Brookhart, G. O. Nelson, G. Scholes, and R. A. Watson, *J. Chem. Soc., Chem. Commun.*, 195 (1976); M. Brookhart, G. O. Nelson, G. Scholes, R. A. Watson, and G. Koszalka, *J. Am. Chem. Soc.*, **98**, 8155 (1976); C. R. Graham, G. Scholes, and M. Brookhart, *ibid.*, **99**, 1180 (1977).
(25) G. Deganello, H. Maltz, and J. Kozarich, *J. Organomet. Chem.*, **60**, 323 (1973); G. Deganello, P. L. Sandrini, R. A. Michelin, and L. Toniolo, *ibid.*, **90**, C31 (1975).
(26) T. H. Coffield and R. P. M. Werner, U.S. Patent 3 124 600; *Chem. Abstr.*, **60**, 15914 (1964); R. P. M. Werner and T. H. Coffield, *Chem. Ind. (London)*, 936 (1960).
(27) This study was made possible through the courtesy of Professor Jon Clardy and Dr. Jose Fayos.
(28) J. A. S. Howell, B. F. G. Johnson, P. L. Josty, and J. Lewis, *J. Organomet. Chem.*, **39**, 329 (1972).
(29) P. Crews, *J. Am. Chem. Soc.*, **95**, 637 (1973).
(30) (a) L. A. Paquette, *J. Am. Chem. Soc.*, **92**, 5765 (1970); (b) L. A. Paquette, R. E. Wingard, Jr., and R. K. Russell, *ibid.*, **94**, 4739 (1972); (c) D. R. James, G. H. Birnberg, and L. A. Paquette, *ibid.*, **96**, 7465 (1974).
(31) L. A. Paquette and J. M. Photis, *J. Am. Chem. Soc.*, **98**, 4936 (1976).
(32) J. M. Photis and L. A. Paquette, *J. Am. Chem. Soc.*, **96**, 4715 (1974).
(33) L. A. Paquette, *Org. React.*, in press.
(34) This study was made possible through the courtesy of Professor Jon Clardy and Kirsten B. Gifkins.
(35) L. A. Paquette and G. L. Thompson, *J. Am. Chem. Soc.*, **94**, 7118 (1972).
(36) E. Vogel, W. Maier, and J. Eimer, *Tetrahedron Lett.*, 655 (1966).
(37) J. Kalo, J. M. Photis, L. A. Paquette, E. Vogel, and D. Ginsburg, *Tetrahedron*, **32**, 1013 (1976).
(38) See, for example, (a) L. Roos and M. Orchin, *J. Am. Chem. Soc.*, **87**, 5502 (1965); (b) W. R. Roth and W. Grimme, *Tetrahedron Lett.*, 2347 (1966); (c) M. I. Foreman, G. R. Knox, P. L. Pauson, K. H. Todd, and W. E. Watts, *J. Chem. Soc., Perkin Trans. 2*, 1141 (1972); (d) T. H. Whitesides and J. P. Neilan, *J. Am. Chem. Soc.*, **95**, 5811 (1973); (e) J. W. Byrne, H. U. Blaser, and J. A. Osborn, *ibid.*, **97**, 5871 (1975); (f) M. A. Schroeder and M. S. Wrighton, *ibid.*, **98**, 551 (1976); (g) W. T. Hendrix and J. L. von Rosenberg, *ibid.*, **98**, 4850 (1976); and relevant references cited in these papers.
(39) D. R. Lloyd and E. W. Schlag, *Inorg. Chem.*, **8**, 2544 (1969); R. B. King, *Inorg. Nucl. Chem. Lett.*, **5**, 905 (1969).
(40) C. F. H. Allen and A. Bell, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 812.

Molybdenum(0) Catalysis of [1,5]Sigmatropic Carbon Migration in Unsaturated [4.4.2]Propellanes. Deuterium Isotope Effects, Kinetics, and Mechanism

Leo A. Paquette,* Roger P. Micheli, and James M. Photis

Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210. *Received April 28, 1977*

Abstract: Through assessment of the $Mo(CO)_6$-promoted isomerizations of the *2,5-* and *11,12-d_2* [4.4.2]propella-2,4,11-trienes, it could be unequivocally established that C_{11} of the cyclobutene ring and not C_7 of the cyclohexane moiety is directly involved in formal [1,5]sigmatropic migration. The kinetic behavior of the tetrahapto complexes **17–19** revealed several additional mechanistic features: (a) the presence of deuterium atoms at C_2 and C_5 has little impact on the rate-determining step; (b) the 11,12-dideuterio derivative exhibits, in contrast, an appreciable *intermolecular* isotope effect ($k_H/k_D = 0.92$ at 80.6 °C); and (c) a 2-methyl substituent accelerates rearrangement by a factor of 2. The level of isotopic discrimination realizable during *intramolecular* competition was shown to be entirely comparable ($k_H/k_D = 0.93$ at 80 °C) by making recourse to the monodeuterated propellatriene **30**. The magnitude and inverse nature of these secondary isotope effects has been interpreted to be incompatible with two mechanistic alternatives involving "top-side" complexation of the propellatriene (i.e., syn to the cyclobutene bridge). Rather, a transition state model involving modified [1,5]sigmatropic migration on that molecular face opposite to the site of molybdenum coordination is shown to account best for the experimentally determined Arrhenius parameters, deuterium fractionation factors, regioselectivity, and circumambulation (the latter operative only when both C_{11} and C_{12} carry methyl groups).

The ability of transition metal carbonyl complexes to promote olefin isomerization has constituted an important and extensively studied area of organometallic chemistry.[1] Most commonly, 1,3- and 1,5-*hydrogen* shifts have been observed. Depending upon the substrate and catalyst system employed, concerted migrations or processes involving transient formation of metal hydride intermediates are seen to operate. In either event, the different types of isomerization have provided evidence of complete intramolecularity when this level of mechanistic detail has been sought.[2]

During a study of the reaction of unsaturated [4.4.2]propellanes with molybdenum hexacarbonyl,[3,4] we observed that skeletal rearrangement occurs in those systems which possess a 1,3-cyclohexadiene part structure. Because these reactions proceed much more readily than purely thermochemical rearrangements and involve [1,5]sigmatropic *carbon* migration rather than an intramolecular cycloaddition scheme,[5] we were interested in eludicating the mechanistic details of this little-precedented phenomenon.[6] Here we present the results of kinetic and deuterium labeling studies which, when taken with earlier findings,[3] provide experimental evidence implicating suprafacial [1,5] carbon migration within the coordination sphere of the metal.

Results

Synthesis and Rearrangement of the *2,5-* and *11,12-d_2* [4.4.2.]Propella-2,4,11-trienes. Although our earlier results are rationalizable in terms of a [1,5]sigmatropic shift pathway, no insight has been gained into the timing of this migration. Nor has it been unequivocally established that C_{11} of the cyclobutene ring and not C_7 of the tetramethylene bracket is involved in the translocation. Scheme I illustrates these alternatives for the *2,5-d_2* derivative (**1**) without specifying the relative stereochemistry of the complexing molybdenum or allowing for the possibility that other intermediates are involved. Tetrahapto coordination is also assumed at this time but will receive later substantiation. We see that path a is quite direct, requiring valence isomerization and decomplexation of **2** (not necessarily in that order) to provide the annulated cyclooctatetraene (viz., **3**). Reaction coordinate b requires additional 1,5 deuterium migration in **4** prior to delivering the isomerized product, in this case **6**.

The specifically deuterated propellane **1** was synthesized according to the established sequence (Scheme II). Deuterium incorporation into this hydrocarbon was established to be >90% d_2 by ^1H NMR analysis of its *N*-phenyltriazolinedione

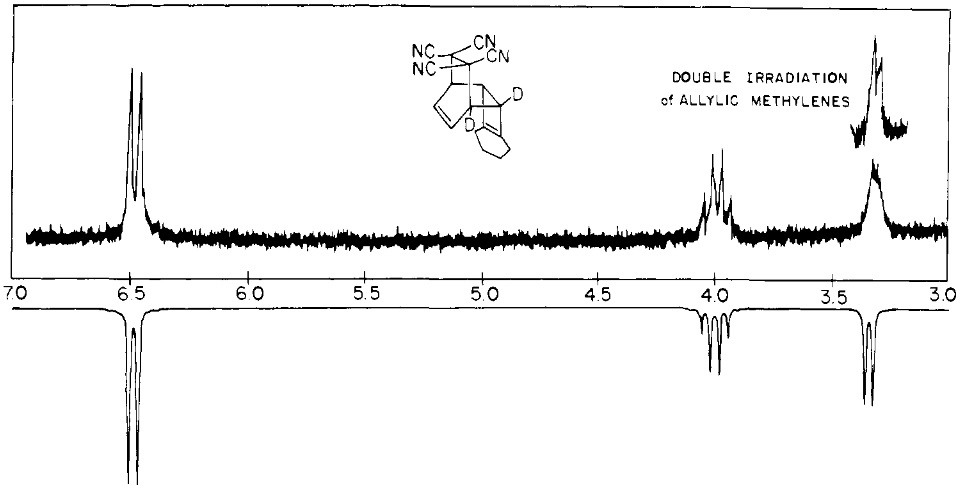
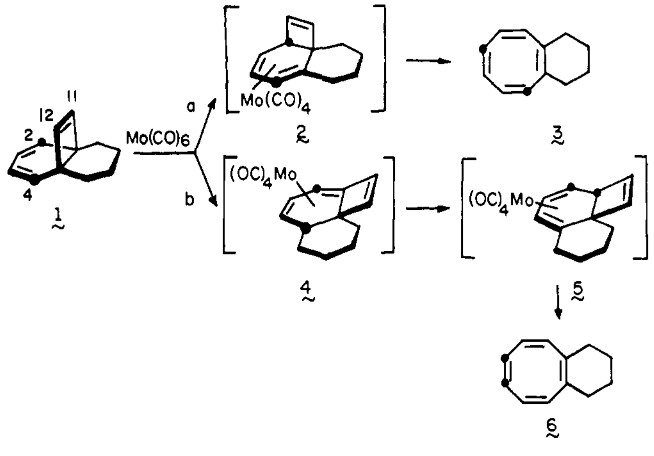
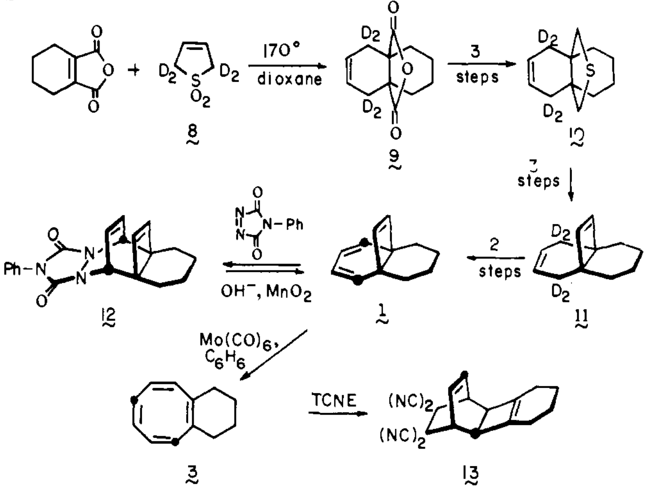


Figure 1. 100-MHz ^{1}H NMR spectrum of **16** (CD_3COCD_3 solution) and the computer simulation thereof by LAOCOON III.[9]

Scheme I



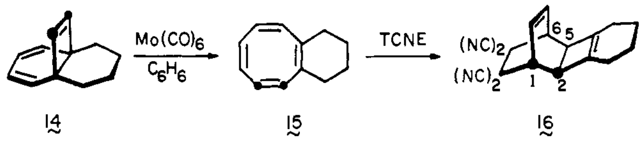
Scheme II



adduct (**12**). When heated with $Mo(CO)_6$ in refluxing benzene for 35 h, **1** was efficiently isomerized to **3** (77% isolated), the positions of isotopic labeling in which were ascertained by formation of the TCNE adduct (**13**). The ^{1}H NMR spectrum of this crystalline derivative displayed an olefinic proton absorption of relative area 1 and proved otherwise identical with that of an authentic sample.[7] Thus, the rearrangement is seen to occur by involvement of C_{11} in a sigmatropic [1,5] migration (path a, Scheme I).

The isotopically labeled propellane **14**[5] was similarly treated with $Mo(CO)_6$ in refluxing benzene. The resulting 1,2-tetramethylenecyclooctatetraene was not isolated but converted directly to its TCNE adduct (Scheme III), the ^{1}H NMR spectrum of which revealed the absence of one proton each from the cyclobutane and bridgehead regions. The 1,2 rather than 1,5 relationship of the deuterium atoms in **16** was established by LAOCOON III simulation of the 100-MHz spectrum (Figure 1).[8] There are major differences in the calculated spectra of **16** and the *1,5-d*$_2$ isomer, particularly in the bridgehead and cyclobutene multiplicities. The unique isolation of **16** is entirely compatible with path a in Scheme I, again in clear contradistinction to the purely thermal reaction channel.[5]

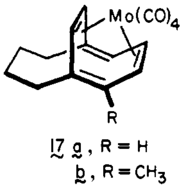
Scheme III



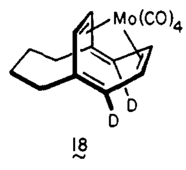
Kinetic Studies. Our intention at the outset was to examine the kinetics of the overall scheme.

$$[4.4.2]\text{propella-2,4,11-triene} \rightarrow Mo(CO)_4\ \text{complex} \rightarrow \text{annulated cyclooctatetraene}$$

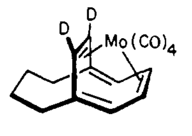
However, pilot experiments revealed this not to be entirely feasible. Thus, when degassed solutions of **14** and $Mo(CO)_6$ in C_6D_6 contained in evacuated ($\sim 10^{-3}$ Torr) NMR tubes were heated in an oil bath at 90 °C, barely detectable amounts (<5%) of the corresponding $Mo(CO)_4$ complex[3] would be formed and no further reaction was seen after prolonged periods of time. These data disclosed that liberation of carbon monoxide is operative during tetrahapto complexation and that this transformation is rather sensitive to the vapor pressure of CO.[9] As a result, we were led directly to a quantitative assessment of the mechanistically more significant rearrangement of such complexes. In this instance, comparable preliminary experiments with **17a** were found to proceed smoothly. Evidently, CO is not now a deterrent to structural isomerization, if it is liberated at all (reversibly or otherwise),



17 a, R = H
b, R = CH_3



18

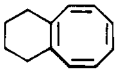
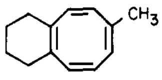
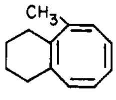
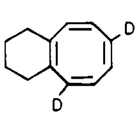
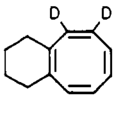


19

Table I. Rate Constants for the Thermal Rearrangement of **17–19** (0.30 M in C_6D_6)

Complex	Temp, °C	$10^4 k_1$, s^{-1}	Other data
17a	80.60 ± 0.05	0.136 ± 0.004	$\Delta H^{\neq} = 31.3 \pm 1$ kcal/mol
		0.142 ± 0.002	$\Delta S^{\neq} = +7 \pm 3$ eu
	100.00 ± 0.05	1.79 ± 0.02	
		1.86 ± 0.03	
	109.99 ± 0.05	4.34 ± 0.03	
		4.30 ± 0.03	
18	100.10 ± 0.05	1.89 ± 0.06	k_H/k_D (100 °C) = 1.03
		1.84 ± 0.04	
19	80.60 ± 0.05	0.148 ± 0.003	k_H/k_D (80 °C) = 0.92
		0.154 ± 0.006	
	100.00 ± 0.05	1.97 ± 0.02	k_H/k_D (100 °C) = 0.90
		2.08 ± 0.02	
17b	100.00 ± 0.05	3.23 ± 0.05	
		3.36 ± 0.05	

Table II. Relative Rates of Formation at 100 °C

	 20	 21	 22
$\underline{k}_{rel}^{100°}$	1.0	1.37	0.44
	 23	 24	
$\underline{k}_{rel}^{100°}$	1.03	1.11	

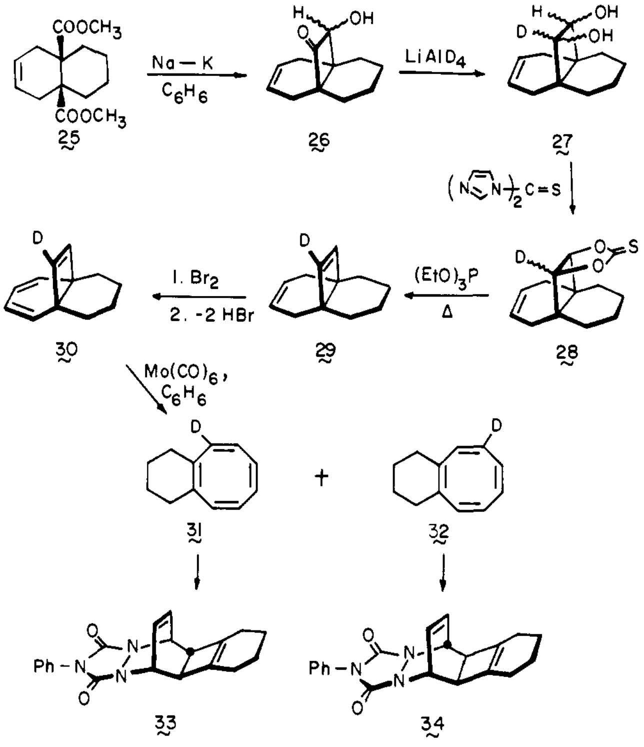
and rate measurements could be suitably conducted in closed systems.

The complexes selected for kinetic study included parent system **17a**, the dideuterated substrates **18** and **19**, and methyl derivative **17b**.[10] Good first-order plots were obtained for the disappearance of all four complexes in C_6D_6 solution as monitored by the gradual disappearance of at least two principal proton signals in their NMR spectra. Good reproducibility was observed in each instance. The relevant rate constants are compiled in Table I.

The kinetic behavior of **17b** at 100 °C reveals the 2-methyl substituent to accelerate rearrangement by a factor of approximately 2 relative to **17a**. However, since **17b** is isomerized to a mixture of **21** and **22** (2.7:1) at this temperature,[3] factoring k_1 for the disappearance of **17b** by these percentage values provides quantitative data for the rates of appearance of these cyclooctatetraenes (Table II). In relative terms, we see that [1,5] shift of the two-carbon bridge toward the methyl group is enhanced while migration away from the alkyl side chain is somewhat decelerated. These computations assume that we are not dealing with two consecutive first-order reactions of the type **17b** → **21** → **22** or **17b** → **22** → **21**. However, the constancy of the percentage composition vs. time and the demonstrated stability of both **21** and **22** to the rearrangement conditions do not allow for this possibility. Rather, all indications are that **21** and **22** result directly from **17b** at reasonably competitive rates.

Our limited study of **18** indicates that labeling of C_2 and C_5 with deuterium introduces minimal if any secondary isotope effect on the rate of isomerization. The data are too limited to judge whether the value of 1.03 at 100 °C is meaningful or within experimental error. On the other hand, the kinetic isotope effect observed with **19** is large and inverse (see Tables I and II). These results are completely consistent with the mechanistic conclusions drawn above. Additionally revealed by these findings is the fact that the C_1–C_{11} or C_6–C_{12} bond is experiencing perturbation during or before the rate-determining step. However, it is not known to what extent the experimentally determined rate constant encompasses the impact of *both* deuterium atoms. To resolve this question, the synthesis of **30** was pursued.

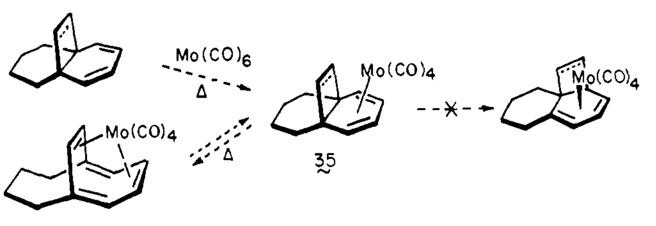
Scheme IV



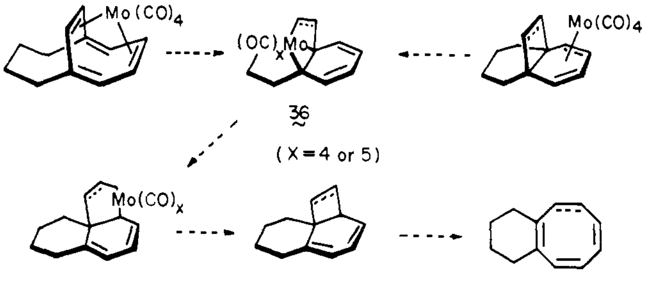
Preparation and Isomerization of [4.4.2]Propella-2,4,11-triene-*11-d*. Determination of an Intramolecular Deuterium Isotope Effect. The $Mo(CO)_6$-promoted rearrangement of **30** constitutes an *intramolecular* competition study because the isotopic discrimination is now required to occur within the same molecule. Experiments of this type are less restrictive than *intermolecular* competition studies (e.g., **17a** vs. **19**), since an isotope effect can be expected to be observed regardless of the timing of the bond breakage.

Access to **30** began by acyloin cyclization of diester **25** according to the literature procedure.[11] Reduction of **26** with lithium aluminum deuteride, followed by reaction of the resulting 1,2-glycol mixture with thiocarbonyldiimidazole,[12] gave the monodeuterated syn and anti thiocarbonates **28** and unreacted *trans*-**27**. Decomposition of **28** in trimethyl phosphite[13] provided **29** which was transformed by well-established

Scheme V



Scheme VI



methodology[14] into **30** having an isotopic purity of ≥98% d_1 (mass spectrometric analysis).

Submission of **30** to the usual rearrangement conditions—$Mo(CO)_6$ in refluxing benzene under a nitrogen atmosphere—produced mixtures of the cyclooctatetraenes **31** and **32** which were treated directly with *N*-phenyltriazolinedione. Through repeated integration of the ^1H NMR spectra of two different samples of adducts **33/34,** identical k_H/k_D values of 0.93 ± 0.05 were obtained after minor correction for isotopic purity. This inverse fractionation factor is closely similar to, if not identical with, that determined previously for **17a.** It therefore is possible that the rate-controlling and product-forming steps are one and the same.

Discussion

In a formal sense, the rearrangements of [4.4.2.]propella-2,4,11-trienes and -2,4-dienes[3] to unsaturated bicyclo[6.4.0]-dodecane derivatives in the presence of $Mo(CO)_6$ correspond to [1,5] sigmatropic shifts proceeding necessarily with migration of an sp^2- or sp^3-hybridized carbon of the four-membered ring. It is now appropriate to raise the question as to how these isomerizations take place. In point of fact, three mechanistic proposals might be advanced to account for the experimental findings.

According to the first alternative, the key intermediate would assumedly be **35,** formed either directly from the propellane substrate through "top-side" bonding to a molybdenum carbonyl fragment or by rebonding and ligand isomerization within stable complexes of the type **17–19** (Scheme V). Although such coordination to the "exo" face might often be favored for steric reasons, the migration of C_{11} (whether sp^2 or sp^3 hybridized) to C_5 within **35** might be impeded by the presence of the metal on the same surface of the molecule. As C_{11} begins its migration across the face of the cyclohexadiene moiety, the $Mo(CO)_4$ fragment must simultaneously be swept away from the seat of reaction. Under these circumstances, one might ask if catalytic action could continue to operate, particularly as it might apply to the twofold circumambulatory rearrangements observed with 11,12-dimethyl derivatives.[3]

A second working hypothesis would involve no reversal of stereochemistry in the α complexation step, but proceed from **17** or **35** to a σ-bonded organometallic intermediate represented by the generalized formula **36** (Scheme VI). In this context, neither a cyclobutane nor cyclobutene carbon subsequently migrates. Rather, they serve as the fulcrum which allows the molybdenum atom to experience [1,5]sigmatropic shifting, the 1,3-cyclohexadiene unit serving as the receptor moiety. Although this mechanism is attractive in its rationalization of the behavior of the 2-methyl- and 11-methyl[4.4.2]-propellatrienes, i.e., the oxidative addition is governed extensively by steric effects, several serious questions can be raised concerning its general operability. Firstly, the entire scheme is predicated on the assumption that molybdenum is capable of oxidative addition in its own right; but no experiments have been reported which clearly demonstrate the capability of molybdenum to insert into carbon–carbon bonds under thermal conditions. However, given the novel structural features of these propellanes, the absence of such corroborative evidence need not have dire significance. Similar considerations apply to the lack of prior findings concerning the feasibility of involvement of Mo in sigmatropic migration.

The most serious disclaimers against the oxidative-addition scheme are the magnitude and inverse nature of the secondary deuterium isotope effect values. Such effects are generally considered to arise from changes in out-of-plane C–H bending force constants which usually are associated with concomitant alterations in hybridization. Since expansion of the four-membered ring by insertion of molybdenum must be at least product determining if not also rate determining, discrimination must be effected at this stage in the case of **30** (and perhaps also with its d_0 and d_2 counterparts). Yet oxidative addition involves a minimal change in rehybridization and should thus give rise to a quite normal isotope effect ($k_H/k_D \sim 1$), although experimental documentation of this assumption is not presently available. The observed fractionation factor of 0.93 is nonetheless considered not to be satisfactorily explained by this model, especially since the transition state might reasonably be expected to be well along the reaction coordinate. Nor is the k_H/k_D value consistent with transient intervention of a biradical intermediate, since a homolytic process should produce but a small isotope effect as well.[15]

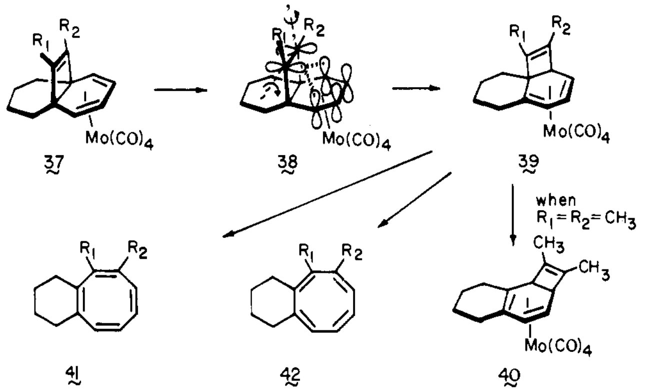
Instead, the isomerization is seen to be particularly isotope sensitive, with C–D migrating some 7–8% more rapidly than C–H. This ordering denotes that the isotopic site becomes more sterically congested or more rigid in the discriminatory transition state, for otherwise the proton-labeled site would pass more rapidly over the energy barrier. Since it is unlikely that **36** is more strained than its precursors, it is seemingly unable to account for the experimental results.

In accord with theory, inverse k_H/k_D values on the order of 10% have become associated with a substantive change in the reactant carbons from sp^2 toward sp^3 in the transition state region.[16] The relative moments of inertia of C–H and C–D are not so altered in proceeding to **36.** Consequently, to the extent that secondary deuterium isotope effects provide a sensitive probe into the mechanistic details of [4.4.2]propella-2,4,11-triene rearrangements, the oxidative addition pathway can be dismissed. This disclaimer does not apply to [4.4.2]propella-2,4-dienes where additional isotope effect studies are required before equally detailed mechanistic analysis is warranted.

The third mechanistic option would involve reversal of stereochemistry in the initial π complexation step. On this basis, the intermediates of consequence would possess structures such as **37,** sigmatropic shifting within which would now necessarily operate on the molecular face opposite to that occupied by the metal (Scheme VII). The new tricyclic system arising in this manner (perhaps through the intermediacy of $Mo(CO)_4$-solvent complexes; noncomplexing solvents do not lead to reaction) could experience electrocyclic ring opening with loss of the $Mo(CO)_4$ fragment and liberation of uncomplexed product. Repetition of the [1,5] shift process would lead via **39** ultimately to a doubly migrated product (**40**) as witnessed under certain conditions of substitution.

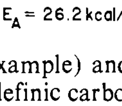
This pathway is particularly attractive in its rationalization of circumambulation. But does it satisfactorily explain why the 11-methyl derivative isomerizes exclusively by migration

Scheme VII

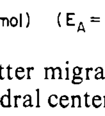


of the unsubstituted cyclobutene carbon? Further, is there a good reason why the 2-methyl isomer should prefer to rearrange by sigmatropic shifting toward the methyl group and at a rate somewhat faster than its unsubstituted counterpart? And does the process conform to the deuterium isotope effect?

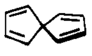
When the Arrhenius parameters for isomerization of **17a** ($\Delta H^{\ddagger} = 31.3$ kcal/mol, $\Delta S^{\ddagger} = +7$ eu) are closely examined, they are seen to compare within reasonable limits to the thermodynamic data obtained by Schiess and Fünfschilling for the thermal rearrangement of the 5-methylcyclohexadienes **43a** and **43b**,[17] by Paquette and Carmody for the isomerization of the *cis*-9,10-dihydronaphthalenes **44a** and **44b** in the 50–90 °C range,[18] and by Semmelhack and co-workers for the spirocyclic tetraene **45** and triene **46**.[19] Each series is characterized by low activation barriers (compare **45** and **46** vs. **47**, for example) and demonstrably better migratory capability for olefinic carbons than for tetrahedral centers. In their study of the thermal reorganization of substituted indenes, Miller, Greisinger, and Boyer noted the preference order H > C_6H_5 > CH_3 to be operative in those [1,5]sigmatropic shifts which prevailed.[20] In agreement with earlier suggestions, we favor a transition state model such as **38** where HOMO-LUMO interaction introduces a level of stabilization adequate to lower the barrier for vinyl shifting.[21] Significantly, this interaction implicates partial bonding of the pπ orbital at the migrating carbon to C_2 and C_6 of the diene moiety at the transition state. Such modification of the more simple [1,5]sigmatropic shift process serves appropriately to decrease torsional modes and enhance steric compression at C_{11} in agreement with the observed isotope effect. Phrased differently, the mechanistic insight provided by **38** can be expected to cause the site with a deuterium label to accumulate at the more sterically congested and rigid position in the transition state (as is observed).



43 a, R = CHO (E_A = 31.0 kcal/mol)
b, R = $COCH_3$ (E_A = 35.2 kcal/mol)

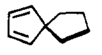


44 a, R = CH_3 (E_A = 26.0 kcal/mol)
b, R = $COOCH_3$ (E_A = 26.7 kcal/mol)



45 (E_A = 26.2 kcal/mol)

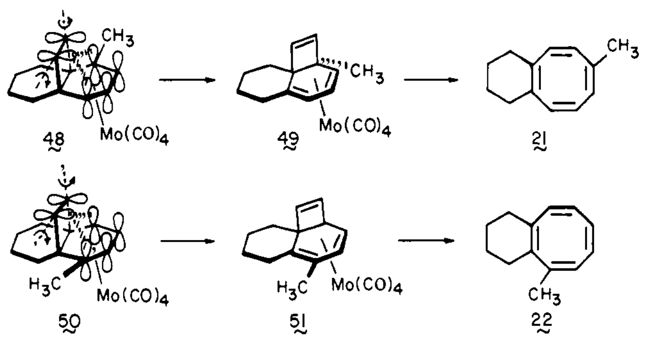
46 (E_A = 27.4 kcal/mol)



47 (E_A = 35.8 kcal/mol)

Since a methyl group at C_{11} will be less inclined than hydrogen to adopt a more sterically encumbered position in the transition state, the unsubstituted vinyl carbon should possess inherently better latent migratory capability in this particular structural situation. Thus, the reactivity pattern of the 11-methyl derivative likewise conforms to this model.

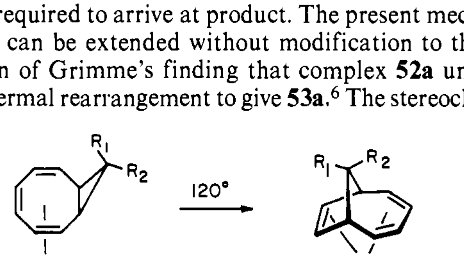
Scheme VIII



The regioselectivity observed in the 2-methyl[4.4.2]propella-2,4,11-triene example is less clear at this time. For the moment, we are inclined to believe that the intramolecular competitions of this sort are governed to a large extent by electronic factors. Thus, both rearrangement pathways are believed to originate with HOMO-LUMO interactions as depicted in **48** and **50**. The extent of long-range interaction in these hypothetical structures need not be, and is likely not, comparable. The observed product distribution (**21**/**22**) provides indication that actual migration within **48** is 2.7-fold faster than that possible in **50** and this despite the inevitable result of positioning the methyl substituent in a rather more congested environment (cf. **49**). Since models clearly show **51** to be less sterically encumbered than **49**, it is unlikely that [1,5] shifting is operating under thermodynamic control. Accordingly, the governing of reactivity by electronic factors within **48** and **50** seems secure, particularly in view of the experimentally established relative rate profile (Table II).

For the present, therefore, these [1,5] carbon shifts can be described as processes involving specific coordination of the unsaturated propellane to molybdenum with suprafacial migration operating under the control of the transition metal. If the rearrangement is indeed dependent upon transitory complexation by a group 6B metal carbonyl fragment on the "underside" of the propellane, then suitable catalysis would expectedly be provided only by the weakly coordinating molybdenum atom. We have previously established that $M(CO)_4$ complexation occurs rapidly on the surface proximal to the cyclobutene ring. When $Cr(CO)_4$ and $W(CO)_4$ residues are involved, the π-complexation strengths are adequate to ensure against reversibility. But this need not be so with $Mo(CO)_4$ which binds less tenaciously.[22]

Schemes VII and VIII serve to explain our experimental observations concisely. In particular, they accommodate in logical orbital-symmetry allowed fashion the overall molecular change required to arrive at product. The present mechanistic analysis can be extended without modification to the interpretation of Grimme's finding that complex **52a** undergoes facile thermal rearrangement to give **53a**.[6] The stereochemistry of this isomerization has more recently been elucidated by Brookhart using the specifically deuterated **52b**.[23] Since conversion to the bicyclo[4.2.1]nonatrienemolybdenum tricarbonyl complex proved stereospecific (**53b** only), a [1,5] shift



52 a, $R_1 = R_2 = H$
b, $R_1 = D, R_2 = H$

53 a, $R_1 = R_2 = H$
b, $R_1 = D, R_2 = H$

with inversion is implicated. Again, both are normal symmetry-allowed processes operating within the coordination sphere of the metal.

Finally, the conversion of **39** ($R_1 = R_2 = CH_3$) to both **41** and **42** ($R_1 = R_2 = CH_3$)[3,4b] is deserving of comment. The latter bond shift isomers give evidence neither of interconvertibility nor of further isomerization under the conditions of their formation. Accordingly, they likely result from **39** by different reaction channels. Should **39** free itself of molybdenum prior to electrocyclic ring opening, then conversion to the cyclooctatetraene will occur disrotatorily under control of the cyclohexadiene unit (in the ${}_{\sigma}2_s + {}_{\pi}2_s + {}_{\pi}2_s$ mode) to deliver only **41**. If metal-ligand coordination of some type persists, however, the molybdenum could prove effective in promoting disrotatory cyclobutene ring opening instead.[24,25] Since it is clear from work in the previous paper that methyl substituents on cyclobutene double bonds effectively block Mo coordination at such sites, the cyclobutene ring might open while the metal remains bound to the cyclohexadiene unit. Independent evidence for a process of this type has not been reported.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^1H NMR spectra were determined with Varian A-60A and Bruker HX-90 instruments, and apparent splittings are given in all cases. Mass spectra were measured on an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Preparative scale VPC separations were performed on a Varian Aerograph Model A-90-P3 instrument equipped with thermal conductivity detectors. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

1,1,4,4-Tetradeuterio-Δ^2-octalin-9,10-dicarboxylic Anhydride (9). A rocking autoclave was charged with 200 g (1.64 mol) of 2,2,5,5-tetradeuteriosulfolene,[26] 200 g (1.32 mol) of cyclohexene-*cis*-1,2-dicarboxylic anhydride, and 600 mL of dioxane and heated at 170 °C for 28 h. The solvent was evaporated and all volatile substances were separated by bulb-to-bulb vacuum distillation at 0.10 mm. The distillate was dissolved in diethyl ether and extracted repeatedly with 10% potassium carbonate solution until the evolution of gases ceased. Evaporation of the dried solution produced a yellow oil which upon trituration with petroleum ether (bp 30–60 °C) gave 52.6 g (19.5%) of **9** as white crystals: mp 66–68 °C (lit[27] mp 68 °C); δ ($CDCl_3$) 5.71 (s, 2 H) and 2.00–1.50 (m, 8 H).

[4.4.2]Propella-3,11-diene-*2,2,5,5-d_4* (11). A solution of 40.0 g (0.19 mol) of anhydride **9** in 150 mL of tetrahydrofuran was added dropwise to a mechanically stirred refluxing mixture of 10.0 g (0.263 mol) of lithium aluminum hydride in 1.5 L of the same solvent. Heating was continued for 7 h after completion of the addition. With ice cooling, a freshly prepared saturated aqueous sodium sulfate solution was added dropwise until the salts became white. The solids were removed by gravity filtration and washed with ether. Evaporation of the combined filtrates gave 38.0 g (100%) of solid diol, mp 139–140 °C (lit.[28] mp 139–141 °C).

To a solution of 50 mL (74.0 g, 0.646 mol) of methanesulfonyl chloride in 900 mL of pyridine chilled to between −5 and 0 °C was added 38.0 g (0.19 mol) of the diol. After 2 h at 0–5 °C, 1.5 L of cold 10% hydrochloric acid was added (gradually at first). The precipitated solid was removed by suction filtration, washed with water, and air dried to give 67.6 g (100%) of dimesylate, mp 123–124 °C (lit.[28] mp 124–125 °C).

An anhydrous slurry of sodium sulfide in hexamethylphosphoramide [prepared from 64.5 g (0.268 mol) of $Na_2S \cdot 9H_2O$ and 450 mL of HMPA by vacuum distillation of an aqueous distillate of maximum bp 110 °C (15 mm)] was cooled, treated with 32.0 g (0.0895 mol) of the dimesylate, and heated at 120 °C for 25 h with mechanical stirring. Cold water and petroleum ether (bp 30–60 °C) were added, the organic layer was separated, and the aqueous layer was extracted twice more with petroleum ether. The combined organic layers were washed four times with water, dried, and concentrated. The residual oil was chromatographed on neutral alumina. Petroleum ether eluted 17.0 g (96.2%) of the colorless sulfide **10**.

To a solution of 15.0 g (0.0757 mol) of **10** in 500 mL of carbon tetrachloride was added 10.1 g (0.0757 mol) of *N*-chlorosuccinimide and the mixture was maintained at the reflux temperature for 90 min. After chilling, the precipitated succinimide was removed by gravity filtration and the solvent was evaporated. Ether (200 mL) was added to dissolve the crude α-chloro sulfide. The solution was chilled to 0 °C and treated dropwise with 240 mL of 0.70 N ethereal monoperphthalic acid solution (0.168 mol). After being stirred at room temperature overnight, the reaction mixture was transferred to a 3-L separatory funnel and extracted repeatedly with 0.5 N aqueous sodium hydroxide until the washings remained basic to litmus, and then washed twice with water. Concentration of the dried ethereal solution gave 20.1 g (100%) of crude oily α-chloro sulfone.

This α-chloro sulfone was dissolved in 1 L of tetrahydrofuran, chilled to −10 °C, and treated slowly with 36.0 g (0.320 mol) of potassium *tert*-butoxide while mechanically stirred. The reaction mixture was allowed to warm to room temperature and heated at reflux for 2 h. Water and pentane were added to the chilled reaction mixture. The pentane layer was separated and washed five times with water, dried, and concentrated in vacuo at 20 °C. The residual red-orange colored oil was vacuum distilled through a short Vigreux column (oil bath 85 °C, 0.15 mm) to give 4.6 g (37.1%) of **11**: δ_{Me_4Si} (CCl_4) 5.77 (s, 2 H), 5.61 (br s, 2 H), and 1.52 (br s, 8 H).

***N*-Phenyltriazolinedione Adduct of 1.** To a magnetically stirred solution of 4.3 g (0.0262 mol) of **11** in 100 mL each of carbon tetrachloride and glacial acetic acid was added 9.24 g (0.0288 mol) of pyridinium hydrobromide perbromide. After 2 h at room temperature, water was added. The organic layer was separated, washed three times with saturated aqueous sodium bicarbonate solution, and dried over anhydrous sodium sulfate. Filtration and evaporation gave a nearly colorless, oily dibromide. This dibromide in hexamethylphosphoramide solution (270 mL) was treated with 11.3 g (0.27 mol) of anhydrous lithium carbonate, and heated with stirring at 90–95 °C for 20 h under a dry nitrogen atmosphere. Water and petroleum ether (bp 30–60 °C) were added, the organic layer was separated, and the aqueous layer was extracted twice with petroleum ether. The combined organic layers were washed three times with water, dried, and concentrated to leave a red-orange oil. This material was distilled (oil bath 80 °C, 0.15 mm) through a short Vigreux column to give 2.6 g (62.0%) of colorless **1**.

A solution of 1.6 g of **1** in 75 mL of pentane was chilled to −78 °C and treated dropwise with a solution of *N*-phenyltriazolinedione in ethyl acetate until the red color persisted. The precipitated adduct was separated by suction filtration to leave 2.7 g (80.5%) of **12** as a tan-colored powder: mp 228–230 °C (lit.[29] mp 230–232 °C); δ_{Me_4Si} ($CDCl_3$) 7.60–7.20 (m, 5 H), 6.20 (s, 2 H), 5.90 (s, 2 H), and 2.10–1.45 (m, 8 H).

[4.4.2]Propella-2,4,11-triene-*2,5-d_2* (1). Hydrolysis–Oxidation of 12. A mixture of 2.0 g (6.0 mmol) of **12**, 2.4 g (6.0 mmol) of sodium hydroxide, and 80 mL of 2-propanol was heated at reflux with magnetic stirring under a nitrogen atmosphere for 3 h. The reaction mixture was chilled in ice water and acidified with 3 N hydrochloric acid. After a few minutes the inhomogeneous mixture was made basic with 3 N aqueous ammonia solution. To the resulting clear solution were added 50 mL of pentane and 5.2 g (60.0 mmol) of manganese dioxide. After 2 h of additional stirring at room temperature, the pentane layer was separated and washed twice with dilute hydrochloric acid and twice with water, dried, and concentrated on a rotary evaporator at 20 °C. The residual yellow oil was distilled bulb to bulb (oil bath 60 °C, 0.10 mm) to afford 0.65 g of pure **1**: δ_{Me_4Si} (CCl_4) 5.85 (s, 2 H), 5.74 (br s, 2 H), and 1.54 (br s, 8 H).

$Mo(CO)_6$-Promoted Rearrangement of 1. Propellatriene **1** (0.65 g, 4.05 mmol) and molybdenum hexacarbonyl (0.535 g, 2.03 mmol) were heated together in refluxing benzene (10 mL) for 35 h. The cooled reaction mixture was passed through Florisil (pentane elution); there was isolated 0.50 g (77.0%) of **3**. To a solution of this rearrangement product (0.50 g, 3.12 mmol) in 15 mL of ethyl acetate was added tetracyanoethylene (0.400 g, 3.12 mmol) and the reaction mixture was heated at reflux for 15 h. The solvent was evaporated and the residual oil was chromatographed on Florisil (ether elution) to give 0.450 g (50.0%) of adduct **13**: δ_{Me_4Si} (CD_3COCD_3) 6.50 (m, 1 H), 3.95 (m, 2 H), 3.28 (m, 1 H), and 1.95–1.50 (m, 8 H).

1,2-Tetramethylenecyclooctatetraene-*3,4-d_2* (15). $Mo(CO)_6$-Promoted Rearrangement of 14. A mixture of 2.0 g (0.0125 mol) of **14**,[5] 2.0 g (0.0076 mol) of $Mo(CO)_6$, and 20 mL of benzene was refluxed under nitrogen for 36 h. Workup as above led to the isolation of 73 mg (36.2%) of **15** and 70 mg (15.2%) of complex **19**: δ_{Me_4Si} ($CDCl_3$) 5.75–5.25 (m, 4 H) and 2.40–1.15 (m, 8 H).

Tetracyanoethylene Adduct of 15. A solution of 52.7 mg (33.0 mmol) of **15** in 4 mL of ethyl acetate was treated with 42.5 mg (33.0 mmol) of tetracyanoethylene at the reflux temperature for 16 h. The solvent was evaporated and the residual oil was chromatographed on Florisil (ether elution) to give 61 mg (64.2%) of **16**: $\delta_{\mathrm{Me_4Si}}$ (CD_3COCD_3) 6.41 (d, J = 4.0 Hz, 2 H), 3.92 (q, J = 4.0 Hz, 1 H), 3.26 (br d, J = 3.5 Hz, 1 H), and 1.95–1.45 (m, 8 H).

[4.4.2]Propella-2,4,11-triene-*11,12-d*$_2$-molybdenum Tetracarbonyl (19). The molybdenum–diglyme carbonyl reagent was prepared by heating 3.0 g (0.0114 mol) of sublimed $Mo(CO)_6$, 10 mL of freshly distilled diglyme, and 3 mL of anhydrous benzene at the reflux temperature under nitrogen for 6 h. The flask was shaken occasionally in order to return the sublimed $Mo(CO)_6$ to the solution. This mixture was allowed to cool, dideuteriopropellatriene **14** (4.0 g, 0.025 mol) was added, and the solution was stirred at room temperatue for 20 h. Pentane was added and the diglyme was removed by repeated extraction with water. The organic phase was dried and evaporated and the residue was chromatographed on Florisil. Elution with hexane returned 2.8 g of unreacted triene, while elution with hexane–benzene (1:1) gave 1.65 g (60.5%) of **19**: $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 5.60 (br s, 2 H), 4.60 (br s, 2 H), 2.40–1.95 (m, 4 H), and 1.75–1.05 (m, 4 H).

[4.4.2]Propella-2,4,11-triene-*2,5-d*$_2$-molybdenum Tetracarbonyl (18). The molybdenum–diglyme complex was prepared as described above. To this reagent was added 0.90 g (5.6 mmol) of **1** in 0.5 mL of anhydrous benzene and the mixture was stirred at room temperature for 12 h under dry nitrogen prior to filtration. The filtrate was diluted with pentane (50 mL) and extracted repeatedly with cold water. After rinsing with brine, the organic phase was dried and concentrated to leave a yellow oil which solidified upon standing. Chromatography on Florisil (benzene–pentane (1:1) elution) gave a yellow fraction, concentration of which gave a yellow solid. Pure complex was obtained by recrystallization from pentane: mp 98.5–99.0 °C dec; $\nu_{\max}$ (KBr) 2010, 1970, 1960, and 1910 cm^{-1}; $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 4.80 (s, 2 H), 4.71 (br s, 2 H), 2.6–1.2 (br m, 8 H); calcd m/e 370.00724, found 370.00775.

Kinetic Determinations. All measurements were conducted in an identical manner and involved degassing solutions of the molybdenum complexes in benzene-d_6 contained in Pyrex NMR tubes with four freeze–pump–thaw cycles on a vacuum line and sealing at pressures below 10^{-3} Torr. The tubes were inserted into a heated rate bath controlled by a Sargent Model T Thermonitor (temperature stabilization to ±0.05 °C), and in each case 60 s was allowed to pass before the timer was activated. The timer was stopped at each instant that the tube was plunged into an acetone–ice bath (−16 °C). Temperatures were measured with a calibrated thermometer (accuracy ±0.01 °C).

All analyses were made by careful integration of ^{1}H NMR spectra obtained with a Varian Model A-60A spectrometer, using the residual protio absorption of benzene-d_6 as internal standard. At least two integral spans were recorded for each time period and the average taken. Also, exactly 5 min was allowed to pass between integrations to ensure essentially complete relaxation. In each case, disappearance of starting material was measured, and first-order rate laws were obeyed.

[4.4.2]Propell-3-ene-11,12-diol-*11-d* (27). Lithium aluminum deuteride (1.36 g, 0.032 mol) was added to 100 mL of anhydrous tetrahydrofuran under dry nitrogen. To this mixture, heated at reflux, was added dropwise 6.0 g (0.031 mol) of **26**[11] in 50 mL of the same solvent. The reaction mixture was allowed to stir at the reflux temperature for 16 h, then cooled in an ice bath, and treated with saturated sodium sulfate solution until the salts turned white. Filtration and concentration of the solution gave a clear, colorless oil which slowly crystallized upon standing. Purification by column chromatography on Florisil (ether elution) gave 5.9 g (97%) of the diol mixture **27**. These compounds do not give a molecular ion.

[4.4.2]Propell-3-ene-11,12-diol-*11-d* Thiocarbonate (28). A solution of the diol mixture (5.0 g, 0.025 mol) and *N,N*-thiocarbonyldiimidazole (5.1 g, 0.028 mol) in toluene (150 mL) was heated at the reflux temperature under nitrogen with magnetic stirring. After cooling, the solvent was removed under reduced pressure and the brownish oily residue was triturated with methanol. The resulting solid was chromatographed on Florisil (elution with 10% ether in hexane). In this fashion, unreacted trans diol was separated from the syn and anti thionocarbonates (1.9 g). The isomers were purified by recrystallization from ether–hexane. For *syn*-**28**: mp 145–146 °C; $\nu_{\max}$ (Nujol) 1290, 1200, and 990 cm^{-1}; $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 5.93 (m, 2 H), 4.90 (s, 1 H), 2.53–1.95 (m, 4 H), and 1.57 (br s, 8 H). For *anti*-**28**: mp 136–137 °C; $\nu_{\max}$ (Nujol) 1290, 1190, and 990 cm^{-1}; $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 6.08 (t, J = 2.5 Hz, 2 H), 4.66 (s, 1 H), 2.05 (d, J = 2.5 Hz, 4 H), and 1.9–1.0 (m, 8 H). The mass spectra of these isomers show M^+ at m/e 237 and an isotopic purity of ≥98%.

[4.4.2]Propella-3,11-diene-*11-d* (29). A solution of the thiocarbonate mixture (1.70 g, 7.17 mmol) in triethyl phosphite (30 mL) was heated at the reflux temperature with stirring for 72 h. Upon cooling, water (40 mL) and potassium hydroxide (10 g) were added (substantial warming) and the mixture was stirred for 1 h before heating on a steam bath. Ether was added, the phases were separated, and the aqueous phase was extracted with ether (3 × 100 mL). The combined ether extracts were in turn washed with water and brine, dried, and evaporated. The propelladiene was freed of residual phosphite by chromatography on silica gel (pentane elution). There was obtained 450 mg (39%) of **29**: $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 5.85 (d of t, J = 3.0 and 1.6 Hz, 2 H), 1.92 (d of d, J = 3.0 and 1.6 Hz, 4 H), and 1.54 (s, 8 H). Mass spectrometric analysis indicated ≥98% of the d_1 species to be present.

[4.4.2]Propella-2,4,11-triene-*11-d* (30). A solution of **29** (0.45 g, 3.0 mmol) in 50 mL of acetic acid and carbon tetrachloride (1:1) was treated with 1.0 g (3.0 mmol) of pyridinium hydrobromide perbromide and stirred at room temperature for 12 h. The predescribed workup gave the dibromide as a clear, pale yellow oil which was directly subjected to dehydrobromination.

Subsequent to heating this dibromide with lithium chloride (1.26 g, 30 mmol) and lithium carbonate (2.22 g, 30 mmol) in anhydrous hexamethylphosphoramide (30 mL) at 90 °C for 19 h, the above workup afforded 410 mg (86%) of **30**: $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 5.85 (s, 1 H), 5.8 and 5.45 (AA′BB′ pattern,[30] 4 H), and 1.54 (br s, 8 H). Again, the mass spectrum indicated ≥98% d_1.

$Mo(CO)_6$-Promoted Isomerization of 30. Two solutions were prepared, each containing 100 mg (0.63 mmol) of **30** and 170 mg (0.63 mmol) of $Mo(CO)_6$ in 25 mL of anhydrous benzene. The stirred solutions were heated under nitrogen at the reflux temperature for 36 h. The solvent was evaporated and the residues were individually chromatographed on Florisil using pentane elution. By this technique, two 50-mg samples of a clear, colorless oil were obtained, the ^{1}H NMR spectra of which indicated them to be the deuterated 1,2-tetramethylenecyclooctatetraenes **31** and **32**.

These samples were each dissolved in 5 mL of ethyl acetate and treated under dry nitrogen with 0.97 g (0.65 mmol) of *N*-phenyltriazolinedione in 5 mL of ethyl acetate. The red solutions were allowed to stir at room temperature for 72 h prior to removal of solvent and chromatography on Florisil (ether elution). The adducts so obtained (31 and 34 mg) were quantitatively analyzed by ^{1}H NMR and determined by relative integrations of the olefinic and bridgehead proton signals to exhibit and inverse secondary isotope effect of 0.93 ± 0.05.

Acknowledgment. This investigation was financed by the National Cancer Institute (Grant CA-12115) and Chevron Research Co.

References and Notes

(1) For reviews, consult N. R. Davies, *Rev. Pure Appl. Chem.*, **17**, 83 (1967); C. W. Bird, "Transition Metal Intermediates in Organic Synthesis", Academic Press, New York, N.Y., 1967, p 67; M. Orchin, *Adv. Catal. Relat. Subj.*, **16**, 1 (1966); C. A. Tolman in "Transition Metal Hydrides", Vol. 1, E. L. Muetterties, Ed., Marcel Dekker, New York, N.Y., 1971, Chapter 6.

(2) For example, see (a) 1,3-hydrogen shifts: L. Roos and M. Orchin, *J. Am. Chem. Soc.*, **87**, 5502 (1965); C. P. Casey and C. R. Cyr, *ibid.*, **95**, 2248 (1973); W. T. Hendrix and J. L. von Rosenberg, *ibid.*, **98**, 4850 (1976); (b) 1,5-hydrogen shifts: W. R. Roth and W. Grimme, *Tetrahedron Lett.*, 2347 (1966); M. I. Foreman, G. R. Knox, P. L. Pauson, K. H. Todd, and W. E. Watts, *J. Chem. Soc., Perkin Trans. 2*, 1141 (1972); T. H. Whitesides and J. P. Neilan, *J. Am. Chem. Soc.*, **95**, 5811 (1973); R. Aumann, *Angew. Chem., Int. Ed. Engl.*, **12**, 574 (1973); G. A. M. Monro and P. L. Pauson, *J. Chem. Soc., Chem. Commun.*, 134 (1976).

(3) L. A. Paquette, J. M. Photis, and R. P. Micheli, *J. Am. Chem. Soc.*, preceding paper in this issue.

(4) (a) L. A. Paquette, J. M. Photis, J. Fayos, and J. Clardy, *J. Am. Chem. Soc.*, **98**, 1217 (1974); (b) L. A. Paquette, J. M. Photis, K. B. Gifkins, and J. Clardy, *ibid.*, **97**, 3536 (1975); (c) L. A. Paquette and J. M. Photis, *Tetrahedron Lett.*, 1145 (1975).

(5) (a) L. A. Paquette and R. E. Wingard, Jr., *J. Am. Chem. Soc.*, **94**, 4398 (1972); (b) L. A. Paquette, R. E. Wingard, Jr., and J. M. Photis, *ibid.*, **96**, 5801 (1974).

(6) W. Grimme, *Chem. Ber.*, **100**, 113 (1967).

(7) R. K. Russell, R. E. Wingard, Jr., and L. A. Paquette, *J. Am. Chem. Soc.*, **96**, 7483 (1974).

(8) The parameters employed in the computer simulation were derived from

the unlabeled adduct[7] and are as follows: $H_{2,5} = \delta$ 3.34; $H_{1,6}$ = 4.02; $H_{7,8}$ = 6.485; $J_{7,8}$ = 8.0; $J_{1,8} = J_{6,7}$ = 6.6; $J_{2,5}$ = 6.0; $J_{1,2} = J_{5,6}$ = 3.5; $J_{1,7} = J_{6,8}$ = 1.2; $J_{1,6} = J_{2,8} = J_{5,7}$ = 0.5 Hz; and all other coupling constants equal zero.

(9) Compare H. D. Kaesz, S. Winstein, and C. G. Kreiter, *J. Am. Chem. Soc.*, **88**, 1319 (1966).

(10) It has not proven possible to prepare the $Mo(CO)_4$ complex of 11-methyl[4.4.2]propella-2,4,11-triene because of the apparent facility of the ensuing rearrangement.[3]

(11) J. J. Bloomfield and J. R. S. Irelan, *J. Org. Chem.*, **31**, 2017 (1966).

(12) H. A. Staab and J. Walther, *Justus Liebigs Ann. Chem.*, **657**, 98 (1962).

(13) E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, **85**, 2677 (1963); E. J. Corey, F. A. Carey, and R. A. E. Winter, *ibid.*, **87**, 934 (1965).

(14) Compare L. A. Paquette and J. C. Philips, *Chem. Commun.*, 680 (1969); L. A. Paquette, J. C. Philips, and R. E. Wingard, Jr., *J. Am. Chem. Soc.*, **93**, 4516 (1971).

(15) (a) M. Matsuoka and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 1260 (1961); (b) M. Takahashi and R. J. Cvetanovic, *Can. J. Chem.*, **40**, 1037 (1962); (c) M. Feld, A. P. Stefani, and M. Szwarc, *J. Am. Chem. Soc.*, **84**, 4451 (1962); (d) W. A. Pryor, R. W. Henderson, R. A. Patsiga, and N. Carroll, *ibid.*, **88**, 1199 (1966); (d) S.-H. Dai and W. R. Dolbier, Jr., *ibid.*, **94**, 3946 (1972).

(16) K. Humski, R. Malojcic, S. Borcic, and D. E. Sunko, *J. Am. Chem. Soc.*, **92**, 6534 (1970), and relevant references cited in this paper.

(17) P. Schiess and P. Fünfschilling, *Tetrahedron Lett.*, 5191, 5195 (1972).

(18) L. A. Paquette and M. J. Carmody, *J. Am. Chem. Soc.*, **97**, 5841 (1975).

(19) M. F. Semmelhack, H. N. Weller, and J. S. Foos, *J. Am. Chem. Soc.*, **99**, 292 (1977).

(20) L. L. Miller, R. Greisinger, and R. F. Boyer, *J. Am. Chem. Soc.*, **91**, 1578 (1969).

(21) Substitution of a cyclobutane ring for cyclobutene in the [4.4.2]propella-2,4-diene series has previously been recognized to require more forcing conditions to achieve isomerization.[3]

(22) D. R. Lloyd and E. W. Schlag, *Inorg. Chem.*, **8**, 2544 (1969); R. B. King, *Inorg. Nucl. Chem. Lett.*, **5**, 905 (1969).

(23) M. S. Brookhart, private communication.

(24) R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, **47**, 71 (1969).

(25) For a review, see L. A. Paquette, *MTP Int. Rev. Sci.: Org. Chem., Ser. One*, **5**, 159 (1973).

(26) A. C. Cope, G. A. Berchtold, and D. L. Ross, *J. Am. Chem. Soc.*, **83**, 3859 (1961).

(27) K. Alder and K. H. Backendorf, *Chem. Ber.*, **71**, 2199 (1938).

(28) L. A. Paquette, R. E. Wingard, Jr., J. C. Philips, G. L. Thompson, L. K. Read, and J. Clardy, *J. Am. Chem. Soc.*, **93**, 4508 (1971).

(29) R. E. Wingard, Jr., R. K. Russell, and L. A. Paquette, *J. Am. Chem. Soc.*, **96**, 7474 (1974).

(30) L. A. Paquette, J. C. Philips, and R. E. Wingard, Jr., *J. Am. Chem. Soc.*, **93**, 4516 (1971).

Formation and Reactivity of Gaseous Acetylium Ions from the Methylation of Carbon Monoxide

Pierluigi Giacomello*[1a] **and Maurizio Speranza***[1b]

Contribution from the Institut für Chemie der Kernforschungsanlage Jülich GmbH, Institut 1: Nuklearchemie, D-5170 Jülich, Federal Republic of Germany, and the Laboratorio di Chimica Nucleare del C.N.R., 00016 Monterotondo Stazione, Rome, Italy. *Received February 18, 1977*

Abstract: Free acetylium ions have been prepared in the diluted gas state at atmospheric pressure, via two different routes, i.e., the methylation of carbon monoxide by CT_3^+ ions from the decay of fully tritiated methane, and the nucleophilic displacement by CO on CH_3M^+ (M = HF, CH_3F) ions, produced from the γ-radiolysis of methyl fluoride. Independently of the preparation methods, the acetyl cation displays a much higher reactivity toward n-type than toward π-type nucleophiles. The reaction of thermalyzed CH_3CO^+ ions with alcohols or phenols yields the corresponding acetates, while no acylation of benzene and toluene was detected. Low yields of ring-acetylated products were obtained from the attack of acetylium ions on anisole and phenol, the reactivity being, however, strongly biased (83.8%) in favor of the oxygen atom of the latter substrate. From these results it appears that the intrinsic intramolecular selectivity of the free acetylium ion, measured in the gas phase, in the absence of the complicating phenomena, such as solvation and ion pairing, invariably affecting solution-chemistry studies, is characterized by a high ortho/para ratio in the acylated products.

In recent years, the gas-phase acetylation of organic compounds by various ionic reagents has been extensively studied in the limited pressure range accessible to mass spectrometric and ICR methods,[2-8] disclosing intriguing features that were not previously observed in ion-molecule reactions of simpler species and cannot be explained by even the most advanced physical models of ion-molecule interactions, but rather recall the complexity and the multifaceted problems of traditional solution chemistry.

In the mass spectrometric investigations the acylating agents are produced by electron impact on molecules such as acetone and 2,3-butanedione,[2-5,8] and species other than CH_3CO^+ ions can be formed, whose efficient acetyl transfer reactions to the substrate may obscure[7] the direct contribution of the free acetylium ion to the adduct formation. Furthermore, an inherent and obvious limitation of these otherwise so powerful and enlightening techniques is the lack of information on the site of attachment of the reacting ion,[3,4] as the isomeric species formed cannot be directly identified. On the other hand, solution chemistry studies[9] suggested that the electrophilic attack of free acylium ions on aromatic substrates represents only one of the conceivable and partly verified mechanisms of Friedel-Crafts acylation reactions. In fact, the nature of the acylating agent and its inherent reactivity and selectivity toward the substrate are strongly affected by several factors—the solvating properties of the environment, the specific features of the catalyst, and the nature of the substituent bound to the carbonyl group—so that the free-ion character of the acylating agent and, consequently, the steric and electronic requirements of the reaction are remarkably variable.[10]

The present paper deals with the formation of the acetylium ion and its reactivity toward some typical organic substrates, studied in the diluted gas state at atmospheric pressure, using the radiolytic[11-14] and the decay[15-17] techniques recently applied to the study of aromatic electrophilic substitutions. Both these approaches are suitable to evaluate the properties of the acylium ion in the absence of the complicating phenomena occurring in solution chemistry, allowing, in addition, the isolation and the identification of *final neutral products*, and their exploitation represents an attempt to establish links, and to substantiate correlations between low-pressure mass spectrometric data and the condensed-phase results.

Methods of Formation. Two different synthetic approaches have been designed for the preparation of gaseous $C_2H_3O^+$ ions, namely, the condensation reaction of CO with the CT_3^+ cations from the β decay of fully tritiated methane, and the