indicate that the organometallic complex cyclobutadiene-iron 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
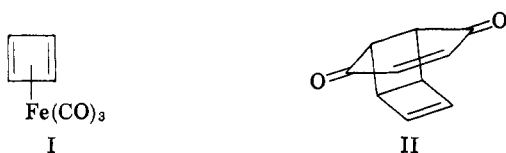
During initial experiments it was observed that cyclobutadieneiron tricarbonyl, when decomposed in the presence of p-benzoquinone, afforded the adduct II. The endo configuration of the adduct II, which was anticipated from earlier studies,[6] was confirmed through ozonolysis of II to cis,cis,cis-1,2,3,4-cyclobutanetetracarboxylic 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°; $\lambda_{max}^{CH_3OH}$ 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.

III   IV

V
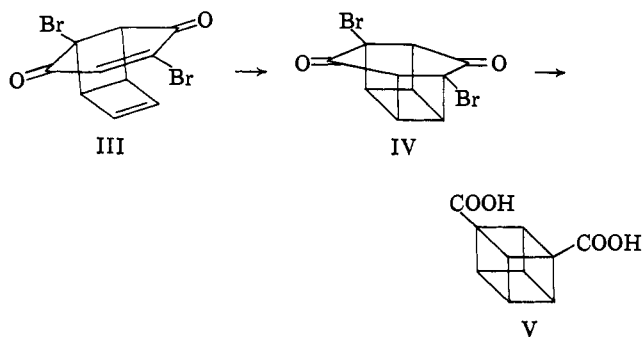
Irradiation of III in benzene with a mercury lamp afforded the colorless isomer IV, 80%; from methanol the material crystallized as white prisms, mp 152–154°, containing one molecule of solvent; $\lambda_{max}^{CH_3OH}$ 210 mμ (log ϵ 3.4). The nmr spectrum of IV consists of a series of complex bands 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]

(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).

James C. Barborak, L. Watts, R. Pettit
Department of Chemistry, University of Texas
Austin, Texas 78712
Received February 9, 1966

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

(1) G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965).
(2) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965).
(3) G. F. Burt and R. Pettit, *Chem. Commun.* (London), 517 (1965).
(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]

(1) S. Ho, I. Unger, and W. A. Noyes, *J. Am. Chem. Soc.*, **87**, 2297 (1965).
(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.
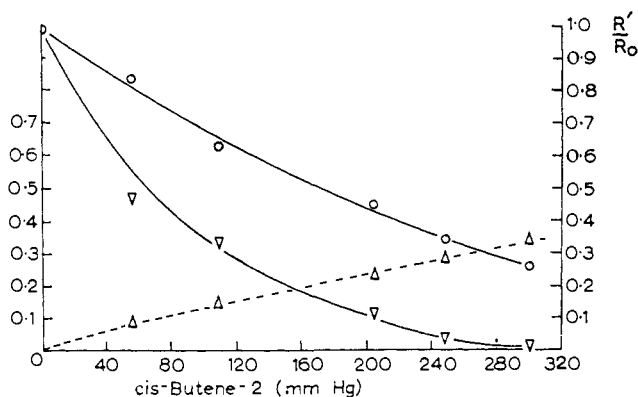(8) R. B. Cundall and A. S. Davies, *Proc. Roy. Soc.* (London), in press.

Figure 1. Dependency of rates of product formation on *cis*-butene-2 pressure at 46°. The left-hand ordinate presents the quantum yield of *trans*-butene-2 production (△). The right-hand ordinate shows the ratio of rate of production of ethylene (▽) and of carbon monoxide (◯) in the presence (R') and absence (R_0) of *cis*-butene-2.

in a cylindrical quartz cell (100 ml) with filtered light from a high-pressure mercury arc providing a beam having a spectral half-band width of 100 A centered upon the 3130-A line. Light intensities were monitored photoelectrically, and absorbed intensities of 10^{-12} einstein ml^{-1} sec^{-1} were employed. The temperature was constant at 46° and the duration of each experiment was 4 hr. The effect of varying pressure of *cis*-butene-2, in the presence of 30 mm of ketene, upon the rates of production of carbon monoxide and ethylene and quantum yield of *trans*-butene-2 is shown in Figure 1.

The reduction in the rate of formation of carbon monoxide is compatible with a direct quenching of an excited state of ketene which would dissociate in the absence of butene-2. Ethylene production diminishes more rapidly and is approaching zero while the yield of carbon monoxide is still finite though decreasing. This behavior is ascribed to the dual effect of the *cis*-butene-2 in quenching the excited ketene molecule and in removing CH_2, yielding products which have been characterized elsewhere.[9] Examination of the yields of addition products at varying *cis*-butene-2 pressures has shown that they pass through a maximum at intermediate butene-2 concentrations. This observation may be interpreted here in terms of the dual mechanism mentioned above.

A consequence of the quenching of excited ketene molecules by olefins will be a temporal effect in the photolysis of ketene alone; *i.e.*, as ethylene concentration increases during irradiation, the rate of decomposition should fall. Of greater importance, in the light of recent work in this field, is the effect of added olefin in quenching excited triplet-state ketene. This alters the distribution of methylene between its singlet and triplet states, which arise out of necessity from the appropriate ketene states by the spin conservation rule, from that which would obtain in the absence of the olefin. Conclusions concerning the behavior of the excited states of the parent ketene molecule, drawn from a study of the distribution of $^3CH_2$ and $^1CH_2$ addition products with added olefin, must be regarded as tenta-

tive unless account has been taken of the triplet-quenching properties of the added gas.

The isomerization of *cis*-butene-2 measured in this investigation may arise from an energy-transfer reaction involving triplet-state ketene molecules or from attack by singlet or triplet methylene upon the olefin. Data, at present available, favor the former mechanism as the major reaction path to isomerization. Thus, the decline in production of ethylene is accompanied by a steady increase in isomerization, while yields of addition products of methylene with *cis*-butene-2 pass through a maximum and are decreasing at higher pressures of added olefin. A further examination of the pressure dependencies of each of these processes will enable the course of isomerization to be characterized, while detailed study of the relative yields of addition produces will elucidate the rate of singlet and triplet methylene in a manner analogous to that described by Rabinovitch, *et al.* In view of the observation that the long wave limit of the ketene absorption spectrum lies at about 4100 A, it may be concluded that the energy possessed by the first excited triplet state will be less than 70 kcal $mole^{-1}$, in which event the efficiency of energy transfer to yield butene-2 triplet (70–72 kcal $mole^{-1}$) will be dependent upon vibrational energy possessed by the ketene triplet (*e.g.*, see ref 8).

R. B. Cundall, A. S. Davies
Department of Chemistry, The University
Nottingham, England

Photoreduction of a β,γ-Unsaturated Ketone[1]

Sir:

Although the excited state corresponding to the ~300-mμ transition of certain β,γ-unsaturated ketones probably involves, in addition to the normal $\pi^* \leftarrow n$ transition, a contribution from a $\pi^* \leftarrow \pi$ type transition of the extended chromophore,[2] the only chemical effect attributed to this interaction of ethylenic and carbonyl linkages in the excited state is the light-induced geometrical isomerization of *trans*-4-hexen-2-one.[3] We now present the second example of such an interaction.

Irradiation of ketone 2 (λ_{max}^{EtOH} 307 mμ (ε 101)) in methylene chloride solution with a mercury arc (Corex filter) provides the saturated ketone 3 (λ_{max}^{EtOH} 300 mμ (ε 22)) in 30–35% yield[4] along with 1,1,2,2-tetrachloroethane, τ 4.08 ppm. When 0.028 M 2 in methylene chloride containing 0.25 M norbornene was irradiated, the rate of formation of 3 over 70% reaction was the same as when no added olefin was present. This result

(1) We are grateful to the Petroleum Research Fund administered by the American Chemical Society for support of this research.

(2) A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962); R. C. Cookson and S. MacKenzie, *Proc. Chem. Soc.*, 423 (1961), and references cited there.

(3) H. Morrison, *Tetrahedron Letters*, 3653 (1964); *J. Am. Chem. Soc.*, **87**, 932 (1965).

(4) The concentration of 3 reaches this maximum value at ~70% reaction. The photochemistry of 3 will be discussed separately.

(9) *E.g.*, see ref 2; also H. M. Frey, *J. Am. Chem. Soc.*, **82**, 5947 (1960); J. W. Simons and B. S. Rabinovitch, *J. Phys. Chem.*, **68**, 1322 (1964).