Table IV. Relative Peak Intensities (*m/e* 42–52) in the Mass Spectra of Samples of Dimethyl Ether[a]

| *m/e* | $CH_3$-$OCH_3$ | $CH_3$-$OCD_3$ | 80° [b] | 135° [c] | 120° [b] | 200° [b] |
|---|---|---|---|---|---|---|
| 42 | 9 | 4 | 8 | 7 | 7 | 7 |
| 43 | 30 | 12 | 27 | 29 | 22 | 23 |
| 44 | 15 | 8 | 22 | 20 | 14 | 13 |
| 45 | 1720 | 22 | 1114 | 1400 | 1060 | 1135 |
| 46 | 781 | 26 | 887 | 683 | 781 | 718 |
| 47 | 23 | 641 | 412 | 240 | 368 | 313 |
| 48 | 2 | 1085 | 220 | 223 | 235 | 264 |
| 49 | 0 | 754 | 93 | 115 | 119 | 156 |
| 50 | 0 | 38 | 3 | 4 | 5 | 6 |
| 51 | 0 | 4 | 0 | 1 | 1 | 1 |
| 52 | 0 | 3 | 0 | 0 | 0 | 0 |

[a] All peak intensities are normalized to the spectrum of $CH_3OCH_3$ taken at a pressure of 49.86 μ. [b] Reaction mixture. [c] Sealed tube.

through the −130° trap showed no absorption at 950 $cm^{-1}$ indicating the absence of ethylene.

**Analysis for Total Deuterium in Dimethyl Ether. Infrared Analysis.** Since the carbon–deuterium bond absorbs in the infrared near 2100 $cm^{-1}$, it was decided to use this band to spectrophotometrically determine the extent of carbon–deuterium bonding in the dimethyl ether obtained from the various pyrolyses at different temperatures. Initially, mixtures of undeuterated and deuterated dimethyl ether were prepared with known concentrations of deuterium. These mixtures were then placed in a gas cell at the same pressure and the absorbance spectrum was recorded for each mixture between 1850 and 2400 $cm^{-1}$. The area under the curves for the sample was determined using a planimeter and a plot of peak are against the percentage of carbon–deuterium bonds present was prepared. The known mixtures were prepared from purified samples of dimethyl ether, dimethyl-1,1,1-$d_3$ ether, and dimethyl-$d_6$ ether.

The standardization graph was prepared in the expected range of per cent deuterium from zero to 16% at a relatively high pressure in the cell so that the areas under the peaks would be large even at low concentrations of deuterium and the error in determining areas would be reduced. The spectra of samples of ether from the pyrolyses were recorded using the same cell at the same pressure as the standard samples and the area under the respective peaks were determined. Using the graph prepared from known mixtures it was found that all the samples contained between 11.3 and 11.9% deuterium. The spectrophotometric results were consistent with a deuterium analyses by the falling-drop method.

**Mass Spectral Analysis.** The mass spectra of undeuterated and half-deuterated dimethyl ether were obtained for comparison with the spectra of the partially deuterated mixtures (Table IV). Examination and comparison of the spectra of undeuterated and half-deuterated ethers provided a basis for some simplifying assumptions which allowed for a rather quantitative analysis of the ether products (Table IV). The spectrum of dimethyl ether showed no peak above *m/e* 46 except a trace of *m/e* 47 whereas the dimethyl-1,1,1-$d_3$ ether showed large peaks at *m/e* 48 and 49. Since the molecular weights of mono- and dideuterated ethers are 47 and 48, respectively, it was assumed that they would contribute little to the characteristic dimethyl-1,1,1-$d_3$ ether peak at *m/e* 49, and, therefore, that the peak at *m/e* 49 in the spectrum of the product ether was due only to dimethyl-1,1,1-$d_3$ ether. Using a sample of pure dimethyl-1,1,1-$d_3$ ether to get the sensitivity of the spectrometer to this material, the per cent of this trideuterated ether was calculated.

After the amount of dimethyl-1,1,1-$d_3$ ether in the mixture was determined, the peaks corresponding to this substance were subtracted from the original spectrum leaving a spectrum which contained all ether other than dimethyl-1,1,1-$d_3$ ether and having no peak above *m/e* 48. Assuming that all of the peak at *m/e* 48 was due to dimethyl-1,1-$d_2$ ether and that the sensitivity of the instrument to dimethyl-1,1-$d_2$ ether was the same as to dimethyl-1,1,1-$d_3$ ether, the amount of dimethyl-1,1-$d_2$ ether was calculated.

Since the total deuterium in the sample is known from elemental analysis and from the infrared data, the amount of deuterium determined as the tri- and dideuterated ether could be subtracted from this total to give the amount of deuterium present as dimethyl-$d_1$ ether. The yield of each of these ethers is presented in Table III.

**Acknowledgment.** We wish to thank the National Science Foundation (GP-1704) and the National Institutes of Health (GM-14062) for supporting this research. We also thank Mr. John Voth and Dr. C. C. Delwiche for the mass spectral data.

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# Mass Spectrometry. I. Evidence for Phenyl, Hydrogen, and Methyl Migrations in the Unimolecular Decomposition of Acetophenone Azine Induced by Electron Impact

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*Contribution from the Departments of Chemistry and Biochemistry,*
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*Received December 4, 1967*

**Abstract:** Evidence is reported in the mass spectrum of acetophenone azine for the occurrence of phenyl, methyl, and hydrogen rearrangements. Multicentered rearrangements are involved in a number of the fragmentations, although in at least two instances the data appear to be consistent with both 1,5 and 1,3 migrations of methyl and phenyl. The driving force for these rearrangements appears to be electron delocalization in both reactant and product ions and the formation of stable neutral molecules.

Mass spectral studies have been reported for a number of nitrogen-containing derivatives of aldehydes and ketones.[4] Such studies assume importance for two reasons. First, considerable attention has been paid

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(1) To whom correspondence should be addressed.

(2) Continental Oil Co., Ponca City, Okla.

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(4) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, Chapter 10, and references cited therein.

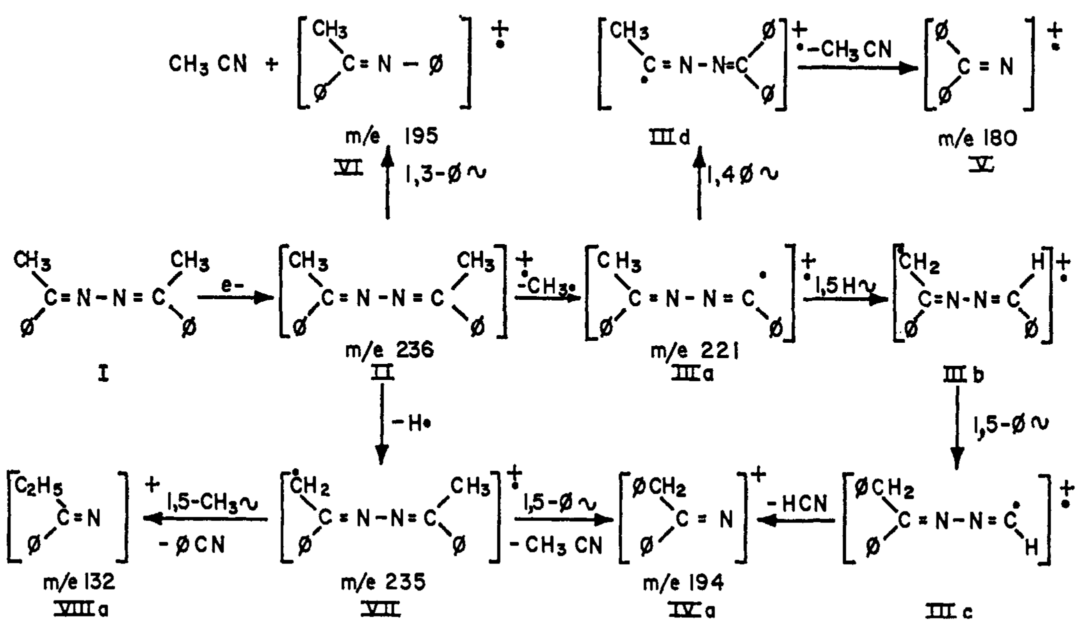

Figure 1. Reaction scheme for fragmentation of acetophenone azine.

to the mass spectral fragmentation patterns of aldehydes and ketones[5] and, hence, it is of mechanistic interest to study the effect of a change in the functional group upon the fragmentation pattern. Second, since these derivatives are useful in the isolation and/or characterization of aldehydes and ketones, general knowledge concerning the fragmentation pattern for such compounds is desirable. The literature reveals no detailed or systematic study of the mass spectrum of azines. Nakata and Tatematsu[6] observed the rearrangement of a number of semicarbazones to the corresponding azines in an all-glass heated inlet system. The occurrence of this process was substantiated by a comparison of the spectra of cyclohexanone semicarbazone and cyclohexanone azine. A number of peaks in the spectrum of cyclohexanone azine was reported but no analysis of the fragmentation pattern was presented.

Of considerable current interest in mass spectrometry are electron-impact-induced migrations of alkyl, aryl, and other functional groups.[7]

We are therefore prompted to report our detailed study of the mass spectral fragmentation pattern of acetophenone azine and evidence for mechanistically interesting migrations of phenyl, hydrogen, and methyl during the fragmentation induced by electron impact.

## Results and Discussion

No thermal decomposition in the mass spectrometer was observed for acetophenone azine (I). Virtually identical spectra were obtained using either a direct probe or a heated inlet system. All reported data were obtained at 70 eV with a direct probe. Tabulated in Table I are the ions present in the spectrum of I whose intensities in per cent ionization ($\Sigma_{38}$%) are greater than 0.7. Elemental compositions for the principal ions of mass 91 or greater are listed in Table II. Metastable peaks were observed for the transitions *m/e* $236^+$ to *m/e* $221^+ + 15$ ($m^* = 206.95$), *m/e* $221^+$ to *m/e* $194^+ + 27$ ($m^* = 170.30$), *m/e* $194^+$ to *m/e* $117^+ + 77$ ($m^* = 70.56$), and *m/e* $118^+$ to *m/e* $77^+ + 41$ ($m^* = 50.25$). Figures 1 and 2 present what appear to be the most reasonable general mechanisms which account for the data.

Table I. Peaks above 0.7% $\Sigma_{38}$ in the Mass Spectrum of Acetophenone Azine

| *m/e* | %$\Sigma_{38}$[a] | RA[b] | *m/e* | %$\Sigma_{38}$[a] | RA[b] |
|---|---|---|---|---|---|
| 51 | 4.4 | 25 | 132 | 2.1 | 12 |
| 76 | 1.1 | 6 | 133 | 1.6 | 9 |
| 77 | 15.1 | 85 | 159 | 4.1 | 23 |
| 91 | 1.6 | 9 | 180 | 2.1 | 12 |
| 103 | 0.8[c] | 5[c] | 194 | 1.2 | 7 |
| 103 | 2.6[d] | 14[d] | 195 | 0.7 | 4 |
| 104 | 2.0[e] | 11[e] | 221 | 17.8 | 100 |
| 104 | 0.7[f] | 3[f] | 235 | 2.5 | 14 |
| 117 | 1.1 | 6 | 236 | 10.1 | 57 |
| 118 | 6.8 | 38 | | | |

[a] Per cent total ionization. [b] Relative abundance. [c] Composition $C_7H_5N$. [d] Composition $C_8H_7$. [e] Composition $C_7H_6N$. [f] Composition $C_8H_8$.

Table II. Peaks Measured at High Resolution

| *m/e* | Δ*m/e* × $10^4$ | Composition |
|---|---|---|
| 91.0548 | 0 | $C_7H_7$ |
| 103.0420 | −2 | $C_7H_5N$ |
| 103.0542 | −6 | $C_8H_7$ |
| 104.0497 | −3 | $C_7H_6N$ |
| 104.0615 | −11 | $C_8H_8$ |
| 117.0581 | 3 | $C_8H_7N$ |
| 118.0651 | −6 | $C_8H_8N$ |
| 132.0811 | −2 | $C_9H_{10}N$ |
| 133.0771 | 5 | $C_8H_9N_2$ |
| 180.0806 | −7 | $C_{13}H_{10}N$ |
| 194.0973 | 3 | $C_{14}H_{12}N$ |
| 195.1046 | −2 | $C_{14}H_{13}N$ |

The extensive conjugation in I suggests formation of the molecular ion, II, *via* loss of a π electron.[8] Although

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(5) Reference 4, Chapter 3, and references cited therein.

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(7) For a recent review see P. Brown and C. Djerassi, *Angew. Chem., Intern. Ed. Engl.*, 6, 477 (1967).

(8) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 51.

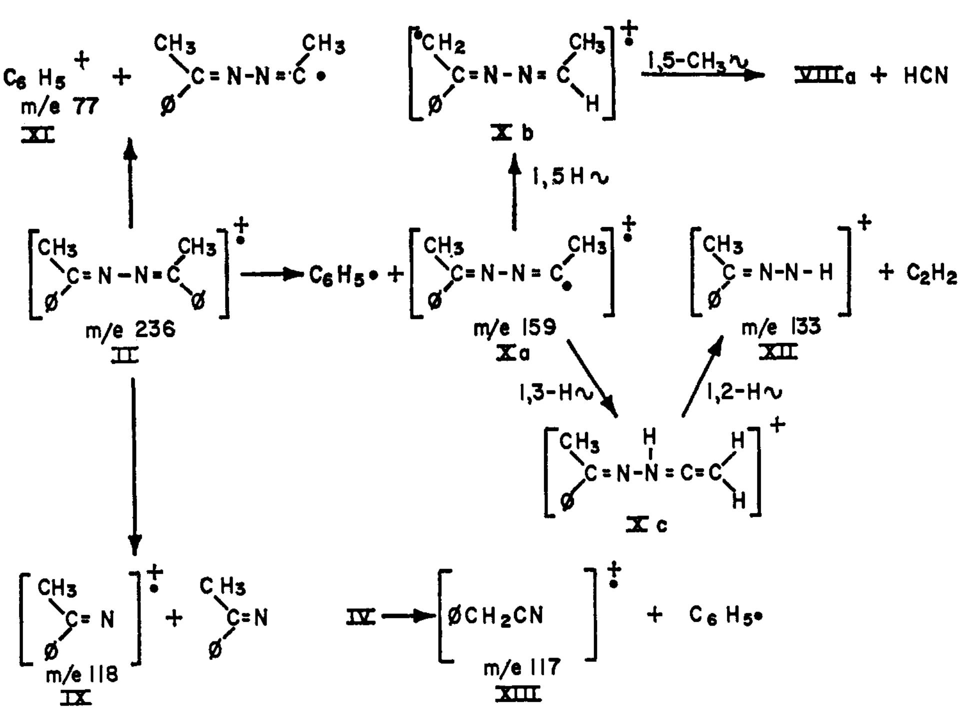
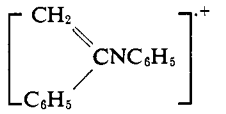


Figure 2. Reaction scheme for fragmentation of acetophenone azine.

II is reasonably stable, comprising 10.1% of the $\Sigma_{38}$ (Table I), the loss of a methyl radical to give the most abundant ion, 17.8% of $\Sigma_{38}$, with mass 221, IIIa, is facile. The metastable peak for the transformation IIIa to IVa and the elemental composition of IVa, Table II, require that this fragmentation involve loss of hydrogen cyanide. Such a fragmentation requiring a double rearrangement is perhaps most easily envisioned (Figure 1) as a 1,5 migration of methyl hydrogen to carbonyl carbon producing IIIb followed by migration of phenyl from this carbon to the methylene carbon with loss of hydrogen cyanide producing IVa. These rearrangements are visualized as proceeding *via* a six-center transition state similar to that in the McLafferty rearrangement.[9] Webster's[10] observation of a 1,5-phenyl migration in the mass spectrum of 3-($\beta$-hydroxy-$\beta$-phenylethyl)-2-iminothiazolidine appears to be the only reported 1,5-phenyl rearrangement.

With some restrictions the data are also consistent with a 1,3-phenyl migration in IIIb to nitrogen with loss of hydrogen cyanide producing IVb. The decomposition pathways for IVb would be expected to be similar to the fragmentation pattern for the possible (M − 1) ion from acetophenone anil. Although the mass spectrum of this compound apparently has not been reported, the anil of benzaldehyde shows, apart from the (M − 1) ion, major fragmentation producing ions of mass 77 and 104.[11] Hence, IVa might reasonably be expected to yield ions of mass 77 (XI) and 117 (XIII). Fragmentation of IVa and/or IVb to produce XIII is confirmed by the presence of the appropriate metastable peak. Assuming a "normal" structure for the benzyl cyanide ion (XIII), its formation from IVb would require either a 1,2- or a 1,3-phenyl migration with loss of phenyl radical. Cleavage of the carbon–nitrogen bond in IVb, if it occurs, would have to proceed exclusively to yield the $C_8H_7$ ion (*m/e* 103$^+$) and phenylnitrene since accurate measurement of the ion with mass 91 showed that only carbon and hydrogen were present. Although the intensity of the $C_8H_7$ ion is not inconsistent with this hypothesis the absence of significant extents of such cleavage in benzaldehyde and various *meta*- and *para*-substituted benzaldehyde anils[11] renders such cleavage improbable.



IVb

A logical and consistent pathway for formation of the ion of mass 180 (V) is the alternate mode of rearrangement in IIIa, a 1,4-phenyl migration to give IIId with loss of acetonitrile.

Das and Kulkarni[12] in a cursory reference to the mass spectrum of I suggest the presence of an ion of mass 195 (VI). High resolution confirms the presence of such an ion with elemental composition $C_{14}H_{13}N$. One mechanism for the formation of VI involves a 1,3-phenyl migration to nitrogen in II with loss of acetonitrile as previously suggested.[12] An alternate route to VI involving a 1,3-phenyl shift to nitrogen in IIIa with loss of a cyano radical is questionable since nitriles are known in general not to undergo $\alpha$ cleavage.[13] Furthermore, such a pathway requires the usually unfavorable formation of an odd-electron ion from an even-electron ion.[14] VI corresponds to the molecular ion derived from acetophenone anil and by analogy[11] could be expected to fragment to give ions of mass 77

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[10] B. R. Webster, *Chem. Commun.*, 124 (1966).

[11] D. J. Elias and R. G. Gillis, *Australian J. Chem.*, **19**, 251 (1966).

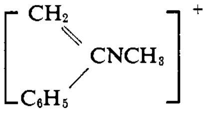
[12] K. G. Das and P. S. Kulkarni, 14th Annual Conference on Mass Spectrometry, American Society of Testing Materials, Committee E-14, Dallas, Texas, 1966.

[13] F. W. McLafferty, *Anal. Chem.*, **34**, 26 (1962).

[14] F. W. McLafferty in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 7.

and 118. Since cleavage of the carbon–nitrogen double bond in the molecular ion from substituted benzaldehyde anils is apparently unimportant, fragmentation of VI, necessarily yielding the $C_8H_8$ ion, probably can be discounted.

Although the (M − 1) ion VII in principle could be formed by loss of either an aromatic or a methyl hydrogen from II, the latter path appears to have the lower energy requirements. VII is the methyl analog of IIIb and would by analogy be expected to undergo fragmentation *via* a 1,5- or 1,3-phenyl migration with loss of acetonitrile producing IVa or IVb and/or a 1,5-methyl shift with loss of benzonitrile producing the ion of mass 132 (VIIIa). The occurrence of a 1,5-methyl rearrangement would be mechanistically interesting since in the McLafferty rearrangement 1,5 migration of methyl has not been observed for ketones[15] or Schiff bases,[16] the only example being in the mass spectrum of di-*n*-propyl ketoxime.[17] A 1,3-methyl migration to produce VIIIb is possible. VIIIb might reasonably fragment to give


VIIIb

XIII and a methyl radical. The absence of a ion of mass 29 either precludes a cleavage of the other carbon–nitrogen bond or requires that VIIIb produce only the $C_8H_7$ ion and methylnitrene. The cleavage of the phenyl–carbon bond in VIIIb, if it occurs, must proceed to produce the phenyl cation because an ion of mass 55 is not observed.

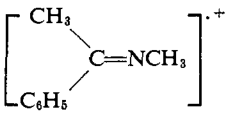
Reasonable reactions producing ion IX (Figure 2) appear to be by fission of the nitrogen–nitrogen bond in II, loss of acetonitrile from Xa, and loss of benzonitrile from IIIa. The first would involve formation of an even-electron ion and a resonance-stabilized odd-electron neutral fragment. The second and third have minimal energy requirements since simple bond cleavage leads to neutral-molecule formation. Although a definite conclusion concerning the relative importance of these pathways is impossible, a simple argument using resonance and neutral-fragment formation appears to favor the latter two.

The molecular ion II apparently decomposes both by loss of phenyl radical producing Xa and fragmentation to give a phenyl cation XI.

The formation of XI by fragmentation of IX with loss of acetonitrile is verified by appearance of the appropriate metastable peak.

A possible precursor of VIIIa or VIIIb (Figure 2) is Xa. This fragmentation would require a 1,5 shift of hydrogen to yield Xb, followed by either a 1,5- or a 1,3-methyl shift and loss of hydrogen cyanide paralleling the transformation of II to IVa or IVb.

The only reasonable precursor of the ion of mass 133 (XII) appears to be Xa. Invoking a 1,3-hydrogen shift to nitrogen to produce Xc followed by a 1,2-hydrogen shift in the ethylenic moiety concomitant with loss of acetylene reasonably accounts for this transformation. It is of mechanistic interest that II undergoes a 1,3-migration of phenyl but not methyl. Migration of the latter would produce XIV and benzonitrile. Such a migration is definitely excluded by high-resolution study


XIV

of the ion of mass 133 (Table II). A possible explanation for this phenomenon is that the transition state for loss of a methyl radical in II, which involves stretching the carbon–carbon bond, is lower in energy than the four-center configuration for rearrangement.

Unfortunately no definite conclusions can be drawn concerning precursors to the hydrocarbon ions of mass 103 and 104. In principle they could be formed from a number of ions in structure II, several of which have been previously discussed.

In addition to other intermediates IVa and IVb are attractive precursor ions of the tropylium ion. Its formation from these ions would lend support to the previously postulated mechanisms for formation of IVa and rearrangement accompanying the fragmentation of IVb.

We suggest that the driving force for the observed rearrangements are extensive electron delocalization and formation of stable neutral molecules[14] hydrogen cyanide, benzonitrile, acetonitrile, and acetylene. The resonance stabilization present in ions II, IIIa, VII, and Xa permits rearrangements to occur which ultimately produce resonance-stabilized ions of reduced mass and stable neutral molecules.

In direct contrast to the fragmentation of I, the electron-impact-induced rearrangements observed for the semicarbazone,[12] thiosemicarbazone,[12] and phenylhydrazone[18] of acetophenone apparently involve only the phenyl group of the hydrocarbon portion of these molecules.

Consequently, azines may be extremely useful in the study of electron-impact-induced rearrangements. A systematic study of the mass spectra of the azine derivatives of ketones and aldehydes is currently in progress.

## Experimental Section

The mass spectrum of acetophenone azine (I), prepared by the method of Cohen, *et al.*,[19] mp 122–123° (lit.[19] 124°), was obtained on the LKB 9000 Prototype and CEC 21-110B mass spectrometers at 70 eV using a direct probe. For measurements using the LKB 9000 instrument, conditions were probe temperature 20°, ion source temperature 310°, filament current 4.0 A, and trap current 65 μA. For the CEC 21-110B the instrument conditions were probe temperature and ion source temperature 95°, filament current 3.5 A, and trap current 100 μA. Virtually identical fragmentation patterns were obtained from both instruments. High-resolution studies to obtain elemental compositions were made on the CEC 21-110B. Data from the LKB 9000 were used to obtain the computer-drawn spectrum and the ion intensities. The intensities of the $C_7H_5N$ and $C_8H_7$ ions, mass 103, and the $C_7H_6N$ and $C_8H_8$ ions, mass 104, were calculated using the total intensities of the 103 and 104 peaks, 3.38 and 2.67% $\Sigma_{38}$, respectively, and the high-resolution ratios of $C_7H_5N$ to $C_8H_7$ and $C_7H_6N$ to $C_8H_8$, 1:3 and 3:1,

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(15) (a) H. Budzikiewicz, C. Fenslau, and C. Djerassi, *Tetrahedron*, 22, 1391 (1966); (b) R. R. Arndt and C. Djerassi, *Chem. Commun.*, 578 (1965).

(16) M. Fischer and C. Djerassi, *Chem. Ber.*, 99, 1541 (1966).

(17) D. Goldsmith, D. Becher, S. Sample, and C. Djerassi, *Tetrahedron Suppl.*, **7**, 145 (1966).

(18) K. G. Das and P. S. Kulkarni, 15th Annual Conference on Mass Spectrometry, American Society of Testing Materials, Committee E-14, Denver, Colo., 1967.

(19) S. G. Cohen, S. J. Groszos, and D. B. Sparrow, *J. Am. Chem. Soc.*, 72, 3947 (1950).

respectively. The mass spectrum of I was also obtained by introduction through the heated inlet system of the CEC 21-110B at 280°.

**Acknowledgments.** We thank Professors O. C. Dermer and E. J. Eisenbraun for discussions relating to manuscript preparation. We acknowledge financial support by the Petroleum Research Fund, Grant 1000-G1, administered by the American Chemical Society, and the Oklahoma State University Research Foundation.

# Syntheses and Optical Rotatory Dispersion Studies of Asymmetric Thiepan-2-ones

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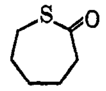
*Contribution from the Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York 11201.* *Received July 24, 1967*

**Abstract:** Optically pure (*R*)-(−)-4-methylthiepan-2-one and (*R*)-(+)-5-methylthiepan-2-one were prepared from pulegone. Racemic 5-methylthiepan-2-one was independently prepared from 4-methylcyclohexanone. The two optically pure thiolactones have complex optical rotatory dispersion spectra in dioxane and in methanol. Between 200 and 620 m$\mu$ two Cotton effects were observed for each compound. They are centered around 234 and 298 m$\mu$, respectively, but only the lower wavelength transitions are definitely observed in the ultraviolet spectra. Solvent effects indicate that the former transition is of type $\pi-\pi^*$ and the latter of type n-$\pi^*$. The relation between the absolute configuration of the asymmetric center and the sign of the low-wavelength Cotton effect is discussed in terms of cyclic *vs.* linear molecular structure. The conformation of the thiolactone ring appears to be the same in both isomers studied.

Several thiolactones with five- and six-membered rings have been known for some time.[2] A number of $\beta$-thiolactones (four-membered rings) have also been reported in the past.[3,4] In a recent paper from this laboratory[5] the synthesis and polymerization of thiepan-2-one ($\epsilon$-thiocaprolactone, I), containing a seven-membered ring, were described. It is the parent compound of the methyl-substituted, asymmetric thiolactones presented in this paper. These optically active thiepan-2-ones were synthesized from an optically active natural product. Their preparation served a double purpose. First, an investigation of the ultraviolet and optical rotatory dispersion spectra was effected. No such study of cyclic thiol esters had yet been undertaken, and little was known of the optical properties of thiolactones. Secondly, these compounds proved to be the most suitable monomers for the preparation of linear, structurally homogeneous poly(thiol esters).[6]



I

## Results

Since Eisenbraun and McElvain[7] converted (+)-pulegone into (−)-$\alpha$-methylglutaric acid, which Fredga[8] has previously correlated with (−)-lactic acid, the terpene has been known to be optically pure and of *R* configuration. (*R*)-(+)-Pulegone (II) was therefore a suitable starting material. Throughout the syntheses, care was taken to avoid reaction conditions that might cause racemization, and no transformations were used which involved the asymmetric carbon or the carbon atoms in $\alpha$ position to it.

(*R*)-(+)-Citronellic acid (III) was prepared from pulegone (II) according to a modified procedure of Plesek[9] (Figure 1). Compound III was esterified with methanol in the presence of a catalytic amount of sulfuric acid. The ozonide of (*R*)-(+)-methyl citronellate (IV) was prepared at −30° in methanol and reduced with sodium borohydride at 0° to give (*R*)-(+)-methyl 6-hydroxy-3-methylhexanoate (V). By bromination of V with phosphorus tribromide, VI was obtained in 43% yield. Esters V and VI were prepared in preference to the corresponding acids because a stable and distillable product which does not undergo cyclization and polymerization was desired after each step. Bromo ester VI was converted to the mercapto acid VII with thiourea according to a general method.[10]

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(1) (a) Author to whom inquiries should be sent at The University of Michigan, Ann Arbor, Mich. 48104. (b) This paper comprises a portion of the dissertation submitted by J. K. Weise in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemistry) to the Graduate School of the Polytechnic Institute of Brooklyn, 1966.

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