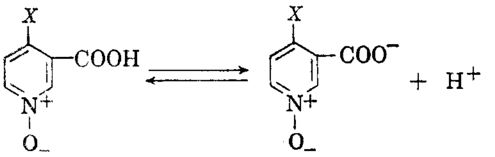
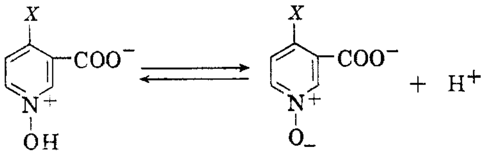


(b)



(c)

successfully correlated by the Hammett equation.

It should be pointed out that, when a compound has substituents both *meta* and *para* to the reacting group, the substituent constants are additive.[5] In the present instance, the *meta* substituent (the —COO⁻ group) is the same in every case.

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# By-products Formed during the Hunsdiecker Decarboxylation and Debromination of Linolenic Acid Hexabromide[1]

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*Received June 15, 1961*

Gas chromatographic analysis of 1-bromo-*cis,cis,cis*-8,11,14-heptadecatriene, a precursor of α-linolenic-1-$C^{14}$ acid, showed it to be contaminated by two compounds in addition to the hydrocarbon described by the original investigators.[3] The combined quantity of these impurities varied according to the conditions used in the synthesis, and ranged from 10 to 25% of the desired bromide. The concern that these two components might become labeled during the $C^{14}$ carbonation to linolenic acid and thus interfere with metabolism studies compelled us to identify them.

The infrared spectrum of a pure sample of each of the unidentified impurities (obtained as gas chromatographic fractions) permitted the identification of one as an ether (strong absorption at 8.95 μ) and the other as a chloro compound (13.7 μ). Positive identification of these as 1-ethoxy- and 1-chloroheptadecatriene was obtained by comparative gas chromatographic behavior.

The synthetic sequence involves a Hunsdiecker reaction on silver hexabromooctadecanoate with subsequent debromination to the unsaturated bromide. Using conditions for the decarboxylation specified by the original investigators (addition of bromine to a refluxing carbon tetrachloride suspension of the silver salt), the chloro compound was obtained in a yield of 20% of the bromide. By modifying these conditions so that the bromine was added to a carbon tetrachloride suspension of the silver salt in an ice bath followed by slow heating to reflux, the yield of chloride was reduced to 8%. During this modified procedure, decarboxylation occurred below reflux temperature.

The formation of alkyl chloride could result either from an intrusion of solvent into a radical-chain mechanism or by attack on solvent by radicals escaping from the solvent cage of a radical-recombination-type mechanism for the Hunsdiecker reaction.[4] The effect of forming the hypobromite in the cold was two-fold. The decarboxylation occurred below reflux temperature, and secondly, the concentration of hypobromite was higher during decarboxylation. Assuming that the reaction proceeds by a radical-chain mechanism, a chain transfer to carbon tetrachloride, being inversely proportional to concentration of the hypobromite,[4c] would account for the decrease in chloroheptadecatriene formation with increased concentration of hypobromite. In deference to the radical-recombination mechanisms, however, it should be stated that an escape-to-recombination ratio which was proportional to temperature would also explain the observed decrease in chloro compound formation.

The 1-ethoxyheptadecatriene presumably arises *via* solvolysis of the 1-bromide during the seven hours of refluxing with zinc in ethanol to affect removal of vicinal bromine substituents from the heptabromoheptadecane. The yield of ether was 2–5% of that of the 1-bromoheptadecatriene.

Neither one of these impurities interferes in the carbonation of the Grignard of the 1-bromoheptadecatriene (to form α-linolenic-1-$C^{14}$ acid) or effect the radio-purity of the product, but knowledge of their presence and concentrations is important in making efficient use of $C^{14}O_2$.

## EXPERIMENTAL

*1-Bromo-cis,cis,cis,-8,11,14-heptadecatriene* was prepared according to the method of Nevenzel and Howton.[3] In some runs the conditions for the Hunsdiecker reaction were modified as given in the text.

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[1] (1) Supported by grant H-4120 from the United States Public Health Service.

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[3] (3) J. C. Nevenzel and D. R. Howton, *J. Org. Chem.*, **23**, 933 (1958).

[4] (4) (a) S. J. Cristol, J. R. Douglass, W. C. Firth, and R. E. Krall, *J. Am. Chem. Soc.*, **82**, 1829 (1960); (b) C. Walling, *Free Radicals in Solution*, John Wiley and Sons, Inc., New York, 1957, p. 389; (c) *Free Radicals in Solution*, p. 148; (d) C. V. Wilson in *Org. Reactions*, **9**, 332 (1957); (e) R. G. Johnson and R. K. Ingham, *Chem. Revs.*, **56**, 219 (1956).

Fractionation of the 1-bromoheptadecatriene in a Babcock-type apparatus[5] was effective in removing the hydrocarbon, but did not give pure samples of any of the other components. Passing a pentane solution of a mixture of 1-ethoxy-, 1-chloro-, and 1-bromoheptadecatriene through an activated silicic acid column effectively removed the ether from the eluted halides. Carbonation of the Grignard reagent[6] prepared from the mixed halides gave linolenic acid, the purity of which was established by gas chromatography of the methyl ester.

An Aerograph Model A-100 chromatograph with a 5-ft. polyester column was used for the isolation of pure samples of 1-ethoxy- and 1-chloroheptadecatriene. The elution characteristics of the various fractions were obtained using a Barber-Coleman Model 10 Chromatograph with a 6-ft. Pyrex column containing 15% succinic acid-ethylene glycol polymer on siliconized Johns-Manville Chromosorb, 80–100 mesh.

*1-Ethoxy- and 1-chloroheptadecatriene* were identified by comparing a hydrogenated sample of each with a homologous series of 1-ethoxy- and 1-chloroalkanes from which the elution time of the $C_{17}$ homolog was determined by extrapolation. The homologous series of ethers was prepared from sodium ethoxide and a mixture of $C_{12,14,16,18}$ 1-bromoalkanes. The chloride series was made by a lithium aluminum hydride reduction of a mixture of $C_{14,16,18,20}$ acids followed by refluxing the alcohols with thionyl chloride–pyridine. The relative retention times for the various fractions at 190° and 139 ml./minute were 1-ethoxy-*cis,cis,cis*-8,11,14-heptadecatriene, 0.42; 1-chloro-*cis,cis,cis*-8,11,14-heptadecatriene, 0.66; and 1-bromo-*cis,cis,cis*-8,11,14-heptadecatriene, 1. Hydrogenation of the mixture over 10% palladium-on-carbon in ethanol gave the 1-substituted heptadecanes with relative retention times of ethoxy, 0.45; chloro, 0.66; and bromo, 1.

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(5) M. J. Babcock, *Anal. Chem.*, **21**, 632 (1949).

(6) D. R. Howton, R. H. Davis, and J. C. Nevenzel, *J. Am. Chem. Soc.*, **76**, 4970 (1954); J. C. Nevenzel and D. R. Howton, *J. Org. Chem.*, **22**, 319 (1957).

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# Conformations of 3,3-Dimethyl-2,4-pentanedione

JOHN B. ROGAN AND DAVID J. ELLIS

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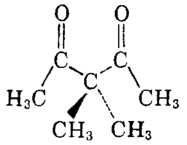
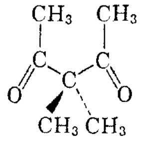
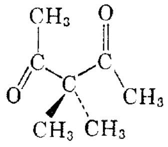
Recently, a number of investigators have reported splitting of the carbonyl band in the infrared spectra of ketones.[1,2] The majority of these cases appear to be due to conformational effects.[3] We wish to report a similar splitting in the carbonyl band of the symmetrical, nonenolic β-diketone, 3,3-dimethyl-2,4-pentanedione (I). This result, coupled with ultraviolet spectral evidence, suggests that I exists as an equilibrium mixture of two conformations (C and D).

As the pure liquid, I exhibits absorption at 5.81 (1721 cm.$^{-1}$) and 5.88 $\mu$ (1701 cm.$^{-1}$) with the more intense band at the higher wave length. Under these conditions the two bands are resolved; however, in carbon tetrachloride solution the lower wave length absorption is present only as a less intense shoulder with both bands at the same positions observed in the pure liquid. By way of comparison, methyl *tert*-butyl ketone (neat) shows a single symmetrical band at 5.85 $\mu$ (1709 cm.$^{-1}$).

A consideration of the possible conformations of I reveals the probable cause for the two bands. Conformation A is unlikely due to the opposed carbonyl dipoles. With conformation B, severe interference results from the proximity of the terminal methyl groups.[4] Form C, on the other hand, is not unduly strained. A final conformation (D, not shown) may be obtained by rotation of the acetyl groups so that the oxygens are both eclipsed by each of the methyls of the *gem*-dimethyl group. This form has no opposed methyl groups and appears to contain the least number of nonbonded interactions.


A


B


C

Conformation C corresponds closely in geometry to a cyclohexanone with an equatorial acetyl group in the α-position. Based upon the well known shift of the carbonyl band observed with cyclohexanones having α-equatorial halogen,[7] the less intense low wave length band of I may be assigned to conformation C.[8] Similarly, the other likely conformation, D, corresponds to an axial α-acetylcyclohexanone with its associated band at 5.88 $\mu$. The effect of

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(1) R. N. Jones and E. Spinner, *Can. J. Chem.*, **36**, 1020 (1958) and references cited therein.

(2) J. L. Adelfang, P. H. Hess, and N. H. Cromwell, *J. Org. Chem.*, **26**, 1402 (1961).

(3) For an exception, see P. Yates and L. L. Williams, *J. Am. Chem. Soc.*, **80**, 5896 (1958).

(4) It has been suggested[5] that conformations of β-diketones corresponding to B may be readily attained. Measurements on Dreiding models reveal that with B there is always a pair of hydrogens on the two methyl groups at internuclear distances of 1.0 Å or less. The van der Waals' radius of the hydrogen atom is 1.2 Å.[6]

(5) G. S. Hammond, *Steric Effects in Organic Chemistry*, M. S. Newman, ed., J. Wiley and Sons, Inc., New York, 1956, p. 447.

(6) L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, 1960, p. 260.

(7) (a) R. N. Jones, D. A. Ramsay, F. Herling, and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 2828 (1952); (b) N. L. Allinger and J. Allinger, *J. Am. Chem. Soc.*, **80**, 5476 (1958).

(8) It might be expected that C could undergo intramolecular hydrogen bonding between the carbonyl oxygen on the right and the activated hydrogens of the left terminal methyl group. However, the position of the infrared band and the ultraviolet spectrum indicate that hydrogen bonding contributes little, if anything, to the structure. For a discussion of the influence of hydrogen bonding on the spectra of ketones, see G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, W. H. Freeman and Co., San Francisco, 1960, pp. 137–139 and 160–164.