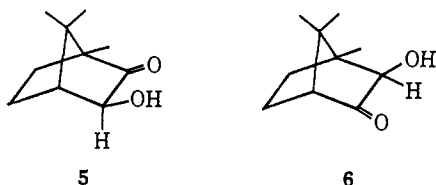
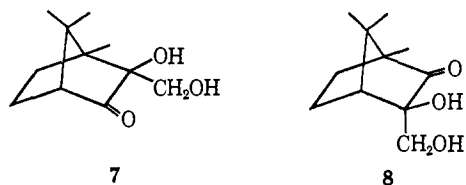


the diketone under a nitrogen atmosphere in isopropyl alcohol solution gave a mixture of **5** and **6**, the two *endo*-hydroxy ketones formed by reduction of **1** with zinc and acetic acid.<sup>7</sup> The *endo*-hydroxy ketones were identified by vapor chromatography and by comparison of the infrared and nuclear magnetic resonance spectra of the mixture with those of a mixture produced by reduction of **1** with zinc and acetic acid.<sup>3</sup> Using 2537-Å light in runs carried to 12% or less conversion, a quantum yield of  $0.06 \pm 0.01$  was measured for the reaction.



Although this result is entirely consistent with the results of Rubin and La Barge,<sup>8</sup> who studied photoreduction of **1** by *o*- and *p*-xylenes, puzzling discrepancies appear on comparison with those of Meinwald and Klingele.<sup>2</sup> 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 ( $0.018 \pm 0.005$ ) 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.<sup>9</sup> The hydroxymethyl radical is apparently less reactive in the hydrogen-transfer reaction.

(7) M. O. Foster and P. Prohashanker, *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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(10) National Institutes of Health Postdoctoral Fellow, 1966-1967.

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## Reactions of Hydridopentacyanocobaltate with the Anions of $\alpha,\beta$ -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.<sup>1</sup> It is generally believed<sup>1</sup> that the active reducing species is the corresponding hydride,  $[\text{HCo}(\text{CN})_5]^{3-}$ , which is in equilibrium with  $[\text{Co}(\text{CN})_5]^{3-}$ , and molecular hydrogen.<sup>2</sup> 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<sup>2,3b</sup> of pentacyanocobaltate(II) with water (and  $\text{D}_2\text{O}$ )<sup>4</sup> using  $\text{CN}^-:\text{Co} = 6$ . The reactions of the hydride (and deuteride) with a series of  $\alpha,\beta$ -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  $\alpha$  substituent (compounds **1**, **3**, **7**, and **8**) form  $\sigma$  complexes, the nmr spectra of which unequivocally establish their structures as  $\text{RCH}_2\text{CH}(\text{CO}_2^-)\text{Co}(\text{CN})_5^{3-}$ . Kwiatek and Seyler<sup>1j,5</sup> 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  $\sigma$  complex, the proton spectrum of which corresponds to an ABC spin system with  $\delta_A$  2.815,  $\delta_B$  2.78, and  $\delta_C$  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  $-\text{Co}(\text{CN})_5^{3-}$  group and the vicinal  $-\text{CO}_2^-$  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. Kamball, *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<sup>3</sup> 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.

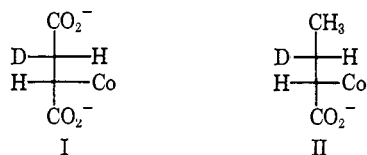
(5) J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.* (Amsterdam), 3, 421 (1965).

Table I. Reactions of  $\alpha,\beta$ -Unsaturated Carboxylate Ions (0.15 M) with  $[\text{HCo}(\text{CN})_5]^{3-}$  (0.15 M)

Substrate	Time, hr	Products, %			D in $\beta$ position(s) in final product		Half-life of carboxylate, <sup>f</sup> hr
		R <sup>a</sup>	C <sup>b</sup>	I <sup>c</sup>	CH <sub>2</sub> -	-CH <sub>2</sub> -	
1, CH <sub>2</sub> =CHCO <sub>2</sub> <sup>-</sup>	2	0	50		2 <sup>b</sup>		1.5
2, CH <sub>2</sub> =CMeCO <sub>2</sub> <sup>-</sup>	6	50	0		2.5		0.1
3, <i>trans</i> -MeCH=CHCO <sub>2</sub> <sup>-</sup>	320	5	20			1.0 <sup>a,b</sup>	>350
4, <i>cis</i> -MeCH=CMeCO <sub>2</sub> <sup>-</sup>	15			50 <sup>d</sup>	2.1 <sup>a</sup>	1.8 <sup>a</sup>	12
5, <i>trans</i> -MeCH=CHCO <sub>2</sub> <sup>-</sup>	100	50	0		2.0	1.5	20
6, CH <sub>2</sub> =CEtCO <sub>2</sub> <sup>-</sup>	0.5		0	50 <sup>d</sup>	2.6 <sup>a</sup>	1.2 <sup>a</sup>	0.5
7, <i>cis</i> -O <sub>2</sub> CCH=CHCO <sub>2</sub> <sup>-</sup>	216	12	44	13		1.0 <sup>a,b</sup>	180
8, <i>trans</i> -O <sub>2</sub> CCH=CHCO <sub>2</sub> <sup>-</sup>	216	9	36			1.0 <sup>a,b</sup>	260
9, <i>cis</i> -O <sub>2</sub> CCH=CMeCO <sub>2</sub> <sup>-</sup>	340	38	0		2.2	1.0	250
10, <i>trans</i> -O <sub>2</sub> CCH=CMeCO <sub>2</sub> <sup>-</sup>	100	50	0		2.2	1.0	100
11, CH <sub>2</sub> =C(CO <sub>2</sub> <sup>-</sup> )CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	7	50	0	17 <sup>a</sup>	2.83 <sup>a</sup>	0.0 <sup>a</sup>	1.3

<sup>a</sup> Reduction product. <sup>b</sup>  $\sigma$  complex. <sup>c</sup> Isomerization. <sup>d</sup> Tiglate 5. <sup>e</sup> Mesaconate 10. <sup>f</sup> These values include the exchange processes and are hence a measure of the rate of initial attack.

broad singlet at  $\delta$  2.80 ppm with no detectable absorption at 2.46 and is hence the *threo* isomer I. Thus,  $\sigma$ -complex formation involves a stereospecific *cis* addition. Maleate yields a mixture containing ca. 80% of the *erythro* isomer, the *threo* isomer arising at least in part from fumarate produced by isomerization during the reaction. Similarly, *trans*-crotonate 3 and the deuteride give the complex II characterized by  $J = 12$  Hz for the coupling between the  $\alpha$  and  $\beta$  protons. Isomerization



occurs in several of the systems investigated (compounds 4, 6, 7, and 11). That isomerization is not stereospecific is indicated by the observation that angelate 4 is isomerized by the deuteride to tiglate 5, a significant fraction (>10%) of which retains the olefinic proton. If the isomerization involved a stereospecific addition of deuteride and elimination of hydride, complete exchange of the olefinic proton would have occurred.<sup>6</sup>

The reduction with the deuteride of both mesaconate 10 and citraconate 9 affords an equimolecular mixture of the *erythro* and *threo* isomers of  $-\text{O}_2\text{CCHD}(\text{CO}_2^-)\text{CH}_n\text{D}_{3-n}$  with  $n = 0.8$  whereas itaconate 11 gives  $-\text{O}_2\text{CCH}_2\text{CD}(\text{CO}_2^-)\text{CH}_n\text{D}_{3-n}$  with  $n = 0.17$ . These results indicate that, although citraconate and mesaconate isomerize to itaconate, some reduction of these two substrates occurs without the intervention of itaconate and the direct reduction is nonstereospecific. Experiments relating to the steric course of reduction in other substrates are in progress.

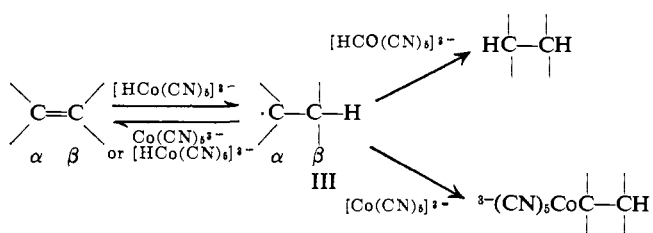
It is noteworthy that 4,5,5-trimethylcyclopent-1-ene-1,4-dicarboxylate, in which presumably both  $\sigma$ -complex formation and reduction are impossible for steric reasons, still undergoes exchange at the  $\beta$  position (37% in 312 hr).

We report two further results of mechanistic significance. Firstly, within experimental error the rate of catalytic hydrogenation of  $\alpha,\beta$ -unsaturated acids is un-

(6) Retention of the proton cannot be due to addition of hydride, formed in the elimination step, to another molecule of tiglate since the rate of exchange between  $[\text{HCo}(\text{CN})_5]^{3-}$  and  $\text{D}_2\text{O}$  is certainly very much faster<sup>2</sup> than the addition reaction (Table I).

affected by changing  $\text{CN}^-:\text{Co}$  from 6 to 100 at constant ionic strength. Thus,  $\pi$ -allyl type complexes which are implicated at lower values of this ratio<sup>1e</sup> are not involved in the reactions considered here. Secondly, we have been unable to reduce  $[\text{Co}(\text{CN})_5\text{OH}]^{3-}$  with molecular hydrogen in the presence of the  $[\text{Co}(\text{CN})_5]^{3-}$  so that the former complex cannot be involved in the catalytic hydrogenation.<sup>7</sup> This result disposes of a mechanism in which  $[\text{HCo}(\text{CN})_5]^{3-}$  functions as a hydride ion donor yielding a carbanion and  $[\text{Co}(\text{CN})_5]^{2-}$ , since the carbanion would be protonated by the solvent and  $[\text{Co}(\text{CN})_5]^{2-}$  would yield the hydroxo complex, thus destroying the catalyst. It is also unlikely that  $[\text{Co}(\text{CN})_5]^{4-}$  is an intermediate since the observation of an nmr signal for the proton of the hydride<sup>2,3a</sup> indicates the absence of rapid (on the nmr time scale) proton exchange with water, and furthermore such an intermediate would not account for the observed orientation in the  $\sigma$  complexes.

The results presented here lend support to the mechanism proposed by Simandi and Nagy,<sup>1h,1</sup> and considered by Kwiatek,<sup>1j</sup> in which the hydride is a hydrogen atom donor which generates the organic free-radical intermediate III. Reduction is completed by attack at the



$\alpha$  position by a second hydride molecule. Exchange and isomerization involve removal of a hydrogen atom from the  $\beta$  position by either  $[\text{Co}(\text{CN})_5]^{3-}$  or  $[\text{HCo}(\text{CN})_5]^{3-}$ , the latter giving molecular hydrogen which subsequently regenerates the hydride.  $\sigma$ -Complex formation, which is stereospecific, can be formulated either as a concerted addition<sup>1j</sup> or as collapse of a "cage" at a

(7) The observation of an "autocatalytic reduction" of  $[\text{Co}(\text{CN})_5\text{OH}]^{3-}$  has been reported,<sup>1i</sup> although no details have been given. In any event, the observed rate for the forward stage of the reaction<sup>2</sup>



coupled with the fact that the equilibrium, if such exists, lies well to the right, indicates that the reverse process is far too slow to be involved in the catalytic reduction of reactive substrates.

rate substantially greater than the rate of rotation about the  $\alpha,\beta$ -carbon-carbon single bond.

In accord with this mechanism, the rate of attack by hydride (*cf.* Table I) is facilitated by  $\alpha$ -alkyl groups as these will stabilize the radical III.  $\beta$  Substituents retard the reaction presumably by sterically hindering the approach of the hydride.<sup>8</sup>

(8) The authors express their thanks to the referees for helpful comments and for drawing their attention to ref 1j.

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## Cyclodimerization of Styrene<sup>1</sup>

Sir:

The dimerization of styrene occurs thermally,<sup>2</sup> photochemically,<sup>2</sup> and by ionic mechanisms, either cationic<sup>3</sup> or anionic,<sup>4</sup> with characteristic product patterns. It is thus of potential mechanistic significance to identify dimeric radiolysis products of styrene. The benzene-sensitized radiolysis, if actuated by triplet benzene as in *cis-trans* isomerizations of olefins,<sup>5</sup> should correlate with the photosensitized dimerization. In this communication it is shown that the correlation has limited validity. The argument rests mainly on the previously uncharacterized stereochemistry of diphenylcyclobutane formation in variously initiated dimerizations.

The new measurements (Table I) were made at low conversions (0.1–0.5% dimer) to minimize subsequent isomerization of the radiation-sensitive and thermally labile diphenylcyclobutanes. In dilute solutions at these conversions, high polymer formation was not qualitatively noticeable or detectable by analysis for unreacted monomer. The C<sub>16</sub> fractions were analyzed, with bibenzyl as internal standard, by chromatography on lightly loaded QF-1 columns at 135°.  $\gamma$  Irradiations were performed at a dose rate of  $4 \times 10^{17}$  eV/g min with total doses of  $4 \times 10^{19}$  to  $4 \times 10^{20}$  eV/g. Ultraviolet irradiations utilized a high-pressure mercury lamp and appropriate filters with solutions in sealed Pyrex cells at 30°. Yields of *cis*- and *trans*-1,2-diphenylcyclobutanes (**1** and **2**, respectively) were satisfactorily reproducible but the relative yields of 1-phenyltetralin (**3**) and 1-phenyl-1,2-dihydronaphthalene (**4**) in the thermal and radiolytic reactions were somewhat erratic despite care to exclude air. Addition of *t*-butylcatechol, considered as a possible antioxidant, actually increased the yield of **4** and decreased **3**. The yield of 1-phenyl-naphthalene was appreciable in direct photolysis (7% of total dimer) but small in other cases and unobserved in sensitized photolysis. In radiolysis, two unidentified components, eluting between **1** and **3**, contributed together less than 10%.

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) F. R. Mayo, *J. Am. Chem. Soc.*, **90**, 1289 (1968).

(3) B. B. Carson, J. Dorsky, J. E. Nickel, W. M. Kutz, and H. I. Thayer, *J. Org. Chem.*, **19**, 17 (1954).

(4) A. Zwierzak and H. Pines, *ibid.*, **28**, 3392 (1963).

(5) E. Fischer, H. P. Lehmann, and G. Stein, *J. Chem. Phys.*, **45**, 3905 (1966), and earlier literature therein cited.

Table I. Composition of Styrene Dimer Fractions<sup>a</sup>

Conditions	1	2	3	4
A. Radiolysis <sup>b</sup>				
0.04 M styrene in benzene	3.1	1.1	5.3	1.1
0.2 M, 0.1% <i>t</i> -BC, <sup>c</sup> in benzene	7.4	3.7	11.1	11.0
0.2 M, 1 atm N <sub>2</sub> O, in benzene	7.2	3.3	6.2	6.6
Neat, with 0.1% <i>t</i> -BC	22.8	25.9	4.1	11.2
B. Sensitized Photolysis <sup>d</sup>				
Sensitizer <sup>e</sup> 0.01–0.02 M	0.22	0.75	0.03	...
C. Direct Photolysis <sup>f</sup>				
Benzene	0.75	0.10	0.08	...
Methylene chloride	0.72	0.14	0.07	...
D. Thermal <sup>g</sup>				
No additive	0.09	0.21	0.59	0.02
0.1% <i>t</i> -BC	0.18	0.36	0.11	0.29

<sup>a</sup> Products: **1**, *cis*-1,2-diphenylcyclobutane; **2**, *trans*-1,2-diphenylcyclobutane; **3**, 1-phenyltetralin; **4**, 1-phenyl-1,2-dihydronaphthalene; composition given as mole fraction, except in radiolysis. <sup>b</sup> Cobalt-60  $\gamma$  irradiation at 25°; yields as *g* values  $\times 100$ . <sup>c</sup> *t*-Butylcatechol. <sup>d</sup> Photosensitized (uranium glass filter); 0.2 M styrene in benzene. <sup>e</sup> Averaged results for benzophenone, xanthone, phenyl cyclopropyl ketone, and anthraquinone. <sup>f</sup> Direct photochemical, 0.8 M styrene, various solvents. Similar results were found in methanol, diethyl ether, and isohexane at 30° or at –80°. <sup>g</sup> Thermal, 0.2 M styrene in benzene, 110°, 120 hr.

Dimer yields in the radiolysis of dilute solutions are low compared with *g* values for benzene triplet production of **5** and higher from *cis-trans* isomerizations,<sup>6</sup> and even in neat styrene the total dimer represents a *g* of less than 1. The dimerization in dilute solution is more than the fractional energy absorbed by monomer would account for and can thus be described as benzene sensitized. Cationic mechanisms are evidently not involved, since the characteristic open-chain olefins and indan derivatives are absent, but an anionic, or solvated electron, mechanism is admissible for at least part of the observed 1-phenyltetralin.<sup>7</sup>

The products of primary interest are **1** and **2** since they are the main products in sensitized photolysis and presumably arise by an excited-state mechanism. There is disagreement in the isomer yields; *cis* predominates in radiolysis by a factor of 2 whereas photolysis, with any of the sensitizers tried, favors *trans* by a factor of 3.4. In direct photolysis, with singlet excitation by absorption in the long-wavelength band of styrene, the situation is again reversed, *cis* being favored under widely different conditions by a factor of  $\sim 6$ . This is evidently an example, not the first,<sup>8</sup> of dimerization through strong *cis*-pairwise complexing of the excited singlet. A *cis/trans* ratio in radiolysis that is midway between the two photochemical situations is the basis for concluding that cyclobutane formation in the radiolysis of benzene solutions occurs about equally by triplet and singlet excitation.

The thermal formation of diphenylcyclobutanes, not allowed<sup>9</sup> as a one-step process, may be related to photosensitized dimerizations through a common inter-

(6) M. A. Golub and C. L. Stephens, *J. Phys. Chem.*, **70**, 3576 (1966).

(7) The supposedly anionic dimerization, in refluxing styrene with potassium *t*-butoxide, to 1-phenyltetralin only<sup>4</sup> was under conditions that would allow thermal dimerization and isomerization of primary products.

(8) D. O. Cowan and R. L. Drisko, *J. Am. Chem. Soc.*, **89**, 3068 (1967).

(9) R. Hofmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).