

Characterization of 5,6-*cis*-Diphenylbicyclo[3.1.0]hexan-2-one (IXb).—Photoketone IXb recrystallized to constant m.p. 116.5–117.5°, from 95% ethanol. Prominent peaks in the infrared are located at 3.31, 3.39, 5.80 (s), 6.24, 6.70, 6.91, 7.10, 7.74, 8.10, 8.55, 9.31, 9.75, 11.21, 11.90, and 14.38 μ . The ultraviolet (EtOH) spectra shows strong end absorption (ϵ at 215 $m\mu$, 17,010; at 220 $m\mu$, 15,100; at 230 $m\mu$, 10,810).

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.10; H, 6.45. Found: C, 86.89; H, 6.40.

A 2,4-dinitrophenylhydrazone was obtained; m.p. 119–119.5° (orange needles from chloroform–hexane); λ_{max}^{EtOH} 370 $m\mu$ (ϵ 26,470), 226 $m\mu$ (ϵ 14,230), and end absorption.

Degradation of 5,6-*cis*-Diphenylbicyclo[3.1.0]hexan-2-one (IXb).—The procedure used for the oxidation of photoketone IXa was employed. In a typical run 233 mg. of photoketone IXb (0.943 mmole) was dissolved in 100 ml. of dioxane and treated with a cold mixture of 4.6 g. (81 mmoles) of potassium hydroxide and 1.3 ml. (4.0 g., 26 mmoles) of bromine in 30 ml. of water, first for 3 hr. at room temperature and then for 8.5 hr. at reflux. The usual work-up gave 59 mg. of nonacidic material and 190 mg. of acidic material. Acid IXb crystallized to a constant melting point of 200–210° from methanol–water. Prominent peaks in the infrared spectrum (KBr pellet) are located at 2.95, 3.30, 3.42, 3.72, 5.90 (s), 6.22, 6.71, 6.87, 6.98 (s), 7.73, 7.85, 8.21 (s), 9.32, 9.81 (s), 13.03 (s), and 14.3 (s) μ . The n.m.r. spectrum in acetone- d_6 with TMS as an internal standard is recorded in Table II.

Ester XIIb was prepared using diazomethane as described above for the stereoisomer. A series of oxidations in which 2.24 g. (9.05 mmoles) of photoketone from liquid–liquid partition chromatography was used and in which nonacidic material was recycled through the oxidation procedure yielded 2.195 g. of acidic material. This was converted with diazomethane to an oil weighing 1.808 g. This material was placed on a 3 \times 94 cm. silica gel column slurry-packed in 5% ether in hexane. The ester was eluted in eight 250-ml. fractions of 20% ether–hexane, after elution with 500 ml. of hexane, 500 ml. of 1% ether–hexane, 500 ml. of 2% ether–hexane, 1000 ml. of 5% ether–hexane, 2500 ml. of 10% ether–hexane, 2000 ml. of 15% ether–hexane, and 250 ml. of 20% ether–hexane. The eight fractions weighed 771 mg. representing a 26% yield of XIIb base on photoketone IXb. A portion of this material was recrystallized four times from methanol to a constant melting point of 112–113°. Prominent peaks in the infrared spectrum are located at 3.30, 3.37, 5.80 (s), 6.24, 6.70, 6.95, 7.40, 7.68, 8.56 (s), 9.30, 9.77, and 14.38 μ .

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.07; H, 6.17. Found: C, 73.85, 74.03; H, 6.23, 6.12.

Ring Opening of XIIb.^{4b}—A solution of 585 mg. of XIIb (1.815 mmoles) and sodium methoxide from 46 mg. of sodium (2.00

g.-atoms) in 10 ml. of dry methanol was stirred under nitrogen at reflux temperature for 4 hr., then for 9.5 hr. at room temperature. From the work-up were obtained 133 mg. of acidic material and 447 mg. of nonacidic material. The acidic portion was treated in ether with an excess of diazomethane to yield an oil weighing 188 mg. This material was combined with the nonacidic product and chromatographed on a 25 mm. \times 1 m. column packed with 234 g. of a mixture of Celatom (400 g.) and stationary phase (161 g.). The eluate was scanned at 260 $m\mu$ and collected in 20-ml. fractions. The optical density trace showed four major peaks plus two minor ones.

Fractions 22–25 were dissolved in methanol and seeded with a small crystal of dimethyl 3,4-diphenyl-3-hexenedioate. The oily crystals that were deposited were recrystallized from methanol to yield 28 mg., m.p. 110–115°. Several recrystallizations gave white prisms, m.p. 114–116°, whose infrared spectrum was identical with that of authentic dimethyl 3,4-diphenyl-3-hexenedioate and with no mixture m.p. depression. In the original filtrate more crystals were deposited; weight 60 mg., m.p. 112–113°. One recrystallization gave white prisms, m.p. 112.5–113°, whose infrared spectrum was identical with that of an authentic sample of ester XIIb.

The infrared spectrum of fractions 26–29 was almost identical with that of the dimethyl 3,4-diphenyl-2-hexenedioate obtained earlier. This oil was subjected to long tube molecular distillation. The n.m.r. of the distillate was identical with that of the earlier samples of this compound with the exception of the earlier-noted minor impurity peaks.

Photolysis of 5,6-*trans*-Diphenylbicyclo[3.1.0]hexan-2-one (IXa).

—Using the same procedure and apparatus as described above, 2.07 g. of photoketone IXa in 500 ml. of 95% ethanol was photolyzed through a Pyrex filter under nitrogen for 48 hr. The crude reaction product was dissolved in 3 ml. of upper phase and chromatographed on a liquid–liquid column 130 \times 3.5 cm. dry-packed with 865 g. of a mixture of 700 g. of Celatom and 280 g. of lower phase. The eluate was scanned at 254 $m\mu$ and collected in 40-ml. fractions. The optical density trace showed seven imperfectly defined peaks. There was isolated 512 mg. of photoketone IXa and 578 mg. of photoketone IXb from fractions 38–45 and 46–51, respectively.

Photolysis of 5,6-*cis*-Diphenylbicyclo[3.1.0]hexan-2-one (IXb).

—In a manner similar to the above, 247 mg. of photoketone IXb in 65 ml. of 95% ethanol was photolyzed for 49 hr. The product was separated into its components by chromatography on a column 100 \times 2.5 cm. packed with 200 g. of a mixture of 300 g. of Celatom and 120 g. of lower phase. The eluate was scanned at 260 $m\mu$ and collected in 20-ml. fractions. The optical density trace showed seven peaks. Fractions 21–24 gave 27 mg. of photoketone IXa and 25–28 gave 32 mg. of photoketone XIb.

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Carbenoid Formation of Arylcyclopropanes from Olefins, Benzal Bromides, and Organolithium Compounds and from Photolysis of Aryldiazomethanes^{1,2}

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A number of arylcyclopropanes have been prepared by the reaction of benzal bromide with alkylolithium in the presence of olefins. The same cyclopropanes have also been isolated from the photolysis of the corresponding arylidiazomethanes in olefins. Aryl substituents investigated include *p*-methyl, *p*-methoxy, *p*-chloro, and *m*-chloro. Olefins used as substrates were 1-butene, isobutene, *cis*- and *trans*-2-butene, and 2-methyl-2-butene. The configurations of the adducts have been determined by n.m.r. Relative rates of olefin additions have been measured. The data have been interpreted in terms of addition to the olefin of (a) a free carbene in the case of the photolysis of the diazoalkanes and (b) the α -bromolithium compounds as the only intermediate in the reaction involving the organolithium compound.

The most common reactions associated with divalent carbon intermediates are insertion into saturated carbon–hetero bonds and addition to unsaturated centers.⁵

(1) Supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

(2) Part of this work was reported in preliminary form: G. L. Closs, R. Moss, and J. J. Coyle, *J. Am. Chem. Soc.*, **84**, 4985 (1962).

(3) A. P. Sloan Foundation Fellow, 1962–1966.

(4) National Science Foundation Predoctoral Cooperative Fellow, 1961–1963.

The latter reaction, in particular the addition to olefins yielding cyclopropanes, has been demonstrated to be of great preparative value. Although cyclopropane formation is conveniently formulated as the addition of a free carbene to a double bond, it is by no means neces-

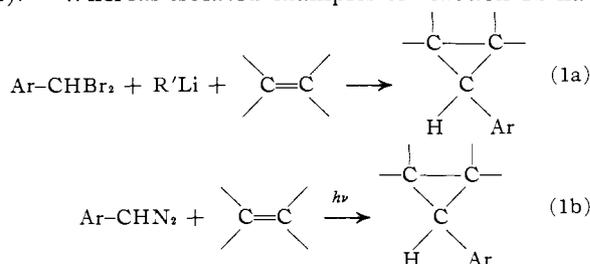
(5) For reviews on the chemistry of divalent carbon see: W. Kirmse, *Angew. Chem.*, **73**, 161 (1961); P. Miginiac, *Bull. soc. chim. France*, 2000 (1962); J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964.

sary to invoke such a mechanism in *all* cases. For example, definite proof exists that the photolysis of certain diazoalkanes produces true divalent carbon species.⁶ However, much less is known about the actual intermediates in reactions of organo alkali metal compounds with certain alkyl halides, although such reactions may also produce cyclopropanes when carried out in the presence of olefins.⁷ Perhaps the best known example of cyclopropane synthesis from olefins in which a free carbene is definitely not involved is the Simmons-Smith reaction.⁸ It is therefore unjustified to use cyclopropane formation as the sole diagnostic test for the intermediacy of divalent carbon species.

It was the aim of the present investigation to learn more about the nature of the intermediates in cyclopropane formation from olefins, suitable alkyl halides, and organolithium compounds, by comparing results from these reactions with those obtained *via* photolysis of the corresponding diazoalkanes. By evaluating substituent effects, relative rate data, solvent effects, and stereochemical observations it was hoped to gain a better understanding of the mechanisms and, in particular, to learn whether or not free carbenes are involved in both reactions types.

Results

Synthesis of Arylcyclopropanes.—The reactions chosen for comparison are outlined in (1a) and (1b). Whereas isolated examples of reaction 1b have



previously been reported,⁹ the use of benzal bromides for the preparation of arylcyclopropanes has not been described.¹⁰ However, this reaction can be considered analogous to the reported synthesis of halocyclopropanes from polyhalomethanes, organolithium compounds, and olefins.^{7b}

The desired benzal bromides I-V were readily available from the corresponding aldehydes on reaction with either anhydrous hydrogen bromide (I and II) or with phosphorus pentabromide (III and IV). These methods failed for the preparation of *p*-methoxybenzal bromide (V), which was finally prepared from the low temperature reaction of *p*-methoxyphenyldiazomethane and bromine.

Reaction of the benzal bromides with alkyllithium compounds, at -10° in the presence of olefins, gave the

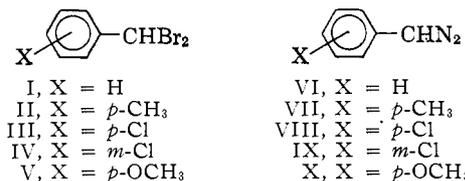
(6) (a) G. Herzberg, *Proc. Roy. Soc. (London)*, **A262**, 291 (1961); (b) R. W. Brandon, G. L. Closs, and C. A. Hutchinson, Jr., *J. Chem. Phys.*, **37**, 1878 (1962); (c) R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. Y. Yager, *J. Am. Chem. Soc.*, **84**, 3212 (1962); (d) A. M. Trozzolo, R. W. Murray, and E. Wasserman, *ibid.*, **84**, 4990 (1962).

(7) Cf. (a) G. L. Closs and L. E. Closs, *ibid.*, **81**, 4996 (1959); **82**, 5723 (1960); (b) W. T. Miller, Jr., and C. S. Y. Kim, *ibid.*, **81**, 5008 (1959); (c) L. Friedman and J. G. Berger, *ibid.*, **82**, 5758 (1960).

(8) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

(9) C. D. Gutsche, G. L. Bachman, and R. S. Coffey, *Tetrahedron*, **18**, 617 (1962).

(10) The reaction of benzal chloride with organolithium compounds is known to take a different course. Proton abstraction proceeds faster than halogen-metal interchange, leading to the formation of phenylchlorocarbene; R. A. Moss, *J. Org. Chem.*, **27**, 2683 (1962); cf. G. L. Closs and L. E. Closs, *Tetrahedron Letters*, **24**, 26 (1960).



expected arylcyclopropanes in yields ranging from fair to good. Cyclopropanes were prepared from I-V and 1-butene, *cis*- and *trans*-2-butene, isobutene, and 2-methyl-2-butene, respectively. Alkyllithium reagents used were methyllithium in ether and butyllithium or amyllithium in pentane. The cyclopropanes were separated from the side products, mainly the corresponding stilbenes, by distillation and were purified by vapor phase chromatography (v.p.c.).

The aryldiazomethanes VI-IX were prepared from the tosylhydrazones of the corresponding aldehydes by base-induced decomposition following essentially the procedure outlined by Bamford and Stevens.¹¹ The *p*-methoxy derivative X was prepared from the hydrazone *via* mercuric oxide oxidation. Photolyses of the diazo compounds were carried out in solutions of the same olefins used in reaction 1a. The resulting arylcyclopropanes were isolated in modest yields by v.p.c. and were found to be identical in all properties with the compounds produced from the corresponding reactions following scheme 1a. The main side products in the photolysis were the benzalazines. Small amounts of phenyl-substituted olefins were also found, probably arising from the insertion of arylmethylene into the carbon-hydrogen bonds of the olefins. These products were not investigated in any detail, because an excellent study of the insertion reaction of phenylmethylene has been published by Gutsche and collaborators.⁹ It should be pointed out that reaction 1a using methyllithium in ether was found to be much superior to 1b as a preparative method for the synthesis of arylcyclopropanes because yields were generally higher and products easier to purify.

The identities of the arylcyclopropanes from reactions 1a and 1b were established by elemental analysis, and infrared and nuclear magnetic resonance (n.m.r.) spectroscopy. In line with expectations, two epimeric cyclopropanes were obtained from each of the addition reactions to 1-butene, *cis*-2-butene, and 2-methyl-2-butene, corresponding to the two possible modes of addition to these olefins. The isomers were separated by v.p.c. and individually identified.

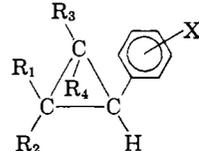
While the infrared spectra of the products gave only limited evidence for the proposed structures and were found useful only for demonstrating the absence of double bonds,¹² the structural information available from the n.m.r. spectra was considerable and merits detailed presentation.

N.m.r. Spectra of Arylcyclopropanes and Assignment of Configurations.—In general, all compounds prepared and listed in Table I gave n.m.r. spectra fully in accord with the proposed structures. Signals originating from cyclopropyl ring hydrogens were separated into two groups. In all compounds the signals arising

(11) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

(12) The "cyclopropane absorption" was found in all compounds but the frequency varied somewhat as a function of the aryl substituent. Limiting values were 1000-1043 cm^{-1} . In view of the fact that aromatic compounds often exhibit bands in this region, the diagnostic value of this band must be considered very dubious.

TABLE I
CHEMICAL SHIFTS OF METHYL PROTONS IN
ARYLCYCLOPROPANES^a



Starting olefin	R _i	Phenyl substituent (X)				
		H	<i>p</i> -CH ₃	<i>p</i> -Cl	<i>m</i> -Cl	<i>p</i> -OCH ₃
Isobutene	R ₁ = R ₂ CH ₃	9.23	9.22	9.23	9.18	9.23
	R ₃ = R ₄ = H	8.80	8.80	8.82	8.87	8.82
<i>trans</i> -2-Butene	R ₁ = R ₄ = CH ₃	9.22	9.24	9.22	9.18	9.22
	R ₂ = R ₃ = H	8.85	8.88	8.83	8.83	8.87
<i>cis</i> -2-Butene	R ₁ = R ₃ = CH ₃	9.05	9.07	9.05	9.03	9.07
	R ₂ = R ₄ = H					
	R ₁ = R ₃ = H	8.87	8.88	8.85	8.85	8.87
1-Butene	R ₂ = R ₄ = H					
	R ₁ = C ₂ H ₅	9.13	9.12	9.12	9.13	9.12
	R ₂ = R ₃ = R ₄ = H	8.98	9.00	8.98	8.98	9.00
2-Methyl-2-butene	R ₁ = R ₃ = R ₄					
	R ₁ = R ₂ = R ₃ =	9.10 ^b	9.12 ^b	9.12 ^b		
	CH ₃ , R = H	8.78	8.82	8.78		
	R ₁ = R ₂ = R ₄ =	9.23	9.25	9.22		
	CH ₃ , R ₃ = H	8.83 ^b	8.85 ^b	8.82 ^b		

^a Measured in carbon tetrachloride solution, with tetramethylsilane as internal reference; numbers are in τ -units.

^b Signal intensity corresponds to two methyl groups.

from the benzylic protons were found at lower field, while resonances of the remaining ring protons overlapped partially with the signals from the methyl protons. The chemical shifts of the methyl protons were of particular interest because of their usefulness in assigning configurations to the stereoisomers.

Figure 1 shows a schematic presentation of 1-phenyl-2,2-dimethylcyclopropane. In the conformation depicted, in which the phenyl plane is normal to the plane defined by C-1, C-2, and the *cis*-methyl carbon, the *cis*-methyl protons are located inside the shielded (+) region, while the *trans*-methyl group is somewhat deshielded (-).¹³ Upon rotation of the phenyl group through 360° the *cis* protons will pass through the shielded area twice, while the *trans* protons will remain deshielded in any conformation. The conformation in Fig. 1 can be expected to be the most stable because nonbonded interactions between the phenyl and methyl groups are at a minimum. Deriving cylindrical coordinates from vector projections based on normal bond angles and bond lengths,¹⁴ and using benzene anisotropy values tabulated by Johnson and Bovey,¹⁶ the differences between the magnetic field strengths experienced by the two methyl groups were calculated. The results indicated that the *trans*-methyl protons should be deshielded by the anisotropy of the phenyl ring by 0.15 p.p.m. while the *cis*-methyl protons should show an increased shielding of 0.37 p.p.m. owing to the same effect.¹⁷ The observed

(13) For an introductory discussion of the relationship of chemical shifts and anisotropy of neighboring phenyl groups, see L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, pp. 112-130.

(14) Because experimental data are not available for arylcyclopropanes, the following parameters were assumed for calculations: bond lengths: C₁-C₂, 1.51 Å.; C₁-Ph, 1.49 Å.; C₂-CH₃, 1.51 Å.; bond angles: C₁-C₂-CH₃ = C₂-C₁-Ph = 118°; CH₃-C-CH₃, 114°. These values were taken from closely analogous systems where experimental data were available.¹⁵ It was also shown that small variations in both bond angles and bond lengths have only very small influence on the calculated values.

(15) O. Bastiansen and M. Traetteberg, *Tetrahedron*, **17**, 147 (1962).

(16) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

chemical shift difference of 0.43 p.p.m. (Table I) is in good agreement with the 0.52 p.p.m. thus calculated. Particularly, the fact that the high-field methyl resonance is found at 0.28 p.p.m. higher field than the methyl signal in 1,1-dimethylcyclopropane (8.95 τ) indicates that the conformation depicted in Fig. 1 contributes heavily to the conformational equilibrium.¹⁸ Once it was established that the *cis*-methyl groups in arylcyclopropanes experience increased shielding, it was possible to use this phenomenon to assign configurations to the epimeric pairs of arylcyclopropanes produced from 1-butene, *cis*-2-butene, and 2-methyl-2-butene. To distinguish molecular configurations from intergroup relationships, we will refer through the remainder of this paper to the configurations with the largest number of alkyl groups *cis* to the aryl substituent as the *syn* configuration while giving the opposite configuration the prefix *anti*. As shown in Table I, the methyl proton resonances of the epimeric adducts of I-V to *cis*-2-butene differ by 0.2 p.p.m. On the basis of the arguments presented above, those compounds with the stronger shielded methyl protons must be assigned the *syn* configuration. The somewhat smaller difference in shielding between the methyl groups in *syn* and *anti* epimers compared to the *cis*- and *trans*-methyl groups of 1-phenyl-2,2-dimethylcyclopropane is to be expected if the reasonable assumption is made that the most stable conformation of the *syn* compounds is the one in which the molecules have a plane of symmetry bisecting both the phenyl and cyclopropane rings. In this conformation the *cis*-methyl groups will be somewhat outside the maximum diamagnetic zone. The assignments of configurations to the isomers resulting from additions to 2-methyl-2-butene and to 1-butene were made on the basis of identical considerations. In the latter the chemical shift differences of the methyl protons in the spectra of the epimers are further reduced because of their larger distance from the phenyl ring.

The more conventional method of assigning configurations to cyclopropane derivatives, by analysis of the spin-spin couplings,¹⁹ was not generally applicable to the compounds considered here. Overlap of the chemical shifts of the methyl protons with those of the vicinal cyclopropyl ring hydrogens prevented determination of the spin-coupling constants. Although the benzylic ring proton signals were visible, highly complex and poorly resolved splitting patterns resulted from virtual coupling²⁰ between the methyl and ring protons in the spectra of most compounds. Only for a few cases could the magnitude of the vicinal coupling constants be estimated. Thus, the adducts of I-III to

(17) These calculations assume a conformation of the *cis*-methyl protons in which two hydrogens are equidistant from the phenyl plane while the third is farthest removed from it. This conformation appeared to us the most likely one because not only is the methyl group staggered with respect to adjacent bonds, but also the nonbonded interactions between phenyl and methyl are at a minimum. Averaging over-all methyl conformation yields the somewhat larger value of 0.44 p.p.m. The value for the deshielding of the *trans*-methyl group is almost independent of the methyl conformation assumed.

(18) It should be pointed out that the conformation in Fig. 1 yields the maximum shielding of the *cis*-methyl protons. Rotation of the phenyl group through 90° will result in a substantial deshielding of the same protons. Consequently, the observation that 76% of the calculated shielding is actually observed corresponds to a significantly higher proportion of molecules in this preferred conformation.

(19) H. M. Hutton and T. Schaefer, *Can. J. Chem.*, **40**, 875 (1962); J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962).

(20) J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

TABLE III
RELATIVE RATES OF ARYLCYCLOPROPANE FORMATION FROM BENZYL BROMIDES, ALKYL LITHIUM, AND OLEFINS AT -10°
IN HYDROCARBON MEDIUM^a

Olefin	Addition mode	Phenyl substituent				
		<i>m</i> -Cl	<i>p</i> -Cl	H	<i>p</i> -CH ₃	<i>p</i> -OCH ₃
1-Butene	<i>syn</i>	0.92 (0.94)	1.1 (0.97)	1.1 (1.1)	1.3 (1.2)	0.95 (0.83)
	<i>anti</i>	0.36 (0.37)	0.52 (0.46)	0.53 (0.51)	0.50 (0.47)	0.31 (0.28)
<i>cis</i> -2-Butene	<i>syn</i>	2.8 (3.0)	2.6 (2.5)	2.2 (2.2)	2.7 (2.5)	2.4 (2.5)
	<i>anti</i>	0.76 (0.82)	0.90 (0.87)	0.91 (0.90)	0.60 (0.56)	0.29 (0.31)
<i>trans</i> -2-Butene		1.00	1.00	1.00	1.00	1.00
Isobutene		2.0	1.8	1.7	1.8	2.0
2-Methyl-2-butene	<i>syn</i>			2.0	2.2	
	<i>anti</i>			1.4	1.6	

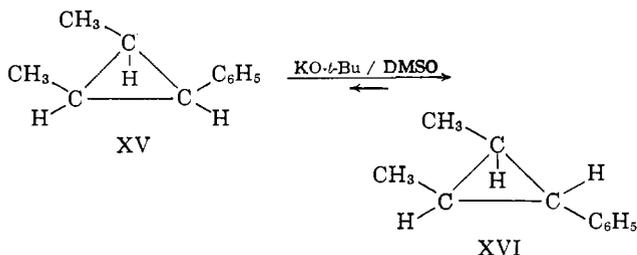
^a The numbers are derived from competitions with *trans*-2-butene. Numbers in parenthesis were determined in competitions with isobutene.

TABLE IV
RELATIVE RATES OF ARYLCYCLOPROPANE FORMATION FROM PHOTOLYSIS OF ARYLDIAZOMETHANES IN OLEFIN SOLUTIONS AT -10° ^a

Olefin	Addition mode	Phenyl substituent				
		<i>m</i> -Cl	<i>p</i> -Cl	H	<i>p</i> -CH ₃	<i>p</i> -OCH ₃
1-Butene	<i>syn</i>	0.71 (0.68)	0.60 (0.59)	0.51 (0.51)	0.48 (0.42)	0.40 (0.43)
	<i>anti</i>	0.59 (0.58)	0.54 (0.55)	.51 (0.51)	0.41 (0.36)	0.28 (0.30)
<i>cis</i> -2-Butene	<i>syn</i>	1.0 (0.95)	1.0 (1.1)	.96 (0.92)	1.1 (1.2)	1.2 (1.2)
	<i>anti</i>	0.82 (0.80)	0.89 (1.0)	.88 (0.85)	0.66 (0.69)	0.43 (0.44)
<i>trans</i> -2-Butene		1.00	1.00	1.00	1.00	1.00
Isobutene		1.2	1.1	0.91	0.83	0.77
2-Methyl-2-butene	<i>syn</i>			1.7	1.3	
	<i>anti</i>			1.6	1.1	

^a The numbers are derived from competitions with *trans*-2-butene. Numbers in parenthesis originate from competitions with isobutene.

with the data from Table II, shows that both reactions 1a and 1b are kinetically controlled, with a preference for the formation of the less stable isomer.



The question of stereospecificity of addition, as introduced by Doering and Skell,²² was examined for both reaction types. All the additions involving organolithium reagents were found to be completely stereospecific within the limit of detection. However, in agreement with the findings of Gutsche and co-workers,⁹ the photolysis of the diazo compounds in the presence of the 2-butenes produced small amounts of adducts in which the relative configuration of the methyl groups deviated from that in the starting olefins. Thus, addition to *cis*-2-butene gave 3-5% 1-aryl-*trans*-2,3-dimethylcyclopropanes, whereas the amount of non-stereospecific addition to *trans*-2-butene was considerably smaller (0.5-1%). In view of the recently reported photoisomerization of certain arylcyclopropanes,²³ it should be pointed out that checks were carried out which established that the nonstereospecific adducts were not artifacts resulting from subsequent rearrangements of the arylcyclopropanes.²⁴

Finally, the relative rates of addition to different olefins were determined for each reaction type (1a and

1b). This was accomplished in the standard manner²⁵ by allowing the reaction to proceed in the presence of large excess of two olefins present in known mole ratios, and analyzing the reaction mixtures for product ratios by v.p.c. The data thus accumulated are presented in Tables III and IV. Addition rates are listed relative to *trans*-2-butene, the rates of which are set equal to unity in each series. In those cases where two addition modes to the olefin exist, the data are broken down into relative rates of the *syn* and *anti* modes, and are normalized by a factor of two for statistical correction. Furthermore, cross-checks were carried out by double measurements in which olefins were allowed to compete with isobutene. The internal consistency of the data is satisfactory.

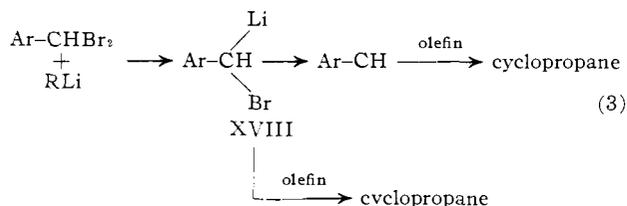
Analysis of the relative rate data shows, first of all, relatively minor variations of the rate with degree of olefin substitution in both reaction types. Furthermore, it can be seen that no great changes in discrimination result from substitution of the aryl ring in either series. Nevertheless, certain differences between the two reaction types are quite apparent, and trends within each series are noticeable. Thus the photolysis reaction (1b, Table IV) shows a relatively clear electrophilic behavior, inasmuch as the addition rate increases with increasing alkyl substitution on the olefins. Although such a trend can still be discovered for reaction 1a (Table III), it is largely obscured by the apparently equally important factor of steric addition mode. For example, the favorable *syn* addition to 1-butene proceeds faster for all phenyl substituents than the *anti* addition to *cis*-2-butene, and is comparable in rate to the addition to *trans*-2-butene. Also, no further rate increase over the *syn* addition to *cis*-2-butene is produced by the additional alkyl group in 2-methyl-2-butene. Another dissimilarity of the two reaction types is the response of the relative addition rates to

(22) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956); W. von E. Doering and P. LaFlamme, *ibid.*, **78**, 5447 (1956).

(23) W. von E. Doering and M. Jones, Jr., *Tetrahedron Letters*, 791 (1963).

(24) Because the possibility of photoisomerization had been recognized at the beginning of this work, all photolyses were carried out using photo-flood filament lamps with negligible output of ultraviolet light, thus eliminating any possibility of direct photolysis of the products.

(25) Cf. W. von E. Doering and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, **80**, 5274 (1958); P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).



Comparison of the data summarized earlier shows unambiguously that the same intermediate cannot be involved in both reaction types. Significant differences exist in stereoselectivities and stereospecificities, relative addition rates, and in the capability of forming insertion products. In general, the photolysis appears to give the more reactive intermediate. It is possible to argue that both reactions proceed through free divalent carbon compounds, but that photolysis produces a "hot" methylene with excess vibrational and translational energy, whereas (1a) yields a methylene in thermoequilibrium with its environment. We find this argument unattractive on the basis of a number of considerations. In the first place, the competition data show that a nonnegligible activation barrier exists for the addition of the methylene in the photolysis reaction. The intermediate methylene must therefore have a considerable lifetime, probably long enough to

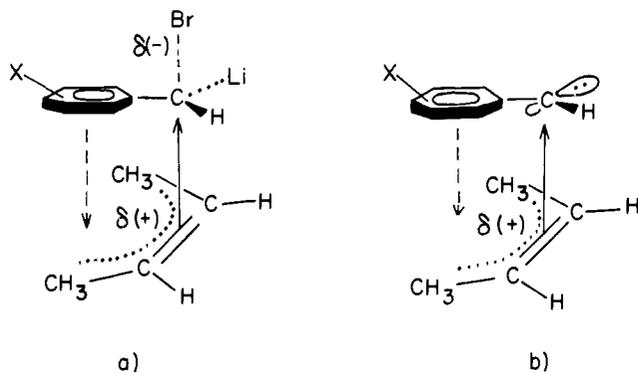


Figure 3.

allow thermoequilibrium to be established by the high collision rate obtaining in solution. Secondly, a certain portion of the methylene produced in 1b apparently lives long enough to reach the triplet state, known to be the true ground state, as evidenced by partial non-stereospecific addition. In contrast, the intermediate in (1a), although on the basis of this argument less reactive and consequently longer lived, remains completely in the singlet state. As a matter of fact, all addition reactions reported so far, involving α -eliminations on alkyl halides, have been reported to be completely stereospecific, even in those cases where the photolysis of the corresponding diazoalkane has a substantial non-stereospecific component,³⁰ and the free carbene is known to possess a triplet-ground state.³²

Fully aware of the somewhat speculative nature of the proposal, we wish to suggest that the observed differences between the two reaction types should be attributed to the intermediacy of a free carbene in the

(32) In view of these facts it does not appear permissible to draw any conclusions about the ground states of free carbenes from the observation of stereospecific addition to olefins when the hypothetical carbene has been generated *via* base-induced elimination reactions on alkyl halides. Correspondingly, arguments aiming at rationalization of relative stabilities of the two states with different multiplicities³³ are meaningless as long as they are only based on this kind of experimental observation.

(33) Cf. U. Schöllkopf and H. Kuppers, *Tetrahedron Letters*, 105 (1963).

photolysis and that of an α -halolithium compound XVIII in (1a). In this latter intermediate, both carbon-lithium and carbon-halogen bonds are expected to be strongly polarized by the mutual inductive effect of the lithium and halogen atom. Although undoubtedly both bonds are relatively weak, it is postulated that the free energy of this intermediate is lower than that of the triplet-ground state of the carbene. Consequently, no *unassisted* elimination of lithium halide occurs. The reaction of intermediate XVIII with the olefin can then be visualized as a displacement reaction in which the π -electrons of the olefins act as a nucleophile. Attack by the olefin is assumed to occur from the opposite side of the halogen atom in analogy to a normal S_N2 reaction. The transition state of the addition step can be pictured, as in Fig. 3a, to involve a nearly sp^2 -hybridized carbon atom. Collapse of this state to the cyclopropane would occur by complete breakage of the carbon-halogen and carbon-lithium bonds.

The addition of the free carbene, as generated in the photolysis reaction, should proceed through a transition state resembling Fig. 3b in analogy to previous suggestions,³ at least if a singlet state is assumed to be the reacting state.

The suggestion that a free carbene is bypassed in reactions of alkyl halides and organolithium compounds is not a new one and has been made previously by one of us and by other investigators.^{30,34} Direct and compelling evidence for this hypothesis, however, does not yet exist and, as a matter of fact, can be expected to be difficult to obtain. The reactivities of an intermediate like XVIII should closely resemble those of a free carbene. Quantitative, rather than qualitative, differences will distinguish the two intermediates.

Because of this expected similarity of chemical reactivities, and because it appears desirable to distinguish a free carbene from a somewhat less reactive species like XVIII, we propose the use of the term "carbenoid" for the description of intermediates which exhibit reactions qualitatively similar to those of carbenes without necessarily being free divalent carbon species.³⁵

The data accumulated in this study can hardly be expected to constitute compelling evidence for the sole intermediacy of a carbenoid XVIII in reaction 1a, but they are at least highly compatible with this hypothesis. Thus, the observed electrophilic addition sequence is in line with expectations for additions proceeding through either carbenoid or free carbene intermediates, because the olefin moiety experiences a certain degree of electron depletion in both transition states. Perhaps more remarkable is the difference observed for the relative addition rates to isobutene and *trans*-2-butene in the two reaction types. Reaction 1a, in analogy to other α -elimination reactions leading probably to the formation of carbenoids, shows a distinct preference for the unsymmetrically substituted olefin.³⁶ This tend-

(34) (a) G. L. Closs and J. J. Coyle, *J. Am. Chem. Soc.*, **84**, 4350 (1962); (b) G. L. Closs and L. E. Closs, *ibid.*, **85**, 99 (1963); (c) V. Franzen, *Chem. Ber.*, **95**, 1964 (1962); (d) H. Hoberg, *Ann.*, **656**, 15 (1962); (e) H. D. Hartzler, *J. Am. Chem. Soc.*, **86**, 526 (1964).

(35) The term carbenoid as an adjective was first used by L. Friedman and H. Shechter, *ibid.*, **81**, 5512 (1959), to describe the base-catalyzed decomposition of tosylhydrazones in aprotic solvents, implying the probable intermediacy of carbenes. We believe that our proposal to use "carbenoid" as a noun, as defined above, does not interfere with this previous use.

(36) H. D. Hartzler, *J. Am. Chem. Soc.*, **83**, 4997 (1961), and references cited therein.

ency has previously been interpreted in terms of an unsymmetrical transition state with the main concentration of the positive charge on the tertiary carbon atom of the olefin moiety.²⁵ Although this concept was proposed for additions of a free carbene, it can be easily adapted for a carbenoid.

The free carbene, as generated by photolysis, shows a reduced ability to distinguish between symmetrically and unsymmetrically substituted olefins. This behavior is to be expected for a more energetic species forming a transition state in which bond formation has not progressed very far. Effects of aryl substituents on the isobutene/*trans*-2-butene ratio are in agreement with our hypothesis. The observed sequence (*m*-Cl > *p*-Cl > H > *p*-CH₃ > *p*-OCH₃) for reaction 1b indicates a larger fraction of negative charge on the carbene carbon in the transition state for the addition of isobutene than for that of *trans*-2-butene addition. This is to be expected if one assumes that the conjugate positive charge is more easily accommodated on the isobutene than on the *trans*-2-butene moiety. No such regularities exist for carbenoid additions. Adopting our model which resembles that accepted for nucleophilic displacement reaction, one would not anticipate any correlation with Hammett substituent constants, since even for the much simpler case of displacements on benzylic halides such correlations are known to fail.³⁷

Perhaps the most striking result of the present study is the observation that both reaction types lead to the preferential formation of the thermodynamically less stable *syn* adduct in those cases where two addition modes exist. Admittedly the stereoselectivities are not large, particularly for the photolysis reaction. But since normal steric hindrance in the transition state would lead to the prevalence of the opposite configuration, some other effect must be operative to counteract thermodynamic product control. Among the previously reported carbene additions, several examples exist in which the stereochemistry of the adducts has been examined. Thus chlorocarbene adds to olefins with predominant formation of the *syn* product² as does phenylthiocarbene³⁵ and phenylselenocarbene,³³ whereas phenoxy carbene³⁹ prefers *anti* addition. All four carbene additions involve α -eliminations induced by alkyl-lithiums and therefore should probably be called additions of carbenoids. If chlorocarbene is generated by photolysis of chlorodiazomethane, almost all stereoselectivity is lost.⁴⁰ Carbethoxycarbene generated either by photolysis or copper-induced decomposition of ethyl diazoacetate has been reported to prefer the *anti* addition mode.⁴¹ From these data it is apparent that the configuration of the predominant product is mainly dependent on the nature of the carbene substituent, and only quantitative changes are observed with variation of the method employed to generate the carbene or carbenoid.

To account qualitatively for the observed stereochemistry, we have previously suggested³ that the charge separation in the transition state, produced by

the flow of electrons from the olefin to the carbenoid carbon, is less severe in the *syn* configuration. This argument was based on the assumption that the positive charge in the olefin moiety will be dispersed over the alkyl groups by either hyperconjugative or inductive effects; that, similarly, the corresponding negative charge may leak into the carbene substituent; and that if a transition state of the geometry as indicated in Fig. 3 is adopted, the *syn* configuration will be of lower energy. In addition to pure electrostatic attraction between the olefin and carbene substituents, it is quite likely that London dispersion forces are also operative. These should be particularly pronounced when strongly polarizable atoms such as sulfur and selenium are attached to the carbenoid atom. Finally, charge-transfer interactions between the substituents may also add to the over-all attractive forces (represented in Fig. 3 by the arrow extending from the phenyl ring toward the alkyl groups.) The observed stereoselectivities are usually small and therefore indicate either weak effects or a delicate balance between attractive and repulsive forces as represented by the common steric effects. It is therefore not surprising to find both addition modes can predominate depending on the nature of the substituents. The data accumulated in this work show that substituents on the phenyl ring generally increase the stereoselectivities. Particularly effective appear to be *p*-methyl and *p*-methoxy groups (Table II), suggesting the relative importance of charge transfer for those substituents.⁴²

Naturally, the stereoselectivity will also be influenced by the ground-state stabilities of the carbene or the carbenoid because the degree of actual bond formation in the transition state and consequently the distance of the interacting groups are determined by this parameter. Part of the observed substituent effects should probably be attributed to their capabilities in stabilizing the ground state. The free carbene will be relatively more stabilized by electron-donating substituents than the carbenoid. The larger discriminating ability of the carbenoid, on the other hand, is easily understood on the basis of the postulated transition state (Fig. 3a) which demands a greater proximity of the reacting partners than that of the free carbene addition. Similar considerations can be used to explain the solvent effects of reaction 1a. The displacement of bromide ion from the carbenoid will require a decreasing activation energy with increasing solvation of the lithium atom and the degree of bond making in the transition state will be correspondingly reduced, leading to lower stereoselectivity.

Lastly, it should be pointed out that the hypothesis of carbenoid addition to olefins has the attractive advantage of permitting a continuum in the reactivity scale. On one side of this scale are the completely free carbenes, as produced by photolysis or pyrolysis of diazoalkanes, and on the other side the very inert α -halomercurials which undergo addition only at elevated temperatures.⁴³ In between, with decreasing reactivities, one would have in order the α -halosodium, α -halolithium, α -haloaluminum, and α -halozinc compounds. In summary, one would expect increasing co-

(37) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 18.

(38) U. Schöllkopf, A. Lerch, and W. Pitterdorf, *Tetrahedron Letters*, 241 (1962).

(39) U. Schöllkopf and G. T. Lehmann, *ibid.*, 165 (1962).

(40) G. L. Closs and J. J. Coyle, *J. Am. Chem. Soc.*, **84**, 4350 (1962).

(41) W. von E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960); P. S. Skell and R. M. Etter, *Proc. Chem. Soc.*, 443 (1961).

(42) For a similar relationship in π -complex formation, see R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

(43) D. Seyferth, M. A. Eisert, and L. J. Todd, *ibid.*, **86**, 121 (1964).

valency of the metal-carbon bond to decrease the reactivity of the carbenoid.

As mentioned above, most of these suggestions should be considered hypothetical at this time, particularly in the case of the alkali metal compounds where a distinction between a free carbene and a carbenoid may be rather subtle. However, the hypothesis is more than a *useless* speculation since in principle it is subject to experimental verification. The whole situation of carbenoid *vs.* free carbene additions resembles rather closely the much more familiar question of SN2 *vs.* SN1 mechanism in nucleophilic substitution, where many reactions can be easily classified to proceed by either one or the other path, but a large number of reactions must be considered borderline cases. Considerably more work and better reactivity criteria are needed in the carbene field before it can be claimed to be as well understood as the subject of nucleophilic displacement reactions.

Experimental

All melting points and boiling points are uncorrected. Infrared spectra were recorded on a Beckman IR-7 instrument; spectra were recorded on a Varian DP-60 spectrometer, at a radiofrequency of 60.00 Mc./sec. Calibration of the spectra was carried out by the usual side-band technique. The spectra were measured in carbon tetrachloride solutions containing tetramethylsilane as internal standard. Vapor phase chromatograms were obtained on a Wilkens Instrument and Research, Inc., Aerograph 90-P instrument, and were recorded with a Brown recorder equipped with disk integrator.

Benzal Bromide and *p*-Methylbenzal Bromide.—Benzal bromide was prepared by the method of Vorlander.⁴⁴ *p*-Methylbenzal bromide was prepared in a similar manner. Hydrogen bromide was added to *p*-tolualdehyde (264 g.) contained in a liter flask and stirred magnetically. Weight increase ceased after the uptake of 141 g. and the addition was discontinued. The resulting dark liquid (which solidified upon cooling) was distilled over a tantalum spiral column at 11 mm. A forerun (17 g.) was removed between 50 and 60°. *p*-Tolualdehyde (230 g.) was recovered at 90°. The residue was transferred to a 100-ml. round-bottom flask and distilled at 0.50 mm. over a short glass tube into a second flask which was cooled by running tap water. A forerun (7 g.) was removed and the distillation was resumed at 0.18 mm. affording a clear liquid (71 g.) which solidified upon standing. This material was recrystallized from 80 ml. of boiling pentane, yielding white crystals (66.5 g.), m.p. 65–66°.² The yield, based on unrecovered aldehyde, was 89%; infrared spectrum: 1216, 1518, 1143, and 840 cm.⁻¹ (in CCl₄).

Anal. Calcd. for C₈H₅Br (263.94): Br, 60.55. Found: Br, 60.35.

***p*-Chlorobenzal Bromide and *m*-Chlorobenzal Bromide.**—Phosphorus pentabromide (0.2 mole) was prepared by the method of Koslow.⁴⁵ This material was suspended in 100 ml. of methylene chloride and *m*-chlorobenzaldehyde (22 g.) was added. The reaction mixture was stirred mechanically and refluxed for 19 hr. (the *p*-chlorobenzaldehyde did not require refluxing.) The resulting dark, homogeneous solution was poured into ice-water; the organic phase was removed and washed with a saturated solution of sodium bisulfite until the bromine color was discharged. It was then washed with water, several times with a saturated solution of sodium bicarbonate until the evolution of carbon dioxide ceased, once more with water, and then dried over anhydrous sodium sulfate. Solvent was removed by distillation and the residue was vacuum distilled over a micro Vigreux column. After removal of a small forerun, 32.9 g. of clear liquid was collected at 62° and 0.02 mm. Redistillation, followed by fractional freezing, afforded an analytical sample. The yield, based on starting aldehyde, was 74%⁴⁶; infrared spectra: *m*-chlorobenzaldehyde (neat), 1590, 1490, 1405, 1145, 1013, 833,

and 720 cm.⁻¹; *p*-chlorobenzaldehyde (neat), 1590, 1575, 1477, 1430 (doublet), 1145, 890, 787, and 690 cm.⁻¹.

Anal. Calcd. for C₇H₅ClBr₂ (*meta*) (284.40): 20.1 mg. of sample should give 36.6 mg. of silver chloride and silver bromide. Found: 35.9 mg. Calcd. for C₇H₅ClBr₂ (*para*): 34.6 mg. of sample should give 63.2 mg. of silver chloride and silver bromide. Found: 62.8 mg.

***p*-Methoxybenzal Bromide.**—*p*-Methoxyphenyldiazomethane (see below) obtained from anisaldehyde (8.5 g.) was dissolved in 50 ml. of pentane and contained in a 250-ml. 3-neck flask, fitted with mechanical stirrer, addition funnel, and low temperature thermometer. The stirred solution was maintained at -15° by a Dry Ice-acetone bath and a solution of bromide (5.0 g.) in 40 ml. of pentane was slowly added. When the red color of the diazo compound had disappeared, the addition was discontinued; the resulting solution was filtered and dried over sodium sulfate. Removal of solvent afforded 5.0 g. of slightly yellow oil. The infrared spectrum of this material was similar to the spectra of the other benzal bromides. The yield was 28.5% based on starting aldehyde.

p-Methoxybenzal bromide is extremely reactive toward moisture and must be stored under nitrogen and at low temperature. It distills at 84° and 0.05 mm., but appears to suffer decomposition in the process. In the α -elimination reactions, it was used without further purification. An analytical sample was prepared by fractional freezing; infrared spectrum: 1595, 1495, 1405, 1305–1230, 890, 810, and 730 cm.⁻¹.

Anal. Calcd. for C₈H₅Br₂O (279.94): Br, 57.1. Found: Br, 52.9.⁴⁷

Tosylhydrazones of Arylaldehydes.—Tosylhydrazine (0.2 mole) was dissolved in 50 ml. of boiling methanol. The methanolic solution was cooled to 50° and added at once to an equimolar quantity of the appropriate arylaldehyde. The exothermic reaction was moderated by a Dry Ice bath so that the reaction temperature remained below 50°. After a 3-min. reaction time the solution was cooled at -70° for 2 hr. The resulting tosylhydrazone was filtered off, recrystallized from boiling methanol, and dried under vacuum. Properties of the newly synthesized tosylhydrazones are given in Table V.

TABLE V
SUBSTITUTED BENZALDEHYDE TOSYLHYDRAZONES

Substituent	M.p., °C.	Yield, %	Mol. wt.	Calcd., %		Found, %
				C =	H =	
<i>p</i> -Methyl	115–116	71	288.36	C = 62.48	62.33	
				H = 5.32	5.32	
				N = 9.72	10.20	
<i>p</i> -Chloro	170–171	84	308.78	54.45	54.55	
				4.24	4.44	
				9.07	9.47	
<i>m</i> -Chloro	124–125	74	308.78	54.45	54.47	
				4.24	4.24	
				9.06	9.46	

Aryldiazomethanes from Tosylhydrazones.¹¹—The indicated tosylhydrazone (57 mmoles) and sodium methoxide (100 mmoles) were placed in a 250-ml. flask; 90 ml. of triethylene glycol (technical) was added and methanol was removed under vacuum. The reaction mixture was stirred magnetically and warmed by an oil bath, as directed in Table VI. The resulting red solution was poured into ice-water and extracted twice with 20-ml. portions of pentane. The combined extract was centrifuged to

TABLE VI
ARYLDIAZOMETHANES

Aryl	—Reaction—		Yield, %	λ_{\max} , m μ ^a	Vis.-ultraviolet, ϵ
	°C.	Min.			
H	60	45	55	491, 275	26, 2.2 × 10 ⁴
<i>p</i> -Cl	60	30	32	488, 281	57, 5.9 × 10 ³
<i>m</i> -Cl	60	25	40	480, 282	54, 4.9 × 10 ³
<i>p</i> -CH ₃	62	45	40	495, 275	25, 2.3 × 10 ⁴

^a The spectra were determined in *n*-pentane solution. The extinction coefficients were calculated on the assumption of 100% purity.

(47) Several other analyses did not improve this value. Hydrolysis on handling for analysis probably explains the low bromine value, since briefest exposure to air was sufficient to allow production of hydrogen bromide.

(44) D. Vorlander and C. Siebert, *Ann.*, **341**, 15 (1905).

(45) C. E. Koslow and M. M. Marsh, *J. Org. Chem.*, **12**, 456 (1947).

(46) *p*-Chlorobenzal bromide: b.p. 66° at 0.015 mm., m.p. ca. 15°, yield 64%.

remove precipitated aldazine and then cooled in an acetone-Dry Ice bath for a few minutes. (The unsubstituted and *p*-methyl compounds were cooled to -40° , the chloro compounds to -20°). The cooled solution was quickly filtered under suction and the solvent was removed on a rotary evaporator at 0° , yielding a red oil or solid. Diazo compounds in this series must be stored over Dry Ice.

***p*-Methoxyphenyldiazomethane.**⁴⁸—Because *p*-methoxybenzaldehyde hydrazone is very unstable, it was not purified and was used *in situ*. *p*-Anisaldehyde (8.5 g.) was dissolved in 50 ml. of dry ether; 4 ml. of anhydrous (95+%) hydrazine was added and the reaction mixture was allowed to stir overnight at $0-10^{\circ}$. After an additional hour of stirring at room temperature, the aqueous base was removed; the ethereal phase was washed twice with 10-ml. portions of water and dried over sodium sulfate. After removal of the drying agent, the solution was transferred into a 250-ml. reaction flask, and fitted with a mechanical stirrer and drying tube. Anhydrous sodium sulfate (6 g.) and yellow mercuric oxide (20 g.) were added, followed by a solution of potassium hydroxide in methanol (0.1 g., 3 ml.). The reaction temperature was maintained below 10° by an ice bath and the mixture was stirred for 40 min. in the dark. The resulting red solution was filtered twice by suction in order to remove all solid and then dried over sodium sulfate. Ether was evaporated at 0° and the resulting red oil was extracted four times with 12-ml. portions of pentane. The combined pentane extracts were cooled to -20° in a Dry Ice-acetone bath for several minutes and then quickly filtered under suction. Pentane was evaporated at 0° , affording a red oil (4.5 g.). The yield, assuming 100% purity, was 49%; λ_{\max} (pentane) 507 (27) and 276 μ (2.9×10^4).

p-Methoxyphenyldiazomethane is sensitive to shock, when neat, and can detonate. It should be stored at -80° . Even at this temperature, however, it slowly decomposes.

Arylcyclopropanes from Benzal Bromides, Olefins, and Alkyl-lithium (General Procedure).—A 3-neck, round-bottom flask was fitted with a low temperature thermometer, dropping funnel, Dry Ice condenser, and magnetic stirring bar. The assembly was evacuated, flamed dry, and allowed to fill with dry nitrogen. The olefin (1 mole) was distilled into the reaction flask from a cold trap which was used for weighing the olefin. The benzal bromide (0.1 mole) was then added to the reaction vessel. The alkyl-lithium (0.11 mole; methyl-lithium in diethyl ether, *n*-butyl-lithium in *n*-pentane, and *n*-amyllithium in *n*-pentane) was added *via* the dropping funnel at a rate of about 1 drop every 2 sec. The temperature was kept at -10° and the solution was vigorously stirred. After addition was complete the reaction product was washed twice with water and dried over sodium sulfate. The excess olefin and the solvent were distilled off. The residue was distilled without a column under vacuum at 0.05 mm. The distillation residue was shown in the unsubstituted series to consist mainly of *trans*-stilbene, which was purified by chromatography, and identified *via* m.p. and comparison of its infrared spectrum with that of an authentic sample. In those cases where epimeric cyclopropanes were formed, the isomer ratios were determined by v.p.c. on the crude material. For purification the distillate was fractionated over a Vigreux column under vacuum. Final purification of the analytical and spectral samples was afforded by v.p.c. and trapping in the conventional manner.

TABLE VII
CYCLOPROPANES FROM BENZAL BROMIDE

Olefin	Alkyl-lithium	B.p.		V.p.c.	Yield, %	Analyses, %	
		$^{\circ}\text{C}$.	Mm.			Calcd.	Found
1-Butene	MeLi	40	0.5	2	17	C, 90.35	90.53
						H, 9.65	9.62
<i>cis</i> -2-Butene	MeLi	64	3.8	2	21	C, 90.35	90.45
						H, 9.65	9.71
<i>trans</i> -2-Butene	MeLi	55	3.5	2	14	C, 90.35	89.99
						H, 9.65	9.48
Isobutene	BuLi	30	0.3	2	20	C, 90.35	90.05
						H, 9.65	9.72
2-Methyl-2-butene	MeLi	61	3.5	2	23	C, 89.94	89.73
						H, 10.06	10.26

(48) This procedure follows closely a procedure recommended to us by C. D. Gutsche.

TABLE VIII
CYCLOPROPANES FROM *p*-METHYLBENZAL BROMIDE

Olefin	Alkyl-lithium	B.p.		V.p.c.	Yield, %	Analyses, %	
		$^{\circ}\text{C}$.	Mm.			Calcd.	Found
1-Butene	BuLi	39	0.4	1	12	C, 89.94	89.80
						H, 10.06	10.19
<i>cis</i> -2-Butene	BuLi	59	.7	3	22	C, 89.94	90.24
						H, 10.06	10.30
<i>trans</i> -2-Butene	BuLi	32	.2	1	18	C, 89.94	89.75
						H, 10.06	10.13
Isobutene	BuLi	39	.2	1	26	C, 89.94	89.68
						H, 10.06	10.39
2-Methyl-2-butene	BuLi	43	.8	3	21	C, 89.59	89.46
						H, 10.41	10.60

TABLE IX
CYCLOPROPANES FROM *p*-METHOXYBENZAL BROMIDE

Olefin	Alkyl-lithium	B.p.		V.p.c.	Yield, %	Analyses, %	
		$^{\circ}\text{C}$.	Mm.			Calcd.	Found
1-Butene	MeLi	55	0.3	3	58	C, 81.77	81.73
						H, 9.17	9.17
<i>cis</i> -2-Butene	MeLi	50	.2	3	55	C, 81.77	81.44
						H, 9.17	9.37
<i>trans</i> -2-Butene	MeLi	49	.7	3	59	C, 81.77	81.81
						H, 9.17	8.90
Isobutene	MeLi	35	.2	3	60	C, 81.77	81.87
						H, 9.17	9.35

TABLE X
CYCLOPROPANES FROM *p*-CHLOROBENZAL BROMIDE

Olefin	Alkyl-lithium	B.p.		V.p.c.	Yield, %	Analyses, %	
		$^{\circ}\text{C}$.	Mm.			Calcd.	Found
1-Butene	BuLi	65	0.3	1	23	C, 73.12	73.16
						H, 7.24	7.37
<i>cis</i> -2-Butene	BuLi	55	.1	3	21	Cl, 19.62	19.64
						C, 73.12	73.10
<i>trans</i> -2-Butene	BuLi	59	.2	3	19	C, 73.12	73.32
						H, 7.25	7.54
Isobutene	BuLi	45	.2	3	19	Cl, 19.62	19.52
						C, 73.12	73.16
2-Methyl-2-butene	BuLi	70	.2	3	7	C, 74.02	73.81
						H, 7.76	7.96
						Cl, 18.21	17.80

TABLE XI
CYCLOPROPANES FROM *m*-CHLOROBENZAL BROMIDE

Olefin	Alkyl-lithium	B.p.		V.p.c.	Yield, %	Analyses, %	
		$^{\circ}\text{C}$.	Mm.			Calcd.	Found
1-Butene	BuLi	39	0.03	1	35	C, 73.12	73.00
						H, 7.25	7.50
<i>cis</i> -2-Butene	BuLi	38	.03	4	41	Cl, 19.62	19.22
						C, 73.12	73.35
<i>trans</i> -2-Butene	BuLi	32	.03	4	51	H, 7.25	7.59
						C, 73.12	73.39
Isobutene	BuLi	32	.03	4	39	Cl, 19.62	19.26
						C, 73.12	73.22
						H, 7.25	7.01
						Cl, 19.62	19.50

Boiling points, yields, analyses, and v.p.c. columns used are listed in Tables VII-XI. The v.p.c. column and temperatures, coded in the tables as 1-4 are: (1) RCA-B6A polyadipate, 35% on firebrick, 6 ft., $15-16^{\circ}$; (2) Wilkens QF-1, 25% on firebrick, 9 ft., 140° ; (3) Dow-Corning silicone 710, 20% on firebrick, 6 ft., 170° ; (4) GE SF-96, 25% on firebrick, 6 ft., 160° .

Competition Experiments with Benzal Bromides.—The procedure for these experiments paralleled exactly that described above

for the synthetic procedure, except that two olefins selected for the competition replaced the single olefin employed in the synthesis. In general, the competitions were carried out on a smaller scale than the synthetic procedure; only 2 to 3 g. of the appropriate benzal bromide was employed. Enough butyllithium in pentane was added to achieve about a 10% excess.

After flask-to-flask distillation (which was shown not to affect the product ratios), the distillate was immediately subjected to v.p.c. analysis. The retention times of the adducts, with respect to the order of earliest elution, were invariant over all five substituent series, and on the four columns used; isobutene adduct, *trans*-butene adduct, 1-butene adduct, *cis*-butene adduct. The 2-methylbutene-2 adducts fell in the general region of the 1-butene and *cis*-butene adducts. The isobutene and *trans*-butene adducts, which had the most similar retention times, were best separated by the SF-96 column. This column was also employed in most of the other competition analyses. It was not, however, capable of separating the two isomers of the 1-butene adducts. A 12-ft., QF-1 column was used for this purpose. In all cases, the identities of the various adducts were established by comparison of the retention time and n.m.r. spectrum of trapped samples with those of the single adducts, prepared in the synthetic runs. The thermoconductivity detector was calibrated with standard mixtures of purified arylocyclopropanes. Relative rates were determined from the expression

$$\frac{K_1}{K_2} = \frac{P_1}{P_2} \times \frac{O_2}{O_1}$$

Here, the P_1 quotient represents the cyclopropane product ratio, as determined by v.p.c., whereas the O_1 quotient represents the mole ratio of the starting olefins 1 and 2. Results of the competition are listed in Table IV.

Photolysis of Aryldiazomethanes (General Procedure).—The photolysis vessel was a 3-neck, round-bottom flask equipped with cold temperature thermometer, stirring bar, and nitrogen inlet tube. The vessel was immersed in a crystallizing dish containing methanol. The methanol was circulated through a copper heat exchanger immersed in a Dry Ice-acetone bath. The circulation was effected by a small pump whose speed was controlled by a Variac, so that it was possible to balance quickly the reaction temperature. The flask was illuminated by a General Electric, Photoflood, PH/RFL-2, 500-w. lamp, which was positioned directly beneath the cold bath. In a typical run 0.25 mole of the olefin was condensed in the reaction flask and 0.01 mole of the aryldiazomethane was added. During irradiation the temperature was kept at -10° . Illumination was continued for 3 to 4 hr. At the end of this period the remaining aryldiazomethane was quenched by pouring the solution into a solution of maleic anhydride (1 g.) in ether (30 ml.).⁴⁹ The ethereal solution was filtered and stirred for 1 hr. with a solution of potassium hydroxide in water (1 g. in 30 ml.). This procedure removed both pyrazoline and excess maleic anhydride. The organic phase was washed with water and dried over sodium sulfate. The ether was distilled off and the residue was distilled in a flask-to-flask distillation under vacuum (0.1 mm.). The distillation residue was shown to be mostly aldazine. The distillate was subjected to v.p.c. and the cyclopropanes were trapped in the conventional manner. Besides cyclopropanes small amounts (2–5%) of olefins were also present in the reaction mixture. In those cases where the olefins interfered with v.p.c. separation of the cyclopropanes the olefins were removed by ozonization. The ozonization was carried out by dissolving the crude distillate in methanol and passing ozone through the solution at -70° . Excess ozone was then destroyed by adding pentene to the solution before the solution was allowed to warm up. The ozonides were removed by adding ether to the reaction mixture and extracting the solution several times with saturated sodium bisulfite solution. The solvent was then evaporated and the residue was subjected to v.p.c. The yields of the arylocyclopropanes in the photolysis runs, calculated on the basis of converted aryldiazomethane, ranged from 10–40%. Each arylocyclopropane was characterized through comparison of its infrared and n.m.r. spectra with those of the corresponding products from the benzal bromide reactions.

(49) This method of removing excess aryldiazomethane was found to be superior to quenching with acids. The latter method gave consistently increased quantities of aryl-substituted olefins.

Competition Experiments with Aryldiazomethanes.—The apparatus and procedure for these experiments paralleled exactly that described above for the synthetic procedure, except that two olefins selected for the competition replaced the single olefin employed in the synthesis. Work-up procedures were also identical with those described above.

Checks were carried out to demonstrate that the products and isomer ratios remained unchanged under the reaction conditions and the work-up procedure. Thus, weighed samples of purified cyclopropanes were irradiated in pentane solutions under conditions identical with those of the photolytic competitions. The runs were worked up as described above, including low temperature ozonization, and were analyzed by v.p.c. No change in product ratio occurred in these control runs.

Analysis by v.p.c. and computation of the relative rates was carried out in the same manner as described for the benzal bromide competitions.

Equilibration of *syn*- and *anti*-1-Phenyl-*cis*-2,3-dimethylcyclopropane.—*anti*-1-Phenyl-*cis*-2,3-dimethylcyclopropane (23 mg.) was dissolved in 2 *N* potassium *t*-butoxide in dimethyl sulfoxide (0.4 ml.). The solution was sealed into an ampoule. The same was done with the *syn*-1-phenyl-*cis*-2,3-dimethylcyclopropane. The ampoules were kept in a bath heated to 100° for 17 hr. Each solution was worked up by hydrolysis, extraction with ether, and evaporation of the ether; v.p.c. analysis of the residue on an SF-96 column showed for both runs one major component with the retention time of the *anti* isomer. A small peak was visible with the approximate retention time of the *syn* adduct. The ratio of these peaks was found to be about 50:1. The major component was trapped and its infrared spectrum was identical with that of *anti*-1-phenyl-*cis*-2,3-dimethylcyclopropane. No attempts were made to trap the minor component of the reaction mixture.

Synthesis of *trans*-1-Phenyl-2-ethylcyclopropane. (a) *trans*-1-Phenyl-1-butene.⁵⁰—Cinnamyl chloride⁵¹ (21.7 g., 0.14 mole) was added dropwise to a refluxing solution of methylmagnesium iodide prepared from methyl iodide (22.2 g., 0.16 mole) and magnesium (3.8 g., 0.16 g.-atom) in 100 ml. of ether. After addition was complete, the solution was hydrolyzed, washed with ammonium chloride, and dried. The solvent was removed and the residue was distilled at 15 mm. The main fraction distilled from 80 – 85° (10.2 g., 55%). The *trans* configuration of the olefin was supported by a strong band in the infrared at 965 cm.^{-1} .

(b) Simmons-Smith Reaction⁵² on *trans*-1-Phenyl-1-butene.—Zinc-copper couple (4.2 g.) was prepared as described by Shank and Shechter.⁵² To a suspension of the couple in ether (40 ml.) was added dropwise methylene iodide (15 g.) containing iodine (0.04 g.). After refluxing the mixture for an additional 0.5 hr., *trans*-1-phenyl-1-butene (2.05 g.) was added. The reaction mixture was heated to reflux temperature overnight, filtered, washed with dilute hydrochloric acid, water, and bicarbonate solution, and dried over sodium sulfate. The solvent was removed and the residue subjected to v.p.c. analysis. The v.p.c. trace showed about 50% of unreacted olefin. The olefin was removed by low temperature ozonolysis as described above for the photolysis reactions. The remaining product was distilled under vacuum and purified by v.p.c. on a polyadipate column at 145° . A 30% conversion of the olefin to cyclopropane was estimated on the basis of the v.p.c. analysis. The infrared and n.m.r. spectra of this material were found to be identical with those of the compound obtained from the reaction of 1-butene with benzal bromide to which the *anti* configuration had been assigned.

Synthesis of *trans*-1-*p*-Methoxyphenyl-2-ethylcyclopropane.—*trans*-1-*p*-Methoxyphenyl-1-butene was prepared using the method of Bateman and Cunneen.⁵⁰ A solution of anisaldehyde (136 g.) in ether (100 ml.) was added to a solution of propylmagnesium bromide prepared from *n*-propyl bromide (123 g.), magnesium (26 g.), and ether (300 ml.). The addition was carried out at -5° . Hydrolysis and removal of ether yielded the crude carbinol which was subjected to dehydration without further purification. Dehydration was carried out by dissolving the carbinol in benzene (200 ml.), addition of *p*-toluenesulfonic acid (0.5 g.), and heating to reflux. The dehydration water was removed with the aid of an azeotrope water separator. The

(50) Cf. L. Bateman and J. I. Cunneen, *J. Chem. Soc.*, 2283 (1951).

(51) "Dictionary of Organic Compounds," Vol. I, I. Heilbron, Ed., Oxford University Press, New York, N. Y., 1953, p. 553.

(52) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1823 (1959).

solution was refluxed for 6 hr. The solvent was distilled off and the residue was chromatographed on alumina and then fractionated over a 2-ft. spiral column. The central fraction was collected between 92 and 102° (1.25 mm.) (59 g., 36%); v.p.c. analysis on two columns indicated the olefin to be 90% pure. The *trans* configuration of the olefin is supported by a strong infrared band at 965 cm.⁻¹ and by the method of preparation.⁵⁰

The Simmons-Smith reaction⁸ on the olefin was carried out in the same manner as described above for the 1-phenyl-1-butene. The resulting cyclopropane was separated by v.p.c. on a QF-1 column from the unreacted olefin. The conversion of olefin to cyclopropane was 70%. The material isolated from v.p.c.

trappings was compared *via* its infrared and n.m.r. spectra with the 1-butene adduct of *p*-methoxybenzal bromide to which the *anti* configuration had been assigned. The spectra were found to be identical in every respect.

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[CONTRIBUTION FROM THE PROCTER & GAMBLE CO., MIAMI VALLEY LABORATORIES, CINCINNATI 39, OHIO]

The Photochemical Properties of a 2-Methyl-1,4-dien-3-one¹

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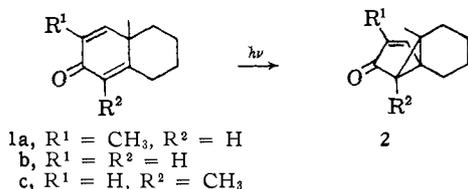
In an effort to learn more about the nature of the effects of alkyl substituents in the photochemical rearrangements of cross-conjugated cyclohexadienones, the photochemical properties of the 2-methyl-1,4-dien-3-one **1a** in both neutral and acidic media were studied. Irradiation of **1a** in dioxane gave the linearly conjugated isomer **5** as the principal product. This unprecedented transformation was resolved into a sequence of at least three distinct photochemical rearrangements involving the cyclopropyl ketones **2a** and **4** as intermediates. In 45% acetic acid the sequence of rearrangements leading to the dienone **5** was again observed, but the principal photoproduct under these conditions was the spiro ketone **17a**. No evidence for the formation of any significant amount of the 5/7-fused ketone **18a** could be detected. This contrasts with 4-methyldienones **1c**, which give predominantly 5/7-fused ketone products **18c**, and with unsubstituted dienones **1b**, which give approximately 1:1 mixtures of the two products **17b** and **18b**. The present results substantiate the view that hydroxy ketone formation is directed by the electronic effects of A-ring alkyl substituents in the cyclopropyl intermediate **16**. Both the dienone **5** and the spiro ketone **10** were obtained in methanol. Two minor products formed in both acidic and neutral media were the phenols **6** and **13**. The former product was shown to arise from the cyclopropyl ketone **4**, which is also the immediate precursor of the dienone **5**. The intermediate **4** showed a marked sensitivity to the nature of the medium, giving a significantly higher ratio of phenol **6** to dienone **5** in acidic media than in neutral media. The formation of **13** is significant in that it does not arise *via* either of the cyclopropyl ketones **2a** or **4**, and thus represents a third reaction pathway for the dienone **1a**, of a type heretofore unrecognized. The role of the 2-methyl substituents in the photochemical properties of **1a** is discussed.

Under the influence of ultraviolet irradiation cross-conjugated cyclohexadienones of type **1** undergo a series of complex, and extremely fascinating, rearrangements.² One of the most surprising results from recent studies of these rearrangements has been the discovery that the presence or absence of a methyl substituent at C-4³ of these dienones has a marked influence on their photochemical behavior.^{4,5} In an effort to learn more about the nature of this substituent effect, we have examined the photochemical properties of a 2-methyl-substituted dienone (**1a**) in both neutral

and acidic media. The results of this study, which are described below, reveal several new intriguing photochemical properties and provide additional insight into various mechanistic aspects of these rearrangements.

The required dienone **1a**⁶ was prepared in 50% yield from the octalone **3**⁷ by oxidation with selenium dioxide.⁸ The results from the irradiation of **1a** are summarized in Table I.¹⁰

Neutral Media.—The photochemical properties of several 4-methyl-1,4-dien-3-ones (type **1c**) in dioxane or ethanol have been studied; in each case initial rearrangement to a single photoproduct (type **2c**, commonly known as the "lumiproduct") occurred in yields as high as 70%.² On the other hand, the one unsubstituted dienone (type **1b**) to be studied gave in dioxane a complex mixture of ketonic and phenolic products, including the lumiproduct **2b**, with no single product being formed in more than 18% yield.^{4a} The irradiation of **1a** in dioxane or methanol resembled that of the 4-methyl derivatives in that a predominate photoproduct



(1) (a) Part IV of the series: Photochemical Rearrangements of Cross-Conjugated Cyclohexadienones; (b) for Part III see P. J. Kropp, *J. Am. Chem. Soc.*, **85**, 3779 (1963); (c) presented in part before the Organic Division, 147th National Meeting of the American Chemical Society, Philadelphia, Penna., April 9, 1964.

(2) For a recent review of the photochemistry of cross-conjugated cyclohexadienones, see O. L. Chapman in "Advances in Photochemistry," Vol. 1, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Eds., John Wiley and Sons, Inc., New York, N. Y., p. 323 ff.

(3) The steroid numbering system is used throughout the Discussion section.

(4) (a) H. Dutler, C. Ganter, H. Ryf, E. C. Utzinger, K. Weinberg, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 2346 (1962);

(b) C. Ganter, E. C. Utzinger, K. Schaffner, D. Arigoni, and O. Jeger, *ibid.*, **45**, 2403 (1962).

(5) P. J. Kropp and W. F. Erman, *J. Am. Chem. Soc.*, **85**, 2456 (1963).

(6) R. Futaki, *J. Org. Chem.*, **23**, 451 (1958), previously obtained **1a** in 36% yield as a pale yellow oil from bromination-dehydrobromination of *cis*-3,9-dimethyl-2-decalone. In the present work **1a** was obtained as a crystalline solid.

(7) J. Cologne, J. Dreux, and J.-P. Kehlstadt, *Bull. soc. chim. France* 1404 (1954).

(8) 2,3-Dichloro-5,6-dicyanobenzoquinone is normally a more convenient reagent for the oxidation of monoenones to cross-conjugated dienones (ref. 9). Quite surprisingly, however, we found that the octalone **3** is totally inert toward this reagent in refluxing benzene.

(9) D. Burn, D. N. Kirk, and V. Petrow, *Proc. Chem. Soc.*, 14 (1960).

(10) Throughout the course of this work the necessary control runs were conducted to show that all rearrangements classified as being light-induced did not occur under the reaction conditions in the absence of light.