200-μg. amounts of stable terbium, gadolinium and europium were added to make spectrographic identification of the peaks possible. The column used was 20 cm. long and 5 mm. in diameter and a flow rate of 0.3 ml./sq. cm./min. was maintained. The Eu and Gd activities appear as a single broad peak; however, spectrographic analyses make possible the construction of the dashed curves for Eu, Gd and Tb. It is evident on comparing this elution with Fig. 6c of ref. 1 that the activity labeled Gd by Ketelle and Boyd is very likely a terbium activity and that any gadolinium activities they may have had are under the front of the europium peak.

It should be noted that the very small separation of gadolinium from europium and the much greater separation of terbium from gadolinium agrees very well with the expected effect of the half-filled 4f electron configuration as was first pointed out by Boyd.[1]

This work was performed under the auspices of the U. S. Atomic Energy Commission.

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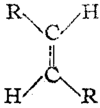
RECEIVED JUNE 19, 1950

The Stereochemical Configuration of the Δ^{22}-Ergostenyl Side Chain

BY R. NORMAN JONES

Althouch the chemical structures of ergosterol and its photo-irradiation products have been known for several years, the stereochemical configuration of the substituents about the Δ^{22}-bond has not been fully established. From a study of the X-ray diffraction pattern of calciferol 4-iodo-5-nitrobenzoate, Crowfoot and Dunitz[1] have assigned a *trans* configuration to the C_{22} and C_{23} hydrogen atoms, and it is the purpose of this communication to draw attention to certain features of the infrared absorption spectra of steroids containing the Δ^{22}-ergostenyl side chain which confirm this structure.

Sutherland and co-workers[2] have observed that the out-of-plane deformation modes of vibration of the olefinic hydrogen atoms in the *trans*-ethylene structure I give rise to a strong absorption band near 965 cm.$^{-1}$, whereas in the *cis*-ethylene structure II, a characteristic band occurs at 690 cm.$^{-1}$. The spectra of several steroids containing the Δ^{22}-ergostenyl side chain have recently been measured in this Laboratory, and in all cases a prominent band is observed at 974–970 cm.$^{-1}$. This band is lacking from the spectra of the corresponding 22,23-dihydro derivatives and from the spectra of analogous compounds containing the cholestanyl side chain.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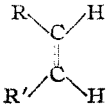
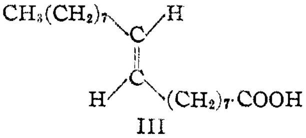

II

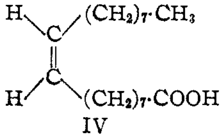
An example is provided by the spectra of ergostane and Δ^{22}-ergostene shown in Fig. 1. A band at the position designated A in Fig. 1 is observed also in the spectra of ergosterol, ergosteryl acetate, lumisteryl acetate and calciferol, all of which contain a Δ^{22}-ergostenyl side chain, but it is lacking from the spectra of Δ^{14}-ergostene, ergostanol-3β, ergostanyl acetate, cholestane, Δ^5-cholestene, cholesterol, cholestenyl acetate, 7-dehydrocholesterol, 7-dehydrocholestenyl acetate and vitamin D_3 which do not contain this group. The 974–970 cm.$^{-1}$ band must be distinguished carefully from a weaker band, designated B in Fig. 1, which is observed at 962–958 cm.$^{-1}$ in most of the above compounds. None of the Δ^{22}-ergostenyl derivatives possess any bands of significant intensity between 700 and 680 cm.$^{-1}$.

It is therefore to be inferred that the 974–970 cm.$^{-1}$ band is associated with the presence of the Δ^{22}-double bond in the molecule which must possess the *trans* configuration.

The olefins listed in the A.P.I. "Catalog of Infrared Spectrograms" on which these correlations are principally based[2] are of a much simpler structure than the steroids considered here. It may therefore be relevant to note that in elaidic acid (III), a band occurs at 968 cm.$^{-1}$ which has been attributed to the *trans*-disubstituted olefin group.[3,4] The spectrum of a liquid film of oleic acid (IV) does not exhibit any pronounced band near 968 nor in the 700–680 cm.$^{-1}$ region, but when such a film is cooled with liquid nitrogen the whole spectrum sharpens to a remarkable degree and a strong band appears at 705 cm.$^{-1}$.

A fuller discussion of the spectra of the compounds mentioned in this paper will be published later; the spectra of calciferol and vitamin D_3 have been published elsewhere.[5]


III


IV

Experimental.—The steroid spectra were determined in carbon disulfide solution using a Perkin-Elmer Model 12C spectrometer.

NOTE ADDED IN PROOF.—Subsequent to the acceptance of this mss. for publication, a similar observation has been reported by Turnbull, Whiffen and Wilson (*Chem. and Ind.*, **33**, 626 (1950)).

Acknowledgments.—The author is indebted for the gift of compounds to Sir Ian Heilbron and Dr. D. H. R. Barton of Imperial College, London; Dr. M. L. Tainter of Winthrop Chemical Co., Rensselaer, N. Y.; and Professor E. R.

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(1) Crowfoot and Dunitz, *Nature*, **162**, 608 (1948).

(2) Barnard, Bateman, Harding, Koch, Sheppard and Sutherland, *J. Chem. Soc.*, 915 (1950).

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(5) Jones, *Chemistry in Canada*, **6**, 26 (94) (1950).

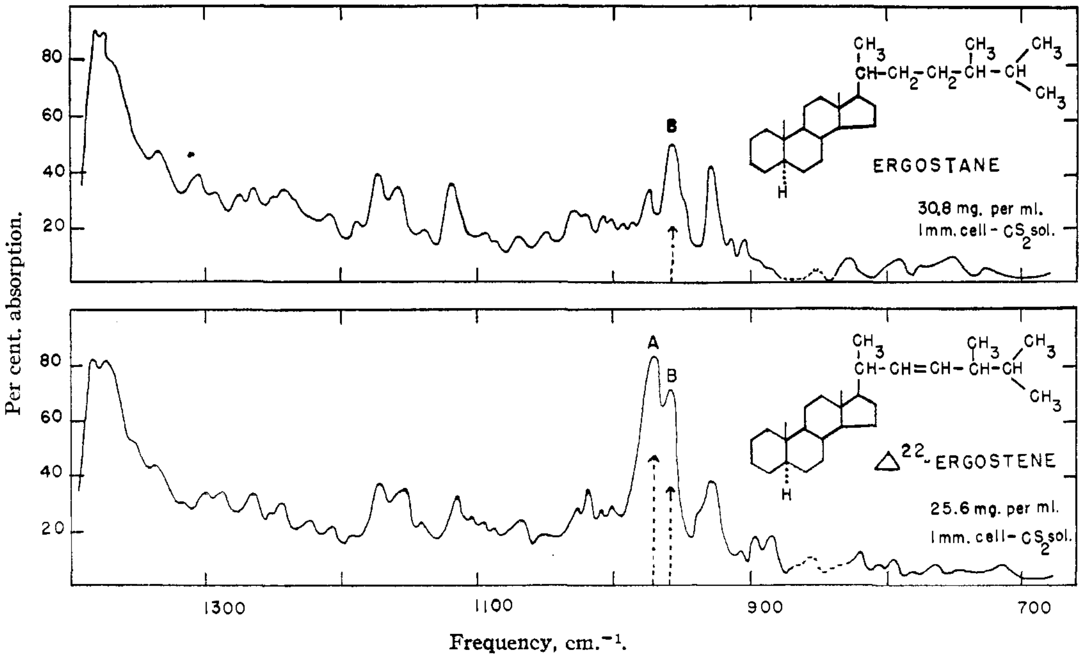

Fig. 1.

H. Jones of Manchester University. His interest in this problem was stimulated by discussion with Dr. Barton.

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Received June 14, 1950

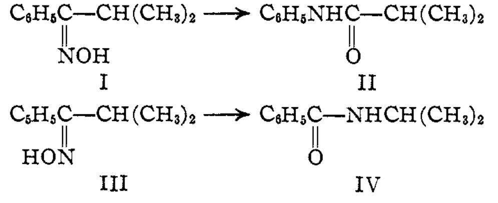
The Geometric Isomers of Isobutyrophenone Oxime

By Henry M. Kissman and John Williams

The melting point of isobutyrophenone oxime has been reported as 58°,[1] 61–62°,[2] 75°[3] and 94°.[4] We have now found that isobutyrophenone oxime when prepared in the usual manner from isobutyrophenone, hydroxylamine hydrochloride and sodium acetate in ethanol melts at 58–60°. When this material was recrystallized slowly from pentane, there could be isolated two sets of crystals. The less soluble variety formed large prisms which melted at 96°, while the more soluble form crystallized in small plates and melted at 90°. A mixture of these two substances melted between 58–60°. Analyses showed these two compounds to be isomeric. Both substances could be cleaved with phthalic anhydride[5] to regenerate isobutyrophenone which was identified by its 2,4-dinitrophenylhydrazine derivative.[6]

It seemed probable that we were dealing with the *syn*- and *anti*-isomers of isobutyrophenone oxime. This possibility was confirmed through the application of the Beckmann rearrangement. The higher melting form rearranged easily with benzenesulfonyl chloride in pyridine[7] at room temperature into isobutyranilide (II), but the lower melting material had to be heated on the steam-bath with the same reagents in order to effect rearrangement. It yielded a compound which was identified through a mixed melting point as N-isopropylbenzamide (IV). This amide, which has not been previously reported, was prepared from isopropylamine and benzoyl chloride.

The results of these rearrangement reactions indicate that the higher melting form is the *anti*-phenyl (I) and the lower melting substance the *syn*-phenyl isomer (III) of isobutyrophenone oxime.



$$\begin{array}{ccc} C_6H_5\underset{\underset{\text{NOH}}{\|}}{C}{-}CH(CH_3)_2 & \longrightarrow & C_6H_5NH\underset{\underset{O}{\|}}{C}{-}CH(CH_3)_2 \\ \text{I} & & \text{II} \\ C_6H_5\underset{\underset{\text{HON}}{\|}}{C}{-}CH(CH_3)_2 & \longrightarrow & C_6H_5\underset{\underset{O}{\|}}{C}{-}NHCH(CH_3)_2 \\ \text{III} & & \text{IV} \end{array}$$

A few attempts toward a chromatographic separation of these isomers were made. A very low degree of separation could be obtained when a hexane solution of the oxime mixture was passed through a column of alumina. The lower melting form was adsorbed slightly less strongly than the other isomer. This method was, however, useless for actual separation since it did not give the higher melting isomer in pure form.

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