5) Although the optical rotatory dispersion curves of (+)-II and (+)-IV were very similar, no Cotton effect was exhibited, so these data alone could not be used as configurational evidence.

(6) A. Fredga in "Thé Svedberg," Almquist and Wiksells, Uppsala, Sweden, 1955, pp. 261 ff.; *Arkiv. Kemi*, **11**, 23 (1957).

(7) K. Mislow and M. Heffler, *J. Am. Chem. Soc.*, **74**, 3668 (1952); K. Mislow and W. C. Meluch, *ibid.*, **78**, 5920 (1956). We are much indebted to Professor Kurt Mislow for pointing out the utility of the Fredga Method and for the interpretation of our data in this connection reported in ref. 4.

(8) R. Huisgen and R. Rüchardt, *Ann.*, **601**, 21 (1956).

(9) E. H. White, *J. Am. Chem. Soc.*, **77**, 6011, 6014 (1955); E. H. White and C. A. Aufdermarsh, *ibid.*, **80**, 2597 (1958).

(10) (a) C. J. Collins and W. A. Bonner, *ibid.*, **75**, 5372, 5379 (1953); (b) **77**, 92, 99, 6725 (1955); (c) **78**, 5587 (1956).

mechanism of the thermal decomposition of the N-nitrosoacyl compound III. These data, which have been referred to before^{3,4} in a preliminary manner, are now recorded.

Methods and Results

1,2,2-Triphenylethylamine (I) and 1,2,2-triphenylethyl-1-C¹⁴-amine (Ia) were prepared and resolved as previously reported,^{1,4} then converted to the isotope position isomers IIc and IIa. The optically active N-acetyl-N-nitroso-1,2,2-triphenylethylamines IIIa and IIIc were prepared by a modification of the method of France, Heilbron and Hey,¹¹ and then heated (a) without a solvent, (b) in benzene, (c) in *p*-cymene and (d) in acetic acid with and without added sodium acetate. The products, labeled, partially racemic IV, were repeatedly crystallized to yield in each case an optically pure form and a racemic form. The chemical purity of each carefully crystallized fraction was ordinarily demonstrated by its infrared spectrum. The infrared determinations were very useful in proving the absence of small percentages of amide II in the fractions of acetate. These fractions of IVab (*i.e.*, mixtures of IV labeled in the 1- and 2-positions of the ethyl moiety) were then oxidized to yield benzophenone and benzoic acid. The benzophenone samples were converted to 2,4-dinitrophenylhydrazones and assayed for radioactivity. From these data were calculated the fractions of carbon-14 rearrangement in products of retained and inverted configurations. The optically pure and racemic samples of IVc, obtained by repeated crystallization of the appropriate products, were assayed for radioactivity and from these data were calculated the percentages of original acetate (labeled) which remained with the optically retained and optically inverted forms of IVc. In several runs with D- or L-IIIa, aliquots of product were reduced with lithium aluminum hydride to yield samples of 1,2,2-triphenylethanol (V), whose optical rotations were determined and from which the percentage inversion during each reaction was calculated. In addition, four separate kinetic runs were carried out in which optically active III underwent thermal decomposition in *p*-cymene and in acetic acid at 34.7° and in acetic acid at 40.5°, 47.7° and at 59.0°. The progress of each kinetic run was followed polarimetrically. The first-order rate constants [k_1] with respect to IIIa were calculated by means of the equation

$$k_1 = \frac{1}{t} \ln \frac{\alpha_0 - \alpha_t}{\alpha_t - \alpha_\infty}$$

where t is the time in hours, α_0 , α_t and α_∞ being the respective polarimeter readings at $t = 0$, $t = t$ and $t = \infty$. The rate constants, k_1 , and α_0 and α_∞ were all determined with the assistance of the ORACLE,¹² those values being chosen for which the standard errors in k_1 were minima. Given in Table I are the results of the experiments just described with optically active N-acetyl-N-nitroso-1,2,2-triphenylethyl-1-C¹⁴-amine (IIIa), whereas in Table II are collected the results of the

(11) H. France, I. M. Heilbron and D. H. Hey, *J. Chem. Soc.*, 389 (1940).

(12) Oak Ridge Automatic Computer and Logical Engine. We wish to thank Dr. M. H. Lietzke for his help with these calculations.

TABLE I

SUMMARY OF KINETIC, STEREOCHEMICAL AND CARBON-14 DATA FOR THE THERMAL DECOMPOSITIONS OF OPTICALLY ACTIVE OR RACEMIC IIIa

| Solvent | Temp., °C. | k_1 , ^a hr. ⁻¹ | Inversion, ^b % | C ¹⁴ rearrangement, % | | |
|----------------------------|---------------|----------------------------------------|------------------------------|----------------------------------|----------|--------------------|
| | | | | Retained | Inverted | Gross ^c |
| None | 94-95 | | 24.4 | 15.7 | 29.1 | 18.9 |
| Benzene | 23 | | 23 | 15.4 | 22.4 | 17.0 |
| <i>p</i> -Cymene | 34.7 | $0.067 \pm (1.5 \times 10^{-4})$ | 25, 24 | .. | .. | .. |
| Acetic acid | 34.7 | $.323 \pm (0.9 \times 10^{-4})$ | 29, 30 | .. | .. | .. |
| Acetic acid | 40.5 | $.830 \pm (1 \times 10^{-2})$ | 30, 29.5, 29 | 28.1 | 38.8 | 31.3 |
| Acetic acid | 47.7 | $1.76 \pm (1.3 \times 10^{-2})$ | 29, 28.5 | 28.7 | 40.1 | 32.0 |
| Acetic acid | 59.0 | | 30.5 | 28.9 | 39.4 | 32.4 |
| Acetic acid-sodium acetate | 40.5 | | .. | .. | .. | 31.5 ^d |

^a The uncertainties are standard deviations. ^b Total inversion; *i.e.*, % inversion plus % retention = 100%. ^c Calculated from data of columns 4, 5 and 6. ^d Reactant IIIa in this run was racemic; this value is therefore an observed value.

experiments with optically active N-(acetyl-2-C¹⁴)-N-nitroso-1,2,2-triphenylethylamine (IIIc). In addition, in both Tables I and II results are listed with racemic IIIa and IIIc performed as check experiments.

TABLE II

SUMMARY OF STEREOCHEMICAL AND CARBON-14 DATA FOR THE THERMAL DECOMPOSITIONS OF OPTICALLY ACTIVE OR RACEMIC IIIc

| Solvent | Temp., °C. | Carbon-14 in product, % | | |
|----------------------------------------------|---------------|-------------------------|-----------------------|-------------------|
| | | Retained ^a | Inverted ^a | Gross |
| Acetic acid ^b | 40.5 | 41.7 | 11.0 | 32.5 ^c |
| Acetic acid ^b | 40.5 | 42.2 | 12.3 | 33.2 ^c |
| Acetic acid ^d | 34.5 | .. | .. | 32.5 |
| Acetic acid ^d | 40.5 | .. | .. | 31.8 |
| Acetic acid ^d | 60.2 | .. | .. | 28.7 |
| Acetic acid ^d - sodium acetate | 50.5 | .. | .. | 31.0 |

^a These values were obtained by dividing the molar radioactivities of the products of retained or inverted configuration by the molar radioactivity of reactant IIIc and multiplying by 100. ^b Reactant optically active. ^c Calculated from the data of columns 3 and 4, assuming 30% inversion. ^d Reactant IIIc racemic.

Next, two experiments were carried out in which *rac*-IIIb (labeled in 2-position of ethyl moiety) and L-(+)-IIIb were thermally decomposed in propionic acid-sodium propionate at 40.5°. In the rearrangement of *rac*-IIIb, the isotope-dilution technique was employed to ascertain yields of acetate and propionate formed. The percentages scrambling of carbon-14 in acetate and propionate were then determined as described in the Experimental section. In the rearrangement of L-(+)-IIIb, the mixed product of acetate and propionate was reduced with lithium aluminum hydride, and the optical rotation of the carbinol so obtained was used in the calculation of the percentages inversion and retention. The results of these experiments are given in Table III.

TABLE III

CARBON-14 DATA OBTAINED UPON THERMAL DECOMPOSITION OF RACEMIC N-NITROSO-N-ACETYL-1,2,2-TRIPHENYLETHYL-2-C¹⁴AMINE (IIIb) AT 40.5° IN PROPIONIC ACID-SODIUM PROPIONATE MEDIUM

| Yield of product, ^a % | C ¹⁴ rearrangement, % in |
|----------------------------------|-------------------------------------|
| IVab | VIab |
| 46.4 | 54.6 |
| 26.5 | 37.7 |

^a In a run with L-(+)-IIIb, the total inversion was 27%.

Finally, the deaminations of racemic or optically active 1,2,2-triphenylethyl-1-C¹⁴-amine (Ia) or of

1,2,2-triphenylethyl-2-C¹⁴-amine (Ib) were carried out (a) in acetic acid to which was slowly added potassium nitrite and (b) in acetic acid saturated with sodium acetate to which was slowly added potassium nitrite. In separate experiments the percentages inversion and retention, the fraction of carbon-14 rearrangement in product of retained and inverted configurations, or the gross rearrangement of the carbon-14 label were determined. The results of all experiments with enantiomers and isotope position isomers of (±)-I and (-)-I are summarized in Table IV.

TABLE IV

SUMMARY OF STEREOCHEMICAL AND CARBON-14 DATA FOR THE DEAMINATIONS OF 1,2,2-TRIPHENYLETHYLAMINE (I)

| Reactant | Solvent | Temp., °C. | Inver- sion, % | C ¹⁴ rearrangement in product | | |
|---------------------|----------------|---------------|----------------------|------------------------------------------|---------------|-------|
| | | | | Re- tained | In- verted | Gross |
| L-(-)-Ia | Acetic acid | 23 | 30 | 24.9 | 29.3 | 26.2 |
| D-(+)-Ia | Acetic acid | 23 | 30.1 | 20.2 | 28.8 | 22.8 |
| (±)-Ib ^a | Acetic acid- | 40.5 | .. | .. | .. | 30.3 |
| (±)-Ib ^a | sodium acetate | 40.5 | .. | .. | .. | 31.0 |
| (±)-Ib | Acetic acid- | 40.5 | .. | .. | .. | 29.2 |
| (±)-Ia | sodium acetate | 40.5 | .. | .. | .. | 29.5 |
| (±)-Ia | Acetic acid- | 40.5 | .. | .. | .. | 29.2 |
| L-(-)-Ia | sodium acetate | 40.5 | 34 | .. | .. | .. |
| L-(-)-Ia | Acetic acid- | 40.5 | 37 | .. | .. | .. |
| L-(-)-Ia | sodium acetate | 40.5 | 35.5 | .. | .. | .. |

^a Labeled with deuterium in 2-position.

The yields of ester (IV or, in the results listed in Table III, IV plus VI) for the decomposition of III in acetic acid or in propionic acid were always quantitative and unaccompanied by the formation of olefin. Similarly, when the amine I was subjected, in acetic acid, to deamination with potassium nitrite the ester IV was obtained quantitatively. The absence of olefin was demonstrated by failure to isolate it through the same chromatographic techniques which previously⁴ demonstrated the presence of small percentages of 1,1,2-triphenylethylene upon deamination of the hydrochloride of I in aqueous medium.

Discussion

The significance of Table II, namely, that the enantiomeric product (D-IVc or L-IVc) from any given run and containing the higher fraction of radioactivity has also been formed with *retention* of configuration, has already been discussed.³ The absolute configurations of (+)-I, (+)-II and (-)-III are thus related to the absolute configurations of D-(+)-IV and D-(+)-V which have

been related to D-(-)-mandelic acid.¹³ The assignment of the D-configuration to (+)-I, (+)-II and (-)-III has also been confirmed now by optical rotatory dispersion data, like Cotton effects being exhibited by the N-dithiocarboethoxy derivative of (-)-I and the O-dithiocarbomethoxy derivative of (-)-V.¹⁴

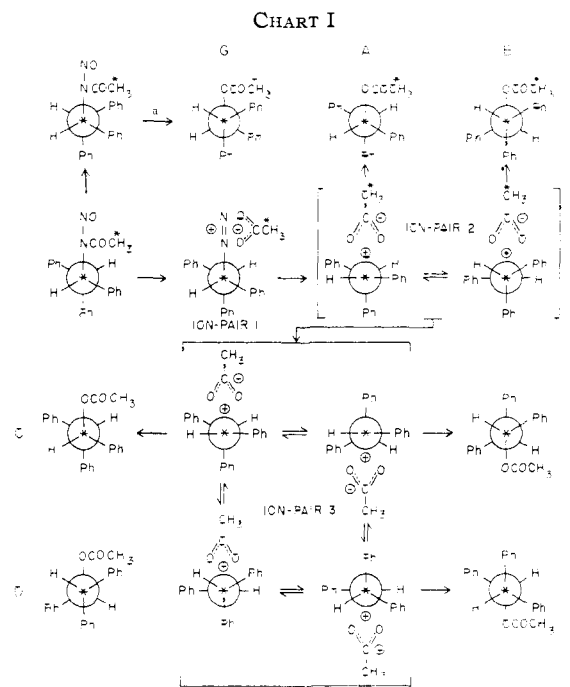
The striking similarity of the results of Table I with the data previously obtained⁴ for deamination of optically active, labeled 1,2,2-triphenylethylamine (I) in aqueous acetic acid is apparent. The results are even in closer agreement with those reported in Table IV for the deamination of I in glacial acetic acid or in acetic acid-sodium acetate. In all three reactions inverted product has suffered more rearrangement than product of retained configuration, and the percentages inversion are roughly the same. The results, in fact, are quite similar despite the wide variation in conditions employed for the thermal decompositions of III. The kinetic data of Table I demonstrate that the thermal decomposition of III is clearly first order with respect to reactant, and that the reaction takes place more rapidly in acetic acid than in the less polar solvent *p*-cymene. Further, it is clear that an increase in temperatures from 34.7° to 59.0° has little, if any, effect upon the fraction of inversion or upon the carbon-14 scrambling exhibited by the product.

The mechanism^{8,9} generally accepted¹⁵ for the thermal decomposition of N-nitrosoamides requires the formation, in the rate-determining step, of a diazoester. In polar solvents it is well established^{8,9,15} that the carboxylic esters are formed from the diazoester through a carbonium ion-ion pair mechanism, whereas in non-polar solvents, in which carbonium ion formation is not favored, α -elimination often occurs. In Chart I is given a scheme for the thermal decomposition, in acetic acid, of D-N-acetyl-2-C¹⁴-N-nitroso-1,2,2-triphenylethyl-1-C¹⁴-amine (IIIac). Formula IIIac is a composite formula signifying double labeling and is used for simplicity to avoid the necessity of a separate chart for IIIa and IIIc. The asterisk in the center of each Newman projection formula signifies labeling with carbon-14 in the front carbon of the ethane moiety. Seven discrete and separate paths (A-G) for the rearrangement of D-III are recognized on the basis of the stereochemical and radiochemical results in Tables I and II, and the intermediates are expressed in terms of ion pairs.⁸ The mechanism presented in Chart I implies rearrangement and inversion during the ion-pair stage, whereas White and Aufdermash¹⁵ propose inversion during the time interval between loss of nitrogen and ion-pair formation. Both concepts equally well explain the data. We prefer our own interpretation for decomposition of the nitrosoamide I, however, because of the similar extent of carbon-14 scrambling exhibited during the nitroso-

(13) K. Milow, *J. Am. Chem. Soc.*, **73**, 3954 (1951).

(14) We are indebted to Professor Carl Djerassi for the optical rotatory dispersion curves. The configurations of compounds I-VI have also been confirmed by C. Djerassi, E. Lund, E. Bunnenberg and B. Sjöberg, *J. Am. Chem. Soc.*, **83**, in press (1961), through a direct examination of the optical rotatory dispersion spectrum of L-(+)-III.

(15) E. H. White and C. A. Aufdermash, *J. Am. Chem. Soc.*, **83**, 1174, 1179 (1961).



^a Phenyl migration through the *cis*-transition state followed by ion-pair collapse; see path G-1 of Chart II.

amide decompositions and solvolytic reactions⁴ of 1,2,2-triphenylethyl derivatives. Thus "ion-pair 1" proceeds to "ion-pair 2" by loss of nitrogen. "Ion-pair 2" can collapse to D-IV through A or B. The product formed through path A is unrearranged D-IVac, labeled in the 1-chain position and in the acetoxy group. Although the product formed through path B (D-IVbc) contains also a labeled acetoxy group, the chain label is contained in the 2-position. The products through paths C and D do not possess acetoxy labels, but are the D-forms of unrearranged and rearranged IV, whereas the products formed through E and F are the L-forms of unrearranged and rearranged IV, respectively, also unlabeled in their acetoxy groups. Although it is conceivable⁸ that "ion-pair 1" could suffer exchange for unlabeled acetoxy and thence lose nitrogen directly to "ion-pair 3," such an interconversion is not shown in Chart I, for our data do not allow us to distinguish this pathway from acetoxy exchange with "ion-pair 2."

From the data of Tables I and II it is possible to calculate the stoichiometry of the various paths shown in Chart I, from which we hoped to determine whether or not path B contributed to the mechanism; that is, whether that fraction of product of retained configuration which was associated with labeled acetoxy had also undergone rearrangement. As can be seen from Table V, however, the data allow both the possibilities that $m_A = m_B$ and $m_B = 0$. From Table III it is clear that in the decomposition of III in propionic acid-sodium propionate medium, product IV which has been formed without propionate-acetate exchange has nevertheless suffered rearrangement of its chain label. It seems, therefore, quite impossible that the N-nitrosoamide III should have undergone decomposition in acetic acid or in acetic

TABLE V

STOICHIOMETRY OF THERMAL DECOMPOSITION OF N-NITROSO-N-ACETYL-1,2,2-TRIPHENYLETHYLAMINE (III)
CALCULATED ON BASIS OF MECHANISM OF CHART I

| Mole fraction of reaction proceeding through path | | | | | | | |
|---------------------------------------------------|----------------|-------|-------|-------|-------|-------|--|
| A ^a | B ^a | C | D | E | F | G | |
| 0.148 | 0.148 | 0.363 | 0.047 | 0.178 | 0.082 | 0.034 | |
| 0.296 | 0 | 0.215 | 0.195 | 0.178 | 0.082 | 0.034 | |

^a The contributions of paths A and B have been calculated by assuming $m_a = m_b$ (first line) or that $m_b = 0$ (second line).

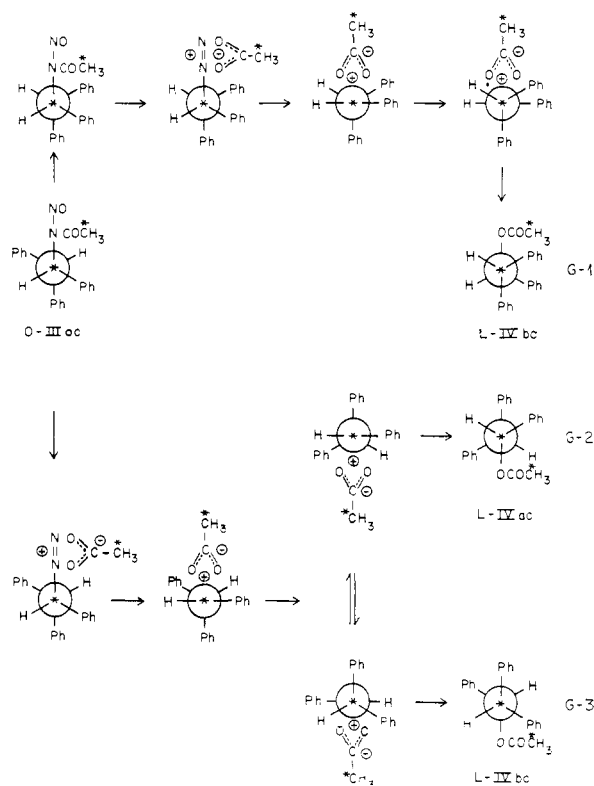
acid-sodium acetate medium with no contribution from path B.

The formation of *inverted* 1,2,2-triphenylethyl acetate-2-C¹⁴ (L-IVbc) through path G requires some comment, for there are three conceivable ion-pair mechanisms outlined in Chart II which would allow the production of inverted 1,2,2-triphenylethyl acetate labeled in the acetoxy group. Path G-1 involves phenyl migration through a *cis*-transition state with inversion at the migration origin. Although path G-1 is shown in Chart II as proceeding through backside attack and a *cis*-transition state, topside migration of phenyl through a *cis*-transition state would lead to the same result. Paths G-2 and G-3 require either (a) that labeled acetoxy can move to the opposite side of the carbonium center through unspecified mechanism, or (b) that the carbonium center itself undergo some degree of inversion. Both paths G-1 and G-3 lead to inverted, acetoxy-labeled product which has undergone 100% isotope-position rearrangement of the chain label, whereas path G-2 produces inverted, acetoxy-labeled, unrearranged L-1,2,2-triphenylethyl-1-C¹⁴ acetate-2-C¹⁴ (L-IVac). Although our present experiments do not allow us to distinguish the possibilities, we favor the mechanism indicated by paths G-2 and G-3 over that of G-1 (Chart II) for the following reasons: (1) White and Aufdermarsh¹⁵ have recently presented compelling evidence for inversion of the carbonium center during the thermal decomposition of N-(1-phenylethyl)-N-nitrosophthamide-carbonyl-O¹⁸ and related compounds; (2) phenyl migration through a *cis*-transition state (G-1) seems unlikely in view of the results of Benjamin, Schaeffer and Collins¹⁶ upon the deamination of stereospecifically phenyl-labeled (+)- and (-)-1,1-diphenyl-2-aminopropanol, through which it was shown that *both* phenyls undergo migration through *trans*-transition states alone, one to the backside, the other to the frontside of the migration terminus; and (3) the stoichiometry of the rearrangements, in acetic acid, of IIIa and IIIc is difficult to reconcile with any appreciable contribution of path G-1 to the formation of inverted product.

Finally, although 1,2,2-triphenylamine (I) hydrochloride, when treated with potassium nitrite in aqueous medium yields carbinol V plus about 4% of 1,1,2-triphenylethylene,⁴ no olefin was observed during the thermal decomposition of I in acetic or propionic acids, nor during the deamination of I in acetic acid. Since even small amounts of olefin are very easy to isolate by chromatography with alumina⁴ or Florisil, our failure to iso-

(16) B. M. Benjamin, H. J. Schaeffer and C. J. Collins, *J. Am. Chem. Soc.*, **79**, 6160 (1957).

CHART II



late it in the present instance can be taken as prime evidence for its non-formation. A referee has suggested that *trans*-elimination is the normal path for olefin formation, and that, therefore, the important conformation in these reactions is that in which the hydrogens, rather than the number 1 nitrogen and number 2 hydrogen are *trans*.

To sum up: (1) the data of Table II serve³ as a radiochemical criterion for assigning the D-configuration to (+)-I, (+)-II, (-)-III, (+)-IV and (+)-V, and these assignments are supported by optical rotatory dispersion data¹⁴; (2) the ion-pair mechanism proposed by others^{8,9,15} for the thermal decomposition of N-nitrosoamide satisfactorily accounts; in the decomposition of III, for all of our results, and (3) the similarity of the radiochemical and stereochemical consequences of both the thermal decomposition of III and the deamination of I in acetic acid-sodium acetate solutions is strongly suggestive that both reactions take place through common intermediates.

Experimental

Resolution of 1,2,2-Triphenylethanol. Method A.—A solution of 110 g. (0.29 mole) of the acid succinate^{10a} of 1,2,2-triphenylethanol and 87 g. (0.29 mole) of cinchonidine was prepared in 3 liters of benzene. After 2 days (room temperature) the crystals of cinchonidine (50 g.) which separated were collected on a filter, and the filtrate was reduced in volume to 500 cc. Subsequently, 30 g. of the cinchonidine salt was obtained which, when crystallized from benzene-hexane (1:1) then benzene, afforded 14 g. of salt, m.p. 168–169°, $[\alpha]_D^{25}$ -52° (pyridine), -83° (ethanol). The melting point and rotation did not change with further crystallization. A solution of 13.5 g. of the foregoing salt in 200 cc. of benzene was treated with 1.8 cc. of 37% HCl in 200 cc. of water. The two-phase solution was stirred for 1 hour, and an additional 6 drops of concentrated HCl was added. The benzene layer was separated, evaporated, and

TABLE VI
 CARBON AND HYDROGEN ANALYSES^a OF COMPOUNDS PREPARED DURING RESOLUTIONS OF 1,2,2-TRIPHENYLETHANOL (V)

| Compound (+)-V or derivative | Empirical formula | Carbon, % | | Hydrogen, % | |
|---------------------------------------|------------------------------------------------------------------------------------|-----------|--------------|-------------|------------|
| | | Calcd. | Found | Calcd. | Found |
| (+)-V | C ₂₀ H ₁₈ O | 87.56 | 87.51, 87.47 | 6.60 | 6.58, 6.64 |
| Acid succinate | C ₂₄ H ₂₂ O ₄ | 77.00 | 76.63, 76.72 | 5.91 | 5.79, 5.84 |
| (-)-1,1-Diphenyl-2-aminopropanol salt | C ₁₉ H ₁₉ N ₂ O ₅ | 77.83 | 77.98, 77.75 | 6.53 | 6.55, 6.42 |
| (-)-V or derivative (-)-V | C ₂₀ H ₁₈ O | 87.56 | 86.30 | 6.61 | 6.65 |
| Acid succinate | C ₂₄ H ₂₂ O ₄ | 77.00 | 76.94, 76.61 | 5.91 | 5.84, 5.69 |
| (+)-1,1-Diphenyl-2-aminopropanol salt | C ₁₉ H ₁₉ N ₂ O ₅ | 77.83 | 77.99, 77.96 | 6.53 | 6.47, 6.53 |
| Cinchonidine salt | C ₄₃ H ₄₄ O ₅ N ₂ ·1/2H ₂ O | 76.2 | 76.29, 76.56 | 6.69 | 6.66, 6.51 |

^a Performed by Huffman Microanalytical Laboratory, Wheatridge, Colo.

the solid which remained was washed with water, dried, and crystallized from a 1:1 benzene-hexane solution to yield 3 g. of material whose melting point was 165–166° (depression when mixed with cinchonidine salt), $[\alpha]_D^{25}$ –84° (benzene), –33° (ethanol), unchanged on further crystallization. The ester was reduced with lithium aluminum hydride to produce a quantitative yield of (–)-1,2,2-triphenylethanol which upon one crystallization from hexane had a melting point of 80–81° and an $[\alpha]_D^{25}$ –123° (ethanol).

Method B.—A solution containing 53 g. (0.142 mole) of the acid succinate ester^{10a} of *rac*-V and 32.1 g. (0.142 mole) of (–)-2-amino-1,1-diphenylpropanol-1¹⁷ in 200 cc. of ethanol was set aside for several days, after which 20 g. of material had accumulated, $[\alpha]_D^{25}$ +14° (ethanol). After five crystallizations from ethanol, 3.4 g. of salt, $[\alpha]_D^{25}$ +25° (ethanol), was obtained. An additional 6 g. was obtained on concentration of the mother liquors. The rotation of this material did not change on further crystallization from ethanol. The salt was hydrolyzed as described in the preceding section for the cinchonidine salt. Reduction of the ester $[\alpha]_D^{25}$ +34° (ethanol) afforded 1.6 g. of (+)-1,2,2-triphenylethanol [V], $[\alpha]_D^{25}$ +120° (ethanol), m.p. 80–81°. The carbon and hydrogen analyses of all pertinent compounds are given in Table VI.

D- and L-N-Nitroso-N-acetyl-1,2,2-triphenylethyl-1-C¹⁴-amine (IIIa).—An adaptation of the method of France, Heilbron and Hey¹¹ was used for these preparations. In a typical experiment, a solution containing 3.07 g. (0.01 mole) of L-(–)-N-acetyl-1,2,2-triphenylethyl-1-C¹⁴-amine⁴ (L-IIa, $[\alpha]_D^{25}$ –105° (dioxane) 7.07 ± 0.01 mc./mole) in 30 cc. of dry pyridine was cooled to 10–15°, and to it was added, dropwise with vigorous stirring, 45 cc. of cooled dry pyridine through which nitrosyl chloride (Matheson Co., Carlstadt, N. J.) had been bubbled for 10 minutes. The mixture was then stirred for 15 minutes (the flask was immersed in an ice-bath), removed from the ice-bath and stirred an additional 15 minutes, then poured over 500 g. of cracked ice with stirring; the bright-yellow solid obtained thereby was collected on a filter and washed with cold water. The solid was air-dried, then washed with six 50-cc. portions of hexane. The washings were dried with anhydrous magnesium sulfate, filtered, then concentrated in a stream of dry air in a flask immersed in an ice-bath. Normal precautions were taken to exclude moisture during the concentration of the hexane solution. In this way, 2.9 g. (85%) of crude L-(+)-N-nitroso-N-acetyl-1,2,2-triphenylethyl-1-C¹⁴-amine was obtained, whose melting point was 110–114° (with decomposition), and which exhibited an $[\alpha]_D^{25}$ of +324° (benzene). The samples were always contaminated with N-acetyl-1,2,2-triphenylethylamine (II), as shown by the isolation of II in the product of thermal decomposition of the N-nitrosoamide. Unfortunately, attempts to crystallize the crude material led to its thermal decomposition as exhibited by the evolution of nitrogen and a sharp drop in optical rotation. For this reason, and also because the N-nitrosoamide decomposed on standing, adequate carbon and hydrogen analyses could not be obtained. Radioactivity analyses of freshly prepared samples indicated the molecular weights: 348, 341, 344, 341, 344 (calcd. 344.4). The nitrosation was repeated many times. The yield of crude product varied from 70 to 98% and seemed to depend upon the amount of water present and the length of time the reaction mixtures were stirred after addition of the pyridine-nitrosyl chloride solutions. Usually the nitrosyl chloride was partially dried by bubbling it through 85% H₃PO₄ before its addition to pyri-

dine. After stirring for 30 minutes, the reaction mixture was poured onto cracked ice; further stirring resulted in decomposition of the product. The enantiomeric D-(–)-N-nitroso-N-acetyl-1,2,2-triphenylethyl-1-C¹⁴-amine (IIIa) was prepared from 3.0 g. of D-(+)-IIa ($[\alpha]_D^{25}$ 109° in dioxane) in yield of 3.15 g. (96%), m.p. 112–118°, $[\alpha]_D^{25}$ –320° (benzene).

Thermal Decompositions of Carbon-14 Labeled D, L- or Racemic N-Acetyl-N-nitroso-1,2,2-triphenylethylamine (IIIa, IIb or IIc). (a) **Work-up Procedure.**—In all of the thermal decompositions the sole isolable product was 1,2,2-triphenylethyl acetate (IVa, IVb or IVc). The reactant N-nitrosoamide, however, could not be obtained completely free of the N-acetyl-1,2,2-triphenylethylamine (II) from which it had been prepared (see previous section), so the acetate IV, obtained upon thermal decomposition of III, was also contaminated with small amounts of II, which could be removed in large part by reason of its lesser solubility in ether. In order to determine the fractions of inversion and retention in runs with optically active material, the product was reduced with lithium aluminum hydride; the ether fraction from the work-up was washed with dilute HCl, then water and then concentrated to dryness. The product was dissolved in hexane and poured onto a column of alumina. Elution with hexane revealed that no olefin was present. The carbinol V was washed from the column with ethanol and the solution was taken to dryness. The pure, dry carbinol usually crystallized at this point, and its optical rotation was then taken. The purity of the carbinol was checked by infrared analysis of the carbinol fraction itself and of reacylated material. It was shown independently that II could easily be detected in a mixture of 2% II and 98% IV, since II shows a strong absorption at 6.2–6.3 μ (Perkin-Elmer Infracolor). It was also shown independently that neither optical rotation nor carbon-14 label was affected by the deacetylation, chromatographic, reacylation and work-up procedures. In the runs with optically active reactant and product, resolution of the partially racemic 1,2,2-triphenylethyl acetate (IV) was effected by crystallization of the reacylated samples from ethanol. Racemic IV concentrated very rapidly in the crystalline fractions, and three or four crystallizations usually sufficed to produce completely racemic IV, m.p. 158°. From the combined mother liquors the enantiomer, $\pm 61^\circ$, was tediously obtained by repeated crystallizations through which racemic IV was concentrated in the crystalline fractions. When the acetate present in the mother liquors possessed an optical rotation $[\alpha]_D^{25} \cong 55^\circ$, it was then possible by further crystallization to concentrate the enantiomer in the solid fraction to an optical rotation $[\alpha]_D^{25} \pm 61^\circ$. The progress of the resolution of the enantiomer could be followed by melting point determinations, for even a small portion of racemate raised the melting point of D- or L-IV above 121–122° (hotbench) or 128–129° (capillary). The racemic and enantiomer fractions were then assayed for radioactivity (if acetoxy labeled IVc) or, when chain labeled, oxidized to benzophenone and benzoic acid, and the benzophenone fractions were converted to their 2,4-dinitrophenylhydrazones and assayed for carbon-14 content; these procedures have been described previously.⁴

(b) **Decomposition without Solvent.**—A dry, 250-cc. flask containing 3.0 g. (0.0087 mole) of L-(+)-IIIa was heated in an oil-bath to 94–95°, at which point the solid decomposed explosively. The solid residue, 2.6 g., was treated as described in part a, and the results are given in Table I.

(c) **In Benzene.**—To 2.5 g. (0.0072 mole) of D-(–)-IIIa was added 250 cc. of dry, pure benzene. The solution was

(17) B. M. Benjamin, H. J. Schaeffer and C. J. Collins, *J. Am. Chem. Soc.*, **79**, 6160 (1957).

allowed to stand in a temperature-controlled room (23°) for 3 weeks. The benzene was removed by evaporation, and the solid was worked up and treated as in part a, and the results are given in Table I.

(d) In *p*-Cymene.—The *p*-cymene used (Distillation Products Industries) was washed with cold, concentrated sulfuric acid until there was no further color change. It was then washed repeatedly with water, dried over anhydrous MgSO₄ and K₂SO₃, and then distilled. The fraction boiling over the range 174–175° was collected and then passed through a column of alumina (Fischer, 80–200 mesh) 1/2 × 18". The optical rotation decreased from +0.11° (neat, 1 dm.) to zero upon the foregoing treatment. Then 0.503 g. (0.0015 mole) of D-(–)-III was dissolved in 50 cc. of previously warmed *p*-cymene and allowed to remain in a flask in the thermostat at 34.70° for 5 days. The mixture was then evaporated and the solid remaining was treated as described in part a, in order to determine the fraction of inversion. The extent of carbon-14 scrambling was not determined. The results are given in Table I.

(e) In Glacial Acetic Acid.—The acetic acid (analytical reagent, Mallinckrodt) was subjected to further purification by boiling with potassium permanganate for several hours, followed by distillation over triacetyl borate as described by Fieser.¹⁸ The thermal decompositions were carried out at 34.7°, 40.5°, 47.7° and 59.0°. In a typical experiment 2.12 g. of L-(+)-IIIa was added to 200 cc. of purified acetic acid which had previously been warmed in the thermostat to 40.5°. A kinetic run was carried out concurrently. When the reaction was complete, as demonstrated by the kinetic results, the acetic acid was removed in an air stream, and the resulting 1,2,2-triphenylethyl-1,2-C¹⁴ acetate (IVab) was treated as described in part a. The results are listed in Tables I and II. In one run (at 40.5°) the reactant IIIa was racemic; in this case the product was repeatedly crystallized from alcohol then subjected to oxidative degradation as previously⁴ described.

(f) Kinetic Runs.—The 2.0-dm. polarimeter tube was equipped with Neoprene washers for the glass end-plates, and a central T-tube fitted with an air condenser. A thermometer was suspended through the condenser so that the bulb was immersed in the liquid in the tube; it was raised before each observation of optical rotation. The polarimeter tube was also fitted with a metal jacket through which water from the thermostat could be circulated by means of a pump. The rubber condenser tubes leading from the thermostat to the condenser jacket were thickly insulated with asbestos tape wrappings, as was the polarimeter jacket itself. In this way the temperature gradient between the polarimeter tube and the thermostat bath was kept to a minimum. Temperature control was ±0.01° except for brief excursions of a few hundredths of a degree during periods of unusual conditions (power overloads, large variations of air-conditioning requirements, etc.) and in no case worse than ±0.1°. The solution for filling the tube was usually made up in a 100-cc. or 200-cc. volumetric flask (about 1 g. of D- or L-IIIa or -IIIc in 100 cc. of purified acetic acid) with acetic acid which had previously been brought to the required temperature in the thermostat bath. The solution was then quickly pipetted into the polarimeter tube, which was tipped back and forth a few times to remove air bubbles and to assure complete mixing. The fate of the carbon-14 label was determined by work-up of the solution in the volumetric flask plus the contents of the polarimeter tube after decomposition was complete. The change in optical rotation of the solution was observed until no further change took place. The times required for each reaction to reach completion varied from six days (at 34.5°) to 6 hours (at 47.7°). The number of separate observations was never less than 20 nor more than 40. The kinetic results were calculated as discussed in the Methods and Results Section and are given in Table I.

(g) Decompositions of III in Acetic Acid–Sodium Acetate Solutions.—The procedure was identical with that outlined in part e, except that for each 100 cc. of glacial acetic acid there was dissolved 10 g. of anhydrous sodium acetate which had been oven dried for 2 weeks.

(h) Decomposition of IIIb in Propionic Acid–Sodium Propionate Solutions.—N-Acetyl-N-nitroso-1,2,2-triphenylethyl-2-C¹⁴-amine (IIIb) was thermally decomposed in pro-

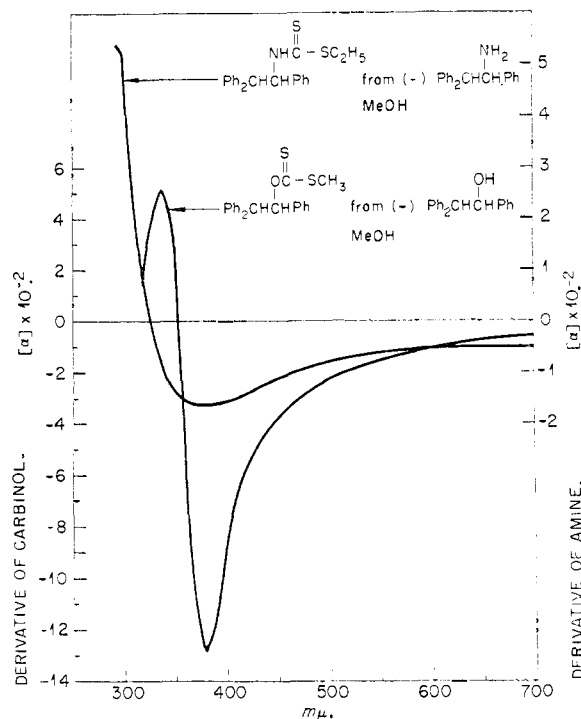


Fig. 1.—Optical rotatory dispersion curves for derivatives of (–)-I and (–)-V.

pic acid containing 10 g. of oven-dried sodium propionate per 100 cc. of acid according to the same procedures employed for the thermal decompositions in acetic acid, part e. Thus 3.5 g. of IIIb (racemic) was dissolved in 250 cc. of propionic acid-sodium propionate solution and maintained at 40.45 ± 0.05° for 3 days. The mixture was poured onto 500 g. of ice and water, then filtered and the collected solid was washed with water and dried. Aliquots of the product were subjected to isotope-dilution analysis to give the yields of acetate IVab and propionate VIab listed in Table III. Another aliquot was dissolved in the least amount of benzene-hexane, placed on a 1/2 × 20" column of Florisil and eluted with benzene-hexane. Several fractions were taken, some were combined and resubjected to Florisil chromatography. In this way IVab and VIab were separated sufficiently so that crystallizations from hexane-petroleum ether (30–60°) and hexane yielded a pure sample of racemic VIab, m.p. 125–126.5°, not depressed by admixture with authentic VI.

Anal. Calcd. for C₂₃H₂₂O₂: C, 83.83; H, 6.73; O, 9.55. Found: C, 83.57; H, 6.74; O, 9.69.

The distribution of carbon-14 in VIab (Table III) was determined by lithium aluminum hydride reduction to Vab, followed by oxidative degradation⁴ to benzophenone and benzoic acid. Another aliquot of reaction product was reduced with lithium aluminum hydride to Vab and the carbon-14 distributions was again determined.⁴ From the fractions of scrambling in VIab and in the gross product, it could be calculated that the 1,2,2-triphenylethyl-1,2-C¹⁴ acetate [IVab] produced had undergone 26.5% scrambling of its carbon-14 label. The gross inversion during thermal decomposition of D-(–)-N-acetyl-N-nitroso-1,2,2-triphenylethylamine in sodium propionate-propionic acid at 40.45° ± 0.05° was determined in a separate experiment in which the combined product IV and VI was reduced to partially racemic D-(+)-1,2,2-triphenylethanol (V), whose optical rotation was determined. The results of all experiments described in this section are listed in Table III.

Deamination of Labeled 1,2,2-Triphenylethylamine (Ia or Ib).—In a typical experiment, a solution of 3.0 g. (0.011 mole) of (–)-1,2,2-triphenylethyl-1-C¹⁴-amine, [α]_D²⁵ –73° (Ia), in 150 cc. of glacial acetic acid was placed in the thermostat bath at 23–24°. To the solution was added 15.7 g. (0.19 mole) of potassium nitrate over a period of 20 minutes. The reaction mixture was stirred vigorously for an

(18) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1955, p. 281.

additional hour. The mixture was then poured into 600 cc. of water and the mixture was extracted with ether. The ether solution was washed with water, bicarbonate solution, then water and concentrated. The solid product IVab was worked up as described in part as in the previous section. The results and conditions are listed in Table IV.

Optical Rotatory Dispersion Data Relating the Configuration of (-)-I and (-)-V.—The optical rotatory dispersions

of derivatives of (-)-I and (-)-V were performed in the Laboratory of Professor Carl Djerassi.¹⁴ The derivatives, prepared by Dr. B. Sjöberg,¹⁹ are shown in Fig. 1, together with the optical rotatory dispersion curves which exhibit like Cotton effects.

(19) For details see B. Sjöberg, A. Fredga and C. Djerassi, *J. Am. Chem. Soc.*, **81**, 5002 (1959).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY, STANFORD, CALIF.]

The Vapor Phase Reaction of 2,3-Dimethyl-2-butene and Ozone¹

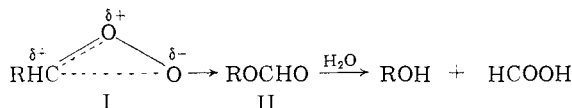
BY HOWARD E. SMITH² AND RICHARD H. EASTMAN

RECEIVED APRIL 10, 1961

In the vapor phase reaction of 2,3-dimethyl-2-butene and ozone the complex mixture of products was found to contain formic acid, formaldehyde, acetone, methanol, carbon dioxide, esters, and either acetic acid or a substance yielding acetic acid on hydrolysis. On the basis of the stoichiometry of the reaction, slightly more than two moles of olefin being required for the complete reaction of one mole of ozone, and the analysis of the mixture of products, it is suggested that two reactions, ozonolysis and allylic oxidation of the olefin, occur simultaneously.

Introduction

The recent appearance^{3,4} of work dealing with the reaction of olefins and ozone in the vapor phase prompts us to report the results of some experiments performed some time ago. This work was a continuation of that reported in a previous communication⁵ concerning the vapor phase ozonolysis of cyclohexene, from which there was obtained an ozonide with different properties from those formed in condensed systems, and which in turn gave the normal product, adipic acid, and the abnormal products, formic acid and *trans*-1,2-cyclohexandiol. It was proposed that the formic acid may be formed through a mechanism suggested by Criegee⁶ in which the intermediate I⁷ rearranges to a formate ester II. Alternatively, there may have been an



ozone-catalyzed allylic oxidation of cyclohexene leading to the formation of cyclohexen-3-ol, the ozonolysis of which would lead to formic acid.⁸

Now we report the vapor phase ozonolysis of 2,3-dimethyl-2-butene. It was chosen as most suitable in that it has no hydrogen attached to the doubly-bonded carbon atoms, is easily prepared in a very pure state, and has a relatively high vapor pressure.

(1) This material is taken from the thesis of Howard E. Smith offered in partial fulfillment of the requirements for the degree of Master of Science, Stanford University, 1954.

(2) Department of Chemistry, Vanderbilt University, Nashville 5, Tenn.

(3) A. E. Heath, S. J. Broadwell, L. G. Wayne and P. P. Mader, *J. Phys. Chem.*, **64**, 9 (1960).

(4) T. Vrbaski and R. J. Cvetanovic, *Can. J. Chem.*, **38**, 1053, 1063 (1960).

(5) R. H. Eastman and R. M. Silverstein, *J. Am. Chem. Soc.*, **75**, 1493 (1953).

(6) R. Criegee, 120th Meeting of the American Chemical Society, New York, N. Y., September 7, 1951, Abstract 22M; *Rec. Chem. Progr.*, **13**, 111 (1957).

(7) The mechanism for the initial attack of ozone at the double bond and the structure and rearrangement of I have recently been discussed by P. S. Bailey, *Chem. Revs.*, **58**, 926 (1958). For Criegee's zwitterion, Bailey suggests the resonance hybrid I.

(8) J. E. Leffler, *Chem. Revs.*, **45**, 400 (1949).

Method and Results

The 2,3-dimethyl-2-butene was prepared by dehydration⁹ of pinacolyl alcohol, and was purified by careful fractional distillation. The correctness of its assigned structure and its purity were demonstrated by comparison of its infrared absorption spectrum with that of 2,3-dimethyl-1-butene, the side product in the dehydration reaction.

The ozonization apparatus was that described⁵ previously. The olefin, as the vapor from a calibrated, thermostated bubbler, was introduced in a metered stream of dry nitrogen to the top of a 10 cm. \times 8 mm. vertically oriented reaction tube, the rate being varied by changes in the flow of nitrogen through the bubbler. The ozone was introduced by passing a metered stream of dry oxygen through a voltage variable, iodometrically calibrated,¹⁰ corona discharge ozonizer and thence into the reaction tube.

At the confluence of the olefin and ozone containing gas streams reaction took place immediately and, as measured by an iron-constantan thermocouple in the reaction tube, the steady-state temperature was 240° at a distance of 0.5 cm. below the point of mixing decreasing to 166° at 5 cm. In addition, as was observed previously in the gas phase ozonolysis of cyclohexene⁵ and 1-hexene,¹¹ an aerosol was produced a short distance down the reaction tube. In order to get complete consumption of ozone it was necessary to use slightly more than twice the molar equivalent of olefin, a stoichiometry similar to that found¹² in the vapor phase ozonolysis at room temperature of 1-hexene, cyclohexene and ethylene.

The reaction conditions under which our observations were made and during which a convenient amount of products could be collected in a reasonable length of time were: nitrogen flow rate, 250

(9) F. C. Whitmore and H. S. Rothrock, *J. Am. Chem. Soc.*, **55**, 1106 (1933).

(10) C. M. Birdsall, A. C. Jenkins and E. Spadinger, *Anal. Chem.*, **24**, 662 (1952).

(11) R. D. Cadle, *Air Pollution Foundation*, Rept. **2**, No. 3, 27 (1956); *C. A.*, **51**, 9984c (1957).

(12) R. D. Cadle and C. Schadt, *J. Am. Chem. Soc.*, **74**, 6002 (1952)