(9 mm). The product exhibited ir and nmr spectra in accordance with its structure.

The α-halocarboxylic acids and esters are exceedingly valuable intermediates, providing routes to the corresponding α-amino acids and a host of other α-substituted derivatives. The dialkylacetic acids are also valuable intermediates. This new synthesis evidently provides a highly convenient route to these intermediates which should greatly enhance their synthetic utility. Of even greater significance may be the implication that this new method of forming carbon–carbon bonds is of considerable generality for α-halogen-substituted carbanions.

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Mechanisms of Photochemical Reactions in Solution. LII.[1] Photoreduction of Camphorquinone

Sir:

Camphorquinone (1) is of potential interest in photochemistry because it is optically active, is nonenolizable, and has its carbonyl functions in a rigid *cis* configuration. In addition, a recent report[2] indicated that, in the absence of oxygen, the compound has little or no reactivity in photoreduction reactions. These properties suggest that the diketone would be of interest as an optically active sensitizer and also raise interesting questions concerning structure–reactivity relationships in the photoreduction reaction. In the course of an investigation of 1, we have found that the compound does in fact undergo photoreduction and that an interesting, symmetrical radical is an intermediate.

1
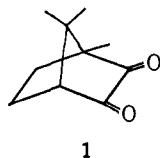
Irradiation of 1 was carried out in the cavity of an epr spectrometer with samples degassed by five freeze–thaw cycles under high vacuum. In methanol solution the signal was of an intensity too low to be resolved. However, in isopropyl alcohol, a species having a spin resonance signal with an easily resolvable hyperfine structure was observed. The spectrum is shown in Figure 1, along with a theoretical reconstruction based on the splitting constants listed in Table I. Symmetri-

Table I. Coupling Constants of Radicals in Gauss

	A_{CH_3}	A_{H_4}	A_{H_5}	A_{H_6}	$A_{H(endo)}$
2[a]	0.55, 0.15	2.08	3.01	3.01	0.221
3	0.7	2.0	3.4	3.4	...

[a] From ref 3.

(1) Part LI: G. Ziegler and G. S. Hammond, *J. Am. Chem. Soc.*, **90**, 513 (1968).

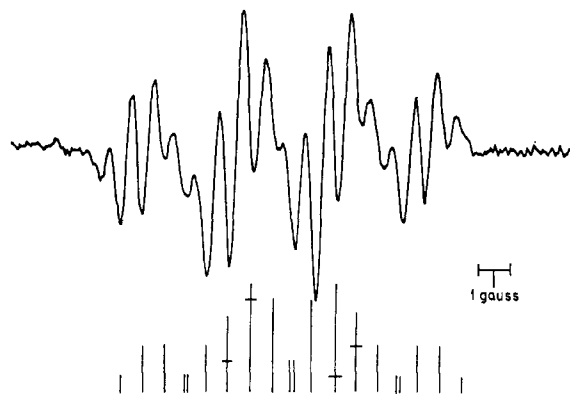(2) J. Meinwald and M. O. Klingele, *ibid.*, **88**, 2071 (1966).

Figure 1. Esr spectrum of radical produced from camphorquinone on irradiation in isopropyl alcohol (top); calculated spectrum based on splitting constants (bottom) given in Table I.

cal structure 3 is assigned to the radical because of the simplicity of the spectrum and the good agreement of the splitting constants for 3 with those of semidione 2, produced by reduction of 1 with alkali metals.[3] In this connection it should be noted that, for the corresponding radicals derived from biacetyl,[4] the two methyl groups are not equivalent, showing very different A_{CH_3}
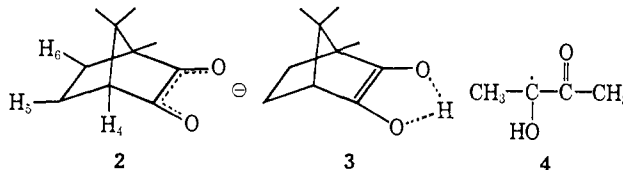
values. An additional splitting of 2.07 gauss, assigned to the hydroxyl hydrogen, is observed. While it is possible that the splitting constant assigned to H_4 in the spectrum of 3 is due to the hydroxyl proton, it is unlikely in view of the similarity of the splitting constants for H_5 and H_6, and that for one of the methyl groups of 2. It seems reasonable to propose that these differences stem from the fact that 4 probably has its carbonyl group in the *trans* configuration, while those of 3 are held rigidly *cis*. Under our experimental conditions a splitting constant as low as 0.5 gauss would most likely not have been observed. Thus we believe that the simplicity of the hyperfine pattern would be compatible with two unsymmetrical structures that interconvert rapidly by oscillation of the bridging hydrogen atom between two positions, which might explain our failure to observe an interaction with the hydroxyl hydrogen. We note that Prichett[5] has observed conversion of the spectrum of 4 to a symmetrical splitting pattern at pH 0.5. This must be associated with protonation to form a conjugate acid of 4 without disturbing the *trans* configuration since the one value of A_{CH_3} in strong acid is 8.3 gauss.

The reaction has every characteristic of a normal photoreduction reaction with isopropyl alcohol serving as a hydrogen donor. The triplet state of the diketone is probably involved because the reaction can be sensitized by benzophenone.[6] Irradiation of a solution of

(3) G. A. Russell, E. T. Strom, E. R. Talaty, K. Y. Chang, R. D. Stephens, and M. C. Young, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **27**, 3 (1966).

(4) H. Zeldes and R. Livingston, *J. Chem. Phys.*, **47**, 1465 (1967).

(5) R. J. Prichett, *Mol. Phys.*, **12**, 481 (1967).

(6) Interesting kinetic complications arise from the chemical crossing of the paths of reduction of the substrate and sensitizer. These results will be described later in a full report. The inference concerning mechanism is drawn from experiments under conditions that lead to essentially complete energy transfer to the diketone.

the diketone under a nitrogen atmosphere in isopropyl alcohol solution gave a mixture of **5** and **6**, the two endo-hydroxy ketones formed by reduction of **1** with zinc and acetic acid.[7] The endo-hydroxy ketones were identified by vapor chromatography and by comparison of the infrared and nuclear magnetic resonance spectra of the mixture with those of a mixture produced by reduction of **1** with zinc and acetic acid.[3] Using 2537-Å light in runs carried to 12% or less conversion, a quantum yield of 0.06 ± 0.01 was measured for the reaction.
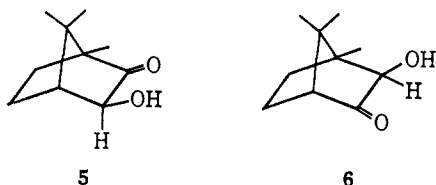
Although this result is entirely consistent with the results of Rubin and La Barge,[8] who studied photoreduction of **1** by o- and p-xylenes, puzzling discrepancies appear on comparison with those of Meinwald and Klingele.[2] The latter found that no reaction occurred when **1** was irradiated in oxygen-free methanol but that both photoreduction products and products of oxidation of the diketone appeared in experiments conducted in the presence of oxygen. Reduction products were also obtained in isopropyl alcohol, although experimental details were not reported. We find that irradiation of a solution of **1** under nitrogen in methanol does, in fact, lead to formation of a mixture of hydroxy ketones (66%) along with a mixture of two new compounds (34%). Infrared and nmr spectra are consistent with assignment of structures **7** and **8** to the products, although we have no firm basis for confirmation of the indicated stereochemistry.
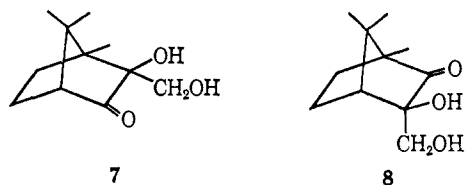
The results indicate that photoreduction follows a normal course in methanol, although the quantum yield (0.018 ± 0.005) is even lower than in isopropyl alcohol. We postulate that the reduction observed by Meinwald and Klingele probably occurred at stages in the reaction when the system became oxygen starved. Their failure to observe reaction in deoxygenated solution is probably due to some fortuitous combination of experimental circumstances related to the low quantum yield and possibly the complexity of the product mixture.

Formation of **7** and **8** in methanol and the failure of analogous products to appear in isopropyl alcohol can be attributed to the occurrence of facile hydrogen transfer from the 2-hydroxy-2-propyl radical to the diketone.[9] The hydroxymethyl radical is apparently less reactive in the hydrogen-transfer reaction.

(7) M. O. Foster and P. Probhashanker, J. Chem. Soc., 127, 1855 (1925).

(8) M. B. Rubin and R. G. La Barge, J. Org. Chem., 31, 3283 (1966).

(9) The reaction would be analogous to the transfer from the same radical to benzophenone, reported by J. N. Pitts, Jr., et al., J. Am. Chem. Soc., 81, 1068 (1959).

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Reactions of Hydridopentacyanocobaltate with the Anions of α,β-Unsaturated Acids

Sir:

The homogeneous hydrogenation of a variety of conjugated olefins catalyzed by aqueous pentacyanocobaltate(II) has been the subject of a number of investigations.[1] It is generally believed[1] that the active reducing species is the corresponding hydride, $[HCo(CN)_5]^{3-}$, which is in equilibrium with $[Co(CN)_5]^{3-}$, and molecular hydrogen.[2] We now describe experiments which throw some light on the mechanism of this reaction.

Solutions of the hydride (and deuteride) were conveniently prepared by the "aging" reaction[2,3b] of pentacyanocobaltate(II) with water (and D_2O)[4] using $CN^-:Co = 6$. The reactions of the hydride (and deuteride) with a series of α,β-unsaturated carboxylate ions were followed in situ by nmr, and the principal findings are presented in Table I.

It is found that carboxylate anions lacking an α substituent (compounds **1**, **3**, **7**, and **8**) form σ complexes, the nmr spectra of which unequivocally establish their structures as $RCH_2CH(CO_2^-)Co(CN)_5^{3-}$. Kwiatek and Seyler[1j,5] have also shown that complexes are formed by the additions of the hydride to conjugated olefins, in particular to acrylonitrile, acrylate, and the dimethyl esters of maleic and fumaric acids. Maleate **7** and fumarate **8** yield the same σ complex, the proton spectrum of which corresponds to an ABC spin system with δ_A 2.815, δ_B 2.78, and δ_C 2.46 ppm; $J_{AB} = 12.5$, $J_{AC} = -17.0$, and $J_{BC} = 3.9$ Hz. The values of the two vicinal coupling constants (J_{AB} and J_{BC}) indicate that one conformation about the central single bond is strongly preferred, and it is reasonable to assume that it is that in which the $-Co(CN)_5^{3-}$ group and the vicinal $-CO_2^-$ group are antiperiplanar. The monodeuterio complex derived from fumarate and the deuteride consists of a

(1) (a) M. Iguchi, J. Chem. Soc. Japan, 63, 1752 (1942); (b) B. de Vries, Koninkl. Ned. Akad. Wetenschap. Proc., Ser. B, 63, 443 (1960); (c) J. Kwiatek, I. L. Mador, and J. K. Seyler, J. Am. Chem. Soc., 84, 304 (1962); (d) J. Kwiatek, I. L. Mador, and J. K. Seyler, Advances in Chemistry Series, No. 37, American Chemical Society, Washington D. C., 1963, pp 201–215; (e) J. Kwiatek and J. K. Seyler, Proceedings of the 8th International Conference on Coordination Chemistry, Vienna, 1964, p 308; (f) A. F. Mabrouk, H. J. Dutton, and J. C. Cowan, J. Am. Oil Chemists' Soc., 41, 153 (1964); (g) A. F. Mabrouk, E. Selke, W. K. Rohwedder, and H. J. Dutton, ibid., 42, 432 (1965); (h) L. Simandi and F. Nagy, Magy. Kem. Folyoirat, 71, 6 (1965); (i) L. Simandi and F. Nagy, Acta Chim. Acad. Sci. Hung., 46, 137 (1965); (j) J. Kwiatek, Cat. Rev., 1, 37 (1967).

(2) M. G. Burnett, P. J. Connolly, and C. Kemball, J. Chem. Soc., A, 800 (1967), and references therein.

(3) (a) W. P. Griffiths and G. Wilkinson, J. Chem. Soc., 2757 (1959); (b) N. K. King and M. E. Winfield, J. Am. Chem. Soc., 83, 3366 (1961).

(4) It has been reported[3] that the pentacyanocobaltate ion (II) can be directly and rapidly reduced by borohydride. We have shown by nmr, magnetochemical, and catalytic hydrogenation studies that this reaction does not occur other than through the slow hydrolysis of the borohydride to molecular hydrogen.

(5) J. Kwiatek and J. K. Seyler, J. Organometal. Chem. (Amsterdam), 3, 421 (1965).