the illustrated reaction scheme.

$$\begin{tikzcd}
 & & \mathrm{RD(H)} \\
\mathrm{RH(D)} \arrow[r, "k_{\mathrm{H(D)}}\ \mathrm{MeO^-}", "\mathrm{MeOD\ (MeOH)}"'] & \mathrm{R^-} \arrow[ur, "k_{\mathrm{d(h)}}"] \arrow[dr, "k_{\mathrm{e}}"'] & \\
 & & \mathrm{R\cdot}
\end{tikzcd}$$

Within experimental error, $k_1 = k_2$ (subscripts are run numbers) and $k_3 = k_4$, demonstrating that in runs 2 and 4 the reaction is ionization limited. Moderate changes in acceptor concentration produced no change in rate constant, supporting this conclusion. Because $k_5 = k_{\mathrm{H}}$ and $k_4 = k_{\mathrm{D}}$, the primary isotope effect is $k_5/k_4 = k_{\mathrm{H}}/k_{\mathrm{D}} = 5.7$ (in MeOH). Similarly, $k_2/k_7 = k_{\mathrm{H}}/k_{\mathrm{D}} = 5.3$ (in MeOD). Solvent isotope effects are $k_2/k_5 = k_{\mathrm{H(MeOD)}}/k_{\mathrm{H(MeOH)}} = 2.4$ and $k_7/k_4 = k_{\mathrm{D(MeOD)}}/k_{\mathrm{D(MeOH)}} = 2.6$.

The isotope effect for carbanion protonation is calculated as follows: for loss of RH in MeOH, $k_6 = k_{\mathrm{H(MeOH)}}k_{\mathrm{e}}/(k_{\mathrm{e}} + k_{\mathrm{h}})$ and $k_5/k_6 = (k_{\mathrm{e}} + k_{\mathrm{h}})/k_{\mathrm{e}}$, giving $k_{\mathrm{h}}/k_{\mathrm{e}} = 19.7$. The same method gives $k_{\mathrm{d}}/k_{\mathrm{e}} = 3.7$, and, therefore, $k_{\mathrm{h}}/k_{\mathrm{d}} = 5.3$. (A value of 5.2 was obtained at 0.81 *N* KOMe.) If microscopic reversibility is assumed, two conclusions are suggested: first that the change from H to D produces about the same change in zero-point energy for OH in methanol as for CH in 9-methoxyfluorene and second that the change in solvent (MeOH *vs.* MeOD) does not affect the electron-transfer rate. These conclusions are not independent; rather the assumption of one requires the other and the incorrectness of one requires a fortuitously compensating incorrectness in the other.

If both k_{H} and k_{D} are measured in the same solvent, $k_{\mathrm{H}}/k_{\mathrm{D}} \cong 5.5$. If k_{H} and k_{D} are measured in isotopically different solvents, $k_{\mathrm{H}}/k_{\mathrm{D}}$ is modified by the solvent isotope effect, for example, $k_{\mathrm{H(in\ MeOH)}}/k_{\mathrm{D(in\ MeOD)}} = k_5/k_7 = 2.2$. This shows that the isotopic nature of the medium affects the free-energy difference between the starting state (RH(D) and $\mathrm{MeO^-}$) and the transition state in a manner independent of covalent bond-breaking processes. As the free-energy difference between the product state ($\mathrm{R^-}$ and MeOH(D)) and the transition state is affected by the isotopic nature of the medium only to that extent expected for the primary, bond-breaking isotope effect ($k_{\mathrm{h(MeOH)}}/k_{\mathrm{d(MeOD)}} = 5.3$), it may be inferred that the product state and the transition state are similarly solvated, whereas the starting state, in particular methoxide ion, must be appreciably desolvated enroute to the transition state.

It should be made clear that the reverse isotope effect measured in this manner does not necessarily indicate that the carbanion would select MeOH molecules in preference to MeOD molecules if exposed to a mixture of both. We have merely demonstrated a longer lifetime[12] for 9-methoxyfluorenide ion in the deuterated solvent. Although this could result from a greater fraction of productive encounters in MeOH *vs.* MeOD, it could also indicate a situation in which all encounters lead to protonation but where the average time between encounter and protonation is greater in MeOD. This point deserves further study in that the latter alternative could allow the occurrence of intramolecular reprotonation even in the case of trappable anions.

Acknowledgment. We wish to thank the National Science Foundation for a grant (GP-17465) supporting this work.

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[12] Although we can determine only relative lifetimes, reprotonation of the carbanion must be well below the diffusion-controlled limit. Ionization is rate limiting for the electron-transfer reaction at concentrations of 3,5-dichloronitrobenzene down to 0.05 *M*. Stoichiometric studies show clearly that complexation between the reagents and the acceptor is not important and that the acceptor is therefore acting as a true bimolecular interceptor for the anion.

Reaction of Methylenecyclopropanes with Tetracyanoethylene. A New Cycloaddition Involving Three- and Two-Carbon Units

Sir:

Most thermal [2 + 2 + 2] cycloadditions[1] hitherto presented are viewed as involving either a symmetry-allowed $[{}_{\pi}4_{\mathrm{s}} + {}_{\pi}2_{\mathrm{s}}]$ process (Diels–Alder reaction)[2] or a $[{}_{\pi}2 + {}_{\pi}2 + {}_{\pi}2]$ reaction.[3] Comparatively few examples are known of the intermolecular $[{}_{\sigma}2 + {}_{\pi}2 + {}_{\pi}2]$ cycloaddition where a C–C single bond participates as a two-electron component.[4,5] This paper describes a thermal cycloaddition of methylenecyclopropanes to tetracyanoethylene (TCNE) which, at least formally, falls into this category, and the substituent dependency of the reaction mode.

When a mixture of 2-phenyl-1-methylenecyclopropane (**1a**) and TCNE (1:1.2 mole ratio) in benzene was heated at 100° for 5 days under nitrogen atmosphere, five-membered cycloadducts, **2a** [mp 151–152°; uv ($\mathrm{C_2H_5OH}$) $\lambda_{\max}$ 261 (log ϵ 4.26) and 293 nm (shoulder); nmr ($\mathrm{CDCl_3}$, TMS) δ 3.63 (broad s, 4 H, $\mathrm{CH_2}$), 6.78 (m, 1 H, $=\mathrm{C}H\mathrm{C_6H_5}$), and 7.37 (m, 5 H, $\mathrm{C_6H_5}$)] and **3a** [mp 97.5–98.5°; nmr ($\mathrm{CDCl_3}$) δ 3.68 (m, 2 H, $\mathrm{CH_2}$), 4.65 (m, 1 H, $\mathrm{C}H\mathrm{C_6H_5}$), 5.29 and 5.62 (m, 1 H each, $=\mathrm{CH_2}$), and 7.48 (s, 5 H, $\mathrm{C_6H_5}$)][6,7] were obtained in 40 and 25% yields, respectively (eq 1). Similarly, reaction of 2,2-diphenyl-1-methylenecyclopropane (**1b**) and TCNE (100°, 3 days) gave **2b** (45%) [mp 142.5–143.5°; uv ($\mathrm{C_2H_5OH}$) $\lambda_{\max}$ 260 nm (log ϵ 4.07); nmr ($\mathrm{CDCl_3}$) δ 3.51 (s, 4 H, $\mathrm{CH_2}$) and 7.35 (m, 10 H, $\mathrm{C_6H_5}$)] and **3b**

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[1] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[2] Reviews: (a) A. Onishchenko, "Diene Synthesis," Oldbourne Press, London, 1964; (b) A. Wassermann, "Diels–Alder Reactions," Elsevier, Amsterdam, 1965.

[3] (a) A. T. Blomquist and Y. C. Meinwald, *J. Amer. Chem. Soc.*, **81**, 667 (1959); (b) R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *Tetrahedron Lett.*, 615 (1962); (c) R. C. Cookson, J. Dance, and J. Hudec, *J. Chem. Soc.*, 5416 (1964); (d) H. Hearney and J. M. Jablonski, *Tetrahedron Lett.*, 2733 (1967); (e) H. K. Hall, Jr., *J. Org. Chem.*, **25**, 42 (1960); (f) J. K. Williams and R. E. Benson, *J. Amer. Chem. Soc.*, **84**, 1257 (1962).

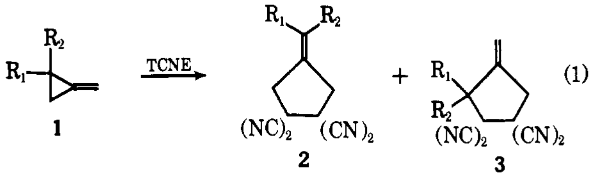
[4] For possible $[{}_{\sigma}2 + {}_{\pi}2 + {}_{\pi}2]$ cycloadditions previously reported: (a) S. Sarel and E. Breuer, *ibid.*, **81**, 6522 (1959); (b) F. W. Fowler, *Angew. Chem., Int. Ed. Engl.*, **10**, 135 (1971); (c) J. E. Baldwin and R. K. Pinschmidt, Jr., *Tetrahedron Lett.*, 935 (1971).

[5] For the $[{}_{\sigma}2_{\mathrm{a}} + {}_{\sigma}2_{\mathrm{a}} + {}_{\pi}2_{\mathrm{s}}]$ cycloaddition, see C. D. Smith, *J. Amer. Chem. Soc.*, **88**, 4273 (1966).

[6] All new compounds gave correct elemental analyses and consistent spectral data (ir, uv, nmr, and mass spectra). The authors thank Professor A. Tatematsu, Meijo University, for measurement of the high-resolution mass spectra.

[7] Careful ozonolysis of **2a** at −78° followed by reductive work-up[8] gave 3,3,4,4-tetracyanocyclopentanone [mp 127–129° dec; ir (KBr) 2240 (CN) and 1778 $\mathrm{cm^{-1}}$ (C=O)][6] and benzaldehyde, whereas **3a** was converted into 3,4,4-tricyano-2-phenylcyclopentenone [mp 161.5–163.5° dec; ir (KBr) 2240, 2220 (CN), and 1745 $\mathrm{cm^{-1}}$ (C=O)].[6]

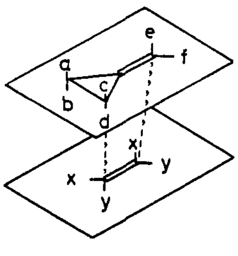
[8] J. J. Pappas, W. P. Keaveney, E. Gancher, and M. Berger, *Tetrahedron Lett.*, 4273 (1966).



a, $R_1 = C_6H_5$; R_2 = H
b, $R_1 = R_2 = C_6H_5$

(35%) [mp 127–129°; nmr ($CDCl_3$) δ 3.76 (m, 2 H, CH_2), 5.60 and 5.75 (broad s, 1 H each, $=CH_2$), and 7.40 (s, 10 H, C_6H_5)].[6] Thus, the methylenecyclopropanes are shown to undergo the cycloaddition to TCNE at the exocyclic methylene and one of the cyclopropane methylenes.

A concerted mechanism consisting of the synchronous cyclopropane cleavage and the cyclopentane formation by way of transition states of type **4** or **5** would reasonably account for the present reaction. Based on first-order orbital-symmetry arguments,[1] there are *a priori* four possible modes of combination of the two components: (i) $[({}_\sigma 2_s + {}_\pi 2_s) + {}_\pi 2_s]$, (ii) $[({}_\sigma 2_a + {}_\pi 2_a) + {}_\pi 2_s]$, (iii) $[({}_\sigma 2_s + {}_\pi 2_a) + {}_\pi 2_a]$, and (iv) $[({}_\sigma 2_a + {}_\pi 2_s) + {}_\pi 2_a]$ processes, the stereochemical requirements for methylenecyclopropanes being designated in parentheses.[9] At this point, closer scrutiny of the stereochemical results to distinguish the mechanistic pathway is not possible, since substrates suitable for such elucidation are not at hand.[12]



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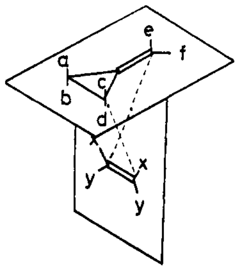

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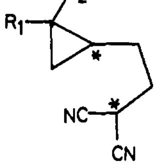

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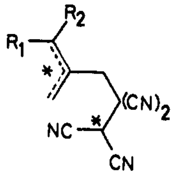

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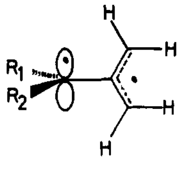

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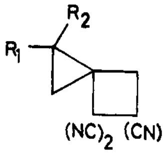
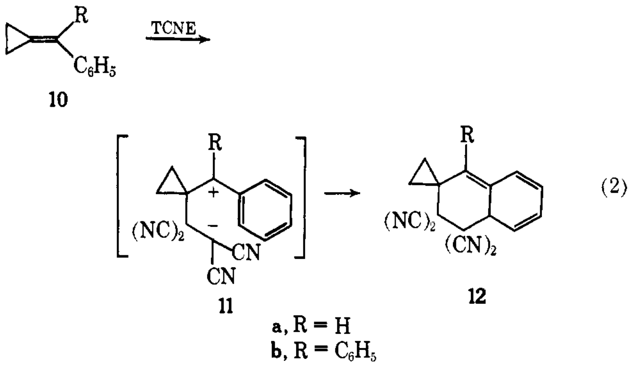


9

Alternatively, nonconcerted mechanisms involving diradical intermediates such as **6** or **7** (* = ·) might be operative, though no confirmative evidences have been obtained. Phenyl-substituted methylenecyclopropanes which enter into the cycloaddition undergo facile degenerate rearrangements,[13,14] and TCNE might be trapping the intermediary, nonplanar trimethylenemethane diradicals **8**.[13b,d] However, the structure of **8** having a plane of symmetry might result in the formation of a single type of adduct (**2** or **3**).[15,16] A stepwise conversion *via* the dipolar ions **7** (* = + and −) seems unlikely, because the reaction was not accelerated with an increase in the polarity of the solvent:[17] relative rates of the reaction of **1a** and TCNE at 100° in cyclohexane, benzene, chloroform, and acetonitrile are approximately 1.0, 1.8, 1.8, and 1.0, respectively. A two-step transformation involving the formation of the cyclobutane **9**[18] and the subsequent rearrangement to the methylenecyclopentane **2** or **3**[19] also seems not to be operative, since monitoring the reaction by nmr provided no evidence for the intervention of **9** which would be expected to survive long enough to allow its spectroscopic detection.

Finally, it should be noted that the reaction of TCNE with **10a** and **10b** (in benzene, 25°) proceeds in a completely different manner to afford **12a** (80% yield) [mp 108–110°; uv ($CHCl_3$) λ_{max} 269 (log ϵ 4.23) and 278 nm (4.21); nmr ($CDCl_3$) δ 1.28–1.75 (m, 4 H, CH_2), 4.58 (broad s, 1 H, >CH), 5.05 (d, J = 5 Hz, 1 H, =CH), and 5.70–6.48 (m, 4 H, =CH)] and **12b** (90%)



a, R = H
b, R = C_6H_5

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[9] Thermal rearrangement of vinylmethylenecyclopropane[10] and **1b**[11] would provide examples of the intramolecular type iii transformation.

[10] (a) T. C. Shields, W. E. Billups, and A. R. Lepley, *J. Amer. Chem. Soc.*, **90**, 4749 (1968); (b) T. C. Shields and W. E. Billups, *Chem. Ind.* (*London*), 619 (1969).

[11] M. Jones, Jr., M. E. Hendrick, J. C. Gilbert, and J. R. Butler, *Tetrahedron Lett.*, 845 (1970).

[12] TCNE which has a symmetrical structure is a sole olefin capable of forming the cycloadducts. Under similar conditions, fumaronitrile, acrylonitrile, maleic anhydride, dimethyl maleate, dimethyl fumarate, methyl acrylate, styrene, or dimethyl acetylenedicarboxylate did not give adducts of type **2** or **3**.

[13] *Cf.* (a) E. F. Ullman, *J. Amer. Chem. Soc.*, **82**, 505 (1960); (b) J. J. Gajewski, *ibid.*, **90**, 7178 (1968); (c) J. C. Gilbert and J. R. Butler, *ibid.*, **92**, 2168 (1970); (d) W. von E. Doering and H. D. Roth, *Tetrahedron*, **26**, 2825 (1970), and references cited therein.

[14] Optically active **1a** racemizes with a half-life of 22 min at 100° in $CHCl_3$ [R. Noyori, H. Takaya, Y. Nakanisi, and H. Nozaki, *Can. J. Chem.*, **47**, 1242 (1969)]. **1b** undergoes a degenerate rearrangement with the activation parameters $\Delta H^{\ddagger}_{52°}$ 22.1 kcal/mol and $\Delta S^{\ddagger}_{52°}$ −11.5 eu.[13c]

[15] For the possible cycloaddition of trimethylenemethane to TCNE, see J. S. Ward and R. Pettit, *Chem. Commun.*, 1419 (1970).

[16] The cycloaddition was not quenched by radical scavengers such as thiocresol, 2,6-di-*tert*-butylphenol, or galvinoxyl. Under comparable thermal conditions neither **1a** nor **1b** rearranges into the isomers benzylidenecyclopropane (**10a**) or diphenylmethylenecyclopropane (**10b**), respectively.

[17] (a) R. Gompper, *Angew. Chem., Int. Ed. Engl.*, **8**, 312 (1969); (b) P. D. Bartlett, *Quart. Rev., Chem. Soc.*, **24**, 473 (1970).

[18] (a) Cycloaddition of tetrafluoroethylene and methylenecyclopropane: B. C. Anderson, *J. Org. Chem.*, **27**, 2720 (1962); (b) related reactions of TCNE with methylenecyclobutenes [J. K. Williams, *J. Amer. Chem. Soc.*, **81**, 4013 (1959)] and with triisopropylidenecyclopropane [G. Köbrich, H. Heinmann, and W. Zündorf, *Tetrahedron*, **23**, 565 (1967)] are known.

[19] Symmetry-allowed $[{}_\sigma 2_s + {}_\sigma 2_a]$ process: J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1561 (1970).

[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, $>$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**, $k_{\mathrm{CH_3CN}}/k_{\mathrm{C_6H_{12}}}$ at 25° $\simeq 10^2$), the cycloaddition would be rationalized as a stepwise reaction involving the dipolar ions **11**.[17,20,21]

[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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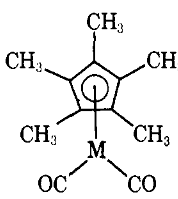
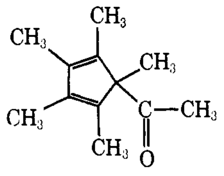
A Convenient Synthesis of Pentamethylcyclopentadienylmetal Carbonyls

Sir:

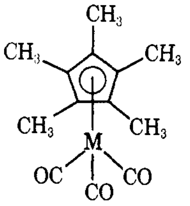
We required gram quantities of several pentamethylcyclopentadienylmetal carbonyls for a comparison of their chemistry with that of the unsubstituted cyclopentadienylmetal carbonyls.[1] Previously reported syntheses of pentamethylcyclopentadienylmetal carbonyls either required the difficultly accessible 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



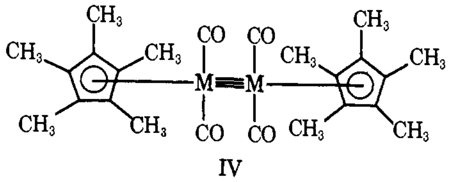
II



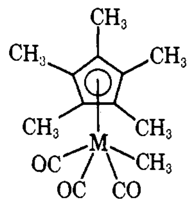
III

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°.

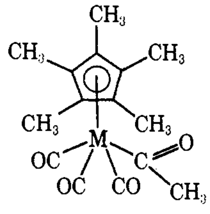
In the original work[3] with pentamethylcyclopentadienylmetal carbonyl derivatives, the reaction between pentamethylcyclopentadiene and $Mo(CO)_6$ was of interest because it gave a product $[(CH_3)_5C_5Mo(CO)_2]_2$, which was not analogous to the unsubstituted cyclopentadienyl derivative $[C_5H_5Mo(CO)_3]_2$. 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).