

Here k_α is the isotope effect per deuterium for PhCD_2 migration where CH_3 is the nonmigrating group; k_β is that for PhCH_2 migration where CD_3 is the nonmigrating group. K_H/K_D refers to the respective equilibrium isotope effects for addition to the carbonyl. In order to obtain values for the α and β isotope effects, we must measure or simulate values for K_H/K_D .

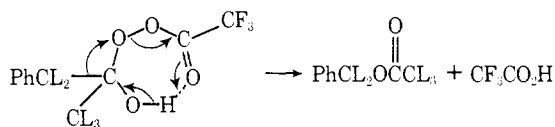
Jones and Bender^{10a} measured the isotope effect for methyl hemiketal formation for acetone in methanol-dioxane and for cyclopentanone in methanol. We applied their method to phenyl-2-propanone in 3 M methanol in dioxane. We measure $(K_H/K_D)_{\text{D}_2} = 0.87 \pm 0.03$ and $(K_H/K_D)_{\text{D}_5} = 0.68 \pm 0.04$. These may be compared to Bender's measurements^{10a} of 0.78 for acetone- d_6 and 0.69 for cyclopentanone- d_4 and to Lamaty's value of 0.790 for K_H/K_D for formation of the bisulfite adduct for phenyl-2-propanone- d_5 .^{5,13}

Inserting the values of K_H/K_D into eq 3-5, we calculate $k_\alpha^2 = 1.071 \pm 0.030$ (1.035 ± 0.014 per deuterium), and $k_\beta^3 = 1.166 \pm 0.070$ (1.052 ± 0.010 per deuterium). The comparable values in the pinacol rearrangement of 1,1-diphenyl-2-methylpropane-1,2-diol are 1.195 for CD_3 migration (1.061 per deuterium) and 0.970 for CD_3 as the nonmigrating group (0.990 per deuterium).⁴

The isotope effect on the migrating group in the Baeyer-Villiger reaction is smaller than expected; the general trend predicts a larger per deuterium isotope effect for RCH_2 than for CH_3 .¹ This is consistent with a smaller decrease in the HCH bending force constant or a larger increase in HCO bending force constant for benzyl migration in the Baeyer-Villiger reaction than for methyl migration in the pinacol reaction. This implies less positive charge delocalized onto the migrating group in the former reaction. The large positive β isotope effect for CD_3 is definitive; it must be due to $\text{C}=\text{O}$ or $\text{C}=\text{OH}^+$ bond formation¹⁴ in the transition state for breakdown of the tetrahedral intermediate. In the pinacol reaction the β isotope effect is not significantly different from 1.0. This suggests a later transition state for migration of benzyl in the Baeyer-Villiger reaction than for methyl migration in the pinacol rearrangement.

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(14) Proton transfer steps in the Baeyer-Villiger reaction in nonprotic media remain to be elucidated. Proton transfer to the trifluoroacetate carbonyl simultaneous with the departure of that group during the



migration step would lead to $\text{C}=\text{O}$ and not $\text{C}=\text{OH}^+$ formation.

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Uses of Benzocyclopropenes in Synthesis. Catalysis by Silver Ion

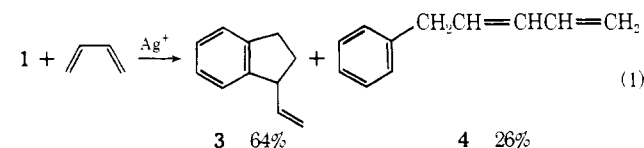
Sir:

Since the novel hydrocarbons benzocyclopropene (1)^{1a} and naphtho[b]cyclopropene (2)^{1b} have become



readily available, we have been studying their chemistry and report here some of our results.² Particularly interesting are the silver ion catalyzed reactions of these hydrocarbons with various substrates.³

Thus, reaction of 1 with butadiene and 1 mole % $\text{Ag}(\text{I})$ in benzene (0° , 30 min) gives 3 and 4 (eq 1).⁴



These products are rationalized in terms of intermediates 5 and 6 (Scheme I). In this scheme, 3 and 4 arise from 6 by ring closure and proton transfer, respectively.⁵ In contrast, the thermally induced reaction of 1 and buta-

(1) (a) E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Lett.*, 3625 (1965); W. E. Billups, A. J. Blakeney, and W. Y. Chow, *Chem. Commun.*, 1461 (1971); (b) W. E. Billups and W. Y. Chow, *J. Amer. Chem. Soc.*, **95**, 4099 (1973).

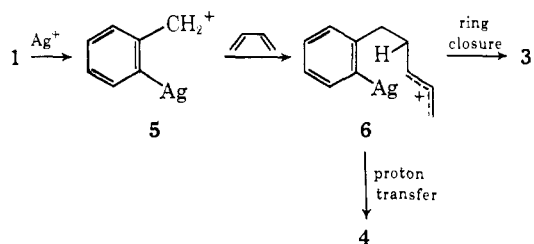
(2) For a review on benzocyclopropenes, see B. Halton, *Chem. Rev.*, **73**, 113 (1973).

(3) Cleavage of strained carbon-carbon σ bonds with transition metals has been investigated extensively; however, much less is known about the metal-catalyzed reactions of these systems with other substrates. Exceptions are found when protic solvents are used where ready solvent incorporation is observed. For relevant references see H. Hogeveen and H. C. Volger, *J. Amer. Chem. Soc.*, **89**, 2486 (1967); W. Merk and R. Pettit, *ibid.*, **89**, 4788 (1967); T. J. Katz and S. A. Cerefice, *ibid.*, **91**, 2405, 6519 (1969); R. Askani, *Tetrahedron Lett.*, 3349 (1970); N. B. Chapman, J. M. Key, and K. J. Toyne, *ibid.*, 5211 (1970); L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 3515, 6366 (1970); L. Cassar and J. Halpern, *Chem. Commun.*, 1082 (1970); K. G. Powell and F. J. McQuillin, *Tetrahedron Lett.*, 3313 (1971); R. Grigg and G. Shelton, *Chem. Commun.*, 1247 (1971); M. Sakai and S. Masamune, *J. Amer. Chem. Soc.*, **93**, 4610, 4611 (1971); R. Noyori, T. Suzuki, Y. Kumagai, and H. Takaya, *ibid.*, **93**, 5894, 5896 (1971); L. A. Paquette, *Accounts Chem. Res.*, **4**, 280 (1971); L. A. Paquette and S. E. Wilson, *J. Amer. Chem. Soc.*, **93**, 5934 (1971); L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, **93**, 2335 (1971); W. G. Dauben and A. J. Kielbania, Jr., *ibid.*, **94**, 3669 (1972); R. J. Roth and T. J. Katz, *ibid.*, **94**, 4770 (1972); P. G. Gassman and T. Nakai, *ibid.*, **94**, 5497 (1972); P. G. Gassman and F. J. Williams, *J. Chem. Soc., Chem. Commun.*, 80 (1972); *J. Amer. Chem. Soc.*, **94**, 7733 (1972); P. G. Gassman, G. R. Meyer, and F. J. Williams, *ibid.*, **94**, 7741 (1972); P. G. Gassman and T. J. Atkins, *ibid.*, **94**, 7748 (1972); P. G. Gassman, T. J. Atkins, and J. T. Lumb, *ibid.*, **94**, 7757 (1972); N. Acton, R. J. Roth, T. J. Katz, J. K. Frank, C. A. Maier, and I. C. Paul, *ibid.*, **94**, 5446 (1972); L. A. Paquette and L. M. Leichter, *ibid.*, **94**, 3653 (1972); L. A. Paquette, S. E. Wilson, R. P. Henzel, and G. R. Allen, Jr., *ibid.*, **94**, 7761 (1972); L. A. Paquette, S. E. Wilson, and R. P. Henzel, *ibid.*, **94**, 7771 (1972); L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, **94**, 7780 (1972), and references therein.

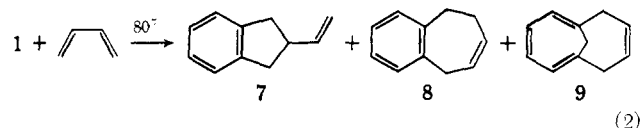
(4) Spectral properties of 3 are: nmr (CCl_4) δ 1.6-2.6 (m, 2 H), 2.86 (d of d, 2 H, $J = 6$, $J = 9$ Hz), 3.7 (q, 1 H, $J = 9$ Hz), 4.89-5.3 (m, 2 H), 5.46-6.2 (m, 1 H), and 7.18 (s, 4 H); ir (neat) 910, 990, and 1638 cm^{-1} . 4 shows nmr signals at δ 3.51 (d, 2 H, $J = 8$ Hz), 4.85-5.48 (m, 2 H), 5.48-7.0 (m, 2 H), and 7.2 (s, 5 H); uv $\lambda_{\text{max}}^{\text{C}_6\text{H}_6}$ 229 nm (ϵ 20,000). The ir is in good agreement with the one reported by Prévost for this compound. See C. Prévost, P. Miginiac, and L. Miginiac-Groizeleau, *Bull. Soc. Chim. Fr.*, **10**, 2485 (1964).

(5) Although formation of carbon-silver σ bonds is frequently invoked³ in rearrangements of strained hydrocarbons which are catalyzed by silver ion, it should be noted that few compounds incorporating this structural feature have been reported.

Scheme I

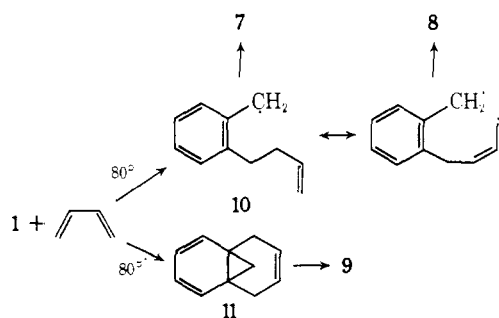


diene has been reported to give 7, 8, and 9 (eq 2).⁶ The

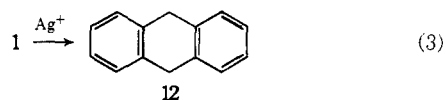


diradical 10⁶ has been invoked as an intermediate in the formation of 7 and 8, whereas 9 probably arises *via* a concerted [4 + 2] or [6 + 4] cycloaddition to give intermediate 11 which would spontaneously rearrange to 9 (Scheme II).

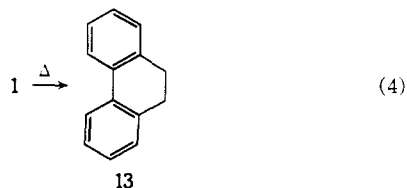
Scheme II



Addition of AgBF_4 (1 mole %) to a solution of 1 in benzene or CHCl_3 at 0° gives 9,10-dihydroanthracene (12) in 45% yield, eq 3. This conflicts with the recent



claim by Shirafuji and Nozaki⁷ that AgOAc and 1 give the isomeric 9,10-dihydrophenanthrene (13). However, it is interesting that 1 dimerizes thermally at 80° to give 13, eq 4.⁶

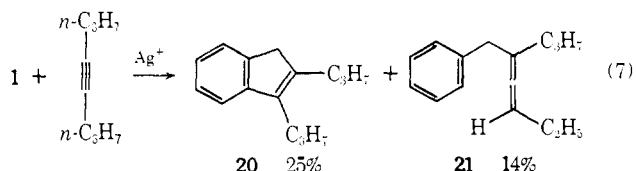
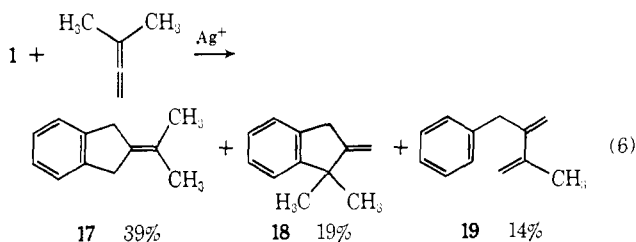
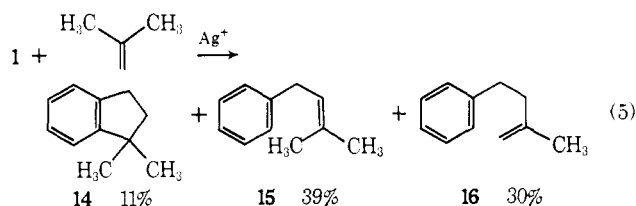


Olefins, allenes, and acetylenes react readily with 1 in the presence of silver ion. Representative examples are illustrated in eq 5, 6, and 7.⁸⁻¹¹ Several features of

(6) S. Korte, Ph.D. Thesis, University of Köln, 1968, as read in ref 2.

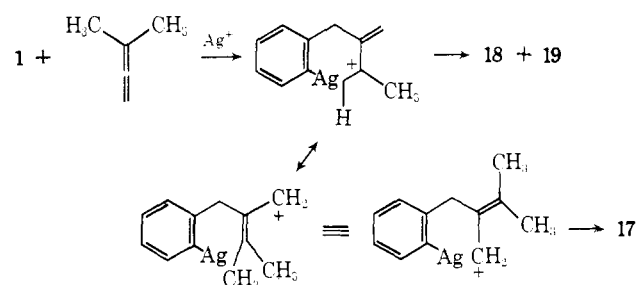
(7) T. Shirafuji and H. Nozaki, *Tetrahedron*, 29, 77 (1973).

(8) Compounds 14,⁹ 15,¹⁰ and 16¹¹ are known and the spectral properties observed here agree with those reported. 17 shows nmr (CCl_4) signals at δ 1.70 (t, 6 H, $J = 2$ Hz), 3.58 (t, 4 H, $J = 2$ Hz), and 7.12 (s, 4 H). 18: nmr (CCl_4) δ 1.32 (s, 6 H), 3.68 (t, 2 H, $J = 2$ Hz), 5.00 (m, 2 H), and 7.05 (s, 4 H). 19: nmr (CCl_4) δ 1.87 (s, 3 H), 3.54 (s, 2 H), 4.83 (broad s, 2H), 5.07 (d, 2 H, $J = 10$ Hz), and 7.06 (s, 5 H); uv $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ 227 nm (ϵ 14,500). 20: nmr (CCl_4) δ 0.94 (t, 6 H, $J = 7$ Hz), 1.56 (sextet, 4 H, $J = 7$ Hz), 2.43 (m, 4 H), 3.2 (s, 2 H), and 6.90-7.32 (m, 4 H). 21: nmr (CCl_4) δ 0.70-1.63 (m, 8 H), 1.63-2.2 (m, 4 H), 3.24 (d, 2 H, $J = 3$ Hz), 5.07 (m, 1 H), and 7.19 (s, 5 H); ir absorption (weak) at 1960 cm^{-1} (allene).



these reactions merit comment. All are rationalized in terms of carbonium ion mechanisms. The products of eq 6 arise from addition of the electrophile to the central carbon of the allene rather than from the more commonly observed addition to the terminal carbon (illustrated in Scheme III).¹² It is interesting that in this

Scheme III



scheme 19 must arise *via* proton transfer to the benzene ring within a cyclic transition state incorporating seven atoms. Products 16 (eq 5) and 21 (eq 7) probably arise by a similar mechanism.

Finally, the thermally initiated reaction of 1 with isobutylene or 1,1-dimethylallene was found to give complex mixtures of products¹³ and efforts to identify these were abandoned.

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(9) F. E. Juge, Jr., and A. Fry, *J. Org. Chem.*, 35, 1876 (1970).

(10) R. C. Haley, J. A. Miller, and H. C. S. Wood, *J. Chem. Soc.*, C, 264 (1969).

(11) R. P. A. Sneeden and H. H. Zeiss, *J. Organometal. Chem.*, 26, 101 (1971).

(12) D. R. Taylor, *Chem. Rev.*, 67, 338 (1967).

(13) For example, reaction of 1 with 1,1-dimethylallene at 100° for 12 hr gave ~20 products as determined by glpc.

(14) Alfred P. Sloan Foundation Fellow, 1973-1975.

(15) National Defense Education Act Fellow, 1970-1973.

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