Solutions of the formyl complex **1** slowly decompose to $HFe(CO)_4^-$ ($t_{1/2}$ (25°) $\geq$ 12 days (Na^+ salt, THF)) but in the solid state ($[N(PPh_3)_2]^+$ salt) there is no apparent decarbonylation after 13 days at 0.2 mm (25°)). Although the related acyl complexes **2** can be protonated forming aldehydes,[4] oxidized ($O_2 + H_2O$) affording carboxylic acids,[6] and alkylated yielding ketones,[5] the formyl complex reacts somewhat differently and is not synthetically useful. However, the reactions of the formyl complex have important mechanistic implications. Protonation of **1** afforded the expected formaldehyde (dimedone derivative). Reaction of **1** with O_2 resulted in an explosion upon acidification suggesting the formation of performic acid.[19] Alkylation of **1** with octyl iodide gave octane (75% isolated yield) but only a trace of nonanal—the product expected on the basis of our earlier ketone synthesis.[5,20] Apparently the neutral intermediate iron(II) complex $[(C_8H_{17})(CHO)Fe(CO)_4]$ loses CO and, following hydride migration to iron, reductively eliminates the octyl and hydride groups forming octane.[21]

These diverse experimental results may arise from differences in migratory insertion equilibria and/or from different tendencies of the pairs R, H; RCO, H; RCO, R′; and R, R′ to undergo reductive elimination. In no instance have we observed the reductive elimination of two σ-bonded alkyl groups—a reaction of enormous potential synthetic significance. Further studies are required to clarify these mechanisms.

Acknowledgment. We wish to thank the National Science Foundation, Grant No. GP20273X1, for financial support and Walter Siegl for helpful discussions.

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[19] Performic acid has been reported to explode on heating with metals: "Dictionary of Organic Compounds," Vol. 4, Oxford University Press, New York, N. Y., 1965, p 2642.

[20] Although $HFe(CO)_4^-$ gives octane when treated with octyl iodide, decarbonylation of **1** to the hydride is too slow to account for the formation of octane by this route.

[21] This neutral iron(II) complex should dissociate CO more easily than the anionic iron(0) formyl complex **1**.

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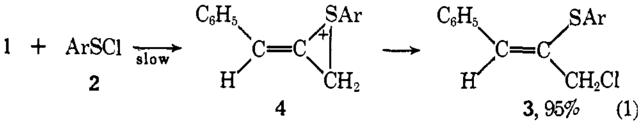
Orientation and Kinetic Secondary Isotope Effects in the Addition of 2,4-Dinitrobenzenesulfenyl Chloride to Phenylallene[1]

Sir:

Allenic compounds show a variety of regioreactivities in electrophilic addition reactions.[2] Phenylallene (**1**) was found to generally give a product of the terminal-bond addition, 2,3 adduct, through the central-carbon attack by an electrophile.[3] However, we have obtained evidence that it is formed in hydrochlorination[3a] and bromination[3b] through a primary electrophilic attack on the internal bond, 1,2 addition, followed by the allylic rearrangement. On the other hand, Jacobs, *et al.*,[4] showed that the allylic rearrangement could not be involved in the sulfenylation of an aliphatic allene. We have found that 2,4-dinitrobenzenesulfenyl chloride (**2**) adds to **1** to give a 2,3 adduct by a direct rate-determining addition to the terminal bond.

The addition of **2** to **1** has been investigated in glacial acetic acid. The product obtained at ~20° was predominantly the 2,3-adduct **3**. The yield was ~95% by nmr spectroscopy. Recrystallization from CCl_4 gave yellow needles in 64% yield, mp 118–119°. *Anal.* Calcd for $C_{15}H_{11}N_2O_4ClS$: C, 51.34; H, 3.16; N, 7.99; Cl, 10.11; S, 9.14. Found: C, 50.98; H, 3.10 N, 8.04; Cl, 10.10; S, 9.15. Nmr ($CDCl_3$): δ 4.44 (2 H, s, CH_2Cl), 7.46 (1 H, s, -CH=), 7.53 (5 H, m, C_6H_5), 7.73 (1 H, d, J = 9 Hz, 6-H of $C_6H_3(NO_2)_2$), 8.33 (1 H, dd, J = 9 Hz, 2.5 Hz, 5-H of $C_6H_3(NO_2)_2$), 9.13 (1 H, d, J = 2.5 Hz, 3-H of $C_6H_3(NO_2)_2$).



Ar = 2,4-dinitrophenyl

The adduct **3** was oxidized by H_2O_2–AcOH to the corresponding sulfoxide, mp 173–174°. Nmr ($CDCl_3$): δ 4.22 and 4.52 (2 H, 2d, J = 13 Hz, CH_2Cl), ~7.48 (5 H, m, C_6H_5), 7.83 (1 H, s, -CH=), ~8.73 (m) and 9.10 (d) (3 H, $C_6H_3(NO_2)_2$). The nmr spectrum of the sulfoxide in the presence of 0.65 mol equiv of the shift reagent, $Eu(C_{10}H_{10}F_2O_2)_3$, showed signals at δ 7.83 and ~8.27 (5 H, 2 m, C_6H_5), ~10.11 (m) and 10.68 (d) (3 H, $C_6H_3(NO_2)_2$), 11.08 (1 H, s, -CH=), and 15.78 and 23.86 (2 H, 2d, J = 13 Hz, CH_2Cl). The comparison of the effects of the shift reagent on the chemical shift of the olefinic proton with those observed for closely related compounds[5] confirmed that the olefinic proton is trans to the sulfinyl group. Hence, **3** can be assigned the structure as shown in eq 1.

Small amounts of the 1,2 adduct, $C_6H_5CHClC(SAr)=CH_2$, and its rearranged product, $C_6H_5CCl=C(SAr)CH_3$, were also isolated. Neither of them was found to rearrange to **3**. This fact indicates that **3** is formed kinetically. Stereochemical purity of **3** obtained in the reaction also conforms to the assumption of its kinetically controlled formation.

Data obtained by the experiments on the kinetic secondary isotope effects are further evidence to substantiate the rate-determining 2,3 attack of sulfur forming an intermediate episulfonium ion. The second-order rate constants[6] measured at 30° are given in Table I for **1** and its deuterated derivatives. The large rate enhancement (k_H/k_D = 0.84) was observed by γ,γ dideuteration while the α deuteration had essentially no effect on the rate (k_H/k_D = 1.01).

The secondary deuterium isotope effects observed here can be taken as a direct indication of the predominant 2,3-bond attack by the sufenyl sulfur in the rate-

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[1] Part V of Electrophilic Additions to Dienes. For part IV, see K. Izawa, T. Okuyama, T. Sakagami, and T. Fueno, *J. Amer. Chem. Soc.*, submitted for publication.

[2] For review, see D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967).

[3] (a) T. Okuyama, K. Izawa, and T. Fueno, *Tetrahedron Lett.*, 3295 (1970); *J. Amer. Chem. Soc.*, submitted for publication; (b) K. Izawa, K. Ohashi, T. Okuyama, and T. Fueno, unpublished results.

[4] T. L. Jacobs, R. Macomber, and D. Zunker, *J. Amer. Chem. Soc.*, **89**, 7001 (1967).

[5] K. Ogura and G. Tsuchihashi, *Tetrahedron Lett.*, 1383 (1972). In the case of 1-methylsulfinyl-1-methylthio-2-phenylethylene, 0.51 mol equiv of the shift reagent caused a downfield shift of 8.98 and 2.69 ppm for protons cis and trans to the sulfinyl group, respectively.

[6] The rate is first order in each reactant. Kinetic measurements have been made according to the method of Orr and Kharasch.[7]

[7] W. L. Orr and N. Kharasch, *J. Amer. Chem. Soc.*, **78**, 1201 (1956).

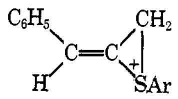
Table I. Second-Order Rate Constants for the Reaction of Deuteriophenylallenes[a]

Allene	$10^4 k_2$, M^{-1} sec^{-1}	k_H/k_D
$C_6H_5CH{=}C{=}CH_2$	9.79 ± 0.08	
$C_6H_5CD{=}C{=}CH_2$	9.68 ± 0.18	1.01 ± 0.03
$C_6H_5CH{=}C{=}CD_2$	11.67 ± 0.14	0.84 ± 0.02 (0.92 per D)

[a] [2] = 0.08 *M*; [allene] = 0.04–0.06 *M*; in acetic acid at 30°.

determining step. Furthermore, rate-enhancing effects by deuteration is interpreted in terms of the partial hybridization change of the carbon atom in question ($sp^2 \rightarrow sp^3$)[8] and thus the formation of a bridged episulfonium ion. Similar secondary isotope effects have recently been observed in the sulfenylation of styrene-*α*-*d*.[9]

In conclusion, in contrast to the hydrochlorination,[3] the addition of **2** to **1** takes place through the rate-determining attack on the terminal 2,3 double bond of **1** by electrophilic sulfur from the side of the phenyl group to form an episulfonium ion **4**. The reason for a favorable formation of **4** as compared with an isomeric intermediate **5** is not obvious at present and further investigations will be needed. Particularly, extention of the study for other sulfenyl halides would be useful.



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Acknowledgment. We wish to thank Mr. Y. Kawashima for his partial assistance in the experimental work.

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[8] *E.g.*, E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

[9] C. L. Wilkins and T. W. Regulski, *J. Amer. Chem. Soc.*, **94**, 6016 (1972).

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On the Mechanism for Photoreduction of Benzophenone in Benzene. Evidence for Self-Quenching of Benzophenone Triplets in Solution and for H Abstraction from Benzophenone Ground State[1]

Sir:

In earlier papers,[2] we reported on the basis of flash experiments that the relatively rapid rate of decay of benzophenone triplets ($^3Ph_2CO^*$), in solution in benzene and substituted benzenes at room temperature, is primarily due to interaction of $^3Ph_2CO^*$ with the aromatic to give a complex which ultimately decays to ground state Ph_2CO and the aromatic.

This decay mechanism is in competition with an inefficient photoreaction in these media which leads mainly to benzpinacol[3–6] and, in the case of benzene solvent, biphenyl.[4–7] The quantum yield for benzpinacol[6] in aromatic solvents decreased as the lifetime of $^3Ph_2CO^*$ decreased.[8] We report here the results of a detailed kinetic investigation on the formation of benzpinacol and biphenyl in benzene, which reveal interesting features of this fundamental reaction[9] not previously disclosed.[2–5,7]

Absolute and relative quantum yields for formation of benzpinacol and biphenyl[6] as a function of benzophenone concentrzation [B^0] over the range 0.01–3.0 *M* were measured in benzene purified by the Saltiel–Metts photochlorination procedure.[8,10] Whereas biphenyl formation is strongly quenched by benzophenone, benzpinacol yields are barely affected.[11] The following mechanistic scheme is proposed.

$$Ph_2CO^0 \xrightarrow{h\nu} {}^1Ph_2CO^* \longrightarrow {}^3Ph_2CO^* \tag{1}$$

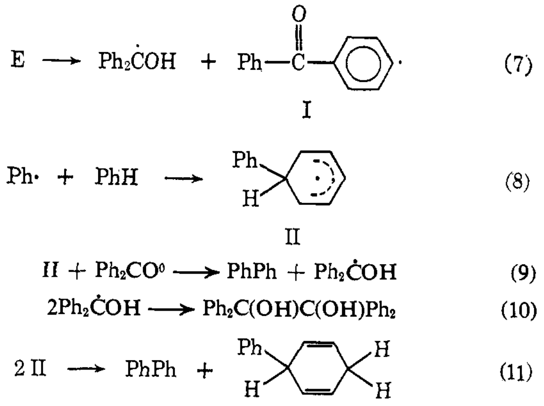
$${}^3Ph_2CO^* + PhH \longrightarrow C \tag{2}$$

$$C \longrightarrow Ph_2CO^0 + PhH \tag{3}$$

$${}^3Ph_2CO^* + PhH \longrightarrow Ph_2\dot{C}OH + Ph\cdot \tag{4}$$

$${}^3Ph_2CO^* + Ph_2CO^0 \longrightarrow E \tag{5}$$

$$E \longrightarrow 2Ph_2CO^0 \tag{6}$$



$$II + Ph_2CO^0 \longrightarrow PhPh + Ph_2\dot{C}OH \tag{9}$$

$$2Ph_2\dot{C}OH \longrightarrow Ph_2C(OH)C(OH)Ph_2 \tag{10}$$

Assuming the steady-state approximation holds for all reaction intermediates, the following relationships can be derived, if step 11 is excluded.[12,13] The rate

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[1] Part XXXVIII of Photochemistry of Ketones in Solution. Part XXXVII: D. I. Schuster and M. D. Goldstein, *J. Amer. Chem. Soc.*, **95**, 986 (1973).

[2] (a) D. I. Schuster, T. M. Weil, and M. R. Topp, *Chem. Commun.*, 1212 (1971); (b) D. I. Schuster, T. M. Weil, and A. M. Halpern, *J. Amer. Chem. Soc.*, **94**, 8248 (1972).

[3] E. J. Bowen and E. L. A. E. de la Praudiere, *J. Chem. Soc.*, 1503 (1934).

[4] J. Saltiel, H. C. Curtis, and B. Jones, *Mol. Photochem.*, **2**, 331 (1970).

[5] J. Dedinas, *J. Phys. Chem.*, **75**, 181 (1971).

[6] Quantitative determination of benzpinacol yields was by rearrangement to benzpinacolone using iodine in acetic acid and analysis for the latter by gas–liquid partition chromatography (glpc) with internal standards. Analysis by glpc for biphenyl was made on the original photolysate.

[7] J. A. Bell and H. Linschitz, *J. Amer. Chem. Soc.*, **85**, 528 (1963).

[8] Full details and data, not included because of space limitations, will be given in the full publication. See also T. M. Weil, Ph.D. Dissertation, New York University, 1973.

[9] See N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965; J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966.

[10] J. Saltiel and L. Metts, private communication of unpublished results. See also J. Saltiel, H. C. Curtis, and B. Jones, *Mol. Photochem.*, **2**, 331 (1970). This method of purification of benzene is the best of many tried by us, as indicated by the fact that it gives the longest measured lifetime of $^3Ph_2CO^*$.[2]

[11] Dedinas[5] made the same observation over a much more limited concentration range. He also found very small yields (∼10^{-4}) of 4-biphenyldiphenylcarbinol.

[12] This assumes that phenylcyclohexadienyl radical (II) reacts exclusively with benzophenone[5] and that the disproportionation reaction (11)[13] plays little role. If step 11 were important at low [B], the yield of $Ph_2\dot{C}OH$ and derived pinacol would fall below the extrapolated line from high [B], which is not observed. The absence of tetrahydroquaterphenyls suggests dimerization of II is also not important, at least over the range [B] = 0.002–0.05 *M*.[5] The fate of I is not yet defined.

[13] E. L. Eliel, S. Meyerson, Z. Welvart, and S. H. Wilen, *J. Amer. Chem. Soc.*, **82**, 2936 (1960); D. F. De Tar, R. A. J. Long, J. Rendleman, J. Bradley, and P. Duncan, *ibid.*, **89**, 4051 (1967).