[mp 129.5–130.5°; uv (CHCl$_3$) λ_{max} 333 nm (log ϵ 3.91); nmr (CDCl$_3$) δ 0.80–1.82 (m, 4 H, CH$_2$), 4.65 (broad s, 1 H, $\geqslant$CH), 5.40–6.50 (m, 4 H, =CH), and 6.80–7.50 (m, 5 H, C_6H_5)],[6] respectively (eq 2). Since the rate is highly sensitive to the solvent polarity (for instance, in the case of **10b**, $k_{CH_3CN}/k_{C_6H_{12}}$ at 25° $\simeq 10^2$), the cycloaddition would be rationalized as a stepwise reaction involving the dipolar ions **11**.[17,20,21]

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(20) *Cf.* L. H. Klemm, W. C. Solomon, and A. J. Kohlik, *J. Org. Chem.*, **27**, 2777 (1962).

(21) Very recently the related [(σ2 + π2) + π2] cycloaddition of alkenylidenecyclopropanes to 4-phenyl-1,2,4-triazoline-3,5-dione was reported [D. J. Pasto and A. Chen, *J. Amer. Chem. Soc.*, **93**, 2562 (1971)]. The intermediary formation of **12b**, though not isolated, in the reaction of **10b** and TCNE at 120° was claimed [J. E. Baldwin and R. E. Peavy, *J. Org. Chem.*, **36**, 1441 (1971)].

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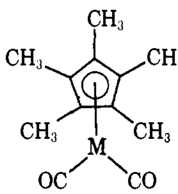
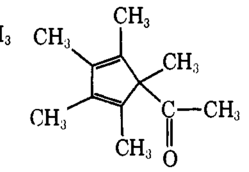
A Convenient Synthesis of Pentamethylcyclopentadienylmetal Carbonyls

Sir:

We required gram quantities of several pentamethylcyclopentadienylmetal carbonyls for a comparison of their chemistry with that of the unsubstituted cyclopentadienylmetal carbonyls.[1] Previously reported syntheses of pentamethylcyclopentadienylmetal carbonyls either required the difficultly accessible pentamethylcyclopentadiene[2] as a starting material[3] or were restricted to the rhodium[4] and iridium[5] derivatives of the type $(CH_3)_5C_5M(CO)_2$ (I, M = Rh and Ir). This communication reports a general synthesis of pentamethylcyclopentadienylmetal carbonyls which utilizes the readily available 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene (II)[6] as a starting material.


I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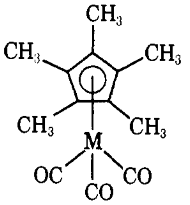
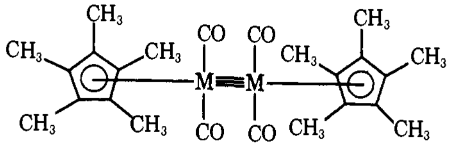
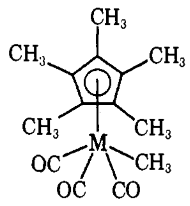
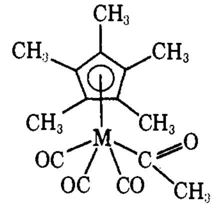

III

The acetyl derivative II reacts with many metal carbonyls in hydrocarbon solvents at elevated temperatures to form pentamethylcyclopentadienylmetal carbonyl derivatives with concurrent loss of the acetyl group. Thus, $Co_2(CO)_8$ reacts with II in boiling cyclohexane (22 hr) to give a 60% yield of the known[3] red crystalline $(CH_3)_5C_5Co(CO)_2$ (I, M = Co), mp 54–55° (lit.[3] mp 56–58°). Similarly, $Mn_2(CO)_{10}$ reacts with II in boiling 2,2,5-trimethylhexane (48 hr) to give a 12% yield of the new[7] pale yellow crystalline $(CH_3)_5C_5Mn(CO)_3$ (III, M = Mn), mp 77.5°.

In the original work[3] with pentamethylcyclopentadienylmetal carbonyl derivatives, the reaction between pentamethylcyclopentadiene and $Mo(CO)_6$ was of interest because it gave a product $[(CH_3)_5C_5Mo(CO)_2]_2$, which was not analogous to the unsubstituted cyclopentadienyl derivative $[C_5H_5Mo(CO)_3]_2$. Structure IV (M = Mo) was postulated for $[(CH_3)_5C_5Mo(CO)_2]_2$, with a metal–metal triple bond[3,8] to give each molybdenum atom the favored 18-electron rare gas configuration.[9] The synthesis of additional compounds related to IV was of obvious interest in order to investigate the properties of this unusual type of compound. Reaction of the acetyl derivative II with $Cr(CO)_6$ in boiling 2,2,5-trimethylhexane (24 hr) gave a 44% yield of deep green crystalline $[(CH_3)_5C_5Cr(CO)_2]_2$, which decomposed at ~200°.[7] This green compound is clearly the analogous chromium compound IV (M = Cr). The acetyl derivative II did not react with $W(CO)_6$ upon prolonged heating in boiling 2,2,5-trimethylhexane in accord with the generally lower reactivity of tungsten carbonyl derivatives relative to corresponding chromium and molybdenum carbonyl derivatives.[10] However, the acetyl derivative II did react with the more reactive[11] acetonitrile complex[12] $(CH_3CN)_3W(CO)_3$ in boiling 2,2,5-trimethylhexane (22 hr) to give the yellow σ-methyl derivative[7] $CH_3W(CO)_3C_5(CH_3)_5$ (V, M = W), mp 170–171° dec in 4% yield. Reaction of the acetyl derivative II with $Mo(CO)_6$ in boiling 2,2,5-trimethylhexane (32 hr) gave both the red bimetallic derivative $[(CH_3)_5C_5Mo(CO)_2]_2$ (IV, M = Mo) in 20% yield and the known[3] yellow σ-methyl derivative $CH_3Mo(CO)_3C_5(CH_3)_5$ (V, M = Mo), which decomposed at 140° (lit.[3] decomposition 141–145°), in 43% yield.


IV


V


VI

The formation of the σ-methyl derivative $CH_3M(CO)_3C_5(CH_3)_5$ (V, M = Mo and W) in reactions of the acetyl derivative II with appropriate carbonyls of molybdenum and tungsten suggests that the acetyl group from II is transferred to the metal atom before

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(1) R. B. King, "Transition-Metal Organometallic Chemistry: An Introduction," Academic Press, New York, N. Y., 1969.

(2) L. de Vries, *J. Org. Chem.*, **25**, 1838 (1960).

(3) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **8**, 287 (1967).

(4) J. W. Kang and P. M. Maitlis, *ibid.*, **26**, 393 (1971).

(5) J. W. Kang, K. Moseley, and P. M. Maitlis, *J. Amer. Chem. Soc.*, **91**, 5970 (1969).

(6) H. N. Junker, W. Schäfer, and H. Niedenbrück, *Chem. Ber.*, **100**, 2508 (1967); L. A. Paquette and G. R. Krow, *Tetrahedron Lett.*, 2139 (1968).

(7) All new compounds gave correct elemental analyses for at least carbon, hydrogen, and oxygen. In addition, the infrared, proton nmr, and mass spectra of all new compounds were consistent with the proposed structures. In particular, the proton nmr spectra of compounds with two or more nonequivalent methyl groups (*e.g.*, V, VIII, and IX) exhibited the expected numbers of methyl resonances of the expected relative intensities.

(8) R. B. King, *Chem. Commun.*, 986 (1967).

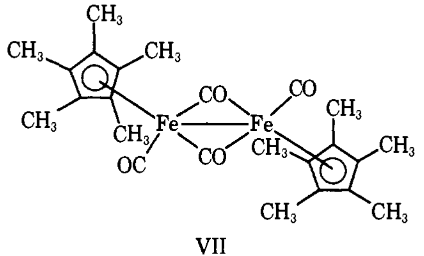
(9) R. B. King, *Advan. Chem. Ser.*, No. **62**, 203 (1967).

(10) R. B. King, *Inorg. Nucl. Chem. Lett.*, **5**, 905 (1969).

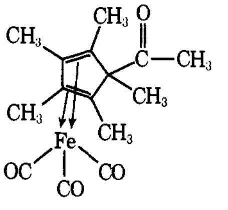
(11) R. B. King and A. Fronzaglia, *Inorg. Chem.*, **5**, 1837 (1966).

(12) D. P. Tate, J. M. Augl, and W. R. Knipple, *ibid.*, **1**, 433 (1962).

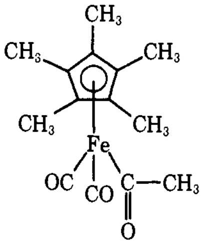
complete loss, since the compounds $CH_3M(CO)_3C_5(CH_3)_5$ (V, M = Mo and W) are the expected thermal decarbonylation products[13] of the σ-acetyl derivatives $CH_3COM(CO)_3C_5(CH_3)_5$ (VI, M = Mo and W) which would be formed if the acetyl group in II was transferred to the metal atom. More specific information on the mechanism of formation of pentamethylcyclopentadienylmetal carbonyl derivatives from reactions of the acetyl derivative II with various metal carbonyls is provided by a study of the reactions of II with various iron carbonyls. Reaction of $Fe(CO)_5$ with the acetyl derivative II in boiling 2,2,5-trimethylhexane (36 hr) gave a 71% yield of the known[8] red-violet crystalline $[(CH_3)_5C_5Fe(CO)_2]_2$ (VII) with complete loss of the acetyl group. However, reaction of $Fe_2(CO)_9$ with the acetyl derivative II in pentane at room temperature gave a 25% yield of the yellow waxy diene–iron tricarbonyl complex[7] $[(CH_3)_5C_5COCH_3]Fe(CO)_3$ (VIII) and a 9% yield of the pale yellow crystalline σ-acetyl derivative[7] $CH_3COFe(CO)_2C_5(CH_3)_5$ (IX), mp 71–72°. Thus the reactions of the acetyl derivative II with iron carbonyls depending upon the reaction conditions can give a compound where II is maintained intact [*i.e.*, the diene complex $[(CH_3)_5C_5COCH_3]Fe(CO)_3$ (VIII)], a compound where the acetyl group in II is transferred from an sp^3 carbon atom to iron [(*i.e.*, the σ-acetyl derivative $CH_3COFe(CO)_2C_5(CH_3)_5$ (IX)], or a compound where the acetyl group is lost completely [(*i.e.*, $[(CH_3)_5C_5Fe(CO)_2]_2$ (VII)].



VII



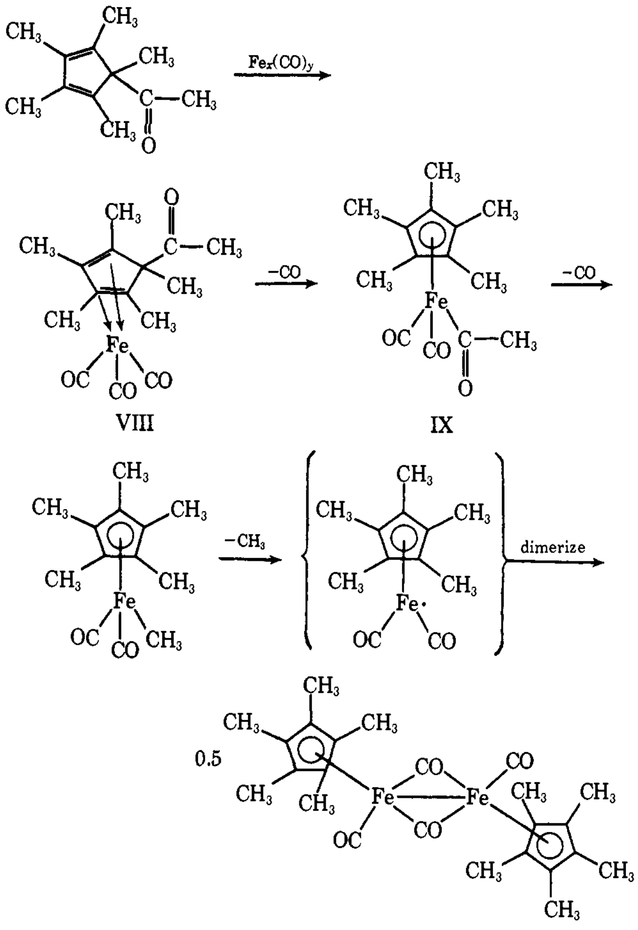
VIII



IX

These experiments suggest the mechanism given in Scheme I for the reaction of the acetyl derivative II with iron carbonyls. Similar mechanisms can be postulated for reactions of the acetyl derivative II with other metal carbonyls. The stabilities of the intermediate diene complexes (*i.e.*, analogs of VIII), σ-acetyl derivatives (*i.e.*, analogs of IX), and σ-methyl derivatives (*i.e.*, analogs of V) relative to the pentamethylcyclopentadienylmetal carbonyl end product will determine whether any of the intermediate compounds can be isolated from a given system. Thus the diene complex VIII and the σ-acetyl derivative IX can be isolated from reactions of II with iron carbonyls, whereas only the σ-methyl derivative V apparently can be isolated from reactions of II with carbonyls of molybdenum and tungsten. These observations on the mechanism of reactions of metal carbonyls with the acetyl derivative II also relate to analogous reactions between metal carbonyls and unsubstituted cyclopentadiene, where the complex $C_5H_6Fe(CO)_3$ from $Fe_2(CO_9)$ and cyclopentadiene[14] exemplifies a diene complex intermediate and the complex $C_5H_5W(CO)_3H$ from $(CH_3CN)_3W(CO)_3$ and cyclopentadiene[11] exemplifies a σ-hydride intermediate, the analog of a σ-acetyl intermediate.

Scheme I. Pathway of the Reaction of 5-Acetyl-1,2,3,4,5-pentamethylcyclopentadiene with Iron Carbonyls



The availability of pentamethylcyclopentadienylmetal carbonyls in larger quantities than before has enabled us to initiate studies on their derivative chemistry. Examples of other pentamethylcyclopentadienylmetal carbonyl derivatives which have been prepared and characterized include the orange $(CH_3)_5C_5Cr(CO)_2NO$, mp 74–75°, the pale yellow $(CH_3)_5C_5Mn(CO)_2P(C_6H_5)_3$, mp 177–180° dec, the red-brown $(CH_3)_5C_5Fe(CO)_2Br$, mp 160–162°, and the yellow $(CH_3)_5C_5Fe(CO)_2C_6F_5$, mp 104–106°. Further details of this work will be reported elsewhere.

Acknowledgment. Portions of this research were supported by the National Science Foundation under Grant No. GP-9662 and by the Petroleum Research Fund,

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[13] R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 15 (1964).

[14] R. K. Kochhar and R. Pettit, *ibid.*, **6**, 272 (1966).

administered by the American Chemical Society, under Grant No. 2838-A1,3.

(15) Postdoctoral research associate, 1968–1971.

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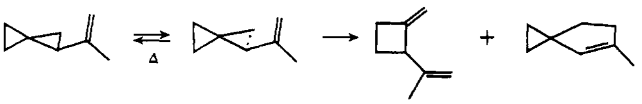
Stereochemistry of and Alteration in the Mechanism of the Spiropentane to Methylenecyclobutane Thermal Rearrangement by Polar Substituents

Sir:

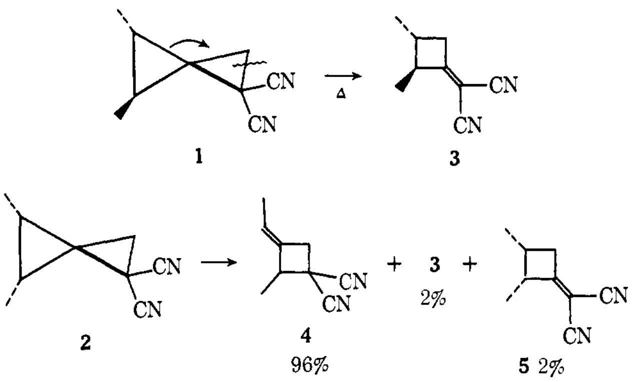
The thermal rearrangement of isopropenylspiropentanes to methylenecyclobutanes and spiro[2.4]hept-4-enes has been shown to proceed by initial reversible 1,2 (peripheral) bond fission followed by a vicinal alkyl shift to give the cyclobutanes.[1]



In an effort to examine the stereochemistry of the alkyl shift in a polarized diradical, *trans*- and *anti-cis*-dimethyl-1,1-dicyanospiropentane, **1** and **2**, respectively,[2] were prepared by addition of dicyanocarbene[3] to *trans*- and *cis*-2,3-dimethylmethylenecyclopropane, respectively.[4] Only one trans compound is possible (as an enantiomeric pair), but only one of the two possible cis compounds, presumably the anti material, was formed, possibly because of the steric effects.

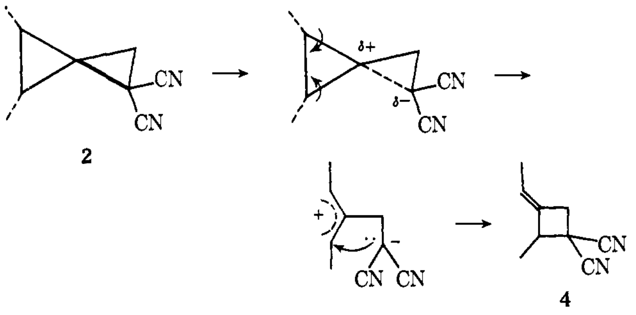
Pyrolysis of **1** at 170° in the vapor phase or in benzene in sealed tubes gave a single product whose pmr was consistent with that of *trans*-2,3-dimethyldicyanomethylenecyclobutane (**3**).[5] This material can be formed by cleavage of what must be one of the weakest bonds in the system, namely, the 1,2 bond, followed by an alkyl shift with retention of stereochemistry of the migrating group.

However, when **2** was pyrolyzed under the same conditions, the major product was of an entirely different type, namely, 2-methyl-3-ethylidene-1,1-dicyanocyclobutane (**4**). There are two stereoisomers of **4**, syn and anti. Both were formed as a 1:1 mixture by cycloaddition of ethylidene malononitrile[6] to methylallene, and these were separated; in addition, two other compounds were formed in this cycloaddition whose pmr spectra were consistent with the *trans*- and *cis*-2,4-dimethyl-3-methylene-1,1-dicyanocyclobutanes. Significantly, only one of the isomers of **4** was produced upon pyrolysis of **2**. Pmr[7] would not allow assignment of stereochemistry although the ^{13}Cmr[8] could be interpreted in terms of the anti stereochemistry for the major rearrangement product from **2**. The pathway for formation of **4** from **2** is, most likely, initial fission of the 1,3 (radial) bond followed by fission of the 4,5 bond and recombination. Because of the high stereospecificity of this reaction, there is the suggestion that it resembles the cyclopropyl to allyl cation rearrangement *via* the appropriate disrotatory motions,[9] thus



1 → **3**

2 → **4** 96% + **3** 2% + **5** 2%



2 → → **4**

Consistent with this interpretation is the direction of rotation of the methyl groups of the cyclopropane ring relative to the departing group[9] and the fact that the rearrangement is at least a factor of ten faster in acetonitrile as in benzene. However, the reaction of **1** to **3** was also dramatically faster in acetonitrile.

Also formed in the pyrolysis of **2** in the vapor phase were two minor products in a 1:1 ratio, representing no more than 4% of the total product. One of these was identical with **3** by nmr and vpc while the other had an nmr consistent with that of *cis*-2,3-dimethyldicyanomethylenecyclobutane (**5**).[10] The 3:5 ratio was

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(1) J. J. Gajewski, *J. Amer. Chem. Soc.*, **92**, 3688 (1970).

(2) Both starting materials were collected by vpc and had m/e 146.085, calcd for $C_9H_{10}N_2$, 146.0844; nmr of **1** (220 MHz) multiplet with a symmetry plane from δ 1.10 to 1.4 (8 H), singlet at 2.05 (2 H); nmr of **2** (220 MHz) doublet at δ 1.11 (6 H, J = 6 Hz), symmetrical multiplet at 1.76 (2 H), singlet at 1.95 (2 H).

(3) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 1979 (1966).

(4) J. J. Gajewski, *ibid.*, **90**, 7178 (1968).

(5) The pmr of **3** (220 MHz) showed: doublet at δ 1.26 (3 H, J = 7 Hz), doublet at 1.37 (3 H, J = 7 Hz), five-line multiplet with 7-Hz separation of lines at 2.14 (1 H), doublet of doublets at 2.60 (1 H, J = 18, 7 Hz), multiplet at 2.91 (1 H), and doublet of doublet of doublets at 3.22 (1 H, J = 18, 8, and 4 Hz); nominal mass 146. For reference, the pmr of *trans*-2,3-dimethylcyclobutanone (220 MHz) showed: doublet at δ 1.12 (3 H, J = 7 Hz), doublet at 1.34 (3 H, J = 7 Hz), five-line multiplet at 1.96 (1 H), doublet of doublet of doublets at 2.58 (1 H, J = 2, 8, and 17 Hz), multiplet at 2.79 (1 H), and doublet of doublet of doublets at 2.98 (1 H, J = 2, 8, and 16 Hz).

(6) Farbenfabriken Bayer Akt-Ges. British Patent 812,240 (1959); *Chem. Abstr.*, **53**, 15,648 (1959).

(7) Pmr of *anti*-**4** (220 MHz) showed: doublet at δ 1.42 (3 H, J = 7 Hz), doublet of quartets at 1.58 (3 H, J = 7 and 2 Hz), broad singlet at 3.34 (2 H), multiplet at 3.64 (1 H), and multiplet at 5.41 (1 H); nominal mass 146. Pmr of *syn*-**4** (220 MHz) showed: doublet at δ 1.53 (3 H, J = 7 Hz), doublet of quartets at 1.62 (3 H, J = 7 and 2 Hz), broad singlet at 3.30 (2 H), multiplet at 3.69 (1 H), and multiplet at 5.37 (1 H); nominal mass 146.

(8) The ring methylene carbon in the anti compound was at 154.7 ppm (relative to CS_2) while in the syn compound it occurred at 153.3 ppm. The ring methine carbon in the anti compound was at 144.4 ppm while in the syn compound it occurred at 145.0 ppm. The shielding effect of a γ substituent (the allylic methyl) appears to give rise to these shifts; B. V. Cheney and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 5319 (1967).

(9) (a) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *ibid.*, **87**, 4006 (1965); (b) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *ibid.*, **87**, 4007 (1965); (c) P. von R. Schleyer, G. W. Van Dine, V. Schöllkopf, and J. Paust, *ibid.*, **88**, 2868 (1966).

(10) Pmr of **5** (220 MHz) showed: doublet at δ 1.15 (3 H, J = 7 Hz), doublet at 1.34 (3 H, J = 7 Hz), multiplet at 2.65 (2 H), multiplet at 3.25 (1 H), and multiplet at 3.50 (1 H). For reference, the pmr of