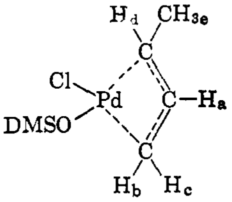
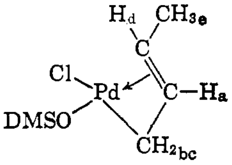
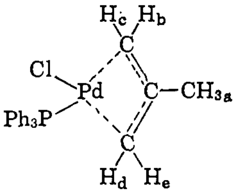
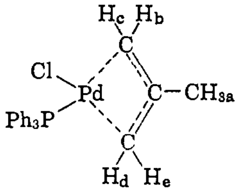
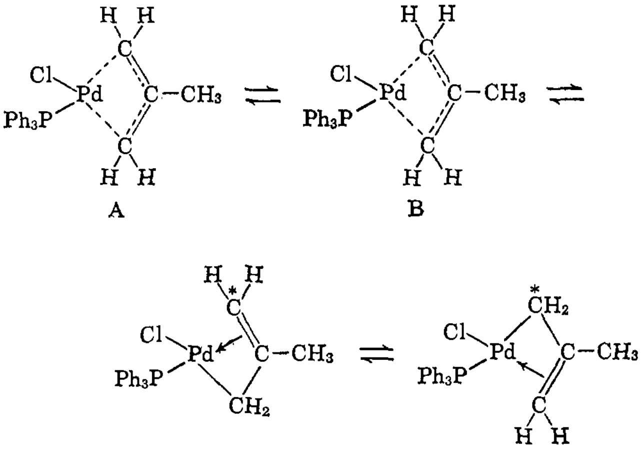
Table I. Nmr Parameters of the Allylic Complexes of Palladium

Predicted structure	Temp, °C	Chemical shifts τ values					Coupling constants, cps
	−20°	a 4.42	b 6.90	c 5.90	d 5.90	e 8.45	J_{ab} = 12.5 J_{ac} = 7.0 J_{ad} = 12.5 J_{dc} = 7.0
	80°	a 4.60	bc 7.24		d 6.01	e 8.63	J_{abe} = 10.0 J_{ad} = 11.0 J_{de} = 7.0
	−20°	a 8.05	b 5.48	c 6.41	d 7.21	e 7.15	J_{be} = 3.0 J_{bP} = 6.0 J_{cP} = 10.0
	60°	a 8.07	be 6.28	cd 6.81			

tons split either by coupling to the phosphorus or by restricted rotation.[1] Comparison of the 60- and 100-Mc/sec spectra shows that the separation between the two components is dependent on field strength which rules out phosphorus coupling. Detailed analysis of the spectrum indicates that the components do not correspond to an AB quartet which rules out the latter postulate. Furthermore, the downfield component centered at τ 7.15 shows an interaction of approximately 3 cps with the proton at τ 5.48. A tentative assignment of the four resonances can be made on the basis of the preferential coupling of phosphorus with protons in the *trans* position[3] and the preferential coupling of protons in a planar zig-zag arrangement.[4,5] The complex is thus in the π-allylic form at room temperature. As the temperature is increased to 60°, the four resonances converge into two. The positions of these new resonances (half-way between b and e, and half-way between c and d) seem to indicate that the π-allylic species A, which has four nonequivalent protons, converts into a second π-allylic species B for which the *cis* protons (b and e) are equivalent and the *trans* protons (c and d) are equivalent. As the temperature is further increased, these resonances first broaden, as illustrated in Figure 2, and then converge into a broad singlet at 140°. The latter spectrum was obtained using *o*-dichlorobenzene as a solvent. The equilibration may be depicted as



The temperature dependence of the nmr spectrum of the triphenylarsine adduct yielded similar results, and a complete study on a number of allylic complexes of palladium will be reported in the near future.

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A Convenient Synthesis of the Cubane System

Sir:

Although cyclobutadiene *per se* is unavailable for purposes of organic synthesis because of its extreme chemical instability, nonetheless initial experiments

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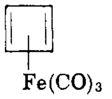
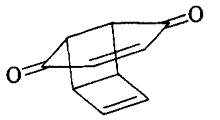
[3] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1625 (1964).
[4] S. Sternhill, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).
[5] M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964).

indicate that the organometallic complex cyclobutadieneiron tricarbonyl[1] (I) seems to afford a useful source of the hydrocarbon. During the course of the oxidative decomposition of I with ceric ion in the presence of dienophiles a molecule of cyclobutadiene can be transferred from the iron atom to the dienophile. For example, when conducted in the presence of various acetylenes the oxidative decomposition of I gives rise to several derivatives of Dewar benzene.[2,3] As a further demonstration of the general utility of this reaction we now wish to report a convenient synthesis of the cubane system,[4,5] in which the cyclobutadiene transfer reaction plays a key role.



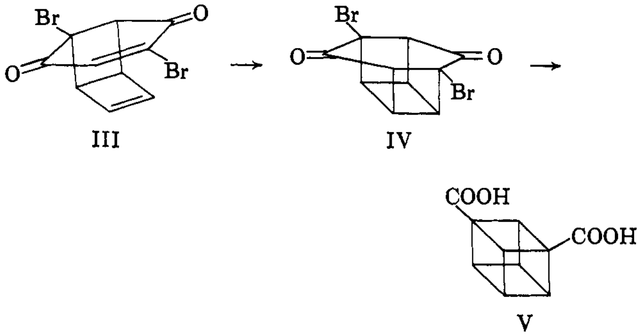
I



II

During initial experiments it was observed that cyclobutadieneiron tricarbonyl, when decomposed in the presence of *p*-benzoquinone, afforded the adduct II. The *endo* configuration of the adduct II, which was anticipated from earlier studies,[6] was confirmed through ozonolysis of II to *cis,cis,cis*-1,2,3,4-cyclobutanetetracarboxylic acid.

Decomposition of I in the presence of 2,5-dibromobenzoquinone yielded the Diels–Alder adduct III, 80%; yellow needles from petroleum ether, mp 127–128°; $\lambda_{\max}^{\mathrm{CH_3OH}}$ 275 mμ (log ϵ 4.0). The nmr spectrum of III displayed absorptions at τ 2.53 (singlet, area 1), 3.75 (complex multiplet, area 2), and 5.97 (broad complex multiplet, area 3). The *endo* configuration of III is indicated by analogy with II and by its subsequent behavior upon irradiation.



Irradiation of III in benzene with a mercury lamp afforded the colorless isomer IV, 80%; from methanol the material crystallized as white prisms, mp 152–154°, containing one molecule of solvent; $\lambda_{\max}^{\mathrm{CH_3OH}}$ 210 mμ (log ϵ 3.4). The nmr spectrum of IV consists of a series of complex bands in the region τ 6.18–6.78; no olefinic protons are evident in particular.

Treatment of IV with aqueous KOH at 100° affords cubane 1,3-dicarboxylic acid (V),[7] 80%; white needles from pentane, mp 171° dec. *Anal.* Calcd for $C_{10}H_8O_4$: C, 62.50; H, 4.20. Found: C, 62.49; H, 4.45.[8] The nmr spectrum in $CDCl_3$ displays a broad absorption at τ 2.4 (area 2) and a complex band between τ 5.30 and 6.10 (area 6). The dimethyl ester (white needles, mp 66–68°) shows in the nmr spectrum a sharp peak at τ 6.30 (area 1) and again a complex absorption in the region τ 5.38–6.15 (area 1).

Convincing proof of the structure of V is established through its decarboxylation to cubane *via* thermal degradation of the di-*t*-butyl perester.[9] The hydrocarbon obtained in this manner displayed a sharp singlet in the nmr spectrum at τ 6.0 and three principal absorptions in the infrared spectrum at 3000, 1231, and 850 cm^{-1}; these properties are identical with those of cubane reported by Eaton and Cole.[5]

Acknowledgments. We thank the National Science Foundation, the U. S. Army Research Office (Durham), and the Robert A. Welch Foundation for financial assistance. We also thank General Aniline and Film Corporation and Badische Anilin und Soda Fabrik for generous gifts of iron carbonyl and cyclooctatetraene, respectively.

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(2) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965).

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(4) P. E. Eaton and T. W. Cole, Jr., *J. Am. Chem. Soc.*, **86**, 962 (1964).

(5) P. E. Eaton and T. W. Cole, Jr., *ibid.*, **86**, 3157 (1964).

(6) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **88**, 623 (1966).

(7) The 1,3 relationship of the carboxylic acid functions has not been proven through mechanistic considerations strongly suggest this orientation.[4]

(8) Satisfactory elemental analyses were obtained on all other compounds described in this paper.

(9) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Am. Chem. Soc.*, **83**, 3998 (1961).

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The Photolysis of Ketene–Olefin Mixtures

Sir:

Two recent communications[1,2] concerning the reactions of methylene with butene-2 suggest that this preliminary report of a detailed investigation of the photochemistry of ketene, at present being undertaken in this laboratory, may be of immediate interest.

It has been shown that the primary dissociative yield is unity when ketene is irradiated with light of 2700-A wavelength and is not diminished by addition of oxygen.[3] At 3650-A dissociation is pressure and temperature dependent, an apparent activation energy for the dissociation being 4 kcal mole^{-1}.[4] Photolysis with the shorter wavelength produces methylene almost exclusively in the singlet state, while at 3650 A more than half the methylene produced is in the triplet state.

The *cis–trans* isomerization of butene-2 has been used in this laboratory to elucidate the intramolecular processes occurring during irradiation of a number of organic photosensitizers, *e.g.*, benzene,[5–7] pyridine,[5] and acetone.[8] In the present study, mixtures of ketene and *cis* butene-2 in the gas phase were photolyzed

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(2) B. S. Rabinovitch, K. W. Watkins, and D. F. Ring, *ibid.*, **87**, 4960 (1965).

(3) A. N. Strachan and W. A. Noyes, *ibid.*, **76**, 3258 (1954).

(4) W. A. Noyes and I. Unger, "Organic Photochemistry," IUPAC, Butterworths, London, 1965.

(5) R. B. Cundall, F. J. Fletcher, and D. G. Milne, *Trans. Faraday Soc.*, **60**, 1146 (1964).

(6) R. B. Cundall and P. A. Griffiths, *ibid.*, **61**, 1968 (1965).

(7) R. B. Cundall and A. S. Davies, *ibid.*, in press.

(8) R. B. Cundall and A. S. Davies, *Proc. Roy. Soc.* (London), in press.