evaporation, the residue was washed thoroughly with water. These aqueous extracts contained monoester, m.p. 137–139°, and dibasic acid, m.p. 235–240°. The water insoluble portion was recrystallized from methanol–water (4:1) to furnish 3.81 g. (55%) of **3,4-bis[(ethylthio)methyl]thiophene-2,5-dicarboxylic acid dimethyl ester**, m.p. 79.5–80.5°; n.m.r. spectrum (CHCl₃): singlets at τ 5.67 and 6.10, triplet at τ 8.62, 8.75, and 8.88, and quadruplet at τ 7.28, 7.40, 7.52, and 7.63, area ratio 2:3:3:2; ultraviolet spectrum: $\lambda_{max}^{95\% \ EtOH}$ 218, 277 mμ (ϵ 22,000, 17,000).

Anal. Calcd. for $C_{14}H_{20}O_4S_3$ (mol. wt. 348.51): C, 48.25; H, 5.78; S, 27.61. Found: C, 47.8, 48.1; H, 5.9, 5.8; S, 27.3, 27.3.

After hydrolysis to the decarboxylic acid, m.p. 235–240°, the decarboxylation was carried out by heating 6.50 g. (0.0203 mole) of the diacid with 2 g. of copper powder in 50 ml. of quinoline. Carbon dioxide evolution commenced at 220°. Removal of the quinoline (from the distillate) with hydrochloric acid and distillation furnished 2.30 g. of VIII as a straw-colored liquid, b.p. 182–183° (15 mm.), n^{20}D 1.5840. 3,4-Bis[(ethylthio)methyl]-thiophene (VIII) was obtained as a colorless liquid, n^{20}D 1.5823, after passage over alumina; n.m.r. spectrum: singlets at τ 6.26 and 3.02, triplet at τ 8.68, 8.80, and 8.92, and quadruplet at τ 7.44, 7.55, 7.70, and 7.80; area ratio 2:1:3:2 (in CCl₄);

ultraviolet spectrum: $\lambda_{max}^{95\% \ EtOH}$ 246 mμ (ϵ 5,600); infrared spectrum: strongest absorption 801 cm.$^{-1}$ (neat).

Anal. Calcd. for $C_{10}H_{16}S_3$ (mol. wt. 232.44): C, 51.67; H, 6.94; S, 41.39. Found: C, 52.2; H, 6.9; S, 40.9.

A mercurichloride derivative, m.p. 111–112° (70% ethanol), was prepared in 90% yield.

1H,3H-Thieno[3,4-c]thiophene-4,6-dicarboxylic Acid Dimethyl Ester 2,2-Dioxide (VI).—A solution containing 2.58 g. (0.01 mole) of Vd in 30 ml. of glacial acetic acid was heated with 3.06 ml. (0.03 mole) of a 30% hydrogen peroxide solution. The solution was refluxed for 30 min., causing disappearance of the pink color. Upon addition of water to the reaction mixture VI precipitated. Recrystallization of the solid (1.5 g., 55% yield) from benzene–petroleum ether (4:1) furnished the sulfone (VI) as colorless crystals, m.p. 199–200°; n.m.r. spectrum (CHCl₃): singlets at τ 5.52 and 6.08, area ratio 2:3.

Anal. Calcd. for $C_{10}H_{10}O_6S_2$ (mol. wt. 290.31): S, 22.09. Found: S, 21.7.

Pyrolysis of VI at 350° in a sublimation apparatus using copper powder or over a heated coil (500°)[13] furnished as the only identifiable product 3,4-dimethylthiophene-2,5-dicarboxylic acid dimethyl ester (infrared spectrum identical with that of IIIc, undepressed mixture melting point).

Mechanisms of Photochemical Reactions in Solution.
XXIV.[1] Photochemical and Catalytic Decomposition of Diazoacetophenone

DWAINE O. COWAN, MATTHEW M. COUCH,[2] KARL R. KOPECKY, AND GEORGE S. HAMMOND[3]

Contribution No. 3076 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California

Diazoacetophenone has been decomposed under a variety of conditions. The sensitized and direct photochemical decomposition both appear to produce the triplet ketocarbene which adds to *cis*- and *trans*-2-butene in a nonstereospecific manner. The ketocarbene is relatively unreactive and exhibits radical properties as characterized by the large amounts of bicyclohexenyl and acetophenone produced in the direct and sensitized photolysis of diazoacetophenone in cyclohexene. Phenacyl chloride was formed in addition to the expected cyclopropanes when metal chlorides were used to catalyze the reaction of diazoacetophenone with olefins.

When diazomethane is photochemically decomposed in solutions the resulting methylene reacts in a stereospecific manner with olefins[4,5] and gives indiscriminate insertion to hydrocarbons.[6,7] These properties are consistent with assigning the singlet state to methylene produced under these conditions. The singlet–triplet decay of methylene has not yet been observed in solution because of the extreme reactivity of methylene, but this decay has been postulated for the gas phase photolysis of diazomethane to explain both spectroscopic[8] and chemical results.[9] The only manner in which triplet methylene has been prepared in solution is by the photosensitized decomposition of diazomethane.[7] In this process, benzophenone is selectively excited to a singlet state, whereupon intersystem crossing takes place to produce excited triplet benzophenone with the nearly unit efficiency. The triplet benzophenone can then transfer its energy (with conservation of spin angular momentum) to ground singlet diazomethane mole-

cules to generate diazomethane in the excited triplet state. The triplet diazomethane then decomposes to give methylene which reacts as predicted for triplet methylene.

The synthetic importance of the photochemical decomposition of substituted diazomethanes (diazo ketones) has been recently emphasized by Meinwald's synthesis of D-norsteroids[10] and the reinvestigation of the photolysis of diazocamphor.[11]

The photochemical decomposition of diazo ketones is intriguing because of the possibility that the triplet ketomethylene could be produced upon direct irradiation. The result is predicted as a consequence of the high rates of intersystem crossing by carbonyl compounds in general.

Results and Discussion

The photolysis of diazoacetophenone in solution gave only traces of the dilactone (m.p. 268–270°) which Wiberg[12] obtained from the photolysis of solid diazoacetophenone. This is reasonable since the postulated mechanism for the formation involves the bimolecular reaction of either diazoacetophenone or the corresponding ketomethylene with phenylketene. The principal products from the direct and sensitized photolysis of diazoacetophenone in cyclohexene were 3,3'-bicyclohexenyl, acetophenone (70% yield), and 7-norcaryl

(1) Part XXIII: G. S. Hammond, P. Wyatt, C. DeBoer, and N. J. Turro, *J. Am. Chem. Soc.*, **86**, 2532 (1964).

(2) National Science Foundation Undergraduate Research Participant, 1962.

(3) To whom inquiries should be addressed.

(4) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

(5) R. C. Woodworth and P. S. Skell, *ibid.*, **81**, 3383 (1959).

(6) W. v. E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *ibid.*, **78**, 3224 (1956).

(7) K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *ibid.*, **84**, 1015 (1962).

(8) G. Hertzberg and I. Shoosmith, *Nature*, **183**, 1801 (1959).

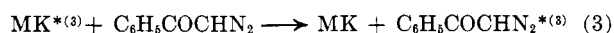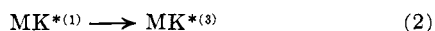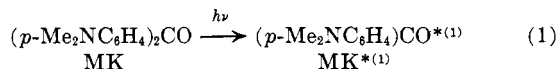(9) H. M. Frey, *J. Am. Chem. Soc.*, **82**, 5947 (1960).

(10) J. Meinwald, G. G. Curtis, and P. G. Gassman, *ibid.*, **84**, 116 (1962).

(11) J. Meinwald, A. Lewis, and P. G. Gassman, *ibid.*, **84**, 977 (1962).

(12) K. B. Wiberg and T. W. Hutton, *ibid.*, **76**, 5367 (1954).

phenyl ketone (10–12%). The high yields of acetophenone and bicyclohexenyl suggest that the ketomethylene is highly reactive in hydrogen abstraction.

Because of the relatively large extinction coefficient of Michler's ketone at 3660 Å., it was possible to activate selectively Michler's ketone (MK) in the presence of diazoacetophenone using light filtered to isolate the 3660-Å. line from a mercury arc. Under these conditions, the triplet ketomethylene should be formed.

$$(p\text{-}Me_2NC_6H_4)_2CO \xrightarrow{h\nu} (p\text{-}Me_2NC_6H_4)CO^{*(1)} \quad (1)$$
$$\text{MK} \qquad\qquad\qquad\qquad \text{MK}^{*(1)}$$

$$\text{MK}^{*(1)} \longrightarrow \text{MK}^{*(3)} \quad (2)$$

$$\text{MK}^{*(3)} + C_6H_5COCHN_2 \longrightarrow \text{MK} + C_6H_5COCHN_2^{*(3)} \quad (3)$$

$$C_6H_5COCHN_2^{*(3)} \longrightarrow C_6H_5COCH{:}(\downarrow\downarrow) + N_2 \quad (4)$$

The process involving transfer of energy from Michler's ketone in the excited singlet state to ground state diazoacetophenone is endoenergetic and, as such, should not compete with intersystem crossing of Michler's ketone from the singlet to triplet state.

Since both the sensitized and direct photolysis in cyclohexene give the same product distribution (see Table I), this again implicates the triplet state in the direct photolysis.

TABLE I

YIELD OF 7-NORCARYL PHENYL KETONE FROM THE REACTION OF
DIAZOACETOPHENONE AND CYCLOHEXENE

Catalyst	Yield, %	$t_{1/2}$	Temp., °C.
Cu_2Cl_2	29	5 min.	28
$Cu_2Cl_2{}^a$	22	6 min.	28
$CuCl_2$	44	85 min.	28
CuO	55	3 + hr.	60
$CuSO_4$	62 (50)	3 + hr.	28
$Cu(DPM)_2{}^b$	19		28 then 60
$Ni(CP)_2{}^c$	5	3 hr.	28
$Ni(CO)_4$	Trace		28
$AgNO_3$	Trace		28
Direct irradiation	10–12^e		28
Photosensitized^d	12^e		28

^{a} Equimolar amounts of Cu_2Cl_2 and diazoacetophenone. ^{b} DPM is dipivaloylmethide. ^{c} CP is cyclopentadiene. ^{d} Michler's ketone was the sensitizer. ^{e} These reactions also produced >70% acetophenone.

The reaction of ketomethylenes produced by direct and sensitized photolysis of diazoacetophenone with cis- and trans-2-butene in isooctane have also been studied. Both methods of photolysis produced low yields of the expected cyclopropanes in a nonstereo

$$(5)$$
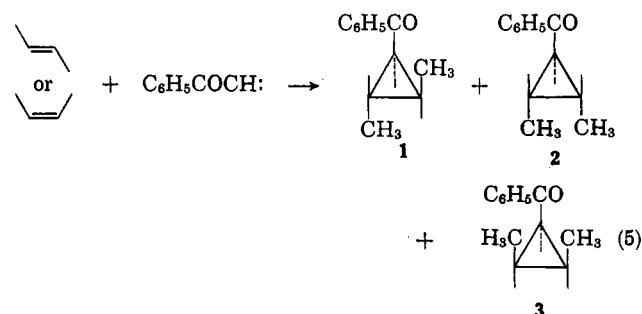
specific manner. The low yield of cyclopropanes in this case could result from the competition with reaction 6, rearrangement of the ketomethylene to the corre

$$(6)$$

$$C_6H_5\overset{O}{\overset{\|}{C}}{-}CH{:} + RH \longrightarrow R{\cdot} + C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}CH_2 \quad (7)$$
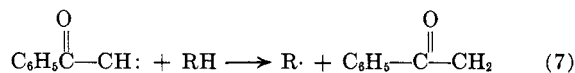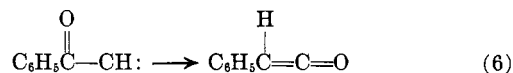
sponding ketene, and reaction 7, radical reaction with either the solvent or olefin molecules.

Doering[18] and Griffin[14] have shown that cyclopropanes can isomerize under the influence of light; to reduce this isomerization as much as possible, the irradiations were carried out for relatively short periods of time. Experimentally it was found that, under our conditions, a very small amount of isomerization does take place during the period of irradiation.

Since the isomer distribution is similar for the sensitized and direct photolysis of diazoacetophenone in a solution with cis- or trans-2-butene, the triplet ketomethylene must be produced by both methods. The triplet ketomethylene apparently adds to the double bond of olefins to produce a short-lived biradical in which the electrons are unpaired. Since cis- and trans-2-butene do not give exactly the same product mixture, the rate of internal rotation is not much larger than the rate of spin inversion. Thus when starting out with cis-2 butene, more 2 is produced than when starting with trans-2 butene (see Table II). Identical product distribution from the reaction of cis- and trans-2-butenes and triplet methylene was not obtained either.[7]

TABLE II

RELATIVE YIELDS OF CYCLOPROPANES FROM PHOTOLYSIS
OF DIAZOACETOPHENONE IN THE PRESENCE OF cis- AND
trans-2-BUTENE

Alkene	Method of photolysis	Relative per cent^a		
		1^b	2	3
cis	Direct	50	40	10
cis	Sensitized	55	35	10
trans	Direct	73	15	12
trans	Sensitized	74	17	9

^{a} The total yield of cyclopropanes varied from 8–12%. ^{b} On long irradiation the relative amount of 1 increased slightly.

Although the results strongly implicate the triplet ketomethylene as the principal reactive intermediate in both reactions, we have no good grounds for specification of a path for its formation in the direct irradiations. Intersystem crossing could occur either before or after decomposition of the diazo compound. Since no phosphorescence of diazoacetophenone could be detected when the compound was irradiated in a hydrocarbon glass at 77° K., we infer that the lifetime of the triplet diazoketone must be very short if it is formed at all.

Ziffer and Sharpless[15] have correlated Horner's[16] data for substituent effects on the quantum yields for photolysis of substituted diazoacetophenones with the Hammett constants of the substituents. The correlation, although rough, is probably statistically significant, but we are unable to understand the author's

(13) W. v. E. Doering and M. Jones, Jr., *Tetrahedron Letters*, 791 (1963).
(14) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *J. Am. Chem. Soc.*, **85**, 1001 (1963).
(15) H. Ziffer and N. E. Sharpless, *J. Org. Chem.*, **27**, 1944 (1962).
(16) W. Kirmse and L. Horner. *Ann.*, **625**, 34 (1959).

rationalization of the results.[17] As we look at the data, which show that maximum quantum yields are actually measured for the parent compound and for two *ortho*-substituted derivatives, it seems that we could provide a rationalization based upon effects of substituents on the efficiency of intersystem crossing. The lowest excited states of these molecules probably have mixed n,π* and π,π* character, and it might be expected that the members of the series of which the triplets have the most nearly "pure" n,π* character would undergo intersystem crossing most efficiently. This prediction follows from both empirical experience and from the fact that the singlet–triplet separation is ordinarily small in n,π* states. Introduction of various substituents which increase conjugative interaction between the aryl moieties and the carbonyl group might well increase the coupling of n,π* and π,π* states with consequent increase in the singlet–triplet splitting and decrease in the efficiency of intersystem crossing. This view is consistent with the fact that an improvement of the correlation by the Hammett equation was obtained when log $\Phi\epsilon$, rather than log Φ, was plotted against σ. The fact that quantum yields tend to be lowest for those compounds that have the largest extinction coefficients for the first allowed transitions makes sense since the high extinction coefficients may reflect considerable mixing of excited states. This explanation (which makes correlation with the Hammett parameters seem almost incidental) does not account perfectly for all the data, and is certainly not persuasive mechanistic evidence. Analysis of the problem is highly complicated by the fact that the fate of the excited molecules is probably determined only after they have decayed from initially formed excited states to lower lying states for which direct excitation is rather highly forbidden.

The mechanism of catalytic decomposition of diazoacetophenone in the presence of metal salts must be different from the photolytic processes. As is shown by the data in Table I, catalytic decomposition in the presence of cyclohexene leads to formation of norcaryl phenyl ketone, usually in much larger yield than was obtained by either direct or sensitized photolysis. Products expected from hydrogen abstraction from the alkene were not found. Catalytic decomposition in the presence of the butenes also led to higher yields (30–45%) of cyclopropanes than were obtained in the photochemical experiments. Furthermore, as is shown in Table III, the relative amounts of **1**, **2**, and **3** were also quite different. Reaction with *trans*-2-butene gives only **1** in a reaction that is entirely stereospecific. Compounds **2** and **3**, which would be expected from stereospecific addition to *cis*-2-butene, are the predominant products when the latter alkene is the substrate, although some **1** was also produced in all experiments. Phenacyl chloride is also produced in reactions in which cuprous chloride was used as the catalyst.

(17) The authors seem, on the one hand, to imply that the existence of a correlation implies that loss of nitrogen is determined by competitive actions of the triplet diazo compound; *i.e.*, that intersystem crossing occurs with constant efficiency. On the other hand, the sign of ρ is discussed as though it were determined by the migratory aptitudes of the aryl groups *in the ketocarbene*. The latter effects should have little relevance to the quantum yields for nitrogen evolution unless loss of nitrogen and rearrangement to a ketene are a single, concerted process. Such a mechanism is obviously not applicable, at least under our reaction conditions, since rearranged products are not obtained in significant yield.

TABLE III
RELATIVE YIELDS OF PRODUCTS FROM THE CATALYZED REACTIONS OF DIAZOACETOPHENONE WITH *cis*- AND *trans*-2-BUTENES

Reaction catalyst	Olefin	Solvent	Relative yields,[a] %		
			1	2	3
Cu_2Cl_2	*cis*	Isooctane	21	54	25[b]
Cu_2Cl_2	*cis*	None	22	57	22[b]
Cu_2Cl_2	*cis*	Isooctane	25	58	17[b]
$CuSO_4$	*cis*	Isooctane	28	67	5
$CuSO_4$	*trans*	Isooctane	100		

[a] The total yield of cyclopropane compounds varied from 30–45%. [b] Component **3** was an unsymmetrical v.p.c. peak, not resolved on any of the columns tried.

The relatively high stereospecificity of catalyzed addition to the 2-butenes might be indicative of the involvement of the singlet ketocarbene. We regard such an explanation as being unattractive, largely because the reagent involved seems to be more selective than the triplet carbene believed to be the active agent in photolysis. It is most probable that the attacking reagent is an organometallic compound such as C_6H_5-COCHCu or $C_6H_5COCHCuCl_2$. The latter species would be a logical precursor of phenacyl chloride and would be structurally analogous to the species Zn-CH_2I_2 formed by the reaction of diazomethane with zinc iodide.[18] The fact that the catalytic reactions with *cis*-2-butene are not entirely stereospecific may indicate that the catalyzed reactions proceed by some mixture of mechanisms.

Experimental

Catalyzed Diazoacetophenone–Cyclohexene Reactions.—All of the metal-catalyzed diazoacetophenone–cyclohexene reactions listed in Table I were carried out in the same manner. The diazoacetophenone used in these reactions was prepared by the method of Newman and Bell.[19] Diazoacetophenone (0.5 g.) was dissolved in 25 ml. of distilled cyclohexene in a 50-ml., one-necked round-bottomed flask connected to a mercury-filled buret. The metal catalyst (50 mg.) was added, and the resulting suspension was stirred magnetically until the reaction was finished. The solution was thermostated in a water bath at 28 ± 1°. Reaction mixtures were analyzed by vapor phase chromatography (v.p.c.) using a diethylene glycol succinate (DEGS) column and an internal standard.

The high boiling component of the copper sulfate catalyzed reactions was isolated by distillation and also by v.p.c. on a DEGS column. The properties of this material agree with those that Mousseron[20] reported for 7-norcaryl phenyl ketone, b.p. 140° at less than 1 mm., reported 145° at 1 mm.; λ_{max}^{EtOH} 244 mμ (log ε 4.5), reported 244 mμ (log ε 4.2); 2,4-dinitrophenyl-hydrazone, m.p. 200.5–202.5°, $\lambda_{max}^{CHCl_3}$ 383 (log ε 4.37), reported m.p. 195–196, $\lambda_{max}^{CHCl_3}$ 383 (log ε 4.42).

Anal. of the 2,4-dinitrophenylhydrazone. Calcd. for $C_{19}H_{19}$-O_4N_4: 14.75. Found: N, 14.80.

The only other product isolated from the metal chloride catalyzed reactions was phenacyl chloride. This material had n.m.r., ultraviolet, and infrared spectra identical with those for authentic phenacyl chloride. The starting diazoacetophenone was tested (v.p.c.) for phenacyl chloride and none was observed; phenacyl chloride was not found in the reactions catalyzed by copper sulfate.

Direct Irradiation in Cyclohexene.—The direct photolysis reactions were carried out in an immersion reactor[7] with a 2900-Å. cut-off filter sleeve. The light source was a 200-w. Hanovia mercury vapor lamp Type S, No. 654A. In a typical experiment, diazoacetophenone (0.5 g.) dissolved in 75 ml. of purified cyclohexene was charged into this reactor and irradiated until

(18) G. Wittig and K. Schwarzenbach, *Ann.*, **650**, 1 (1961).
(19) M. S. Newman and P. Bell, *J. Am. Chem. Soc.*, **71**, 1056 (1949).
(20) M. Mousseron, *Compt. rend.*, **243**, 1880 (1956).

the theoretical amount of nitrogen had been produced, about 2.5 hr. The reaction solution was concentrated by fractional distillation through a short column packed with Pyrex helices to a volume of 25 ml. The products were identified by comparison of v.p.c. retention times on a DEGS column, using known compounds as standards, and by infrared spectrometric analysis of fractions trapped at the proper time from the effluent of the chromatograph. In two determinations an internal standard was added to the irradiated solution before concentration so that the absolute amount of each component could be calculated.

The major products were 7-norcaryl phenyl ketone (10–12%), acetophenone (65–75%), and a considerable amount of 3,3'-bicyclohexenyl. Norcaryl phenyl ketone was isolated by preparative vapor chromatography and identified by comparison of its physical constants with those reported in the literature.[20] The n.m.r. spectrum showed, in addition to the signals expected from the benzoyl group, intense, broad signals at τ 9.0 and ~8.45, and a less intense signal at 7.75. Although the spectra showed, by weak signals in the vinyl proton region, the presence of small amounts of impurities, the integrals of the three high-field signals were approximately in the ratio 2:8:1. Consequently the high-field resonance is attributed to the two protons at the junction of the six- and three-membered rings, and the signal at 7.75 is attributed to the proton attached to the cyclopropane carbon atom which also bears the benzoyl group. The signal at ~8.45 is obviously due to eight methylene protons.

The 3,3'-bicyclohexenyl was isolated by preparative vapor chromatography and compared directly with an authentic sample prepared by reaction of 3-bromocyclohexene with magnesium in ether, b.p. 132–134° at 30 mm., n^{25}D 1.5083.[21]

Catalytic Decomposition of Diazoacetophenone in the Presence of 2-Butenes.—The isomeric 2-butenes were obtained from Phillips Petroleum Company. The specified purities, cis >99 mole % purity and trans 99.47 mole % purity, were confirmed by v.p.c. analysis using a silver nitrate column and a flame ionization detector.

A solution of 20 g. of either cis- or trans-2-butene, 0.5 g. of diazoacetophenone, and 50 mg. of the copper salt was prepared in a 150-ml., three-necked round-bottomed flask fitted with a Dry Ice condenser protected from the atmosphere by a calcium chloride tube. The reaction mixtures were stirred for 24 hr. keeping the temperature of the solution below 0°. Most of the butene was then distilled from the reaction mixture by replacing the Dry Ice condenser with a column packed with helices and warming the solution to 30°. The relative yields of the high-boiling compounds reported in Table III were obtained from a vapor phase chromatogram of a sample from the reaction mixtures. The total yield of components 1, 2, and 3 varied from 15 to 40%. Several minor, low boiling components were noted by using temperature-programmed vapor phase chromatography but these were not further identified.

The reaction solution from an experiment carried out as described above with cis-2-butene using copper sulfate as the catalyst was combined with that from an experiment using 2 g. of diazoacetophenone, 50 g. of cis-2-butene, and the same catalyst. The mixture was concentrated by fractional distillation through a column packed with Pyrex helices to a volume of about 15 ml. The compounds 1, 2, and 3 were isolated by vapor phase chromatography using a column of 10% Ucon Polar on C-22 firebrick. The properties of the major component of the mixture from reaction with cis-2-butene (the second compound off the Ucon Polar column) are consistent with assigning the substance structure 2. The n.m.r. spectrum exhibits signals at τ 2.3 and 2.75 (multiplets), at 8.05 (triplet, $J = 4$ c.p.s.), at 8.5 (multiplet), and 8.82 (doublet). If the integrated area of the aromatic

protons is assigned a weight of 5, then the other signals represent correspondingly 1, 2, and 6 protons. The ultraviolet spectrum (ethanol) is similar to that for the 7-norcaryl phenyl ketone with absorption maxima at 244 mμ (log ϵ 4.06), 280 (2.8) and a shoulder at 315 (2.1). The infrared spectrum exhibits significant bands at 5.95 and 9.75 μ. The n.m.r. spectrum, especially the coupling constant for the triplet at 8.05, and the retention time on a Ucon Polar column strongly support the structure assignment of 2 and not 3 or 1. Component 1 (first off the Ucon Polar column) is identical with the only compound isolated from the copper salt catalyzed reaction of trans-2-butene and diazoacetophenone (retention time, ultraviolet, and n.m.r. spectra) and is therefore assigned structure 1 (vide infra). Inasmuch as component 3 was formed in about 1% yield, not enough of this compound was isolated for a complete analysis. It is suggested that this compound could be the all-cis-substituted cyclopropane 3 since it has an ultraviolet spectrum similar to the other cyclopropanes [244 mμ (log ϵ ≈4), 280 (≈3), and a shoulder at 315 (≈2)] but has a slightly longer retention time on a Unicon Polar column.

It should be noted that phenacyl chloride was formed in about fourfold higher yield in reactions carried out in the presence of cis-2-butene than in reactions in the presence of cyclohexene.

Compound 1 was isolated from the reaction of both cis- and trans-2-butene with diazoacetophenone in the presence of copper sulfate. In the reaction of cis-2-butene, the compound was a minor product (20%), while with trans-2-butene it was the only cyclopropane formed. This is consistent with assignment of the stereochemistry of 1 inasmuch as diazomethane, copper sulfate, and an olefin are known[7] to give a cyclopropane which retains the stereochemistry of the olefin. The ultraviolet and infrared spectra of 1 were very similar to those of 2. The ultraviolet spectrum (ethanol) had absorption maxima at 244 mμ (log ϵ 4.1), at 280 (3.0), and a shoulder at 315 (≈2). The infrared again showed the bands due to carbonyl and cyclopropane ring absorption. The n.m.r. and infrared spectra indicated that the compound had undergone some partial rearrangement or decomposition in the isolation process since, besides the bands assignable to the cyclopropane compound, others were found in the olefinic region. Thus the integral of the n.m.r. signal for this sample could not be interpreted in terms of one simple compound but only in terms of compound 1 and an olefin with the same molecular weight.

Direct and Sensitized Photolysis of Diazoacetophenone in the Presence of cis- or trans-2-Butene.—The irradiations were carried out in an immersion reactor with a uranium glass filter (cut-off, 3300 Å.) for the sensitized reactions and with a pyrex filter (cut-off, 2900 Å.) for the direct photolysis reactions. The reactor was cooled in a bath at 0° and ice–water was circulated through the cooling jacket of the reactor during the experiment.

A solution containing 0.5 g. of diazoacetophenone, 28 g. of trans-2-butene, 10 ml. of anhydrous ether, and 75 ml. of isooctane was saturated with Michler's ketone. The resulting solution was diluted with 10 ml. of isooctane and charged into the reactor. This solution was then irradiated until the theoretical amount of nitrogen had been produced, about 3 hr. The solution was concentrated by fractional distillation to a volume of about 20 ml. and the reaction mixture was analyzed by vapor phase chromatography. The three components listed in Table II had the same v.p.c. retention times on a Ucon Polar column as the three products isolated from the copper catalyzed reactions. They also had the same ultraviolet absorption bands. These three components were formed in from 8 to 12% yields along with a host of other products, such as acetophenone and about ten others. The relative yields of the three cyclopropanes under different experimental conditions are listed in Table II.

(21) A. Berlande, Bull. soc. chim. France, 9, 641 (1942).