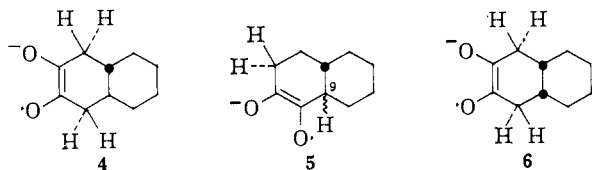


mately three parts of **4** to one of **5** whereas *cis*-2-decalone produced approximately two parts of **5** to one of **6**.

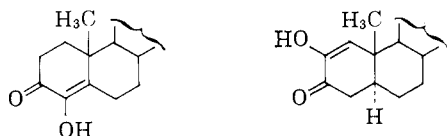


$a_H = 6.49, 6.49, 12.98, \text{ and } 12.98$  gauss     $a_H = 6.96, 12.63, \text{ and } 12.63$  gauss     $a_H = 6.38, 7.14, 12.34, \text{ and } 13.29$  gauss

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  $\sim 9,500$  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,<sup>7,9</sup> 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.<sup>1</sup>

(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)].

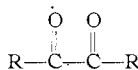
DEPARTMENT OF CHEMISTRY  
IOWA STATE UNIVERSITY  
AMES, IOWA

GLEN A. RUSSELL  
ERACH R. TALATY

RECEIVED AUGUST 31, 1964

### Photoformation and Photosensitized Formation of the Isobutyryl 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.<sup>1</sup> They concluded that the oxidation proceeds *via* a dienolization step and that the acylil anion radical was present in some of the reaction



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

solutions. The presence of several such acylil radicals was confirmed by spectrophotometric,<sup>2</sup> susceptibility,<sup>3</sup> and electron spin resonance (e.s.r.)<sup>4-6</sup> 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<sub>3</sub>)<sub>2</sub>CH-) and pivaloin (R = (CH<sub>3</sub>)<sub>3</sub>C-). 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 butyryl radical (R = C<sub>3</sub>H<sub>7</sub>-). Only the four equivalent  $\alpha$ -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  $n \rightarrow \pi^*$  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 isobutyryl 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  $\alpha$ -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  $\beta$ -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  $\beta$ -protons (coupling = 0.8 Mc., *g* = 2.005). Further amplification revealed the missing proton lines as well as some C<sup>13</sup> satellites.

Titration of the acyloins with sodium phenolindophenol, which oxidizes specifically 1,2-dienols,<sup>7</sup> 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 isobutyryl and pivalil radicals. Moreover, radicals were now formed at wave lengths other than 3130 Å. Thus, the strong

(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.

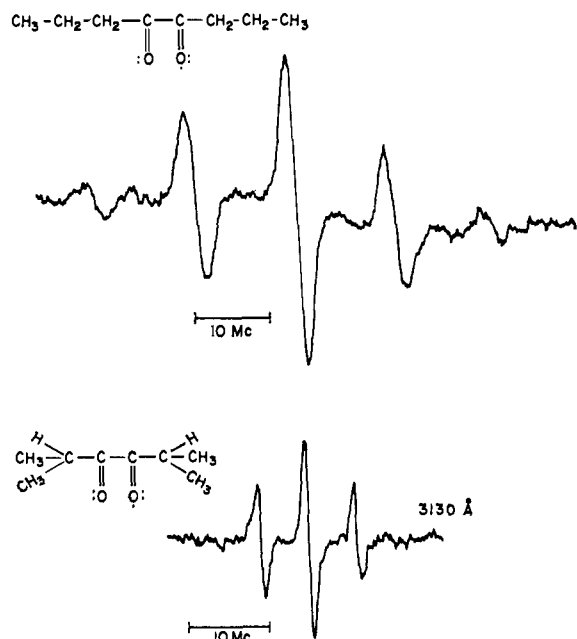


Fig. 1.—Electron spin resonance spectra of butyryl (upper) and isobutyryl (lower) anion radicals.

e.s.r. signals of the isobutyryl radical in Fig. 2 (lower) were produced in an isobutyroin solution containing 0.01 *M* benzophenone, exposed to 3660 Å., the  $n \rightarrow \pi^*$  band of benzophenone. Note that Fig. 1 (lower) and Fig. 2 (lower) were obtained with the same spectrometer settings of microwave power and amplification, and that Fig. 2 shows even  $C^{13}$  lines of the radical. Clearly, there is an order of magnitude increase in the radical concentration in the sensitized run. Comparison of the upper and lower curves of Fig. 2 shows that the benzophenone ketyl anion radical  $(C_6H_5)_2C=\dot{O}$  is also present in the sensitized experiment. The spectrum of the ketyl radical (Fig. 2, upper) was observed in an alcohol-water solution of 0.01 *M* benzophenone and 0.5 *M* NaOH exposed to 3660-Å. light. This radical has been previously observed.<sup>8</sup>

Two tentative mechanisms may be suggested for the photosensitized results:

(1) Triplet-triplet energy transfer from the excited benzophenone to the isobutyroin anion, followed by the enolization and oxidation of the latter. A singlet-singlet transfer can be ruled out, since the singlet state of the former ( $26,000 \text{ cm.}^{-1}$ )<sup>9</sup> is lower than that of the latter (centered at  $34,500 \text{ cm.}^{-1}$ ). The position of the triplet of isobutyroin is unknown but may be assumed to be close to that of acetone, *i.e.*, approximately  $24,500 \text{ cm.}^{-1}$ .<sup>10</sup> Hence, energy transfer from the benzophenone triplet ( $24,250 \text{ cm.}^{-1}$ )<sup>9</sup> is conceivable. In the framework of this mechanism, the formation of the ketyl radical would be an independent process, just as it is in the solution devoid of acyloin.

(2) The effective transfer of an electron from the acyloin anion to the excited, electrophilic benzophenone molecule (probably triplet), resulting in the reduction of the latter and the oxidation of the former without an enolization step. This over-all reaction could proceed either through an actual electron transfer, yielding

(8) P. B. Ayscough and R. Wilson, *J. Chem. Soc.*, 5412 (1963). The excitation energy is not specified in this work.

(9) V. L. Ermolaev, *Soviet Phys.-Usp.* (Engl. Transl.), 6, 333 (1963).

(10) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, 66, 1144 (1962).

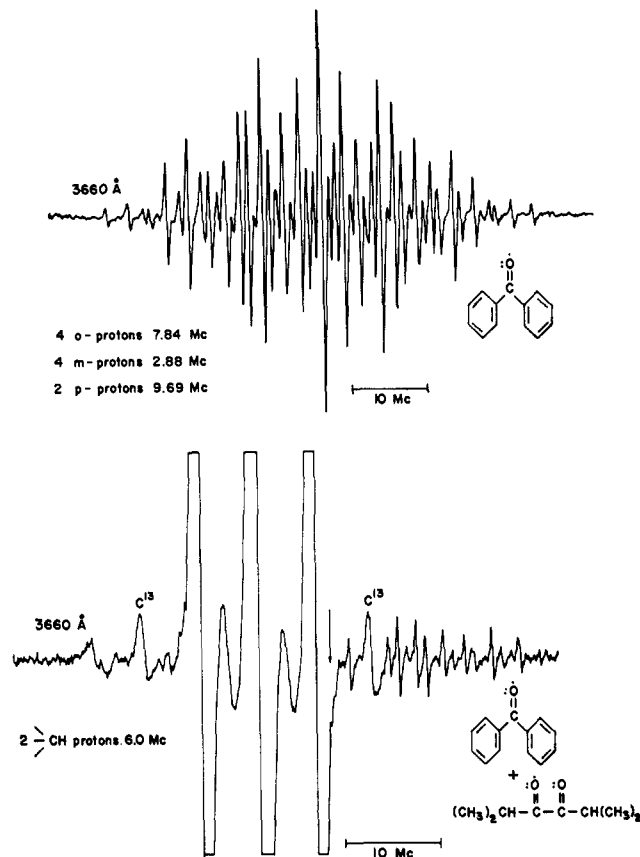


Fig. 2.—Electron spin resonance spectra of the benzophenone ketyl (upper and lower) and isobutyryl anion (lower) radicals; arrow indicates position of center line of the ketyl radical.

directly  $(C_6H_5)_2C=O$ ,  $R-C-C-R$ , and water, or *via* a hydrogen-atom transfer step.<sup>11</sup> In the latter case,  $(C_6H_5)_2\dot{C}-OH$  and the isobutyryl radical would form first, and the former would then give  $(C_6H_5)_2C=\dot{O}$  and  $H_2O$  in basic solution.

Further work on these phenomena, including the use of other sensitizers, is now in progress.

(11) J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *J. Am. Chem. Soc.*, 81, 1068 (1959); W. M. Moore, G. S. Hammond, and R. P. Foss, *ibid.*, 83, 2789 (1961).

(12) In some former publications, C. Heller was used.

SCIENTIFIC LABORATORY  
FORD MOTOR COMPANY  
DEARBORN, MICHIGAN

HANAN C. HELLER<sup>12</sup>

RECEIVED SEPTEMBER 26, 1964

### Structure in the Ionization Efficiency Curves of $Ar_2^+$ by Pulsed Mass Spectrometry

Sir:

Previous observations of the ionization efficiency curves of  $Ar_2^{+1-8}$  (using continuous ion repulsion)

- (1) J. A. Hornbeck and J. P. Molnar, *Phys. Rev.*, 84, 621 (1951).
- (2) J. S. Dahler, J. L. Franklin, M. S. B. Munson, and F. H. Field, *J. Chem. Phys.*, 36, 3332 (1962).
- (3) W. Kaul, U. Lauterbach, and R. Fuchs, *Naturwiss.*, 47, 353 (1960).
- (4) W. Kaul and R. Fuchs, *Z. Naturforsch.*, 15a, 326 (1960).
- (5) W. Kaul and R. Taubert, *ibid.*, 17a, 88 (1962).
- (6) F. H. Field, H. N. Head, and J. L. Franklin, *J. Am. Chem. Soc.*, 84, 1118 (1962).
- (7) M. S. B. Munson, J. L. Franklin, and F. H. Field, *J. Chem. Phys.*, 37, 1790 (1962).
- (8) M. S. B. Munson, J. L. Franklin, and F. H. Field, *J. Phys. Chem.*, 67, 1542 (1963).