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).

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

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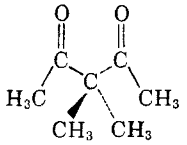
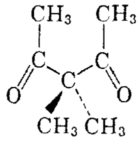
Recently, a number of investigators have reported splitting of the carbonyl band in the infrared spectra of ketones.[1,2] The majority of these cases appear to be due to conformational effects.[3] We wish to report a similar splitting in the carbonyl band of the symmetrical, nonenolic β-diketone, 3,3-dimethyl-2,4-pentanedione (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 μ (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 μ (1709 cm.$^{-1}$).

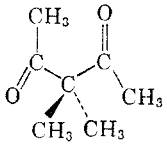
A consideration of the possible conformations of I reveals the probable cause for the two bands. Conformation A is unlikely due to the opposed carbonyl dipoles. With conformation B, severe interference results from the proximity of the terminal methyl groups.[4] Form C, on the other hand, is not unduly 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 μ. 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.

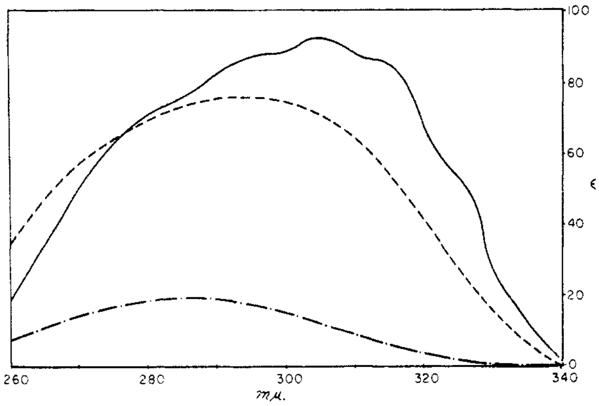

Fig. 1. Ultraviolet absorption spectra of 3,3-dimethyl-2,4-pentanedione in petroleum ether (b.p. 69–96°) (———); 3,3-dimethyl-2,4-pentanedione in absolute ethanol (--------); and methyl *tert*-butyl ketone in petroleum ether (b.p. 69–96°) (-·-·-·)

solvent polarity on the relative concentrations of C and D is consistent with the results obtained with α-bromocyclohexanones.[7b]

The ultraviolet spectra of I in both hydrocarbon and ethanol solvents (Fig. 1) are considerably different from that expected of a compound with a pair of isolated carbonyl groups (*cf.* methyl *tert*-butyl ketone, Fig. 1). In hydrocarbon solvent there is a maximum at 305 mμ (ε 93) and four shoulders—a spectrum that is more complex than that for the normal n → π* transition of simple ketones. With ethanol as solvent the maximum is shifted to lower wave length. This is the usual "blue shift" observed with solvents capable of hydrogen bonding with the carbonyl chromophore.[9]

The presence of an axial α-halogen is known to cause a bathochromic shift in λ_{max} and an increase of the extinction coefficient in the ultraviolet spectra of cyclic ketones.[10] Application of this result to the present case suggests that conformation D is mainly responsible for the observed anomalous ultraviolet absorption. It has been suggested that the shifts observed with axial α-halo ketones are due to hyperconjugation.[10b] While this may also be true with D, another interpretation is that overlap between the p-orbitals on the carbonyl carbons occurs and, in fact, the geometry of D is favorable for this type of overlap. A similar explanation has been used to account for the spectral abnormalities of phenyl and benzyl acetone.[11] In any event, interpretation of the electronic spectra is subject to the usual difficulties in deciding whether a shift in λ_{max} is the result of a change in the ground state or the excited state.

EXPERIMENTAL

3,3-Dimethyl-2,4-pentanedione was prepared essentially by the published method[12] through stepwise dimethylation of acetylacetone. Considerable difficulty was experienced in introducing the second methyl group until it was discovered that reducing the reaction time to 20 min. prior to removal of the ethanol by distillation gave the product in 65–70% yield. Purification by fractional distillation followed by extraction with aqueous cupric acetate yielded material contaminated with 1.5% monomethyl acetylacetone (analysis by gas-liquid chromatography[13]). Low temperature recrystallization from pentane reduced the impurity to < 0.1%.

Infrared spectra were determined on a Beckman IR-5 instrument[14] with an estimated accuracy of ±0.01 μ (± 3 cm.$^{-1}$). Each spectrum was calibrated with the 6.24-μ (1602 cm.$^{-1}$) polystyrene band. Ultraviolet spectra were measured on a Beckman DK-2 spectrophotometer.[15] All solvents used for solution spectra were purified.

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[9] G. J. Brealy and M. Kasha, *J. Am. Chem. Soc.*, **77**, 4462 (1955).

[10] (a) R. C. Cookson, *J. Chem. Soc.*, 282 (1954); (b) E. J. Corey and H. J. Burke, *J. Am. Chem. Soc.*, **77**, 5418 (1955).

[11] R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2303 (1956); S. F. Marsocci and S. MacKenzie, *J. Am. Chem. Soc.*, **81**, 4513 (1959).

[12] R. G. Pearson and E. A. Mayerle, *J. Am. Chem. Soc.*, **73**, 926 (1951).

[13] Separation of acetylacetone from its mono- and dimethylated derivatives was achieved by use of a 10-ft. poly(diethyleneglycol succinate) column operated at 145° with a helium flow rate of 50 ml./min. The compounds emerge in the reverse order of increasing molecular weight.

[14] Purchased with funds from National Science Foundation grant NSF-G16358 for which acknowledgment is gratefully made.

[15] We wish to thank Mr. Wilbert Shimoda for the ultraviolet measurements.

Synthesis of *endo*-2-Carboxy-*endo*-6-aminonorbornane Lactam[1]

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The synthesis of the lactam of *endo*-2-carboxy-*endo*-6-aminonorbornane (III) was of interest because a knowledge of the properties of the monolactam is potentially useful for the solution of the intimate structure of the dilactam of *endo-cis*-2,3-dicarboxy-*endo-cis*-5,6-diaminonorbornane.[2] In the dilactam it is not known whether both the lactam groups are in the usual keto form or whether one of the lactam groups is in the unusual enol form. The lactone of *endo*-2-carboxy-*exo*-5-bromo-*endo*-6-hydroxynorbornane[3] (I) with aqueous sodium hydroxide at room temperature gave *endo*-2-carboxy-6-ketonorbornane (II). Evidence for the structure of the keto acid II is: the elemental analysis; the infrared spectrum, 5.7 μ for the ketone and 5.85

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[1] This work was supported by a research grant, G-11381, from the National Science Foundation.

[2] W. S. Worrall, *J. Am. Chem. Soc.*, **82**, 5707 (1960).

[3] C. D. Ver Nooy and C. S. Rondestvedt, Jr., *J. Am. Chem. Soc.*, **77**, 3583 (1955).