

liberating an H atom regenerates e_{aq}^- by reaction 1.

While no attempt was made to ensure uniform irradiation, the average steady-state (e_{aq}^-)_{ss} concentration is $1.37 \times 10^{-8} M$. This concentration is derived from our optical density of 0.0082, a value of $1.5 \times 10^4 M^{-1} \text{ cm.}^{-1}$ for the molar extinction coefficient of e_{aq}^- and a cell length of 40 cm.

Our demonstration that steady-state concentrations of e_{aq}^- produced by Co^{60} γ -rays may be measured suggests several applications. (1) Accelerators are not required for hydrated electron research. Co^{60} γ -ray sources generating 500–1000 rads/sec. are adequate if multiple-pass irradiation cells are used. (2) Hydrated electron rate constants may be determined by measuring the (e_{aq}^-)_{ss} in the presence of different scavengers. (3) The study of transient spectra such as I_2^- , HO_2 , O_2^- , and other intensely absorbing radicals should be possible. (4) The steady-state measurement of e_{aq}^- offers excellent dosimetric possibilities. The hydrogen saturated alkaline solution can be irradiated indefinitely without change in composition.

Acknowledgment.—The above work was carried out in a remote controlled cave. We gratefully acknowledge the cooperation and technical assistance of Messrs. Harry Youngquist, Howard Harvey, and Joseph Hoe.

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The Structure of Ethylmagnesium Bromide Dietherate. An X-Ray Diffraction Study¹

Sir:

The structure of the Grignard reagent has been the subject of much speculation and intense study in recent years.^{2,3} In our study the crystal and molecular structures of the ethyl Grignard reagent in diethyl ether have been determined by X-ray diffraction techniques. Since various structures for the Grignard reagent have been proposed based in part or wholly on evidence obtained from experiments on the ethyl Grignard reagent, we feel that our results have a strong bearing on this problem.

Crystals of $\text{C}_2\text{H}_5\text{MgBr} \cdot 2(\text{C}_4\text{H}_{10}\text{O})$ are monoclinic with cell constants $a = 13.18 \pm 0.03$, $b = 10.27 \pm 0.03$, $c = 11.42 \pm 0.03 \text{ \AA.}$, and $\beta = 103.3 \pm 0.3^\circ$. The space group is $P2_1/c$ and there are four molecules per unit cell. The data were recorded photographically at about -75° on the Buerger precession camera using molybdenum radiation. The intensities of 626 independent reflections were judged visually. The bromine and magnesium positions were obtained from a Patterson map, and the remaining positions were determined by a combination of the least-squares and Fourier methods. At this point in the structure determination, the discrepancy factor $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ is 0.10. The crystallographic details as well

(1) Contribution No. 1603. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) R. E. Dessy and G. S. Handler, *J. Am. Chem. Soc.*, **80**, 5824 (1958); R. E. Dessy, G. S. Handler, J. H. Wotiz, and C. A. Hollingsworth, *ibid.*, **79**, 3476 (1957).

(3) S. Hayes, *Ann. chim. (Paris)*, **8**, 545 (1963); A. Kirrmann, R. Hamelin, and S. Hayes, *Bull. soc. chim. France*, 1395 (1963); R. Hamelin, *ibid.*, 684, 692 (1961).

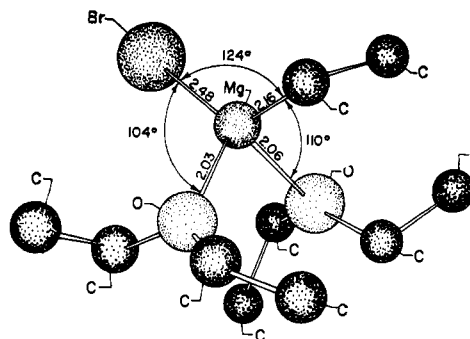
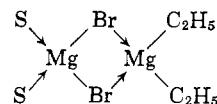


Fig. 1.—The molecular configuration of $\text{EtMgBr} \cdot 2\text{Et}_2\text{O}$.

as the results of further refinement will be reported later.

The structure consists of ethylmagnesium bromide monomers (Fig. 1) with the ethyl group, a bromine atom, and two ether molecules forming a distorted tetrahedron about a single magnesium atom. The bond distances to the magnesium atom as well as some representative angles are shown in Fig. 1. The Mg-O bond distance is among the shortest Mg-O distances known. The next shortest Mg-Br distance is 5.81 Å, which is too long to correspond to any sort of chemical bond and rules out all dimeric structures involving bridging bromine atoms. There is essentially trigonal bonding about the oxygen atoms. For a given ether molecule, the distance from the magnesium atom to a plane defined by the methylene carbons and the oxygen atom is about 0.2 Å. The terminal methyl groups on a given ether molecule are nearly opposed to each other.

Previously,³ the favored structure for the ethyl Grignard in the solid state was



where S represents the solvent. It was proposed that the number of molecules of solvent associated with this species is nonintegral and increases with the basicity of the solvent. Also, it was concluded that no species of definite chemical composition existed in the solid state.

In our study, diffraction photographs were taken of many preparations which were purified to various degrees, and in no case was a species obtained different from the monomeric species described. The evidence for the existence of a species of definite chemical composition, namely, the monomeric species, is therefore strong. These results are consistent with those found with the phenyl Grignard reagent, which is also monomeric in the solid state.⁴ Although the evidence presented here does not apply directly to the liquid state, the observations discussed by Stucky and Rundle⁴ in this regard apply equally well here.

In our experiments crystals were grown from the liquid state by slowly cooling the sample with a stream of cold nitrogen gas. This method is similar to that used by Vreugdenhil.⁵ Other authors³ have based their studies on crystals obtained by evaporation of the solvent from a solution of Grignard reagent. This difference may indeed be significant.

(4) G. D. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 1002 (1963).

(5) A. D. Vreugdenhil and C. Blomberg, *Rec. trav. chim.*, **82**, 453, 461 (1963).

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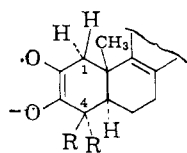
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Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. II. Alicyclic Semiquinones Derived from Steroidal Ketones and 2-Decalones^{1,2}

Sir:

Alicyclic semiquinones $[-\overset{\cdot}{\text{O}}\text{C}=\overset{\cdot}{\text{C}}\text{O}-]$ 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. spectra³ 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 rings⁴ 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 5 α -androstan-3-one gave the 14-line spectrum shown in Fig. 1.^{5,6} The



- 1, R = CH₃
 2, R = H, $\Delta^{8(9)}$ absent

torial) 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 5 α -androstan-3-one gave the 14-line spectrum shown in Fig. 1.^{5,6} The

(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

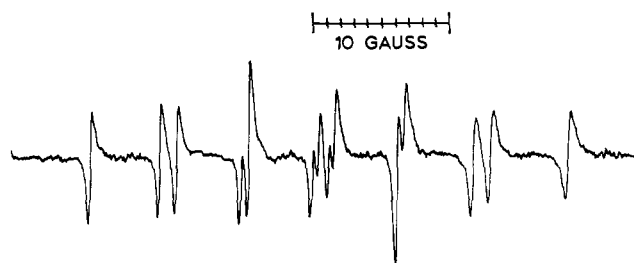


Fig. 1.—First derivative e.s.r. spectrum of radical anion produced by reaction of oxygen with 5 α -androstan-3-one (0.03 *M*) in DMSO in the presence of 0.07 *M* potassium *t*-butoxide. Solution was exposed to air for 1 min. after deoxygenated solutions of the ketone and base were mixed. Above spectrum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

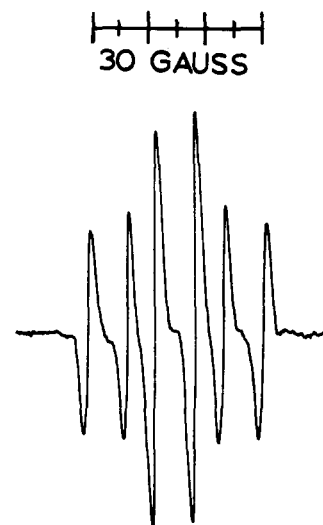


Fig. 2.—First derivative e.s.r. spectrum of radical anion produced by reaction of oxygen with 5 β -pregnan-3-one (0.05 *M*) in DMSO in the presence of 0.1 *M* potassium *t*-butoxide. Solution was exposed to air for 50 sec. before spectrum was recorded.

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, $a_{\text{H}} = 5.69, 7.00, 12.04,$ and 12.66 gauss. Similar e.s.r. spectra were obtained in the oxidation of 5 α -androstan-17 β -ol-3-one, 5 α -androstan-3,17-dione, 5 α -cholestan-3-one, and 5 α -pregnan-3,20-dione, all compounds with a *trans*-A/B ring junction.

Oxidation of 3-keto compounds with a *cis*-A/B ring junction, such as 5 β -androstan-17 β -ol-3-one, 5 β -androstan-3,17-dione, 5 β -cholestan-3-one, 5 β -pregnan-3-one, or 5 β -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-

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 5 β -pregnan-3-one h.f.s.c. were $a_{\text{H}} = 7.46, 12.49,$ and 12.49 gauss, while for 5 β -androstan-17 β -ol-3-one h.f.s.c. were 7.59, 12.71, and 12.71 gauss.