Fig. 1.—Infrared spectrum of D-*ribo*-hexos-3-ulose (2 mg. in 400 mg. KBr).

always moved faster than fructose. We now wish to report the successful isolation of the previously unidentified component of the enzymatic hydrolysis product of 3-ketosucrose and to present data on its isolation, physical constants and structure.

Crystalline 3-ketosucrose (200 mg.) was hydrolyzed with β-D-fructofuranoside fructohydrolase (3 mg.) at pH 5.0 in 0.01 M acetate buffer for 2 hr. at room temperature. The non-fructose moiety of the reaction product reacted readily at room temperature in the arsenomolybdate reaction of Nelson[7] (while fructose required heating at 100° before it would show a positive reaction with this reagent). When the hydrolysis mixture was passed through a charcoal bed (Darco G-60, acid-washed) most of the fructose was found in the effluent while the non-fructose moiety was chiefly retained on the charcoal. The latter component was removed from charcoal with 50% ethanol (v./v.) and concentrated to a sirup (at 32°). Adsorption and elution from charcoal was repeated four times because a small quantity of fructose remained behind on each previous passage. The combined sirups were finally dissolved in water-saturated butanol and, following removal of water under reduced pressure (at 35–37°), the product was precipitated from butanol by refrigeration at −25° for 1–2 weeks. Recrystallization from *n*-butyl alcohol was repeated three times whereupon the product was obtained, fructose-free, in approximately 45% yield as highly hygroscopic, colorless, rhombic crystals. The crystalline material gave a single spot of R_f 0.42 ($R_{fructose}$ 1.16) on chromatography in acetone–AcOH–water (4:1.2:10)[8] and of R_f 0.51 ($R_{fructose}$ 1.36) in methyl ethyl ketone–acetone–water (3:1:0.6).[9] M.p. (in presence of drying agent to reduce hygroscopicity) 58–60° (uncor.), $[\alpha]^{26}D$ +14.8° (*c* 1, H$_2$O). *Anal.* Calcd. for C$_6$H$_{10}$O$_6$·0.5H$_2$O: C, 38.5; H, 5.9. Found: C, 38.9; H, 6.24. Infrared spectrum (KBr disk) gave sharp bands at 1730 and 1626 cm.$^{-1}$ indicative of the presence of a free carbonyl group and water, respectively (Fig. 1).

Periodate oxidation[10] of the new substance consumed 2.9 moles of periodate per mole of starting material with the concomitant formation of 1.7 moles of titrable free acid. Reduction of the isolated material with NaBH$_4$[11] produced two polyols which were identified by paper chromatography and paper electrophoresis as sorbitol and allitol.

From the above data the newly isolated non-fructose product of the enymatic hydrolysis of 3-ketosucrose is identified as D-*ribo*-hexos-3-ulose ("3-ketoglucose").

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A NOVEL PHOTOCHEMICAL REACTION. CONVERSION OF α,β-UNSATURATED KETONES TO ACETONYLCYCLOPROPANES

Sir:

In contrast to the extensive investigations undertaken on photochemical reactions of cyclic α,β-unsaturated carbonyl compounds,[1] the photochemistry of simple acyclic α,β-unsaturated ketones, other than *cis–trans* isomerization, has not been explored.[2] As part of our systematic study of the photochemistry of such ketones, we have examined the photochemical behavior of ketones Ia and Ib. We wish to report that these undergo a novel photochemical reaction, resulting in the formation of derivatives of acetonylcyclopropane.

Ia, R = H   IIa, R = H   III
Ib, R = CH$_3$ IIb, R = CH$_3$
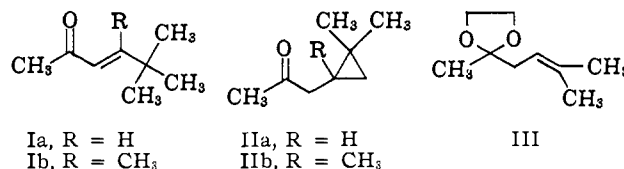
Irradiation of 5,5-dimethyl-3-hexen-2-one (Ia) (5.0 g. in 400 ml. of ether) by means of a Hanovia 450-watt light source, employing a Pyrex filter, led first to a *cis–trans* isomerization, reaching a photostationary state in 2 hr.,[3] followed by the slow formation of a third ketone. The reaction was followed by vapor phase chromatography until the yield of the new ketone reached a maximum, after 46 hr. Distillation, b.p. 52° (15 mm.), and further purification by vapor phase chromatography, afforded 1.5 g. of isomeric ketone (38% based on reacted starting material; approximately 20% of starting ketone recovered) (found: C, 76.11; H, 11.30); $\gamma_{max}^{CCl_4}$ 3055 and 1724 cm.$^{-1}$; semicarbazone, m.p. 145–146° (found: C, 59.03; H, 9.31; N, 22.64). The n.m.r. spectrum exhibited the following peaks: a two-proton doublet at 7.75 τ (J_{AB} = 7.4 c.p.s.); three-proton singlets at 7.97, 8.97 and 9.05 τ; a broad multiplet in the 9.1 τ to 9.7 τ region and a broad triplet at 10.12 τ, corresponding to a total of three hydrogens. This spectrum, in particular the characteristic absorption of cyclopropane methylenic hydrogens at high field, suggested the formulation of the structure of this ketone as IIa. This structure assignment was confirmed by an independent synthesis of 3-(2,2-dimethylcyclopropyl)-2-propanone, carried out in the following manner. Isobutylideneacetone was converted to the ethyleneketal III, shown by n.m.r. analysis to be the β,γ-unsaturated isomer.[4] The ketal was treated in a Simmons–Smith reaction with methylene iodide and zinc–copper couple,[5] resulting in an 80% yield of IIa, identical in every respect with the ketone obtained from the irradiation of Ia.

(1) See, for example, P. De Mayo and S. T. Reid, *Quart. Rev.*, **15**, 393 (1961), for early references; H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962); W. W. Kwie, B. A. Shoulders and P. D. Gardner, *ibid.*, **84**, 2268 (1962); J. J. Hurst and G. H. Whitham, *Proc. Chem. Soc.*, 160 (1959); 116 (1961).

(2) A report by R. Ya. Levina, V. N. Kostin and P. A. Gembitskii, *Zh. Obshch. Khim.*, **29**, 2456 (1959), describing the conversion of 1-acetylcyclohexene and of ketone Ib to their respective β,γ-unsaturated isomers could not be substantiated in our present work. The photochemistry of methyl propenyl ketone in the vapor phase has been investigated [R. S. Tolberg and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **80**, 1304 (1958)]; at room temperature the principal reaction was found to be *cis–trans* isomerization.

(3) The *cis* isomer was isolated by vapor phase chromatography and identified by comparison of its infrared spectrum with the published spectrum of the *cis* ketone, *cf.* R. Heilman, G. de Gaudemaris and P. Arnaud, *Bull. soc. chim. France*, [5], 119 (1957). The *cis–trans* equilibrium ratio was approximately 45:55.

(4) It was shown that double bond migration from the α,β-position to the more stable β,γ-position occurred in the α,β-unsaturated ketal under the ketalization conditions.

(5) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1824 (1959).

The conversion to 3-cyclopropyl-2-propanones appears to be a general reaction of α,β-unsaturated ketones containing a quaternary carbon at the γ-position. Under similar conditions, 4,5,5-trimethyl-3-hexen-2-one (Ib) (1.1 g. in 400 ml. of ether, irradiation for 31 hr.) is converted to the isomeric ketone IIb in 55% yield (based on reacted starting material; approximately 10% starting ketone recovered), isolated by vapor phase chromatography (found: C, 76.96; H, 11.30), $\gamma_{max}^{CCl_4}$ 3055, 1724 and 1712 (shoulder) cm.$^{-1}$, semicarbazone, m.p. 143–144° (found: C, 60.99; H, 9.90; N, 21.00). The n.m.r. spectrum revealed an unsymmetrical two-proton doublet at 7.65 τ (J_{AB} = 3 c.p.s.), three-proton singlets at 7.98, 8.90, 8.96 and 9.00 τ and a characteristic high field cyclopropane methylene singlet at 9.83 τ, corroborating the structural assignment as 3-(1,2,2-trimethylcyclopropyl)-2-propanone (IIb). The mechanism and scope of this reaction are being investigated.

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CONCERNING THE STERIC REQUIREMENTS FOR THE ALLYLIC 1,3-SPIN–SPIN COUPLING OF PROTONS[1]

Sir:

Although the long range 1,3-spin–spin coupling of a vinylic proton with an allylic proton is a well recognized[2-5] phenomenon, there is a paucity of information concerning the steric requirements for such interaction. The only definitive studies that we are aware of involve acyclic Δ^1-olefins with preferred conformations about the C_2–C_3 bond due to dipole repulsions[4] or to steric hindrance[5] and indicate strongly that coupling is minimal when the C-1 methylene group and allylic proton are eclipsed,[4,5] while there appears to be no simple relationship of coupling constants to *cis–trans* geometrical configuration.[3,6] We wish to present evidence that in a
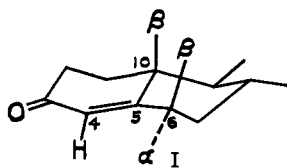
number of Δ^4-3-keto steroids (structure I) the vinylic C-4 proton is strongly 1,3-coupled (J = 1.5–2.0 c.p.s.) to the axial 6β-proton and, in 19-nor steroids, to the axial 10β-proton as well, while coupling with the equatorial 6α-proton is negligible. This defines in a rigid system the conditions for minimal and for significant (probably maximal) 1,3-coupling.

The C-4 vinyl proton of a number of representative Δ^4-3-keto steroids (*e.g.*, testosterone) appears in the n.m.r. spectrum as a single peak at about 344 c.p.s.[7]

(1) Supported in part by Grants A-4044 and CY-4550, U. S. Public Health Service, and T-185, American Cancer Society.

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(3) R. R. Fraser and D. E. McGreer, *Can. J. Chem.*, **39**, 505 (1961), and references therein.

(4) E. B. Whipple, J. H. Goldstein and G. R. McClure, *J. Am. Chem. Soc.*, **82**, 3811 (1960); E. B. Whipple, *J. Chem. Phys.*, **35**, 1039 (1961).

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(6) *Cf.* D. R. Davis and J. D. Roberts, *ibid.*, **84**, 2252 (1962).

(7) All spectra were obtained using a Varian 4300 n.m.r. spectrometer, with field homogeneity control unit, at a frequency of 60 Mc.p.s. The

with an average line width[8] of 3.4 c.p.s. Examination of the C-4 proton peak of the 6β-deuterio derivatives of androst-4-ene-3,17-dione, testosterone and cholest-4-en-3-one revealed a marked sharpening of the peak with a line width of 2.3 c.p.s. in each case which suggested that despite the absence of a split C-4 proton peak there is a 1,3-coupling between the C-4 and C-6β protons in the undeuterated steroid. Three 6β-methyl-Δ^4-3-ketones similarly exhibited sharpened C-4 proton peaks with an average line width of 2.3 c.p.s. (2.1, 2.4 and 2.5 c.p.s.), further indication of C-4, 6β proton–proton coupling in the unsubstituted cases.

In contrast, the examination of four 6α-methyl-Δ^4-3-ketones demonstrated in each case a doublet for the C-4 proton with J = 1.5–2.0 c.p.s.,[9] while the 6α-methyl group itself exhibited the normal doublet splitting pattern of a methyl group on a carbon atom bearing a single proton. These results can be interpreted only as C-4, 6β proton–proton coupling.

A similar pattern was found in the isomeric 6-bromo-androst-4-ene-3,17-diones. The 6β-bromo isomer exhibited a sharpened C-4 proton peak of width 2.4 c.p.s. at 355 c.p.s. (average frequency) while the 6α-proton, due to coupling with the C-7 protons, appeared as a typical ABX quartet centered at 296 c.p.s. The 6α-bromo isomer, however, showed a doublet for the C-4 proton centered at 391 c.p.s., J = 2.0 c.p.s., and an octet for the 6β-proton (center 304 c.p.s.) due to coupling with the two C-7 protons and the C-4 proton.

It is apparent that 1,3-coupling is significant only in the case of the axial 6β-proton while the effect of the 6α-equatorial proton appears to be negligible. Sterically, the 6β-axial C–H bond but not the 6α-equatorial bond is positioned for efficient overlap with the π orbitals of the double bond and the transmission of spin information may be pictured as proceeding *via* the electrons associated with the C-6 proton directly to the π-electrons.[10] These findings appear to confirm the prediction of Karplus[10] that the position of the allylic proton with respect to the π-orbitals of the double bond will be the predominant factor in determining the magnitude of 1,3-coupling. It may be noted that although the 6α-proton in Δ^4-3-keto steroids geometrically approximates the eclipsed conformation of the olefins in ref. 4 and 5, and confirms that coupling is minimal in this position, 1,3-coupling should also be minimal when the two protons are *trans* if the two C–H bonds are in the same plane.

It was predictable that 19-nor-Δ^4-3-keto steroids should exhibit evidence of 10β-hydrogen as well as 6β-hydrogen coupling with the C-4 proton since the C–H bond in both cases is approximately perpendicular to the plane passing through the C-4, 5 and 6 carbon atoms and hence in an optimal position for σ–π overlap. A number of 19-nor-Δ^4-3-ketones, unsubstituted at C-6, were investigated and all exhibited marked broadening of the C-4 proton peak (av. line width 4.3 c.p.s.) indicative of additional coupling with the 10β-proton but no definite splitting was observed. However, the C-4 proton of 6β-methyl-19-norandrost-4-ene-3,17-dione appeared as a sharp doublet at 353.5 c.p.s., J = 2.0 c.p.s.,

samples were dissolved in deuteriochloroform and the spectra were calibrated using the side-band technique. Peak positions are reported in c.p.s. downfield from tetramethylsilane (internal reference).

(8) The full line widths were measured in each case at half-height. The homogeneity of the magnetic field was such that the average line width of the tetramethylsilane reference peak was 1.2 c.p.s. The uncertainty in measurement is estimated to be ±0.2 c.p.s.

(9) 6α-Methyltestosterone, 2.0 c.p.s.; 6α-methylprogesterone, 2.0 c.p.s.; 6α-methyl-17α,21-dihydroxypregn-4-ene-3,20-dione, 1.5 c.p.s.; 6α-methyl-17α-hydroxypregn-4-ene-3,20-dione, 1.5 c.p.s. *J*-values are estimated to be accurate to ±0.2 c.p.s.

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