More research is needed to demonstrate the importance of the monomeric species in ethereal solutions. The "monomeric"[5] molecular weight evidence for dilute ethereal solutions and the "monomeric"[6] molecular weight evidence over a wide range of concentrations in THF strongly suggest that the RMgX species is an important part of the Grignard reagent in solution and should be included in any equilibrium describing this reagent.

We are continuing to study those aspects of the Grignard problem which can be investigated by X-ray diffraction.

(6) E. C. Ashby and W. E. Becker, *J. Am. Chem. Soc.*, **85**, 118 (1963).

(7) Deceased Oct. 9, 1963.

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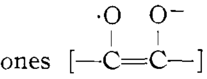
RECEIVED OCTOBER 8, 1964

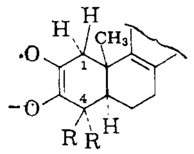
Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. II. Alicyclic Semiquinones Derived from Steroidal Ketones and 2-Decalones[1,2]

Sir:



Alicyclic semiquinones $[-\overset{\cdot O}{\overset{|}{C}}=\overset{O^-}{\overset{|}{C}}-]$ are formed by exposure to oxygen of solutions of decalones and certain steroidal ketones in dimethyl sulfoxide (DMSO) containing potassium *t*-butoxide. Interpretation of the e.s.r. spectra[3] observed in the oxidation of 3-keto steroids defines the nature of the initial A/B ring juncture. Extension of this work may provide a means of establishing the position of the carbonyl functions in the A or D rings[4] as well as the position of certain substituents in a steroidal ketone.

Lanosterone produced a four-line spectrum with peaks of equal intensity. The spectrum is consistent with **1** which contains nonequivalent (axial and equatorial) hydrogen atoms at C-1. On the basis of the theory of β-splittings in aliphatic semiquinones,[1] the larger hyperfine splitting constant (h.f.s.c.) of 12.74 gauss is assigned to the axial hydrogen atom and the smaller interaction of 4.76 gauss assigned to the equatorial hydrogen atom. Oxidation of 5α-androstan-3-one gave the 14-line spectrum shown in Fig. 1.[5,6] The spectrum is consistent with oxygenation at C-2 to give **2**[7] with β-splitting by four different hydrogen atoms at C-1 and C-4, a_H = 5.69, 7.00, 12.04, and 12.66 gauss. Similar e.s.r. spectra were obtained in the oxidation of 5α-androstan-17β-ol-3-one, 5α-androstan-3,17-dione, 5α-cholestan-3-one, and 5α-pregnan-3,20-dione, all compounds with a *trans*-A/B ring junction.



1, R = CH_3
2, R = H, $\Delta^{8(9)}$ absent

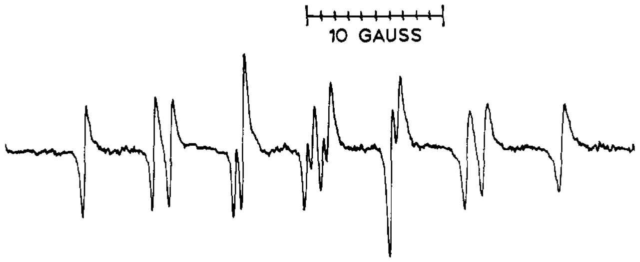


Fig. 1.—First derivative e.s.r. spectrum of radical anion produced by reaction of oxygen with 5α-androstan-3-one (0.03 *M*) in DMSO in the presence of 0.07 *M* potassium *t*-butoxide. Solution was exposed to air for 1 min. after deoxygenated solutions of the ketone and base were mixed. Above spectrum was recorded 1 hr. after exposure of solution to air.

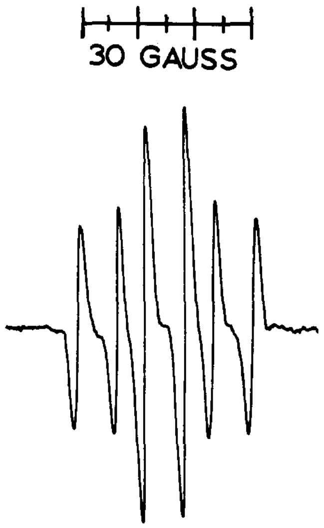


Fig. 2.—First derivative e.s.r. spectrum of radical anion produced by reaction of oxygen with 5β-pregnan-3-one (0.05 *M*) in DMSO in the presence of 0.1 *M* potassium *t*-butoxide. Solution was exposed to air for 50 sec. before spectrum was recorded.

Oxidation of 3-keto compounds with a *cis*-A/B ring junction, such as 5β-androstan-17β-ol-3-one, 5β-androstan-3,17-dione, 5β-cholestan-3-one, 5β-pregnan-3-one, or 5β-pregnane-3,20-dione, produced the 1:1:2:2:1:1 spectrum of Fig. 2.[8] This spectrum demands interaction of the odd electron with a pair of equivalent hydrogen atoms and with one additional hydrogen atom and is consistent with **3**, *i.e.*, oxygenation at C-4. It is not yet obvious whether the equivalent hydrogen atoms are both at C-2 or one at C-2 and one at C-5.

The oxidation of 2-decalones showed considerably lower selectivity than the oxidation of the 3-keto steroids. However, similar directive effects were apparent. Thus, *trans*-2-decalone produced approxi-

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[1] G. A. Russell and E. T. Strom [*J. Am. Chem. Soc.*, **86**, 744 (1964)] is considered to be Part I of the series.

[2] Reactions of Resonance Stabilized Anions. XIV. Work supported by a grant from the National Science Foundation.

[3] All spectra were obtained at 25–28° using a Varian V-4500 spectrometer with 100 kc./sec. field modulation utilizing a flat cell and inverted-U mixing chamber [G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964).

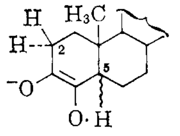
[4] Oxidations of 16- and 17-ketoandrostanes are extremely selective and give different radical anions consistent with oxygenation at C-15 and C-16, respectively.

[5] The same spectrum was obtained when oxygen was introduced simultaneously with the base or when the ketone was allowed to ionize before exposure to oxygen. Experimentally we have found it more convenient to mix deoxygenated solutions of the ketone and potassium *t*-butoxide before exposure of the surface of the solution to air.

[6] Initially and at high radical concentrations <5% of a second radical anion consistent with **3** can be detected.

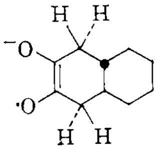
[7] Oxygenation of cholestanone and lanost-8-en-3-one in basic solution to the 2,3-diketones has been described by E. J. Bailey, D. H. R. Barton, J. Elks, and J. F. Templeton, *J. Chem. Soc.*, 1578 (1962).

[8] For 5β-pregnan-3-one h.f.s.c. were a_H = 7.46, 12.49, and 12.49 gauss, while for 5β-androstan-17β-ol-3-one h.f.s.c. were 7.59, 12.71, and 12.71 gauss.



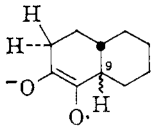
3

mately three parts of **4** to one of **5** whereas *cis*-2-decalone produced approximately two parts of **5** to one of **6**.



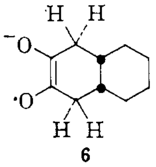
4

a_H = 6.49, 6.49, 12.98, and 12.98 gauss



5

a_H = 6.96, 12.63, and 12.63 gauss



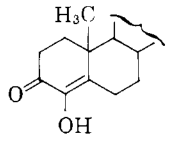
6

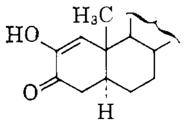
a_H = 6.38, 7.14, 12.34, and 13.29 gauss

The formation of **5** from both *cis*- and *trans*-2-decalone indicates that either an initially formed radical anion or an oxidation intermediate, possibly the 1,2-diketone, underwent epimerization at C-9. Upon standing **5** decayed more rapidly than **4** or **6** so that after 3 hr. only **4** remained in the oxidation product of *trans*-2-decalone. The spectrum of **4** was a 1:2:3:4:3:2:1 heptet while the spectrum of **5** was a 1:1:2:2:1:1 sextet. The spectrum assigned to **6** contained 13 lines and is consistent with four magnetically nonequivalent protons. This observation demands that **6**, a derivative of *cis*-decalin, has a frozen conformation in regard to the spectrometer frequency of ~9,500 Mc./sec.

The results so far obtained suggest that e.s.r. spectroscopy, particularly when used in conjunction with oxidation of ketones in basic solution,[7,9] is a versatile and unique analytical technique for structural assignments in rigid alicyclic systems as well as a powerful tool for conformational analysis in nonrigid alicyclics.[1]

(9) It has been established by ultraviolet spectroscopy that the major products of base-catalyzed oxidation of 3-keto steroids with *cis*- and *trans*-A/B ring junctions are





respectively [B. Camerino, B. Patelli, and R. Sciaky, *Tetrahedron Letters*, 554 (1961)].

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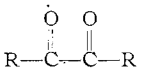
Photoformation and Photosensitized Formation of the Isobutyril and Pivalil Anion Radicals

The oxidation of acyloins (R–CH(OH)–CO–R) to their respective diketones (R–CO–CO–R) in aerated basic solutions was studied some 30 years ago by Weissberger and co-workers.[1] They concluded that the oxidation proceeds *via* a dienolization step and that the acylil anion radical was present in some of the reaction



$$R-\overset{\dot{O}}{\overset{\vdots}{C}}-\overset{O}{\overset{\|}{C}}-R$$

solutions. The presence of several such acylil radicals was confirmed by spectrophotometric,[2] susceptibility,[3] and electron spin resonance (e.s.r.)[4-6] measurements. In this communication some results are presented on the photoformation and photosensitized formation of such radicals in two sterically hindered acyloins, *i.e.*, isobutyroin (R = $(CH_3)_2CH$–) and pivaloin (R = $(CH_3)_3C$–). The sensitization results are of particular interest, since they represent a case in which radicals due to *both* the sensitizing and sensitized molecules have been observed simultaneously. Moreover, these results may provide additional insight into the reaction mechanism of sensitizers with alcohols in basic solutions.

Typical solutions used in the present work consisted of 0.5 *M* acyloin solutions and 0.5 *M* NaOH in alcohol-water (70:30). Such a solution of butyroin readily exhibited the five-line e.s.r. spectrum shown in Fig. 1 (upper). The lines have the approximate intensity ratio of 1:4:6:4:1, and are due to the butyril radical (R = C_3H_7–). Only the four equivalent α-protons interact with the uncoupled electron, which is delocalized over the two carbonyl groups. The proton hyperfine splittings and g-value were found to be 13.5 Mc. and 2.005, respectively.

Attempts to form radicals in solutions of the sterically hindered isobutyroin and pivaloin by simply mixing the reactants were unsuccessful. However, when these solutions were exposed to light (3130 Å.) in the n → π^* absorption bands of the acyloins, the respective radicals formed readily. Selective light irradiation was accomplished with a Bausch and Lomb monochromator equipped with a 200-w. mercury lamp. The isobutyril radical thus formed exhibited the spectrum of Fig. 1 (lower). The three lines with the intensity ratio of 1:2:1 are due to the two α-protons (hyperfine coupling = 6.0 Mc., g-value = 2.005). In some spectra additional incompletely resolved lines (coupling = 0.4 Mc.) were detected in the main lines, suggesting a weak interaction with the twelve β-protons. The spectrum due to the pivalil radical (not shown here) consisted of 11 lines (out of possible 19) due to the interaction of 18 β-protons (coupling = 0.8 Mc., g = 2.005). Further amplification revealed the missing proton lines as well as some C^{13} satellites.

Titration of the acyloins with sodium phenolindophenol, which oxidizes specifically 1,2-dienols,[7] revealed a similar pattern. Deaerated butyroin solutions reduced dilute solutions of this reagent in the absence of light, indicating the dienol character of butyroin in basic solution. Isobutyroin and pivaloin, on the other hand, reduced the phenolindophenol only upon excitation with 3130-Å. light. The results thus far suggest, therefore, that dienolization in sterically hindered acyloins may be accomplished *via* an excited state (singlet or triplet) of their anions.

The addition of a sensitizer, such as benzophenone, greatly enhanced the production of the isobutyril and pivalil radicals. Moreover, radicals were now formed at wave lengths other than 3130 Å. Thus, the strong

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(1) A. Weissberger, E. Strasser, H. Mainz, and W. Schwarze, *Ann.*, **478**, 112 (1930); A. Weissberger, *Ber.*, **65B**, 1815 (1932).

(2) L. Michaelis and E. S. Fetcher, *J. Am. Chem. Soc.*, **59**, 1246 (1937).

(3) J. L. Ihrig and R. G. Caldwell, *ibid.*, **78**, 2097 (1956).

(4) R. Dehl and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 1793 (1963).

(5) G. A. Russell and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 744 (1964).

(6) H. C. Heller, unpublished results.

(7) B. Eistert in Houben-Weyl, "Methoden der Organischen Chemie," Vol. II, E. Muller, Ed., 4th Ed., Georg Thieme Verlag, Stuttgart, 1952, p. 395.