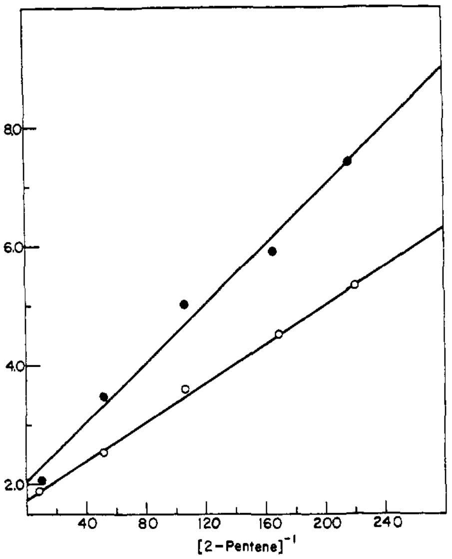

Figure 1. Acetone-photosensitized isomerization of *cis*- and *trans*-2-pentene, open and full circles, respectively.

(Figures 1 and 2). Decay ratios for intermediates produced with each sensitizer were obtained from the ratios of the intercepts in Figures 1 and 2. Excitation ratios were calculated from the decay ratios and the *trans*/*cis* photostationary state ratios. The results are shown in Table I. An independent check of the proposed general mechanism is available in that the ratios of the slopes in the plots predict closely the observed photostationary states as required by eq 8–10. Limiting quantum yields at high pentene concentrations are $\phi_{t\rightarrow c} = 0.49, 0.26$, and $\phi_{c\rightarrow t} = 0.58, 0.50$, for acetone and acetophenone, respectively.[16]

Table I. Sensitized Photoisomerization of the 2-Pentenes

Sensitizer	E_T, kcal/ mole[a]	$\alpha/(1 - \alpha)$	k_6/k_5	$(t/c)_s$ Obsd	$(t/c)_s$ Predicted[c]
Benzene	84	1.0_0[b]	0.92[b]	0.92[b]	
Acetone	80	1.1_7	1.3_0	1.5_2	1.5_2
Acetophenone	74	1.9_0	2.8_5	5.4	4.7

[a] Triplet excitation energies: benzene, ref 3; acetone, ref 10; acetophenone, ref 2. [b] Values for the butenes from ref 3. [c] From the ratios of the slopes in Figures 1 and 2.

We stress here that, in contrast to the stilbenes and the 1,2-diphenylpropenes, a *single decay ratio does not account for observations with different sensitizers in the case of the 2-pentenes.* The variation of photostationary ratios of 2-octenes and 2-pentenes with the triplet energy of sensitizers was incorrectly attributed solely to changes in excitation ratios for alkene triplet formation.[12] Since a common decay ratio does not obtain, it is clear that *different intermediates are produced with different sensitizers.*

The triplet mechanism should be important with sensitizers whose triplet excitation energy is close to that of ethylene, ~82 kcal/mole.[17] With lower energy sensitizers the triplet mechanism should diminish in importance except in cases where nonvertical excitation transfer can occur.[4,7] We propose that *for alkenes* deviation of the decay ratio from unity is a measure of the involvement of Schenck intermediates, **2**, in the photoisomerization. Thus, the small increase of the decay ratio obtained with acetone as sensitizer indicates that at 30° the Schenck intermediate is involved to a minor extent, and that triplet excitation transfer represents the major path for the isomerization.[18] On the other hand, the large decay ratio increase obtained with acetophenone as sensitizer suggests that the Schenck mechanism predominates in this case. It may be more than a coincidence that for acetophenone and other n–π* sensitizers with even lower triplet-state energies the photostationary ratios are very close to the thermodynamic ratio.[12,19] The mechanism accounts for the observations that triphenylene[7] and some carbonyl compounds with π–π* lowest triplet states[12] are ineffective as sensitizers of the *cis–trans* isomerization of alkenes. The possibility that the abnormally *trans*-rich photostationary states obtained for the stilbenes with a few sensitizers[2,5,20] were due to competing decay from Schenck intermediates is under investigation.[20a]

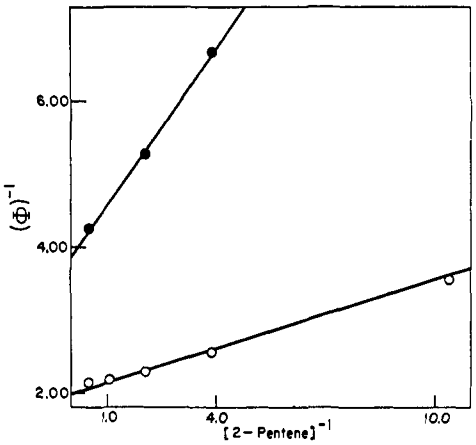

Figure 2. Acetophenone-photosensitized isomerization of *cis*- and *trans*-2-pentene, open and full circles, respectively.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[16] The acetone results are in qualitative agreement with those in ref 10b. The maximum limits of error on our results are: $(t)/(c) = 1.52 \pm 0.12$; sum of limiting quantum yields = 1.06 ± 0.10.

[17] S. Sato, *Pure Appl. Chem.*, **16**, 87 (1968).

[18] This interpretation agrees with that proposed in ref 10b, where two competing mechanisms were suggested on the basis of variation of photostationary state ratios with temperature.

[19] C. Moussebois and J. Dale, *J. Chem. Soc., C*, 260 (1966).

[20] R. Searle, J. L. R. Williams, D. E. De Meyer, and J. C. Doty, *Chem. Commun.*, 1165 (1967).

(20a) Note Added in Proof. Similar conclusions have been reached by Professor N. C. Yang and Dr. J. I. Cohen for the sensitized photoisomerization of the 3-methyl-2-pentenes. We thank Professor N. C. Yang for communicating their results to us.

[21] National Institutes of Health Postdoctoral Fellow, 1968–1969.

[22] Petroleum Research Fund Scholar.

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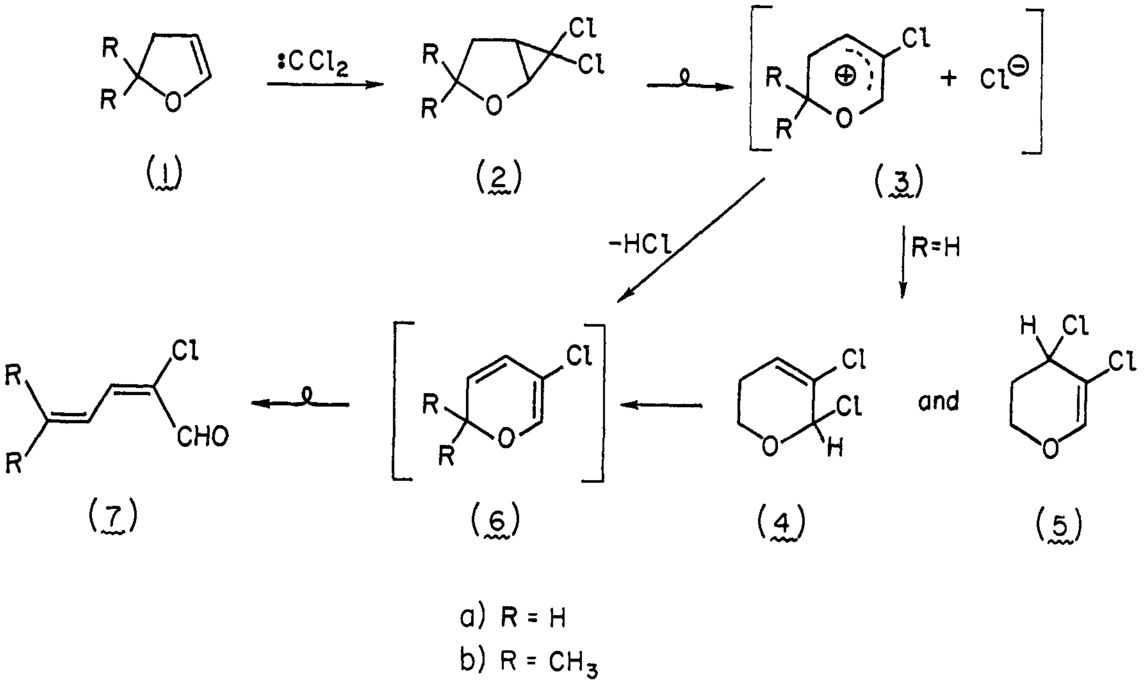
The Thermal Rearrangement of 6,6-Dichloro-3,3-dimethyl-2-oxabicyclo[3.1.0]hexane. A Novel Case of Steric Hindrance to Ionization

Sir:

The recent literature[1] contains a number of reports of attempts to observe steric hindrance to ionization.

(1) (a) Reviewed by H. C. Brown, I. Rothberg, P. von R. Schleyer,

Scheme I



Although some degree of success has been achieved, uncertainties remain regarding the adequacies of the models compared and the absolute relationships of the observed *exo:endo* solvolysis rates. We now report an unambiguous case of steric hindrance to ionization encountered in the rearrangement of 6,6-dichloro-3,3-dimethyl-2-oxabicyclo[3.1.0]hexane (**2b**)[2] (Scheme I).

Theoretical prediction[3] that the *syn* substituent will migrate preferentially in a concerted disrotatory ring opening of (n + 3, n + 3)-substituted bicyclo[n.1.0]-alkanes (**8**) has recently received substantial experimental verification.[4] Evidence has also been presented that there is a minimum energy difference of 15 kcal/mole between allowed and disallowed pathways in related electrocyclic processes.[5] Therefore, the rearrangements (see Scheme II) of such bicyclics should provide a unique probe for observation of steric and other effects provided by substituents in the n ring of **8** on the ionizing group X. Furthermore, studies of these systems are not subject to the same ambiguities encountered in studies of *exo:endo* solvolysis rates and will serve as an independent check on the latter.

The kinetic data for the rearrangements of 6,6-dichloro-2-oxabicyclo[3.1.0] hexane (**2a**)[6] and **2b** are presented in Table I. These first-order rates are for the disappearances of **2** and reflect only the processes involved in going from **2** to the transition state represented as **3**. First-order rates for similar rearrangements have been observed and discussed before[7] and are consistent with this representation. The difference

Scheme II

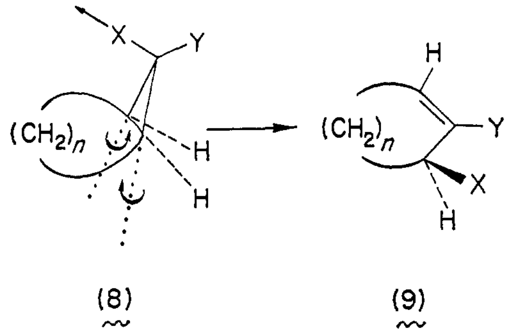


Table I. First-Order Rate Constants and Activation Parameters for the Rearrangements of **2a** and **2b** in C_6H_5CN[a]

Temp, °C	k, sec^{-1} 2a[b]	2b[c]
25.0	4.22 × 10^{-5}	
35.0	1.31 × 10^{-4}	
45.0	2.95 × 10^{-4}	
60.0	2.37 × 10^{-3}	2.62 × 10^{-6}
90.0		7.78 × 10^{-5}
E_a, kcal/mole	22.5	28.3
$\Delta S^{\ddagger}$ (60°), eu	−5.3	−1.2

[a] A difference in initial concentration affects the dielectric constant of the medium and hence also the rate constant.[7a] At the concentrations used here, the differences affect the observed rates only slightly. The $\Delta\Delta G^{\ddagger}$ of 4.5 kcal/mole leaves no question that the observed rate differences are real. [b] Initial concentration 13.0 wt %. [c] Initial concentration 11.8 wt %.

M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1653 (1963); (b) J. P. Schaefer and C. A. Flegal, *J. Am. Chem. Soc.*, **89**, 5729 (1967); (c) H. C. Brown and W. J. Hammar, *ibid.*, **89**, 6378 (1967); (d) H. C. Brown, I. Rothberg, and D. L. Vander Jagt, *ibid.*, **89**, 6380 (1967); (e) H. C. Brown, W. J. Hammar, J. H. Kawakami, I. Rothberg, and D. L. Vander Jagt, *ibid.*, **89**, 6381 (1967).

(2) Nmr (CDCl$_3$-TMS, 60 MHz): H-1, δ 3.97 ($J_{1,5}$ = 6.3 Hz); H-4 and H-5, δ 1.9–2.6 (complex multiplet); 2Me-3, δ 1.26 and 1.30 (singlets); bp 34–36° (0.5 mm). *Anal.* Calcd for $C_7H_{10}Cl_2O$: C, 46.6; H, 5.6; Cl, 39.2. Found: C, 46.6; H, 5.7; Cl, 38.9.

(3) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

(4) (a) T. Ando, H. Yamanaka, and W. Funasaka, *Tetrahedron Letters*, 2587 (1967); (b) L. Ghosez, P. Laroche, and G. Slinckx, *ibid.*, 2767 (1967).

(5) (a) J. I. Brauman and D. M. Golden, *J. Am. Chem. Soc.*, **90**, 1920 (1968); (b) G. A. Doorakian and H. H. Freedman, *ibid.*, **90**, 5310 (1968).

(6) (a) J. C. Anderson, D. G. Lindsay, and C. B. Reese, *Tetrahedron*, 20, 2091 (1964); (b) S. Sarel and J. Rivlin, *Israel J. Chem.*, **1**, 221 (1963); (c) S. Sarel and J. Rivlin, *Tetrahedron Letters*, 821 (1965).

(7) (a) R. C. De Selms and C. M. Combs, *J. Org. Chem.*, **28**, 2206 (1963); (b) L. Gatlin, R. E. Glick, and P. S. Skell, *Tetrahedron*, **21**, 1315 (1965); (c) D. C. Duffey, J. P. Minyard, and R. H. Lane, *J. Org. Chem.*, **31**, 3865 (1966).

of 10^3 in the rates of rearrangement of **2a** and **2b** in benzonitrile at 60° is indeed surprising. We have confirmed this finding using acetonitrile-d_3 as the solvent at 60° and observing first-order rates of 2.30×10^{-3} and 3.62×10^{-6} sec^{-1} for **2a** (16.0 wt %) and **2b** (12.5 wt % initial concentration), respectively.

The amount of rate difference possibly caused by a "*gem* effect"[8] is estimated to be relatively small in the case under consideration. The curious circumstance of one ring system being converted into a second eliminates the general "*gem*-dimethyl effect" discussed by Allinger and Zalkow[8b] since that effect depends on ring–chain transformations and free rotation in the chain form. In this regard also, examination of Dreiding models indicates maximum eclipsing of the substituents in the five-membered ring and hence a tendency to raise the ground-state energy of **2b** relative to **2a**. The "Thorpe–Ingold effect," which is a special case of the *gem* effect involving bond angle deformation, is now thought to contribute a relatively small amount[8c] compared with the differences under consideration. Finally, steric hindrance to solvation is thought to contribute to the *gem* effect.[8d] However, steric hindrance to solvation of the migrating anion, which would be the critical consideration here, is in reality an integral part of, and inseparable from, the ionization process. We therefore conclude that steric hindrance to ionization is the major factor contributing to the rearrangement rate differences of **2a** and **2b**.

While the processes occurring after reaching the transition state (**3**) do not affect the kinetics in the present instances, they are worthy of brief mention. The previous workers[6] have found that **2a** rearranges to **4**[9] thermally and that **4** is converted to **7a** both thermally[6c] and by heating with base.[6a] Under the conditions used here, the rate of conversion of **4** to **7a** is negligible and the first-order rate constants are measured by following the conversion of **2a** to **4**[9] and **5**.[9] On the other hand, the much slower rate for rearrangement of **2b** and the slightly higher temperatures required allow successful competition of the elimination and ring-opening steps, and intermediates corresponding to **4** and **5** are never present in sufficient quantities for detection. The first-order rate constants are therefore measured by following the directly observed conversion of **2b** to 2-chloro-5-methylhexa-2,4-dienal (**7b**).[10]

Acknowledgment. The authors thank Dr. T. M. Regan and Mr. D. F. Ketchum for obtaining nmr spectra and microanalyses, respectively.

(8) (a) T. C. Bruice and W. C. Bradbury, *J. Am. Chem. Soc.*, **90**, 3808 (1968), and previous articles in this series; (b) N. L. Allinger and V. Zalkow, *J. Org. Chem.*, **25**, 701 (1960); (c) P. von R. Schleyer, *J. Am. Chem. Soc.*, **83**, 1368 (1961); (d) F. G. Bordwell, C. E. Osborne, and R. D. Chapman, *ibid.*, **81**, 2698 (1959).

(9) The kinetics studies were done by standard methods using nmr spectroscopy to measure concentrations.[7a] While in ref 6 only formation of **4** by rearrangement of **2a** is reported, we have found not less than 100 times that **2a** neat and in CD_3CN or C_6H_5CN always leads to approximately 1:1 mixtures of both isomers **4** and **5**. Characterization of **4** and **5** will be published elsewhere.

(10) Nmr ($CDCl_3$–TMS, 60 MHz): 2Me-5, δ 2.01 and 2.03 (small couplings each); H-3, δ 6.53 ($J_{3,4} = 11.2$ Hz; small couplings to both methyls); H-4, δ 7.51 ($J_{4,3} = 11.2$ Hz; possible small coupling to a methyl); CHO, δ 9.60 (singlet); mp 70–71°; λ (MeOH) 299 nm (log ϵ 4.58). *Anal.* Calcd for C_7H_9ClO: C, 58.1; H, 6.3; Cl, 24.5. Found: C, 58.2; H, 6.2; Cl, 24.7.

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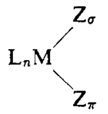
Model Compounds for Transitional Metal Intermediates in Homogeneous Catalysis[1]

Sir:

In many reactions of unsaturated organic compounds catalyzed by metal complexes, species of the type



$$L_nM\begin{matrix}Z_\sigma\\ \\ Z_\pi\end{matrix}$$

where Z_σ is H^- or a σ-bonded organic moiety and Z_π is a π-bonded organic moiety, have often been postulated to be intermediates.[2] In almost all homogeneous catalytic reactions, however, these intermediates are not isolable. Since previous work in this laboratory has shown that cyanocarbons[3] form more stable complexes with noble metal substrates than do the analogous hydrocarbons, it seemed that it might be possible to isolate and characterize compounds analogous to some of these intermediates of catalytic importance by employing cyanocarbons as the organic reactants instead of hydrocarbons. In order to test this hypothesis, reactions of various cyanoolefins and other activated olefins and acetylenes with the five-coordinate complexes $MH(CO)(Ph_3P)_3$ (M = Ir, Rh) have been investigated. These complexes are known to be good catalysts[4,5] for homogeneous hydrogenation of simple olefins and/or acetylenes.

Cyanoolefins and other activated olefins react with $IrH(CO)(Ph_3P)_3$ (I) by displacing one molecule of triphenylphosphine to give hydrido-olefinic complexes of the type $IrH(CO)(Ph_3P)_2$(olefin). For example, addition of a tenfold excess of fumaronitrile, NCCH=CHCN, to a bright yellow benzene solution of I at 50° causes the solution to lighten in color, and in a few minutes a white precipitate forms. Recrystallization of the solid from CH_2Cl_2–CH_3OH gives colorless needles of a compound whose elemental analysis indicates a fumaronitrile/triphenylphosphine/iridium ratio of 1:2:1. *Anal.* Calcd for $C_{41}H_{33}N_2OP_2Ir$: C, 59.77; H, 4.04; N, 3.40; P, 7.52; mol wt, 824. Found: C, 59.39; H, 4.23; N, 3.31; P, 7.53; mol wt, 708 (osmometric in $CHCl_3$). The compound is formulated as a hydrido-olefinic complex (compound IIa of Figure 1) rather than the "insertion" product, $Ir[-CH(CN)CH_2CN]-(CO)(Ph_3P)_2$, which would have the same elemental analysis, on the basis of its infrared spectrum[6] ($\nu_{C\equiv N}$,

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(1) Part VI in the series Metal Complexes of Cyanocarbons: (a) part V, C. Panattoni, G. Bombieri, U. Belluco, and W. H. Baddley, *J. Am. Chem. Soc.*, **90**, 798 (1968); (b) part IV, P. Uguagliati and W. H. Baddley, *ibid.*, **90**, 5446 (1968); (c) part III, W. H. Baddley, *ibid.*, **90**, 3705 (1968); (d) part II, W. H. Baddley, *ibid.*, **88**, 4545 (1966); (e) part I, W. H. Baddley and L. M. Venanzi, *Inorg. Chem.*, **5**, 33 (1966).

(2) For example, see J. Halpern, Advances in Chemistry Series, No. 70, American Chemical Society, Washington, D. C., 1968, p 1; B. R. James, *Coord. Chem. Rev.*, **1**, 505 (1966).

(3) W. H. Baddley, *Inorg. Chim. Acta Rev.*, **2**, 7 (1968).

(4) L. Vaska, *Inorg. Nucl. Chem. Letters*, **1**, 89 (1965).

(5) C. O'Connor, G. Yagupsky, D. Evans, and G. Wilkinson, *Chem. Commun.*, 420 (1968); C. O'Connor and G. Wilkinson, *J. Chem. Soc., A*, 2665 (1968).

(6) Values quoted are for a hexachlorobutadiene mull spectrum. The same type spectrum of the analogous deuterio complex exhibits bands at 2215 s ($\nu_{C\equiv N}$) and 2021 vs ($\nu_{C\equiv O}$) cm^{-1} with no absorption being observed in the 800–900 cm^{-1} range. The fact that $\nu_{C\equiv O}$ in the hydrido and deuterio complexes is different arises from a resonance interaction between Ir—H and C≡O stretching modes, and a *trans* arrangement of hydride and carbon monoxide is indicated as shown in Figure 1. For discussions of the use of resonance interaction to establish stereochemistry, see L. Vaska, *J. Am. Chem. Soc.*, **88**, 4100