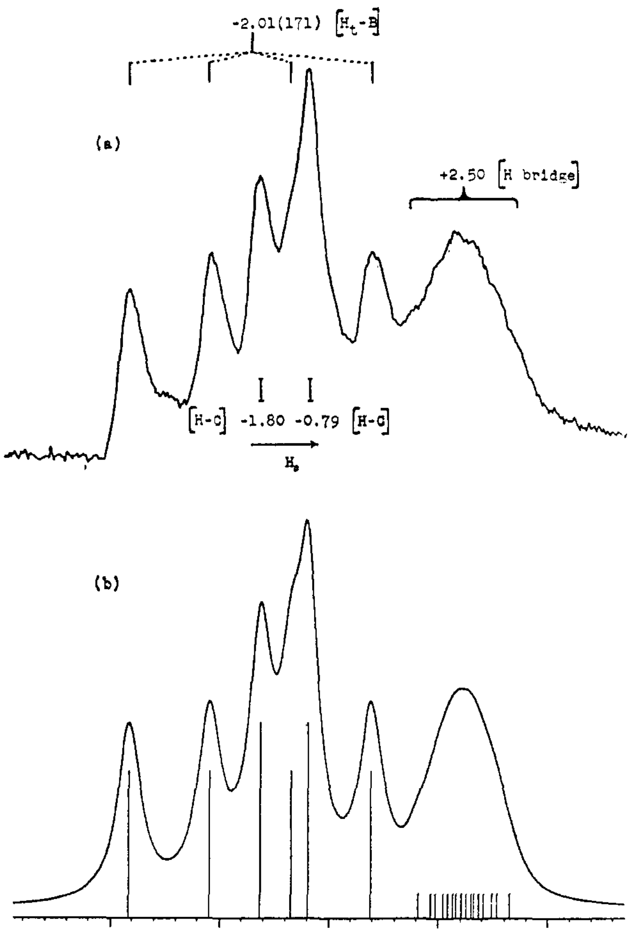

Figure 3. (a) The 100-MHz ^{1}H nmr spectrum of 1,2-$C_2B_3H_7$ (CS_2 solution). Chemical shifts are in ppm relative to external tetramethylsilane, and coupling constants (Hz) are given in parentheses. (b) Computer simulation.

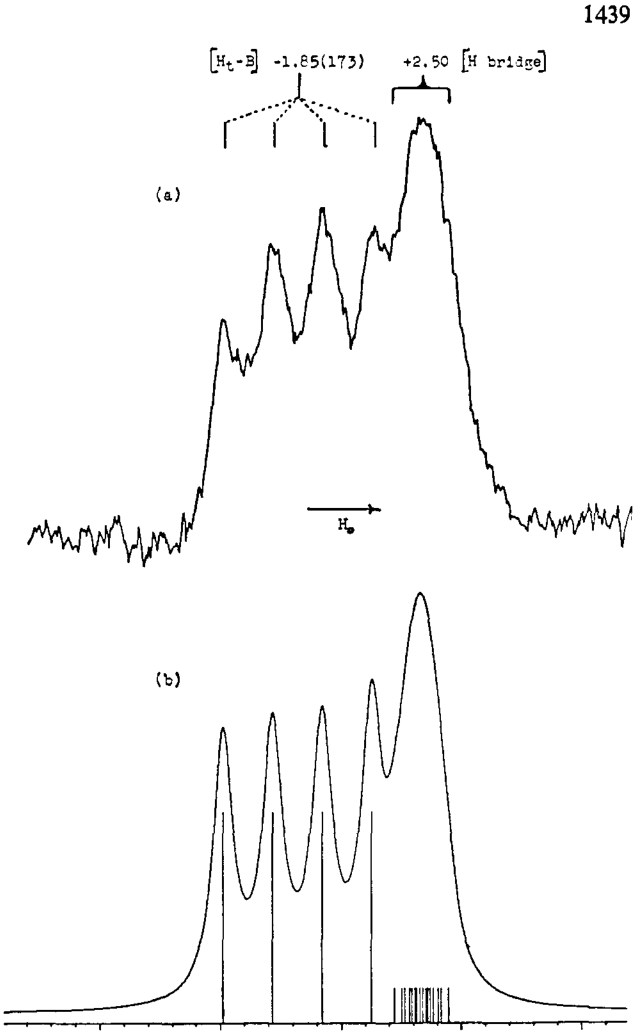

Figure 4. (a) The 100-MHz ^{1}H nmr spectrum of $C_2D_2B_3H_5$ (CS_2 solution). Data are given as in Figure 3a. (b) Computer simulation.

The gas-phase infrared spectrum of I includes principal bands at 3150 (m), 3075 (m), 2610 (vs), 1860 (s, b), 1800 (s), 1565 (vs), 1420 (s, sh), 1370 (vs), 1155 (s), 1050 (m), 980 (s), 895 (s), 840 (vs), 730 (vs, sh), 715 (vs), and 690 (s, sh) cm^{-1}. The bands at 3150 and 3075 cm^{-1}, each having multiplet structure, are assigned to H–C stretching modes, while the absorptions at 2610 cm^{-1} and in the region of 1800 cm^{-1} are attributed to B–H$_t$ and B–H$_b$–B stretching, respectively. The infrared spectrum of II is similar but contains no significant bands above 2610 cm^{-1}, indicating the absence of C–H bonds. A weak absorption at 2350 cm^{-1} is attributed to C–D stretching.

Compound I has shown some unusual properties. In the vapor phase at 50° it is apparently stable, but in the liquid phase it rapidly polymerizes to a white solid at room temperature. The polymerization occurs even in $CDCl_3$ or CS_2 solutions, which complicated the task of obtaining nmr spectra; these data were finally recorded from 20% solutions of I, but even these dilute mixtures became gel-like after 1 hr at room temperature. No reaction was observed between I and B_4H_{10} at 50° in the vapor phase, but I reacts rapidly with B_2H_6 at 50° to yield products as yet unidentified. Further investigations of this carborane are in progress.

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Isotope and Substituent Effects on the Interaction of Benzophenone with Simple Olefins. Apparent Insufficiency of the Schenk Mechanism

Sir:

Recent work[1-3] has demonstrated that the *cis–trans* isomerization of alkylethylenes, photosensitized by n–π* ketone triplets, does not proceed through the triplet state of the olefin as the exclusive[2] or apparently even major[1,3] pathway. Instead, a 1,4 biradical (the Schenk mechanism) has been implicated as an intermediate in this reaction as well as in oxetane forma-

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(1) N. C. Yang, J. I. Cohen, and A. Shani, *J. Amer. Chem. Soc.*, **90**, 3264 (1968).

(2) J. Saltiel, K. R. Neuberger, and M. Wrighton, *ibid.*, **91**, 3658 (1969).

(3) R. A. Caldwell and S. P. James, *ibid.*, **91**, 5184 (1969).

Table I. Quenching of Substituted Benzophenones by *cis*-2-Butene

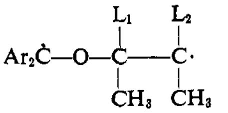
Compound	$\phi_{c\rightarrow t}$[c]	k[a]	$\Sigma\sigma$[b]	E_T,[c] kcal
4,4′-Dimethoxybenzophenone	0.35	4×10^6	−0.54	69.4
Benzophenone	*Ca.* 0.3	7×10^7 [d]	0.00	68.6
4-Trifluoromethylbenzophenone	0.34	2.2×10^8	+0.54	67.6
4-Benzoylpyridine	0.34[e]	3.3×10^8	+0.88[f]	67.1

[a] Measured by the attenuation of *cis–trans* isomerization of 0.3 *M* *cis*-2-butene by isoprene, assuming that k_Q for isoprene is 5×10^9 M^{-1} sec^{-1}. [b] Summation of Hammett substituent constants for the ketone. [c] Triplet energies obtained from D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968). [d] Recalculation of the data of R. A. Caldwell and S. P. James, *J. Amer. Chem. Soc.*, **91**, 5184 (1969). [e] Solutions became noticeably yellow past about 2% conversion. [f] G. B. Barlin and D. D. Perrin, *Quart. Rev.* (London), **20**, 75 (1966).

tion.[4] Since our observation[3] of the isotope effect of vinyl deuteration on the isomerization of 2-butene by benzophenone triplet appeared not to support the formation of a biradical in the *initial* quenching step (eq 1), we have carried out more detailed studies in an attempt to elucidate the quenching mechanism. The present results support the hypothesis that some intermediate X precedes the biradical and suggest its tentative formulation as a species with substantial electron transfer from olefin to ketone.

$$\mathrm{Ar_2C{=}O^3 + CH_3CL_1{=}CL_2CH_3 \xrightarrow{k_1} [X] \xrightarrow{k_x}}$$

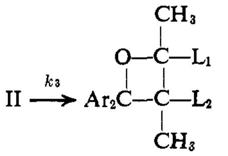
Ia, $L_1 = L_2 = H$
Ib, $L_1 = L_2 = D$
Ic, $L_1 = D$; $L_2 = H$ (≡Id)
Id, $L_1 = H$; $L_2 = D$
Ie, $L_1 = H$; $L_2 = C_2H_5$
If, $L_1 = C_2H_5$; $L_2 = H$



$$\mathrm{Ar_2\dot{C}{-}O{-}\overset{L_1}{\underset{CH_3}{C}}{-}\overset{L_2}{\underset{CH_3}{C}}\cdot} \quad (1)$$

IIa-f

$$\mathrm{II \xrightarrow{k_2} Ar_2C{=}O + CH_3CL_1{=}CL_2CH_3}\ (cis + trans) \quad (2)$$



$$\mathrm{II \xrightarrow{k_3} \begin{array}{l} O{-}\overset{CH_3}{C}{-}L_1 \\ Ar_2C{-}\underset{CH_3}{C}{-}L_2 \end{array}} \quad (3)$$

IIIa-f

We have previously reported[3] the isotope effect on benzophenone-sensitized *cis* to *trans* isomerization of 2-butene as $k(\mathrm{Ia})/k(\mathrm{Ib}) = 1.02 \pm 0.01$. We have now measured the isotope effect on oxetane formation in this system. Benzophenone was irradiated (benzene solution, Pyrex filter) in the presence of a fourfold excess of either Ia–Ib or Ic–Id, and the resulting oxetane was analyzed mass spectrometrically for deuterium content and position. Moderately prolonged irradiation decreased the proportion of IIIa or IIId somewhat, perhaps due to a primary isotope effect on the abstraction of hydrogen L_1 next to oxygen by benzophenone triplet.[5] The isotopic analysis of III was considerably facilitated by the observation that the molecular ion in the low-voltage mass spectrum fragmented virtually quantitatively to an ion of mass 194 for IIIa or IIIc and to an ion of mass 195 for IIIb or IIId, due to loss of $\mathrm{CH_3COL_1}$; precedent for this behavior exists.[6] The analysis for IIIc–IIId was checked by nmr examination of the chromatographed and recrystallized oxetane and by mass spectral examination of both the purified material and the reaction mixture. All these analyses agreed.

The results show low intermolecular isotopic selectivity, $k(\mathrm{IIIa})/k(\mathrm{IIIb}) = 1.03 \pm 0.02$, from *cis*-I, essentially identical with the effect observed[3] on *cis–trans* isomerization of IIb. This identity clearly shows that there is essentially no isotope effect on the partitioning of biradical II in this system. One might have been expected because hybridization arguments[3,7] predict a direct effect for k_2 but an inverse effect for k_3. The observation therefore points to virtually no isotope effect for either k_2 or k_3 and suggests that the transition states resemble biradical II very closely. This is not surprising for these highly exothermic reactions.[8] One may safely conclude that formation of biradical IIb involves a small direct isotope effect, in contrast to expectations based on thermal additions to olefins.[3,7,9]

These experiments alone do not allow the separate determination of the isotope effects at L_1 and L_2; the isotope effects could be any two numbers whose product was equal to our total effect for Ib. If this reaction were comparable to thermal [2 + 2] cycloadditions of ketenes[10] or azodicarboxylates[11] to olefins, one might expect the L_1 effect to be inverse and the L_2 effect to be significant and direct, even if reaction 1 is an elementary reaction. To separate the effects at L_1 and L_2 we have synthesized the *cis* and *trans* isomers of 3-methyl-2-pentene-2-*d* (Ie) and have measured intermolecular isotope effects on benzophenone-sensitized *cis–trans* isomerization. The utility of this molecule comes from the expectation[12] that the tertiary biradical IIe will predominate heavily over the secondary biradical IIf, and therefore that results for this molecule will reflect the L_1 isotope effect. The results for Ie are: k_H/k_D (*cis* → *trans*) = 1.002 ± 0.01 and k_H/k_D (*trans* → *cis*) = 1.007 ± 0.01. Identification of this value as the L_1 isotope effect then allows the conclusion that the L_2 isotope effect as well is small and positive. The straw man derived from cycloadditions[10,11] is thus eliminated.

If reaction 1 is elementary, the isotope effect in intramolecular competition for Ic must, on the basis of the

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[5] W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961).

[6] S. H. Schroeter and C. M. Orlando, Jr., *J. Org. Chem.*, **34**, 1181 (1969).

[7] (a) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Amer. Chem. Soc.*, **80**, 2326 (1958); (b) see J. E. Baldwin and J. A. Kapecki (*ibid.*, **91**, 3106 (1969)) for additional references to inverse isotope effects in addition to olefins.

[8] G. S. Hammond, *ibid.*, **77**, 334 (1955).

[9] R. A. Caldwell and G. W. Sovocool, *ibid.*, **90**, 7138 (1968).

[10] See Baldwin and Kapecki, ref 7b.

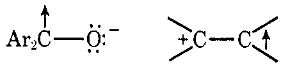
[11] E. Koerner von Gustorf, D. V. White, J. Leitich, and D. Henneberg, *Tetrahedron Lett.*, 3113 (1969).

[12] It is known[4] that the oxetanes from benzophenone and trimethylethylene are formed efficiently ($\phi = 0.45$) and in the ratio of 9:1, favoring the isomer derived from the tertiary biradical. Steric considerations suggest that this is likely to be a minimum ratio for the two biradicals, and that replacing one of the methyl groups by ethyl should make the ratio of IIe to IIf even higher.

results above, be essentially nil. In fact, $k(\mathrm{IIIc})/k(\mathrm{IIId}) = 1.10 \pm 0.01$, indicating a healthy preference for deuterium going next to oxygen, and ruling out the possibility that step 1 is an elementary reaction. The only obvious interpretation consistent with all the isotope effects is that the intermolecular competitions reflect some (irreversible) step k_1 and that the intramolecular competition reflects another step, k_x. The results for the intramolecular competition are readily interpreted on the basis of the preferential collapse of X to IIc over IId, expected on the basis of hybridization arguments[3] as long as L_1 and L_2 are chemically identical in X.

The substituent effects reported in Table I show that the rate of quenching diaryl ketone triplets by *cis*-2-butene increases markedly as electron attracting groups are introduced, even though the triplet energy decreases in this direction. Arnold[4] has observed that the competition between energy transfer and oxetane formation with acetophenones and norbornene is extremely sensitive to ring substituent; the present results suggest that much of this sensitivity may reside in the oxetane-forming reaction.

If the substituent effects reflect the nature of intermediate X, they suggest that it involves significant electron transfer from olefin to ketone. However, Yang[13,14] and Wagner[15] have provided examples of ketone hydrogen-abstraction reactions in which substituent effects similar to these operate, and have concluded that the effects are due to interactions of $\pi-\pi^*$ levels with the $n-\pi^*$ level in the triplet; those triplets which are "purer $n-\pi^*$" react faster. While such an explanation would account for our observations, the available spectroscopic evidence (phosphorescence excitation spectra[14,16] and phosphorescence lifetimes[14]) suggests only rather slight $\pi-\pi^*$ contributions to these diaryl ketone triplets. We accordingly prefer to consider that our substituent effects support the intermediacy of an electron-transfer complex. Electron transfer has for some time been implicated in the quenching of excited states by amines,[17] and more recently by hydrocarbons as well.[18]


X

Further work on the development of model systems for isotope effects on electron-transfer reactions is planned, as well as other experiments to test the proposed intermediate.

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(13) N. C. Yang and R. L. Dusenbery, *J. Amer. Chem. Soc.*, **90**, 5899 (1968).

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Acknowledgment. Support of this work by the donors of the Petroleum Research Fund (Grant No. 3031-A4), administered by the American Chemical Society, is gratefully acknowledged.

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Discovery of a σ Radical in X-Irradiated Malonic Acid

Sir:

We wish to report the discovery by esr of a new σ-radical species in the well-studied system of X-irradiated malonic acid.[1] The existence and structure of a relatively small number of carbon-based σ radicals such as CO_2^-,[2] formyl,[3] phenyl,[4] and acetyl[5] have generated considerable interest in recent years. However, only the former two have been studied as oriented molecules in a single crystal.[2,3d] We have determined carbon-13 and proton hyperfine tensors as well as the g tensor for the oriented σ radical trapped in the malonic acid crystal, and we show that it can be characterized as a monosubstituted acetyl radical, $RCH_2\dot{C}{=}O$ (R = $-COOH$).

Freshly X-irradiated malonic acid has two distinct characteristics: (1) the radiation-induced pink coloration of the crystal disappears within hours; (2) the relaxation time T_{1e} increases dramatically in about the same period.[6] These facts, together with the observation of a more intense pink color from perdeuterated malonic acid, stimulated us to search for unusual features in the spectrum of the deuterated crystal.

An esr spectrum of a malonic acid-d_4 crystal irradiated for 15 min is shown in Figure 1. The previously known $R\dot{C}D_2$ radical[1b,d] gives rise to the five-line pattern marked A at the low-field side of the central spectrum and is the parent of a set of carbon-13 satellites marked B. The single line marked σ is from the new radical and is the parent of two sets of carbon-13 satellites, marked σ(I) and σ(II) in the figure. These four lines have the same g tensor and decay at the same rate as σ.

Diagonalized tensors are (500, 384, 373 MHz) for the ^{13}C(I) hyperfine, (172, 133, 132 MHz) for the

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