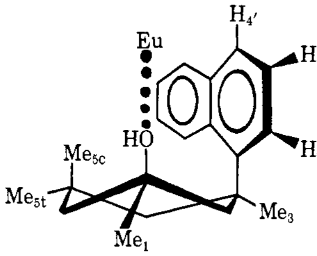
for the *aromatic hydrogen resonances* of the cis isomer (Figure 1d). Large positive (*i.e.*, downfield) shifts are again observed for $H_{2'}$ and $H_{8'}$, but *substantial negative shifts, i.e., to higher applied fields*, are seen for $H_{3'}$ and $H_{4'}$. The $H_{3'}$ shift is very substantial, and the gross, first-order triplet observed for this proton is in fact the highest field absorption in the spectrum at Eu(DPM)$_3$ levels above *ca.* 0.5 molar equiv, and shows a chemical shift at the 0.8-equiv level of δ 2.62. These LIS values observed for cis alcohol II are cleanly rationalized by inspection of eq 1 and examination of the relevant distances and angles as depicted in stereoformula III. In the latter, the $OEuH_{2'}$ angle is seen to be sharply acute, and hence the $(3 \cos^2 \theta - 1)$ angle factor is positive; together with the small $EuH_{2'}$ distance in the naphthyl rotamer shown in III, this should result in a large, positive shift for $H_{2'}$, as is observed. In the case of $H_{3'}$, however, although the $EuH_{3'}$ distance is still relatively small (actually, very similar to that for $H_{2'}$) the OEuH angle has opened up to a value estimated from models to be somewhere in the range 60–75°. Thus $(3 \cos^2 \theta - 1)$ for $H_{3'}$ is negative, and a large, negative shift is in fact observed for this proton. For $H_{4'}$, the OEuH angle is opened up still further, to a value in the 80–95° range. Now, however, the distance factor is smaller, due to $H_{4'}$ being more remote from the europium than either $H_{2'}$ or $H_{3'}$; the resulting shift, although again negative, is thus much smaller than for $H_{3'}$. Finally, $H_{8'}$ gives the modest sized, downfield shift consonant with its again sharply acute OEuH angle and the relatively greater distance.



III (≡II)

The above arguments hold for any reasonable location of the europium atom, *i.e.*, for any OEu bond length above *ca.* 2.5 Å and for any C_1OEu angle and C_2C_1OEu dihedral angle which places the europium outside the perimeter of the cyclohexane ring. The necessary angle and distance relationships to give the above-described behavior are provided by the cis parallel, diaxial disposition of the C_1–O and the C_3-naphthyl bonds together with predominance of the pictured rotational orientation of the naphthalene ring.

The present results, then, underline the theoretically expected importance of the angle factor[5] as well as the distance dependence of these striking and very useful shifts, and tend to support the view that these LIS's are of a cleanly pseudocontact nature describable by eq 1. We further believe that this type of system can be used to make a detailed study of the quantitative aspects of the pseudocontact equation and to put the distance and steric requirements of the lanthanide on a firm quantitative basis, as well as providing numerical values for distance and angle relationships among the constituents of these and other cyclohexanol systems. Such studies are in progress.

Acknowledgments. Major financial support for this work has been provided by The Robert A. Welch Foundation of Houston, Tex., for whose generosity we are deeply grateful. It is also a pleasure to acknowledge helpful conversations with Drs. P. V. Demarco, R. R. Fraser, and M. R. Willcott.

---

(5) The importance of the angle factor has, of course, been pointed out by several authors, *e.g.*, R. R. Fraser and Y. Y. Wigfield, *Chem. Commun.*, 1471 (1970), and J. Briggs, F. A. Hart, and G. P. Moss, *ibid.*, 1506 (1970). These authors have also made important first contributions toward the detailed and quantitative incorporation of the angle factor into incremental shift calculations.

(6) Postdoctoral research fellow of The Robert A. Welch Foundation.

(7) Undergraduate research fellow of The Robert A. Welch Foundation.

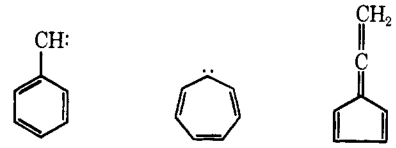
B. L. Shapiro,* J. R. Hlubucek,[6] G. R. Sullivan[7]
Department of Chemistry, Texas A&M University
College Station, Texas 77843
L. F. Johnson
Varian Associates, Analytical Instrument Division
Palo Alto, California 94303

Received March 19, 1971

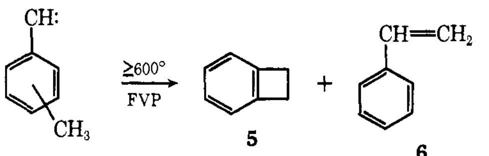
The Thermal Rearrangement of *p*-Tolylcarbene to Benzocyclobutene and Styrene. A Carbon-13 Labeling Study[1]

Sir:

We earlier reported that phenylcarbene (**1**) generated in the gas phase from phenyldiazomethane rearranged either to cycloheptatrienylidene[2a,b] at temperatures ≤600° or ring contracted to fulvenallene (**3**) at temperatures ≥600°.[2a] In contrast, we found that the high-temperature rearrangement for similarly generated *p*-, *m*-, and *o*-tolylcarbenes **4** resulted in benzocyclobutene and styrene in the ratios listed in about 50% overall yields at 700° under flash vacuum pyrolysis (FVP) conditions[3] (**5**:**6**:**4a**, 3; **4b**, 0.80; **4c**, 0.83).



1 **2** **3**



5 **6**

4a, ortho
b, meta
c, para

This remarkable conversion must involve isomerization of *p*- or *m*-tolylcarbene to *o*-tolylcarbene which, in part, undergoes C–H insertion to give **5**. Styrene

---

(1) Flash Vacuum Pyrolysis. IX. Part VIII: E. Hedaya and M. E. Kent, *J. Amer. Chem. Soc.*, **92**, 2149 (1970).

(2) (a) P. O. Schissel, M. E. Kent, D. J. McAdoo, and E. Hedaya, *ibid.*, **92**, 2147 (1970); (b) R. C. Joines, A. B. Turner, and D. M. Jones, *ibid.*, **91**, 7754 (1969).

(3) Similar results were recently reported: W. J. Baron, M. Jones, Jr., and P. P. Gaspar, *ibid.*, **92**, 4739 (1970).

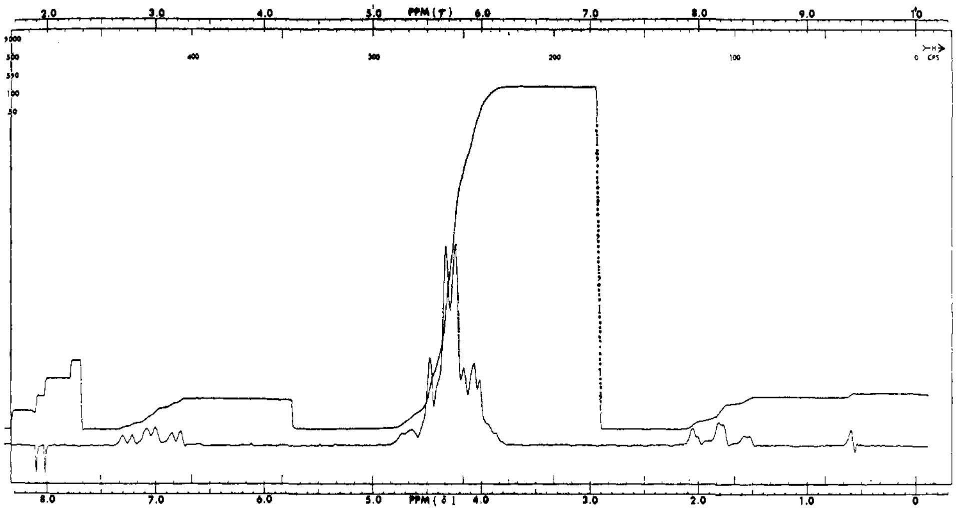
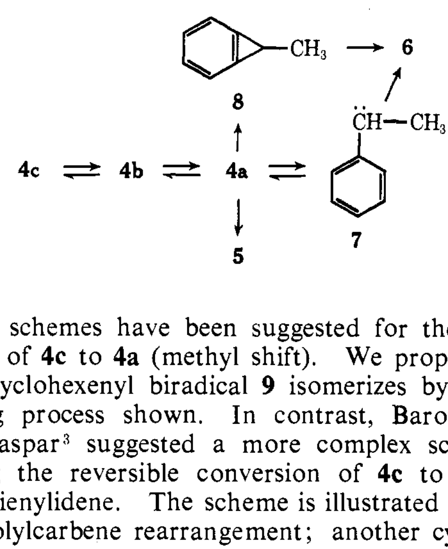
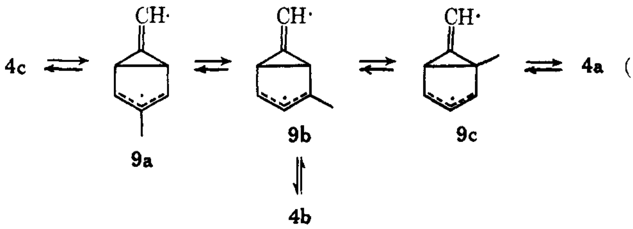


Figure 1. Partial 60-MHz spectrum of ^{13}C-labeled benzocyclobutene in deuteriochloroform; sweep width 250 Hz, CAT output.

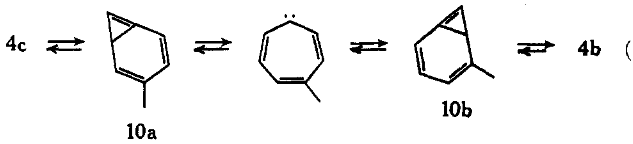
may be formed by further rearrangement to methylphenylcarbene (**7**) or *via* the benzocyclopropene **8** formed from insertion into the exocyclic C–CH_3 bond. Benzocyclobutene itself was found to be stable at 700°.



Two schemes have been suggested for the isomerization of **4c** to **4a** (methyl shift). We proposed that the bicyclohexenyl biradical **9** isomerizes by the ring flipping process shown. In contrast, Baron, Jones, and Gaspar[3] suggested a more complex scheme involving the reversible conversion of **4c** to a cycloheptatrienylidene. The scheme is illustrated for the *p*- to *m*-tolylcarbene rearrangement; another cycle leads to *o*-tolylcarbene while a third gives **7**.



(1)



(2)

The fate of labeled bivalent carbon should unequivocally distinguish these two mechanisms. Equation 1 predicts that the label should be retained in the ethano bridge of benzocyclobutene. The label in the styrene product would either be found in the vinylic carbons if **8** were formed or in the ortho position if **7** were the precursor. Equation 2 predicts that labeled carbon should be found exclusively at the meta 4 position of benzocyclobutene and in the para 4 position of styrene.

p-Tolualdehyde, which was labeled at the aldehydic carbon with 65% excess ^{13}C, was prepared by the modified Gatterman procedure[4] using 65% [^{13}C]-zinc cyanide. This was converted to labeled *p*-tolyldiazomethane by the usual procedure involving pyrolysis of the sodium salt of the tosylhydrazone derivative.[5]

The pyrolysis of *p*-[^{13}C]tolyldiazomethane at 700° in a low-pressure, short-contact time flow system[6] gave labeled benzocyclobutene and styrene in the ratio listed above; these were separated by preparative glpc. The position of the label in the benzocyclobutene was unequivocally established by proton nmr (Figure 1); 65% of one aromatic proton appeared as a ^{13}C satellite ($J_{^{13}C}$ = 79 Hz) with its resonance corresponding to a triplet of doublets (J = 7, ∼3 Hz).[7] The latter pattern rules out the 3-^{13}C isomer and is that predicted for [4-^{13}C]benzocyclobutene. The nmr resonance for the ethano bridge was scanned using the CAT (500 scans) and no excess ^{13}C was detected in this position.

The styrene product was examined by 60- and 220-MHz proton nmr and 22.63-MHz ^{13}C nmr.[8] The 60-MHz spectrum again revealed that 65% of one aromatic proton appeared as a ^{13}C satellite. The 220-MHz spectrum displayed this signal ($J_{^{13}C}$ = 80 Hz) as a complex triplet (J = 7 Hz), which could be correlated with a triplet pattern in the aromatic region centered at 7.43 cps. The relative areas of the latter resonance and the satellites were approximately equivalent suggesting that the ^{13}C was located at the para position. ^{13}C nmr (Fourier transform with protons decoupled) confirmed this assignment; the spectrum of the labeled styrene had one sharply enhanced resonance which corresponded to the para carbon of natural styrene.[9]

[4] T. E. Hinkel, E. E. Ayling, and W. H. Morgan, *J. Chem. Soc.*, 2793 (1932).

[5] G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Schechter, *J. Amer. Chem. Soc.*, 87, 935 (1965).

[6] E. Hedaya, *Accounts Chem. Res.*, 2, 367 (1969).

[7] The differences in shape between the high- and low-field satellites may be ascribed to second-order interactions of the ABCX system.

[8] We thank Brucker Scientific, Elmsford, N. Y., for the use of their instrument.

These results clearly confirm the mechanism summarized by eq 2. A similar mechanism was proposed[10] recently for the rearrangement of diphenylcarbene to fluorene on the basis of methyl labeling experiments. Thus, this process may have considerable generality for aromatic carbenes even though highly strained intermediates such as the bicycloheptatrienes **10** are formally invoked. In fact, the results imply that relatively small energy barriers separate phenylcarbene, cycloheptatrienylidene, and bicycloheptatriene isomers.

Acknowledgment. We thank Dr. P. Green for determining the ^{13}C nmr spectra and Dr. E. B. Whipple for helpful discussions of the nmr data.

---

[9] It is interesting that the mass spectra of labeled styrene and benzocyclobutene both had 55% ^{13}C-enriched C_6H_6 fragments as evidenced by the intensities at *m/e* 78, 79, and 80, even though the parent ions in both cases indicated a 65% enrichment of ^{13}C. The electron-impact induced fragmentation of these molecules to C_6H_6 must occur with randomization of carbon atoms.

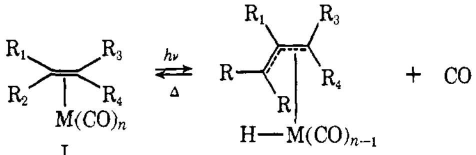
[10] J. A. Myers, R. C. Joines, and W. M. Jones, *J. Amer. Chem. Soc.*, **92**, 4740 (1970).

E. Hedaya,* M. E. Kent
Union Carbide Research Institute
Tarrytown, New York 10591
Received March 15, 1971

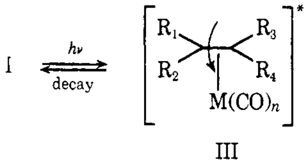
Metal Carbonyl Photoassisted Cis–Trans Isomerization of Stilbene

Sir:

Our work[1] and that of others[2,3] has established the fact that irradiation of metal carbonyl–olefin complexes results in reaction of the olefin. However, the nature of the excited intermediates is in doubt. Two extreme possibilitities exist for intermediates responsible for the cis trans isomerization of olefins complexed to metals: (1) the metal π-allyl hydride (II) formed photochemically as in eq 1 may lead to isomerization *via* thermal reversibility or (2) irradiation of I may produce an excited state which features relatively free rotation about the olefinic bond as in eq 2. Metal–π-allyl hydride intermediates have received a great deal of attention,[4–7] especially as metal hydrides are well-known thermal catalysts for olefin isomerizations.[7] Excited intermediates such as III have been proposed to account for ligand photoisomerization in metalloporphyrin complexes.[8,9] In this communication we present a report of $M(CO)_6$-photoassisted isomerization of the stilbenes. The results suggest strongly that an intermediate similar to III is responsible for the cis–trans photoisomerization of olefins complexed to metal carbonyls.



I   II   (1)



III   (2)

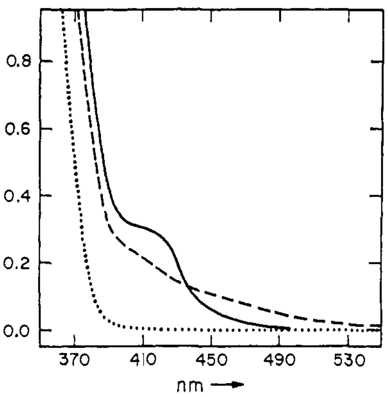


Figure 1. Spectral changes in the uv–visible region due to photochemical formation of $[W(CO)_5(cis\text{-stilbene})]$ (   ) and $[W(CO)_5(trans\text{-stilbene}]$ (———) from 366-nm irradiation of $(WCO)_6$ (· · ·).

Isomerization of the stilbenes has been observed when solutions of either $W(CO)_6$ or $Mo(CO)_6$ and either *cis*- or *trans*-stilbene are irradiated at 366 nm.[10] Olefin isomerization did not occur in the absence of the metal hexacarbonyl. Spectral changes in the uv–visible region occurred upon irradiation, with the solutions turning a greenish yellow. The spectral changes are illustrated in Figure 1. Partial thermal bleaching of the colored solutions occurred when irradiation was terminated. In the initial stages of the photoreaction no significant changes were detected in the ir spectra, but after prolonged or intense irradiations we noted disappearance of the hexacarbonyl and concomitant appearance of ir bands attributable to metal carbonyl–stilbene compounds.[13] In contrast to the $W(CO)_6$-photoassisted isomerization of the conjugated dienes,[1] the stilbenes can be equilibrated photochemically with either $W(CO)_6$ or $Mo(CO)_6$. In Figure 2 we follow the $W(CO)_6$-photocatalyzed equilibration of *cis*- and *trans*-stilbene, starting with solutions of varying initial stilbene compositions.

To determine whether irradiation of the complex results in the cis–trans isomerization, we irradiated at wavelengths where only the metal carbonyl–stilbene

---

[1] M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, **92**, 6068 (1970).

[2] W. Jennings and B. Hill, *ibid.*, **92**, 3199 (1970).

[3] E. K. von Gustorf and F. Grevels *Fort. Chem. Forsch.*, **13**, 366 (1969), and references cited therein.

[4] T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962).

[5] L. Roos and M. Orchin, *J. Amer. Chem. Soc.*, **87**, 5502 (1965).

[6] G. F. Emerson and R. Pettit, *ibid.*, **84**, 4591 (1962).

[7] M. Orchin, *Advan. Catal. Relat. Subj.*, **16**, 1 (1966).

[8] D. G. Whitten, P. D. Wildes, and I. G. Lopp, *J. Amer. Chem. Soc.*, **91**, 3393 (1969).

[9] P. D. Wildes and D. G. Whitten, *ibid.*, **92**, 7609 (1970).

[10] Well-degassed solutions of $\sim 10^{-2}$ *M* stilbene and $\sim 10^{-3}$ *M* $M(CO)_6$ in hydrocarbon solvents were irradiated at 366 nm in a merry-go-round apparatus[11] at room temperature. Light intensity was monitored by benzophenone–piperylene actinometry.[12] Stilbene analysis was by vpc with a 6-ft × 1/8-in. UCW-98 column at 180°. The spectral data were obtained with a Cary 14 spectrometer or with a Perkin-Elmer 225 grating infrared spectrometer.

[11] F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).

[12] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

[13] Metal carbonyl–stilbene complexes have been noted previously: (a) I. W. Stolz, H. Haas, and R. K. Sheline, *J. Amer. Chem. Soc.*, **87**, 716 (1965); (b) G. Drefahl, H. H. Hörhold, and K. Kühne, *Chem. Ber.*, **98**, 1826 (1965); (c) R. Ercoli, F. Calderazzo, and A. Alberola, *Chim. Ind.* (*Milan*), **41**, 975 (1959).