than a hundred times faster in nitromethane than in tetrahydrofuran while several related Diels–Alder reactions[4] are accelerated by a factor of about two for the same solvents. If both I and II were formed from a common, rate-limiting transition state, as would be expected for an intermediate of the type proposed by Woodward for the Diels–Alder reaction collapsing in either of two possible directions, the total rate of reaction would be expected to show only the slight solvent effect which is generally characteristic of Diels–Alder reactions. Since this is not the case, it is necessary to conclude either that a change in mechanism has occurred with a change in solvent or else that I and II are formed in either solvent through separate rate-limiting transition states, quite likely involving, respectively, the *transoid* and *cisoid* configurations of the diene. Attempts at thermal interconversion as demonstrated by Woodward[5] and Roberts[7] in related systems (at the suggestion of Prof. Roberts) were thwarted by the limited thermal stability of I under conditions such that II was virtually unchanged. Decomposition appeared to be accompanied by gas evolution and formation of conjugated structures (strong absorption at 4.5, 6.1, 6.3 microns) and may be related to elimination reactions previously described for tetracyanocyclobutanes.[8]

Acknowledgments.—The author wishes to thank Dr. P. D. Bartlett, in whose laboratories several aspects of this reaction are being investigated, and Dr. J. D. Roberts for helpful discussions.

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(8) J. K. Williams, D. W. Wiley, B. C. McKusick, 139th ACS Meeting, St. Louis, Mo. (1961) abstracts p. 9-O.

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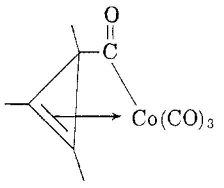
RECEIVED NOVEMBER 15, 1961

CYCLOPROPENYL COMPLEXES OF IRON AND COBALT

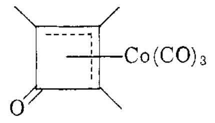
Sir:

π-Bonded metal complexes of the cyclic moieties C_nH_n are known for $n = 4, 5, 6, 7$ and 8. We attempted to prepare a complex containing a cyclopropenyl ligand π-bonded to a metal. Orgel[1] has mentioned the possibility of such complexes and noted the molecular orbitals involved. In practice, we have sought a complex of triphenylcyclopropenyl since triphenylcyclopropenyl bromide is synthesized readily[2] and is highly symmetrical.

Triphenylcyclopropenyl bromide reacted immediately with cobalt tetracarbonylate anion in acetonitrile at room temperature without gas evolution. Processing of the solution gave a 58% yield of yellow, air-stable crystals, m.p. 134–135.5°, soluble in organic solvents. *Anal.* Calcd. for $C_{25}H_{15}CoO_4$: C, 68.50; H, 3.45; Co, 13.4. Found: C, 68.26; H, 3.29; Co, 13.3. An infrared spectrum (KBr pellet) showed seven peaks in the 690–790 cm.$^{-1}$ region, an unsymmetrical doublet at 2015, 2080 cm.$^{-1}$ characteristic of the $Co(CO)_3$ group, and a band at 1710 cm.$^{-1}$ assigned to a ketonic carbonyl. The characteristic triphenylcyclopropenyl cation band at 1400 cm.$^{-1}$ was absent. These data suggest structure I or II for the product.



I



II

Similarly, $Fe(CO)_3NO^{-}$[3] reacted with triphenylcyclopropenyl bromide in methanol, producing a 14% yield of maroon crystals, m.p. 119–21°, somewhat less air-stable than the cobalt compound. *Anal.* Calcd. for $C_{24}H_{15}NFeO_4$: C, 65.94; H, 3.46; N, 3.20; Fe, 12.8. Found: C, 66.10; H, 3.99; N, 2.96; Fe, 13.3. An infrared spectrum showed a symmetrical doublet at 1950, 2005 cm.$^{-1}$ which was assigned to the carbonyl stretches in $Fe(CO)_2$, and an unsymmetrical doublet at 1720(s) and 1680 cm.$^{-1}$ (m) assigned to nitrosyl and ketonic carbonyl groups. Bands characteristic of the phenyl groups were present at 690 and 760 cm.$^{-1}$ with a shoulder at 750 cm.$^{-1}$. Structures analogous to I and II are possible for this complex, with Fe replacing Co and one CO replaced by NO.

Evidence in support of structure I was obtained by oxidizing the iron complex with 1,3-diphenylallyl chloride in hot toluene. This treatment gave yellow crystals of triphenylcyclopropenylium tetrachloroferrate (III), m.p. 253–254°, identified by comparison with the product obtained from triphenylcyclopropenyl bromide and $FeCl_3$ in ethanol. This suggests that the cyclopropene ring is intact in the complexes and therefore that structure I is correct.

These complexes are closely related to the expected $\pi\text{-}(C_6H_5C)_3$ complexes. In fact, the relation is the same as that existing between $RMn(CO)_5$ and $RCOMn(CO)_5$.[4] Complexes of cobalt tricarbonyl with acrylyl and 4-pentenoyl have been prepared.[5] These are similar to structure I in that bonding to cobalt occurs *via* a double bond and a bridging carbonyl.

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PHOTOCHEMICAL REACTIONS OF 1,2-DIKETONES

Sir:

The photolysis of appropriate 1,2-diketones gives 2-hydroxycyclobutanones with striking selectivity and remarkable yields. Only 2-hydroxycyclobutanones, and none of the 1-alkanoylcyclobutanols, are obtained even when the two products might be expected (with 5,6-decanedione). The superiority of these intramolecular reactions over those of monoketones[1-6] and the absence of cleavage reactions[4] may be attributed to the more stable intermediates derived from 1,2-diketones.

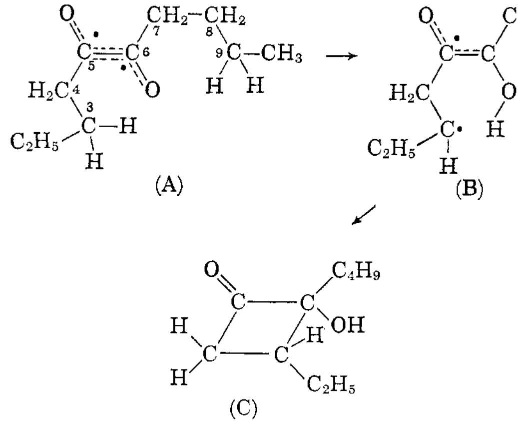
A solution of 5,6-decanedione (35.1 g., 0.21 mole, b.p. 90–91° at 12 mm., n^{25}D 1.4250) in cyclohexane (277.2 g., 3.30 moles) in a Pyrex culture flask (modified) was exposed to sunlight (12 hr.). Analysis of the reaction mixture (v.p.c.) indicated only unreacted diketone (11%) and 2-butyl-3-ethyl-2-hydroxycyclobutanone (Ia, 89%). Distillation gave pure Ia (28.3 g., 0.166 mole, b.p. 83° at 2 mm., n^{25}D 1.4528, infrared 1776 cm.$^{-1}$ and 3400 cm.$^{-1}$) (Found: C, 70.1; H, 10.1; parent mass 170 (Heated Inlet Mass Spectrometer, Consolidated Electrodynamics Corp.)). Its *p*-nitrophenylhydrazone melted at 198–199° (Found: N, 13.9). Ia (1.0 g., 0.006 mole) with periodic acid (1.37 g., 0.006 mole) gave 3-ethyl-4-oxoöctanoic acid (1.2 g., 0.006 mole, n^{25}D 1.4440) identical (infrared) with an authentic sample (b.p. 125–128° at 2 mm., n^{25}D 1.4460) prepared by the peroxide-induced addition[7] of pentanal to 2-pentenoic acid[8] (Found: C, 64.3; N, 10.0). This ketoacid from both sources gave the same semicarbazone (m.p. 176–177°, m.p. of mixture 175–177°; (Found: N, 16.9) and *p*-nitrophenylhydrazone (m.p. 151–152°, m.p. of mixture 151–152°; (Found: N, 13.1). Conditions, yields and identification were similar in experiments with 2,7-dimethyl-4,5-octanedione.

The intramolecular reaction dominates even in solvents highly reactive toward radical attack. Addition of aldehyde to the 1,2-diketone and formation of the acyloin also occur when mixtures of these reactants are irradiated. 4,5-Octanedione (33.8 g., 0.238 mole, b.p. 52–54° at 10 mm., n^{20}D 1.4175) in butanal (137 g., 1.90 mole) was irradiated[9] (2537 Å.) at 30–35° for 23 hours. 5-Hydroxy-4-octanone (8.7%), 2-hydroxy-3-methyl-2-propylcyclobutanone (IIa, 92%) and 5-oxo-4-octanol butyrate (IIb, 7.7%; yields based upon dione used, 75%; irradiation of butanal alone gave 5-hydroxy-4-octanone, 58%, 1-butanol, 9.2% butyl butyrate, 2.9%, and 4,5-octanedione, 1.9%) were obtained. Distillation gave pure IIa (b.p. 67–69° at 1.5 mm., n^{20}D 1.4518, infrared 3400 and 1775 cm.$^{-1}$) (Found: C, 67.3; H, 10.2; m.w. 147 (cryoscopic-benzene; apparently dimerizes, and value given obtained by extrapolation to infinite dilution). IIa with periodic acid gave 3-methyl-4-oxoheptanoic acid (m.w. of IIa assuming 1:1 stoichiometry, 144; infrared identical with that of authentic sample[7]). The same semicarbazone was obtained from this ketoacid from the two sources (m.p. 167–168°, m.p. of mixture 166–167°) (Found: N, 19.5). IIb (b.p. 74–75° at 1 mm., n^{20}D 1.4428; (Found: C, 67.5; H, 10.7; mol. wt., 203) was hydrolyzed to give butanoic acid from which butyranilide (m.p. 94–95°; m.p. of mixture with authentic sample 94–95°) was prepared, and 5-hydroxy-4-octanone that gave its 2,4-dinitrophenylhydrazone (m.p. 110–111°, m.p. of its mixture with authentic sample 109–110°).

Reduction and carbonyl addition were favored in the diketone–aldehyde reaction when cyclobutanone formation involved primary hydrogen atoms. 3,4-Hexanedione (26.3 g., 0.231 mole) in propanal (107 g., 1.85 mole) was irradiated for 37 hours, and conversion (73%) to 4-hydroxy-3-hexanone (23%), 2-ethyl-2-hydroxycyclobutanone (23%) and 4-oxo-3-hexanol propionate (54%) occurred. This diketone (13 g., 0.114 mole) in cyclohexane (153 g., 1.83 mole) in sunlight for 100 hours was converted (73%) to 4-hydroxy-3-hexanone (25%) and 2-ethyl-2-hydroxycyclobutanone (60%, b.p. 75–76° at 4 mm., n^{25}D 1.4353) (Found: C, 62.8; H, 9.2). This cyclobutanone with periodic acid gave 4-oxohexanoic acid (b.p. 89° at 0.4 mm.) that gave the known semicarbazone[10] (m.p. 174–175°) and 2,4-dinitrophenylhydrazone (m.p. 186°).[11]

2,3-Butanedione (51.5 g., 0.60 mole) in 2-propanol (181 g., 3.0 moles) in sunlight (7 days) gave acetone (17.4 g., 0.30 mole, 100%) and 3,4-dihydroxy-3,4-dimethyl-2,5-hexanedione (49.4 g., 0.284 mole, 95%, m.p. 96–97°)[12,13] (Found: C, 55.2; H, 8.3; mol. wt., 173).

Selective formation of 2-hydroxycyclobutanones may be determined by the most facile attainment of the six-membered, cyclic transition state for the hydrogen atom transfer. Whatever excited state (triplet or singlet π*) accomplishes this abstraction, the bond between carbon atoms 5 and 6 must have double bond character. Hence, the two oxygen atoms and carbon atoms 4, 5, 6 and 7 approach coplanarity with the indicated *trans* structure most likely.



The reaction observed then requires further alignment of only carbon atom 3 and a hydrogen atom attached to it, but the alternate path (illustrated

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(13) H. v. Pechmann, *Ber.*, **21**, 1421 (1888).

with the right half of model A) would have involved the further arranging of carbon atoms 8 and 9 and a hydrogen atom on the latter.

The evidence for this selectivity is threefold: (1) one symmetrical peak for the 2-hydroxycyclobutanone with vapor phase chromatography of each reaction mixture; (2) the absorption band at 1775 cm.$^{-1}$, and none at 1700–1720 cm.$^{-1}$, in the infrared spectra of these products; and (3) a single band observed with chromatography on silicic acid[14] of the *p*-nitrophenylhydrazones (prepared with excess reagent and long reaction times). Items 1 and 3 reveal a further specificity. Two asymmetric carbon atoms result from the formation of 2-hydroxy-3-methyl-2-propylcyclobutanone and 2-butyl-3-ethyl-2-hydroxycyclobutanone, but one of the two possible racemates predominates (probably the *trans*).

Preliminary experiments suggest that the excited state A is a triplet since oxygen, naphthalene and anthracene exert a quenching effect. Solutions of 2,7-dimethyl-4,5-octanedione (each 7 ml., 0.84 *M* in ethanol; in 40 ml. serum bottles, soft glass—1% transmittancy at 2900 Å. and 10% at 3000 Å.) with these additives (naphthalene, 0.002 *M*, absorbed ~2% of light from 2900 to 4700 Å.; oxygen, ~0.001 *M;* and anthracene, 0.0005 *M*, absorbed ~5% of this light; control and those containing aromatics swept with nitrogen) were irradiated simultaneously (G. E. Sunlamp, 275 w.; from 12 cm. distance). In all experiments, analyses each hour (F and M Model 500 Chromatograph, 61 cm. Silicone rubber column, 125°, helium flow 70 ml. per min.) showed that 3,3-dimethyl-2-hydroxy-2-(2-methylpropyl)-cyclobutanone was the only product (symmetrical peak, retention time 3.7 min., ultimate yield 95%). All plots of cyclobutanone formed *versus* time were linear through the origin (rates zero order in dione; dependent on constant light intensity completely absorbed). Rate ratios were: control, 1.0; with naphthalene, 0.88; oxygen, 0.62; and anthracene, 0.41 (duplicated to ±0.02 with interchange of vessels). These results imply paramagnetic quenching by oxygen and triplet–triplet conversion by the aromatics,[15,16] and are striking since such destruction of the diketone-derived triplet must compete with an intramolecular reaction.

Supporting evidence is: (1) 2,3-butanedione when irradiated in solution undergoes almost complete intersystem crossing to its phosphorescent triplet state,[17] and (2) a triplet intermediate is suggested since cyclobutane ring formation (B → C) is slow enough to permit domination by conformational factors.

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RECEIVED AUGUST 28, 1961

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[14] B. E. Gordon, F. Wopat, Jr., H. D. Burnham and L. C. Jones, Jr., *Anal. Chem.*, **23**, 1754 (1951). *p*-Nitrophenylhydrazones were used since acidic 2,4-dinitrophenylhydrazine reagent gave partial dehydration to give some α,β-unsaturated hydrazones.

[15] W. G. Moore, G. S. Hammond and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

[16] H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958).

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CARBONIUM ION SALTS. III. SPECTRA AND DECOMPOSITION OF TROPENIUM HALIDES IN METHYLENE CHLORIDE[1]

Sir:

The colors of solid tropenium halides (chloride white, bromide yellow, iodide red) have been attributed to charge-transfer.[2] Winstein[3] has demonstrated charge-transfer complexing between tropenium ion and aromatics, but only one brief report[4] has appeared concerning measurements of the visible solution spectra of the halides.

The ${}^1E_{3u}$ band[5] of tropenium ion in 96% sulfuric acid ($\lambda_{\min}$ 244 (420), $\lambda_{\max}$ 268 (sh), 273.5 (4350), 280 mμ),[6] water ($\lambda_{\max}$ 275 (4350), 280 mμ),[7] and acetonitrile ($\lambda_{\max}$ 275 (4200), 280 mμ)[2c] is not anion dependent, and at spectral concentrations (about 10^{-4} mole/l.) such solutions are colorless unless the anion is colored (as I_3^-, HgI_3^-, etc.). The spectrum of tropenium fluoroborate in dry methylene chloride ($\lambda_{\min}$ 253.5 (785), $\lambda_{\max}$ 271.5 (sh), 278 (4270), 283 mμ (sh)) is similar to that in sulfuric acid, and the solution is colorless. However, tropenium halides dissolve in methylene chloride to give colored solutions at spectral concentrations (chloride light yellow, bromide deep orange, iodide deep violet) with new absorption bands. The new chloride band ($\lambda_{\max}$ 298 mμ (1820)) lies under the tropenium ion band; its position and intensity are estimated by subtracting from the chloride spectrum the absorption of a solution of tropenium fluoroborate of equivalent concentration. The bands of the bromide ($\lambda_{\max}$ 402 mμ (1380)) and the iodide ($\lambda_{\max}$ 422 (1120), 575 mμ (1880))[8] represent discrete new maxima. In addition the tropenium ion ${}^1E_{3u}$ band loses its structure and shows a smooth peak with a higher minimum but almost unchanged maximum (chloride: $\lambda_{\min}$ 249 (2380), $\lambda_{\max}$ 276 mμ (4070); bromide: $\lambda_{\min}$ 253 (1480), $\lambda_{\max}$ 277 mμ (4270); iodide: $\lambda_{\min}$ 264 (3180), $\lambda_{\max}$ 278 mμ (4270)[8]).

We believe that these new colored bands in methylene chloride arise from charge-transfer from halide ion to tropenium ion in the ion pairs or aggregates which should exist[9] in this solvent of low dielectric constant[10] for the following reasons: (1)

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[1] Supported by the Petroleum Research Fund, the National Science Foundation, and Claremont University College.

[2] (a) E. M. Kosower and P. E. Klinedinst, Jr., *J. Am. Chem. Soc.*, **78**, 3493 (1956); (b) W. von E. Doering and L. H. Knox, *ibid.*, **79**, 352 (1957); (c) K. M. Harmon, Ph.D. Thesis, U. of Washington, 1958, *Dissertation Abstr.*, **19**, 1563 (1959).

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[4] K. M. Harmon and A. B. Harmon, *ibid.*, **83**, 865 (1961).

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[6] H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957); in this solvent the ${}^1E_{1u}$ band, at $\lambda_{\max}$ 217 mμ (41,000), may also be seen.

[7] W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

[8] The spectrum of tropenium iodide must be corrected for triiodide ion present from decomposition (see below). This is done by simultaneous solution at two wave lengths to find triiodide concentration, followed by subtraction of the indicated amount of absorption due to triiodide. The position and shape of the tropenium bands can be fixed, but the epsilon values must be compared to an arbitrary standard; values given are relative to 4270 for the 278 mμ absorption of tropenium ion.

[9] C. A. Kraus, *J. Phys. Chem.*, **60**, 129 (1956), and references therein.

[10] Tropenium bromide shows an equivalent conductance at 1 × 10^{-4} moles/l. in methylene chloride of 21 mhos compared with the