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CHEMISTRY OF BIVALENT CARBON INTERMEDIATES—IV[1,2]

COMPARATIVE INTERMOLECULAR AND INTRAMOLECULAR REACTIVITIES OF PHENYLCARBENE TO VARIOUS BOND TYPES

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Abstract—By means of competition experiments phenylcarbene, generated from phenyldiazomethane, has been shown to be approximately equally reactive to the benzene ring (to form phenylcycloheptatriene) and to aliphatic CH_2 bonds, to be approximately six times more reactive to aliphatic CH_2 bonds than to aliphatic CH_3 bonds, and to be very unreactive toward aromatic CH bonds. These data have been used as aids in the interpretation of the results from two previously reported[1b,1c] intramolecular counterparts; they are also used in interpreting the decomposition of 2-n-butylphenyldiazomethane, which yields three cyclic products, 2-ethylindan, 2-methyltetralin, and benzosuberan in a ratio of approximately 6:5:1, and a fourth hydrocarbon product, 1-(*o*-tolyl)-butene-2, representing a new mode of carbene reaction. The effect of temperature and light source on the product ratio from the decomposition of 2-n-butylphenyldiazomethane was studied.

The ability of diazoalkane-generated carbenes to react with unsaturated centers has been known for many years and provides the basis for a number of useful syntheses.[4] More recently, the attack of carbenes on saturated groupings has been recognized,[5–13] and it is mainly with this aspect of carbene reactivity that the present paper deals.

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[1] The following are the first three papers of this series: [a] C. D. Gutsche and M. Hillman, *J. Amer. Chem. Soc.* **76**, 2236 (1954); [b] C. D. Gutsche and H. E. Johnson, *Ibid.* **77**, 5933 (1955); [c] C. D. Gutsche, E. F. Jason, R. S. Coffey and H. E. Johnson, *Ibid.* **80**, 5756 (1958).

[2a] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research; [b] This work was also supported, in part, by a grant-in-aid from The Office of Ordnance Research, U.S. Army (Contract No. DA-23-072-ORD-592).

[3] Postdoctoral Research Associate 1957–58.

[4] For a review of the literature to 1950 see M. Gordon, *Chem. Rev.* **50**, 127 (1952). Reviews covering more recent literature include J. Leitich, *Osterr. Chemiker-Ztg.* No. **6**, 164 (1960); and W. Kirmse, *Angew. Chem.* **73**, 161 (1961).

[5a] H. Meerwein, H. Rathjen and H. Werner, *Chem. Ber.* **75**, 1610 (1942); [b] H. Meerwein, H. Disselnkotter, F. Rappen, H. v. Rintelen and H. van de Vloed, *Liebigs Ann.* **604**, 151 (1957).

[6] M. Vanpee and F. Grard, *Ann. mines. Belg.* **49**, 37 (1950).

[7a] W. H. Urry and J. R. Eiszner, *J. Amer. Chem. Soc.* **74**, 5822 (1952); [b] W. H. Urry, J. R. Eiszner and J. W. Wilt, *Ibid.* **79**, 918 (1957).

[8a] W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, *J. Amer. Chem. Soc.* **78**, 3224 (1956); [b] W. von E. Doering and L. H. Knox, *Ibid.* **78**, 4947 (1956); [c] W. von E. Doering, L. H. Knox and M. Jones, *J. Org. Chem.* **24**, 136 (1959).

[9] F. Greuter, J. Kalvoda and O. Jeger, *Proc. Chem. Soc.* 349 (1958).

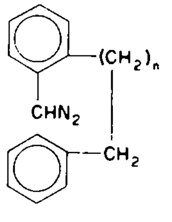
[10a] V. Franzen and L. Fikentscher, *Liebigs Ann.* **617**, 1 (1958); [b] V. Franzen and H. Kuntze, *Ibid.* **627**, 15 (1959); [c] V. Franzen, *Ibid.* **627**, 22 (1959).

[11a] L. Friedman and H. Shechter, *J. Amer. Chem. Soc.* **81**, 5512 (1959); [b] L. Friedman and H. Shechter, *Ibid.* **82**. 1002 (1960); [c] L. Friedman and H. Shechter, *Ibid.* **83**, 3159 (1961).

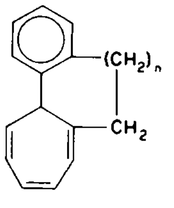
[12a] J. W. Powell and M. C. Whiting, *Tetrahedron* **7**, 305 (1959); [b] J. W. Powell and M. C. Whiting, *Ibid.* **12**, 168 (1961).

[13] D. B. Richardson, M. C. Simmons and I. Dvoretzky, *J. Amer. Chem. Soc.* **82**, 5001 (1960).

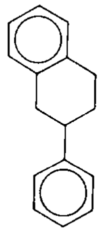
The impetus for this work was provided by several observations in the photolysis of 2-(γ-phenylpropyl)-phenyldiazomethane (IB); e.g. (a) that the tricyclic compound IIB formed only in trace amounts, (b) that the major products of cyclization were 2-phenyltetralin (III) and 2-benzylindan (IV), (c) that the ratio of III : IV appeared to increase as the reaction temperature increased.[1c]



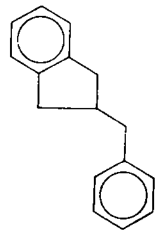
I-A (n=1)
I-B (n=2)



II-A (n=1)
II-B (n=2)



III



IV

It had been anticipated in the photolysis of compounds of type I that the attack at the benzene ring to form II would be the predominate reaction, this feeling having been based on the generally accepted although vaguely delineated notion that aromatic rings are more reactive toward carbenes than are aliphatic C—H bonds. The surprising finding that in the case of compound 1A and 1B the benzene ring is surpassed by the aliphatic bonds as a reaction site led us to undertake experiments designed to explain this fact in terms of inherent reactivity differences, geometrical factors, and reaction conditions.

Inherent reactivity differences. To measure the comparative reactivity of the benzene ring and the aliphatic C—H bond toward phenylcarbene, an equimolar mixture of benzene and cyclohexane containing phenyldiazomethane was photolyzed. The products, consisting of phenylcycloheptatriene and benzylcyclohexane, were quantitatively assayed by reduction (phenylcycloheptatriene to phenylcycloheptane) followed by vapor phase chromatography. The ratio of phenylcarbene attack on cyclohexane vs. benzene was found to be 1·16,[14] thus demonstrating that the aromatic ring is comparable in reactivity to the C—H bond rather than significantly greater.

To measure the comparative reactivity of the benzene ring and the aromatic C—H bond toward phenylcarbene, a solution of phenyldiazomethane in pure benzene was photolyzed. Careful analysis of the product failed to reveal any diphenylmethane accompanying the phenylcycloheptatriene indicating that in the intermolecular case the reactivity of phenylcarbene toward the aromatic ring is much greater than toward the aromatic C—H bond. In suitably constituted molecules where the power of proximity comes into play, however, the latter reaction has been observed. Thus, photolysis of 2-phenyl-phenyldiazomethane provides fluorene in excellent yield.[15] Also, more reactive carbenes may engage in aromatic C—H bond insertion; methylene, for instance, reacts with benzene to give cycloheptatriene and toluene in a ratio of 3·5.[16]

[14] Since the Ar insertion and C—H insertion reactions are different in type from each other it is difficult to apply a statistical correction. Consequently, this ratio is stated without correction.

[15] D. B. Denney and P. P. Klemchuk, *J. Amer. Chem. Soc.* **80**, 3289 (1958).

[16] W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.* **75**, 297 (1953); H. Meerwein *et al.*[6b] failed to detect toluene in this reaction. A more recent study, however, [R. M. Lemmon and W. Strohmeier, *Ibid.* **81**, 106 (1959)], substantiates the cycloheptatriene to toluene ratio of 3·5.

To measure the comparative reactivity of aliphatic CH_3 groups and aliphatic CH_2 groups toward phenylcarbene, a solution of phenyldiazomethane in n-pentane was photolyzed. The ratio of the combined amount of 2- and 3- benzylpentane (CH_2 attack) to 1-phenylhexane (CH_3 attack) was 6·0 ± 0·3, demonstrating that phenylcarbene is quite selective with respect to bond type. Certain other carbenes have been found to be much less selective; methylene, for instance, shows no discrimination[8a,13] or only very slight discrimination[17] between 1°, 2°, and 3° C—H bonds, while carbethoxycarbene exhibits a ratio of only 1·6 between 1° and 2° C—H bonds.[8b] It must be concluded, therefore, that the phenyl group stabilizes the carbene sufficiently to allow it to show a rather large discriminatory ability but not so much as to completely destroy its reactivity toward C—H bonds. Diphenylcarbene, for instance, appears to be unreactive in the C—H insertion reaction except in a few special instances.[18] The structural depiction of the potentiating influence of the phenyl group in phenylcarbene is uncertain and depends upon the multiplicity one assumes for the carbene. While attempts to detect radical character in carbenes by means of electron spin resonance measurements have been unsuccessful,[19] quantum mechanical calculations,[20] spectral evidence,[21] and chemical evidence[7,22–25] indicate that carbenes may have radical character, and it has been suggested[26] that the excited state is a singlet and the ground state a triplet.

Geometrical factors. Having ascertained the reactivity of phenylcarbene toward aromatic rings, aromatic C—H bonds, aliphatic CH_3 bonds, and aliphatic CH_2 bonds, it then becomes possible to assess the geometrical factors operating in the photolysis of I through a study of the product ratio from the photolysis of 2-n-butylphenyldiazomethane (V). The cyclic products from this reaction, obtained in 25 per cent yield, included benzosuberan (VI), 2-methyltetralin (VII), and 2-ethylindan (VIII) formed in the approximate ratio of 1 : 5 : 6 but varying somewhat depending upon the conditions of the decomposition (see later discussion). After adjusting for the relative numbers of hydrogens at the various positions of the n-butyl side chain and for the relative reactivity of CH_3 and CH_2 groups to phenylcarbene (see above) this approximate

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[17] J. H. Knox and A. F. Trotman-Dickenson, *Chem. & Ind.* 268 (1957); H. M. Frey, *J. Amer. Chem. Soc.* **80**, 5005 (1958).

[18] W. Kirmse, L. Horner and H. Hoffman, *Liebigs Ann.* **614**, 19 (1958).

[19] V. Franzen and H. Joschek, *Liebigs Ann.* **633**, 7 (1960), have detected electron spin resonance signals in the photochemical decomposition of diphenyldiazomethane. The resonance, however, is attributed to diphenylmethyl radical and provides only indirect evidence for radical character of the carbene. Similarly, attempts in our laboratories to detect biradical character in diphenylcarbene, generated in a rigid medium at low temperature by photolysis of diphenyldiazomethane, have been unsuccessful even when the half-field technique of J. H. Van der Waals and M. de Groot, *Mol. Phys.* **2**, 333 (1959); 3, 190 (1960) was employed. We are indebted to Professor S. I. Weissman, [see S. I. Weissman, *Ann. Rev. Phys. Chem.* **12**, 164 (1961); for a summary of the half-field technique] for calling our attention to this method and for carrying out the E.S.R. experiments.

[20] G. A. Gallup, *J. Chem. Phys.* **26**, 716 (1957).

[21] G. Herzberg and J. Shoosmith, *Nature, Lond.* **183**, 1801 (1959).

[22] J. Chanmugam and M. Burton, *J. Amer. Chem. Soc.* **78**, 509 (1956).

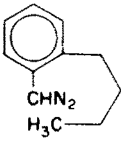
[23] H. M. Frey and G. B. Kistiakowsky, *J. Amer. Chem. Soc.* **79**, 6373 (1957).

[24] R. M. Etter, H. S. Skovronek and P. S. Skell, *J. Amer. Chem. Soc.* **81**, 1009 (1959); P. S. Skell and J. Klebe, *Ibid.* **82**, 247 (1960).

[25] W. von E. Doering and H. Prinzbach, *Tetrahedron* **6**, 24 (1959).

[26] [a] F. A. L. Anet, R. F. W. Bader and A. Van der Auwera, *J. Amer. Chem. Soc.* **82**, 3217 (1960); [b] H. M. Frey, *Ibid.* **82**, 5947 (1960).

ratio becomes 4 : 5 : 6, indicating that the proximity of the reactive site to the carbene has a real but not particularly striking influence on the product formed. The correction of the ratio of VI : VII : VIII for reactivity differences of phenylcarbene toward CH_2 and CH_3 groups assumes that the data obtained from intermolecular reactions can be extended to intramolecular reactions. While it seems reasonable to assume that the intramolecular reaction would involve the phenylcarbene reacting as a singlet species, it is much less certain that the multiplicity of the intermediate in the intermolecular cases is singlet. Were there to be a difference, the reactivity correction would, of course, be quite invalid. To ascertain the character of phenylcarbene as it is involved as an intermediate in intermolecular reactions, the "Skell–Doering" method[24,27,28] was employed. Photolysis of a cyclohexane solution of phenyldiazomethane and *trans*-2-butene gave mainly one isomer of 1,2-dimethyl-3-phenylcyclopropane; a similar experiment employing *cis*-2-butene gave mainly two isomers of 1,2-dimethyl-3-phenylcyclopropane both of which were different from that obtained from the *trans* olefin. Thus, phenylcarbene adds to olefins in a stereoselective manner and, following the Skell–Doering argument, its multiplicity is singlet.[29] Since the olefin addition involves a singlet phenylcarbene it is assumed that the intermolecular C—H insertion involves the same species. Thus, the extension of the results obtained from intermolecular reactions to the intramolecular case seems fairly safe.



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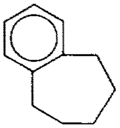
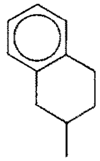
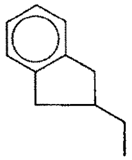


VI



VII



VIII

A number of examples of intramolecular C—H insertion reactions have been reported: 1,2-insertion reactions (equivalent to 1,2-migration of H) result in olefin formation as, for instance, in the conversion of diazocamphane to camphene;[12] 1,3-insertion reactions result in cyclopropane formation as exemplified by the conversion of 1-diazo-2-methylpropane to methylcyclopropane (isobutylene the major product, however);[11a] 1,4-insertion reactions result in cyclobutane formation as exemplified by the two known cases, viz. the conversion of 7,7-dibromobicyclo[4.1.0]heptane to a tricyclic compound containing a four-membered ring (minor product)[30] and the conversion of dimesityldiazomethane to a benzocyclobutene derivative;[31] 1,5-insertion reactions result in cyclopentane formation as in the

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[27] [a] P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.* **78**, 4496 (1956); [b] R. C. Woodworth and P. S. Skell, *Ibid.* **81**, 3383 (1959).

[28] W. von E. Doering and P. LaFlamme, *J. Amer. Chem. Soc.* **78**, 5447 (1956).

[29] It is interesting to note, however, that the product from *trans*-butene-2 was contaminated with about 3% of the two 3-phenyl-*cis*-1,2-dimethylcyclopropanes and that the products from *cis*-butene-2 was contaminated with about 2·5 per cent of 3-phenyl-*trans*-1,2-dimethylcyclopropane. Thus, the addition is not completely stereospecific perhaps indicating that phenylcarbene is intermediate between methylene (completely stereospecific addition) and diphenylcarbene (non-stereospecific addition) with respect to the ease and speed with which it undergoes singlet-triplet transition.

[30] W. R. Moore, H. R. Ward and R. F. Merritt, *J. Amer. Chem. Soc.* **83**, 2019 (1961).

[31] H. E. Zimmerman and D. H. Paskovich, *Abstract of Papers*, 140*th Meeting of the Amer. Chem. Soc.* III; p. 29. Chicago.

formation of fluorene from 2-phenyl-phenyldiazomethane[15] and the formation of hydrindan from the tosylhydrazone of cyclononanone;[11c] 1,6-insertion reactions result in cyclohexane formation as exemplified by the formation of decalin from the tosylhydrazone of cyclodecanone.[11c] The present example of the conversion of V to VIII, VII, and VI provides additional cases of 1,5- and 1,6-insertion reactions involving carbene intermediates and extends the list to include a 1,7-insertion reaction. On the basis of our data and those in the literature the order of preference for intramolecular C—H insertion reactions appears to be $1,2 > 1,3 > 1,5 > 1,6 > 1,7 > 1,4$. This is, of course, not unexpected as a similar preference has been found in other types of ring-forming reactions.[32]

Reaction conditions. The apparent increase in the ratio of III to IV with increasing temperature in the decomposition of I led us to investigate the effect of reaction conditions on the product ratio in the decomposition of V. Table 1 shows the effect on the indan : tetralin ratio (VIII : VII) and the indan + tetralin : benzosuberan (VIII + VII : VI) ratio of changes in light source, solvent, and temperature.

TABLE 1. EFFECT OF REACTION CONDITIONS ON PRODUCT RATIOS IN THE DECOMPOSITION OF V

Temperature	Light source	Solvent	Ratio VIII:VII	Ratio VIII + VII:VI
- 60°	Hg Vapor Lamp	Hexane	1·16 ± 0·01	10·5 ± 1·0
5°	Hg Vapor Lamp	Cyclohexane	1·25 ± 0·05	10·7 ± 1·0
25°	Hg Vapor Lamp	Cyclohexane	1·33 ± 0·03	10·9 ± 1·0
25°	Hg Vapor Lamp	Hexane	1·35 ± 0·01	11·5 ± 1·0
80°	Hg Vapor Lamp	Cyclohexane	1·53 ± 0·04	12·5 ± 1·0
80°	Sun Lamp	Cyclohexane	1·44 ± 0·04	16·0 ± 1·0
80°	None	Cyclohexane	1·14 ± 0·02	22 ± 1·0
200°	None	Eicosane	1·22 ± 0·02	21 ± 1·0

Inspection of Table 1 reveals that a change in solvent from hexane to cyclohexane has no effect on the VIII : VII ratio, that light has a moderately large influence on the ratio, that the type of light source has a very small but probably real effect, and that temperature in the light-induced reaction has a small but real effect. The ratio VIII+VII : VI was measureable with much less accuracy than the ratio VIII : VII, and the only effect that appears to be certain is that of light in favouring the formation of VI. The preferential formation of the smaller ring with increasing temperature (indan > tetralin > benzosuberan) is opposite to the trend in the decomposition of I in which case the geometrical factor must be offset by the special characteristics of the benzyl position.*

From this study of inherent reactivity differences, geometrical factors, and reaction conditions some insight into the chemistry of phenylcarbenes has been gained, particularly with regard to the intramolecular reactions of I and V. It has been ascertained that the failure of IB to yield IIB cannot be due to an inherent reactivity

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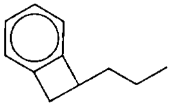
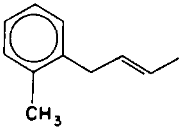
* See ref. 1*c* for a more detailed argument concerning this point.

[32] L. Ruzicka, W. Brugger, M. Pfeiffer, H. Schinz and M. Stoll, *Helv. Chim. Acta.* **9**, 499 (1926) for a discussion and graphic representation (p. 512) of this phenomenon.

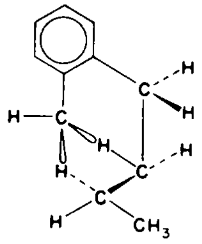
difference of the aromatic ring and a CH_2 group toward phenylcarbene; it has been demonstrated that the geometric or proximity factor is not necessarily the basis for this failure; it has been shown that changes in reaction conditions do not necessarily cause significant changes in product ratios. Thus, the lack of Ar insertion product (IIB) from IB is only partly explained by these data and must be ascribed to something more than a simple proximity factor, possibly the different transition state configurations that may be required for the C—H insertion and the Ar insertion reactions. In the decomposition of V the 1,5-insertion product (VIII) and the 1,6-insertion product (VII) are formed in a ratio of 1·20, while in the decomposition of IA the 1,5-insertion product (IV) and what may be taken as the equivalent of the 1,6-insertion product (e.g. the Ar insertion product IIA) are formed in a ratio of 3·00. From this it would appear that the proximity factor is more severe when C—H insertion competes with Ar insertion than when only C—H insertion is involved. Why this is the case is not apparent but may serve to explain the fact that Ar insertion plays almost no part in the formation of products from the decomposition of IB.

Fourth hydrocarbon photolysis product. The hydrocarbon products from the decomposition of V included, in addition to the bicyclic materials VI, VII, and VIII, a fourth material[33] which was not n-propylbenzocyclobutene (IX),[34] the most logical possibility,[36] but 1-(*o*-tolyl)butene-2 (X). The formation of 1-(*o*-tolyl)butene-2 (ratio of VI+VII+VIII : X is 10 ± 2) represents a new type of carbene reaction, the mechanism of which is obscure. That X does not arise via IX as a precursor was demonstrated by subjecting an authentic sample of IX to photolysis and recovering it unchanged. It seems most probable that X is formed directly from the carbene XI by an intramolecular transfer of hydrogen atoms from the β and γ positions of the side chain to the carbene carbon. Dreiding models and Leybold models show that the molecule can easily assume a conformation which simultaneously brings the β and γ hydrogen atoms close to the carbene center; thus, the hydrogen transfer may be


IX



X



XI

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[33] A fifth hydrocarbon component was identified as 1-(*o*-tolyl)-butane and was present in rather small but widely varying amounts in most of the photolysis mixtures. It is thought to arise not from the photolysis, however, but to be formed at a prior step, probably in the preparation of the aldehyde.

[34] An authentic sample of IX was prepared by a double Arndt-Eistert homologation of benzocyclobutenecarboxylic acid[35] followed by reduction of the terminal carboxyl group to a methyl group. It was different from the fourth photolysis product.

[35] M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.* **80**, 2255 (1958).

[36] Although the experiments of Zimmerman and Paskovich[30] were not known to us at the time, their finding that one of the products from the decomposition of dimesityldiazomethane was a benzocyclobutene derivative would add substance to this surmise.

essentially simultaneous. Further elucidation of the details of this mode of carbene reaction,[37] however, must await additional experiments.

EXPERIMENTAL

M.p. are corrected; b.p. are uncorrected. The I.R. spectra were recorded on a Perker Elmer Model 21 Spectrophotometer; the U.V. spectra were recorded on a Cary spectrophotometer. Analytic vapor phase chromatographic determinations were carried out with a Perkin Elmer Model 154 B instrument containing a ¼″ × 6′ column packed with fire brick and silicone oil (Dow-Corning no. 710) as the adsorbed phase. Preparative vapor phase chromatographic separations were carried out in home made instruments containing a ⅜″ × 10′ column or a ½″ × 16′ column with the same packing as used in the analytical column. (We are indebted to Dr. Robert Barker and Mr. Charles Armbruster for their aid in the construction of the preparative instruments.) Microanalyses were performed by W. Manser's microanalytical laboratory in Zurich, Switzerland and by J. Szcek's microanalytical laboratory in Vienna, Austria.

Photolysis procedures. The photolysis experiments were carried out (a) in an ordinary Pyrex flask with irradiation and heat provided by a General Electric RS sun lamp or (b) in a flask equipped with a water-cooled quartz well containing a 100 W mercury vapor lamp (assembly manufactured by the Hanovia Division of Englehard Industries, Newark, N.J.). In all cases the photolyses were carried out in an atmosphere of nitrogen.

Work-up procedures. After the decomposition of the diazo compound was complete, the large volume of solvent was removed by distillation (under ordinary pressure in most instances but under red press when a cycloheptatriene product was present or when a high boiling solvent was employed). Control experiments indicated that little, if any, of the desired materials were lost by co-distillation during the removal of the solvent. The residue was then distilled under vacuum to a point where all of the hydrocarbon materials had passed over into the distillate. This distillate, containing small amounts of higher boiling products (aldehydes, nitriles), in most cases was further purified by passage through an alumina column followed by elution of the hydrocarbon fraction with petroleum ether (b.p. 63–69°). The eluate was submitted to assay or fractionation by vapor phase chromatographic techniques.

Assay procedures. The analytical vapor fractometer was operated at temperatures and pressures chosen, on the basis of numerous trials, as optimum for maximum resolution in the particular case. The size of sample, the sensitivity, and the chart speed were adjusted to provide suitably large areas under the curves to minimize errors of measurement. The areas were calculated by multiplying the height times the width at half-height and were checked in several cases against the area as obtained by mechanical integration. Correction factors for the specific compounds being assayed were determined on mixtures of accurately known weight composition of authentic samples and were as follows: (a) Benzylcyclohexane (1·14), Phenylcycloheptane (1·12), Diphenylethane (1·00). (b) Phenylhexane (1·00), 2-Benzylpentane (1·03), 3-Benzylpentane (1·03). (c) 2-Ethylindan (1·00), 2-Methyltetralin (1·06), Benzosuberan (1·05). The ratios reported below and in Table 1 represent in each instance the results from two or more replicate experiments, and the limits indicated provide an estimate of the precision of the assay. To rule out the possibility that secondary photochemical reactions were a

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[37] There are numerous examples of migrations to carbene centers from the adjacent position: (a) Hydrogen migration results in olefin formation and is equivalent to 1,2-insertion. (b) Alkyl group and aryl group migration provides the basis for the Wolff rearrangement of diazoketones [W. E. Bachmann and W. S. Struve, *Organic Reactions* Vol. 1, 38 (1942)]. (c) Aryl group migration has been observed in the formation of triphenylethylene from 2,2,2-triphenyl-1-diazoethane [L. Hellerman and R. L. Garner, *J. Amer. Chem. Soc.* **57**, 139 (1935)]. Few examples of migration to carbene centers from non-adjacent positions are known, however. An attempt to detect a 1,3 shift of an aryl group in the decomposition of 3,3,3-triphenyl-1-diazopropane resulted only in the formation of 3,3,3-triphenylpropene-1, the result of a 1,2 hydrogen migration [L. Hellerman and R. L. Garner, *Ibid.* **68**, 819 (1946)]. Only recently have reactions been reported in which a non-adjacent hydrogen migrates to a carbene center: (a) V. Franzen and H. Joschek [*Liebigs Ann.* **633**, 7 (1960)] isolated dibenzofluorene from the thermal decomposition of di-α-naphthlyldiazomethane. (b) Zimmerman and Paskovich[30] isolated a dimesitylmethane derivative from the decomposition products of dimesityldiazomethane.

complicating factor authentic samples of benzosuberan, 2-methyltetralin, 2-ethylhydrindan, and phenylhexane were subjected to the conditions of the photolysis experiments. After several days of irradiation the original compounds were recovered unchanged or, in a few cases, contaminated with no more than a trace of a new substance.

Preparation of diazoalkanes

Phenyldiazomethane was prepared by mercuric oxide exidation of benzalhydrazone according to the procedure of Staudinger and Gaule.[38]

2-n-Butylphenyldiazomethane (V). Following the general procedure of Gottlieb[39] 2-butyroylbenzoic acid was prepared from phthalic anhydride, butyric anhydride and sodium butyrate and obtained in 65–75% yield as colorless prisms after one recrystallization from benzene, m.p. 86–87° (Found: C, 68·65; H, 6·73; $C_{11}H_{12}O_3$ requires: C, 68·73; H, 6·29%). A 44 g sample of the crude 2-butyroylbenzoic acid was heated with 48 g red phosphorus and 176 ml 57% hydriodic acid[40] for 2 days. Another 10 g phosphorus was added, and the mixture was heated an additional day. The crude product consisted of 31–35 g (76–85%) of colourless solid which was used directly in the next step. Recrystallization of a sample from pet ether (b.p. 63–69°) yielded colourless needles, m.p. 40–41° (Found: C, 74·13; H, 7·55; $C_{11}H_{14}O_2$ requires: C, 74·00; H, 7·55%). A 29·0 g sample of crude 2-n-butylbenzoic acid was converted to the acid chloride with thionyl chloride, and the distilled acid chloride was subjected to a Rosenmund reduction[41] to yield, after distillation, 17–20 g (65–75%) of a colorless oil, b.p. 82–84° at 1·5 mm. The *semicarbazone of 2-n-butylbenzaldehyde* was obtained as colorless needles after recrystallization from aqueous ethanol, m.p. 139–140° (Found: C, 65·25; H, 7·87; $C_{12}H_{17}N_3O$ requires: C, 65·72; H, 7·81%). A vapor phase chromatogram of the aldehyde indicated that 2-butyltoluene was present as a minor contaminant. It could be almost completely removed by twice distilling the aldehyde and discarding the first 0·5 ml of distillate.

A 5·0 g sample of 2-n-butylbenzaldehyde was dissolved in 70 ml dry ether and slowly added to a stirred mixture of 5 ml anhydrous hydrazine in 40 ml ether. Stirring was continued for 6–8 hr at 0° and for 2 hr at 25°. The hydrazine layer was separated and extracted twice with ether. The combined ethereal solution was extracted twice with water, dried over sodium sulphate, filtered, and evaporated to give the hydrazone as a greenish oil. This was dissolved in 50 ml dry ether, 15 g anhydrous sodium sulfate and ca. 30 drops of a saturated solution of alcoholic potassium hydroxide[42] were added, and the stirred mixture was cooled to 0–5° and treated over a period of 15–20 min with 10 g yellow mercuric oxide. After the addition was complete, the reaction mixture was allowed to warm to room temp and was stirred an additional 3·5–4 hr. After standing for a short time, the mercury was removed by filtration, the ether was removed by evaporation and the residue containing the diazo compound was taken up in the photolysis solvent. The yield of diazo compound based on the benzoic acid assay[43] or the nitrogen evolution assay was 35–45%.

Photolysis experiments

Photolysis of phenyldiazomethane in benzene. Phenyldiazomethane prepared from 10 g benzalhydrazone was dissolved in 400 ml benzene and irradiated at 25° for 16 days with a mercury vapor lamp. (An infrared spectrum of the reaction mixture after 5 days of irradiation showed that an

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[38] F. Staudinger and A. Gaule, *Ber. Dtsch. Chem. Ges.* **49**, 1906 (1916). Other oxides have been used in hydrazone oxidations;[42] silver oxide has been stated to be particularly effective in the conversion of benzalhydrazone to phenyldiazomethane [R. J. Mohrbacher and N. H. Cromwell, *J. Amer. Chem. Soc.* **79**, 401 (1957)]; active manganese dioxide has been found to be advantageous in the preparation of a bis-diazoalkane of the diphenyldiazomethane type [R. W. Murray and A. M. Trozzolo, *J. Org. Chem.* **26**, 3109 (1961)].

[39] J. Gottleib, *Ber. Dtsch. Chem. Ges.* **32**, 958 (1899).

[40] A. C. Cope and S. W. Fenton, *J. Amer. Chem. Soc.* **73**, 1668 (1951).

[41] E. Mosettig and R. Mozingo, *Organic Reactions* Vol. IV; p. 362. John Wiley, New York (1948).

[42] C. D. Nenitzescu and E. Solomonica, *Organic Syntheses* Coll. Vol. II; p. 495. John Wiley, New York (1943); have noted the accelerating influence of alcoholic potassium hydroxide in hydrazone oxidations. A more recent study [J. B. Miller, *J. Org. Chem.* **24**, 560 (1959)] provides additional details concerning the action of a base in these reactions and suggests that the apparent difference in efficacy between the red and yellow forms of mercuric oxide may be trivial.

[43] F. Arndt, *Organic Syntheses* Coll. Vol. II; p. 166, Note 1. John Wiley, New York (1943).

appreciable amount of diazo compound was still undecomposed.) The benzene was removed under vacuum, and the residue was distilled (3·12 g of material with b.p. 70–100° at 2 mm), and the distillate was passed through an alumina column to give 2·84 g hydrocarbon mixture. A vapor phase chromatogram indicated the absence of diphenylmethane, and the ultraviolet absorption (λ_{max} 235 mu), the hydrogen uptake (0·9 mole equivalents for 3 double bonds) and the vapor phase chromatogram of the reduced (hydrogen and 10% palladium on charcoal) material (one main band corresponding to phenylcycloheptane) indicated that the product was mainly phenylcycloheptatriene.

Photolysis of phenyldiazomethane in cyclohexane. Phenyldiazomethane prepared from 11·5 g benzalhydrazone was dissolved in 1300 ml cyclohexane and irradiated at 25° for 10 days with a mercury vapor lamp. The distilled and chromatographed hydrocarbon fraction amounted to 3·86 g the composition of which was indicated by vapor phase chromatography to be 78% benzylcyclohexane and 22% *cis* stilbene. Conversion of the *cis* stilbene to *trans* stilbene with a trace of iodine and benzoyl peroxide followed by re-chromatography on alumina yielded 2·2 g benzylcyclohexane (identified by comparison with authentic material) in the first fraction and *trans* stilbene in the second fraction.

Photolysis of phenyldiazomethane in benzene and cyclohexane. Phenyldiazomethane prepared from 10 g benzalhydrazone was dissolved in 400 ml of a solution containing equimolar amounts of benzene and cyclohexane and irradiated at 25° for 7 days with a mercury vapor lamp. The distilled and chromatographed hydrocarbon fraction amounted to 4·36 g. Catalytic reduction with 10% palladium on charcoal as catalyst (hydrogen uptake corresponding to 30% phenylcycloheptatriene content) and vapor gas chromatography of the reduced material indicated phenylcycloheptane, benzylcyclohexane, and diphenylethane to be present in the ratio of 2·70 (39·5%), 3·14 (46%) and 1·00 (14·5%). The ratio of benzylcyclohexane : phenylcycloheptatriene, thus, is 1·16.

Photolysis of phenyldiazomethane in n-pentane. Phenyldiazomethane from 10 g benzalhydrazone was dissolved in 450 ml n-pentane (Phillips Co.) and irradiated at 36° for 8 days with a general Electric RS sun lamp. The distilled and chromatographed hydrocarbon fraction amounted to 1·25 g the composition of which was indicated by vapor phase chromatography to be 2-benzylpentane + 3-benzylpentane and 1-phenylhexane in a ratio of 6·10 ± 0·20.

Photolysis of 2-n-butylphenyldiazomethane. The crude diazo compound (1·5–5 g) was dissolved in the appropriate solvent and subjected to photolysis under the various conditions indicated in Table 1. Temperatures were maintained by the refluxing solvent in those reactions carried out above room temp and by appropriate cooling of the reaction vessel and the light source in those reactions carried out at or below room temp. Temperatures were measured by means of a thermocouple contained in a well immersed in the reaction mixture. After the photolysis was completed, the solvent was removed by distillation at atm press (except in the case of eicosane), and the residue was distilled in a Claisen flask, the material boiling up to 160° (15 mm) being collected. The product was quantitatively assayed by means of vapor phase chromatography, the results of which are shown in Table 1. The volatile portion of the photolysis product accounts for 20–35% of the starting 2-n-butylbenzaldehyde and is comprised of 3 parts of the bicyclic products (VI, VII, VIII) and the olefin (X) and 1 part of 2-n-butylbenzaldehyde and 2-n-butylbenzonitrile. The rest of the starting aldehyde is converted to non-volatile products including an unidentified yellow solid which forms during the photolysis and which precipitates from solution, the azine corresponding to 2-n-butylbenzaldehyde, 2,2′-dibutylstilbene (tentative), and other unidentified materials.

In the initial exploratory experiments with this reaction a larger amount of diazo compound was used, and the resulting hydrocarbon product was passed through a preparative vapor phase fractometer. Four fractions were obtained and were identified, in order of increasing retention time, as (a) a mixture of 2-n-butyltoluene and 1-(*o*-tolyl)-butene-2 (X), (b) 2-ethylindan (VIII), (c) 2-methyltetralin (VII), and (d) benzosuberan (VI). The three bicyclic compounds comprising fractions (b), (c) and (d) were identified by comparison of the isolated products with authentic samples. The two compounds of fraction (a) were identified by enriching the photolysis product with authentic samples of 2-n-butyltoluene[44] and 1-(*o*-tolyl)-butene-2. Further identification was provided (a) by the observation that hydrogenation of the photolysis mixture removed the component responsible for the curve

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[44] That 2-n-butyltoluene was not a product of photolysis was indicated by the fact that a sample of hydrazone was shown to contain this material (probably by hydrogenolysis in the preparation of the aldehyde from the acid chloride) and from the fact that a sample of aldehyde purified by chromatography on alumina yielded a diazo compound which upon photolysis produced no toluene.

associated with 1-(*o*-tolyl)-butene-2 and increased the area of the curve associated with 2-n-butyltoluene and (b) by the observation that ozonolysis (with reductive work up) of the photolysis mixture removed the component responsible for the curve associated with 1-(*o*-tolyl)-butene-2 and produced a new component giving rise to a curve at a position identical with that from authentic 2-(*o*-tolyl)-acetaldehyde.

Reaction of phenyldiazomethane and butene-2

(A) *Reaction with* trans-*2-butene.* A sample of phenyldiazomethane prepared from 5 g benzaldehyde was dissolved in 150 ml cyclohexane containing 7·5 g *trans*-2-butene (Matheson Research Grade), and the mixture was photolyzed for 44 hr with a mercury vapor lamp. The solvent was then removed by distillation, the residue was distilled under vacuum with the fraction boiling up to 140° (15 mm) being collected, and the distillate was subjected to ozonolysis in methanol at −70°. The methanol was removed, and the residue was taken up in pet ether (b.p. 63–69°) and chromatographed on alumina (Woelm). The hydrocarbons were eluted with pet ether, the solvent was removed by distillation, and the residue was analysed on a vapor fractometer. One large band (thought to arise from 3-phenyl-*trans*-1,2-dimethylcyclopropane) accompanied by two much smaller bands (thought to arise from *cis* and *trans*-3-phenyl-*cis*-1,2-dimethylcyclopropane) were observed. The ratio of the *trans*-1,2-dimethyl compound:*cis*-1,2-dimethyl compounds was ca. 45. The fraction accounting for the larger peak in the vpc was isolated as a colorless oil (Found: C, 89.95; H, 9·73; $C_{11}H_{14}$ requires: C, 90·35; H, 9·65).

(B) *Reaction with* cis-*2-butene.* An experiment similar to the one described above was carried out using *cis*-2-butene. The vpc of the hydrocarbon portion showed two large and well-resolved bands (thought to arise from *cis*-3-phenyl-*cis*-1,2-dimethylcyclopropane and *trans*-3-phenyl-*cis*-1,2-dimethylcyclopropane) of almost equal intensity accompanied by a much smaller band (thought to arise from 3-phenyl-*trans*-1,2-dimethylcyclopropane). The ratio of the *cis*-1,2-dimethyl compounds to the *trans*-1,2-dimethyl compound was ca. 35. The fractions accounting for the two larger peaks in the vpc were isolated without separation as a colorless oil. (Found: C, 90·52; H, 9·65; $C_{11}H_{14}$ requires: C, 90·35; H, 9·65%). The 3-phenyl-1,2-dimethylcyclopropanes were contaminated in both reaction mixtures with phenylpentene-2 (removed by ozonolysis) and by benzylcyclohexane (considerably higher boiling and completely resolved in the vpc). That the ozonolysis probably had no effect on the cyclopropanes was shown by subjecting an authentic sample of phenylcyclopropane to ozonolysis under the conditions described above and recovering it completely unchanged.

Synthesis of photolysis products

Synthesis of products from phenyldiazomethane photolyses. (A) *Phenylcycloheptane*[1c] was prepared from phenylmagnesium bromide and cycloheptanone[45] followed by dehydration and reduction. (B) *Benzylcyclohexane*[46] was prepared from benzylmagnesium bromide and cyclohexanone followed by dehydration[47] and hydrogenation over palladium on charcoal catalyst. (C) 1-*Phenylhexane*[48] was prepared from benzene, hexanoyl chloride, and aluminium chloride followed by Clemmensen reduction. (D) 2-*Benzylpentane*[49] was prepared from benzylmethyl ketone and n-propylmagnesium bromide followed by dehydration and hydrogenation. (E) 3-*Benzylpentane*[50] was synthesized from ethyl phenylacetate and ethylmagnesium iodide followed by dehydration and hydrogenation.

Synthesis of cyclic products from 2-n-butylphenyldiazomethane photolysis. (A) *Benzosuberan*[51] was obtained by hydrogenolysis of 1-acetoxy-2,3-benzosuberan.[1a] (B) 2-*Methyltetralin* was prepared by the method of Sah and Brull.[52] (C) 2-*Ethylindan*[53] was prepared by alkylation of diethyl

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[45] R. D. Kleene, *J. Amer. Chem. Soc.* **63**, 1482 (1941).

[46] A. Klages, *Ber. Dtsch. Chem. Ges.* **40**, 2360, 2366 (1907).

[47] K. v. Auwers and W. Treppman, *Ber. Dtsch. Chem. Ges.* **48**, 1207, 1218 (1915).

[48] J. v. Braun and H. Deutsch, *Ber. Dtsch. Chem. Ges.* **45**, 2171, 2181 (1912).

[49] E. Bjelouss, *Ber. Dtsch. Chem. Ges.* **45**, 625, 632 (1912).

[50] H. Stenzl and Fr. Fichter, *Helv. Chim. Acta.* **17**, 669, 680 (1934).

[51] W. Borsche and A. Roth, *Ber. Dtsch. Chem. Ges.* **54**, 174 (1921).

[52] P. P. T. Sah and W. Brull, *Ber. Dtsch. Chem. Ges.* **73**, 1430 (1940).

[53] T. Wagner-Jauregg, H. Arnold, F. Huter and J. Schmidt, *Ber. Dtsch. Chem. Ges.* **74**, 1522, 1524 (1941).

benzylmalonate with ethyl iodide and sodium ethoxide followed by saponification and hydrolysis; cyclization of the α-ethylphenylpropionic acid followed by Clemmensen reduction yielded the product.

1-n-Propylbenzocyclobutene. A 2·0 g sample of benzocyclobutene-1-carboxylic acid was converted to the acid chloride with thionyl chloride and then to the diazoketone with ethereal diazomethane. Employing the method of Newman and Beal[54] the diazoketone was submitted to Wolff rearrangement, and the resulting ester was saponified to yield 1·93 g (89%) of a pale yellow solid. Recrystallization from pet ether (b.p. 63–69°) yielded benzocyclobutene-1-acetic acid as colorless needles, m.p. 61·5–62·5° (Found: C, 74.00; H, 6.41; $C_{10}H_{10}O_2$ requires: C, 74·05; H, 6·22%). A 1·52 g sample of this material was subjected to a second Arndt-Eistert homologation to yield 1·27 g (77%) of benzocyclobutene-1-propionic acid which was obtained as colorless needles after recrystallization from pet ether (b.p. 62–69°), m.p. 47–48° (Found: C, 75·27; H, 6·97; $C_{11}H_{12}O_2$ requires: C, 74·97; H, 6·86%). Reduction of this acid to benzocyclobutene-1-propanol with lithium aluminium hydride, conversion to benzocyclobutene-1-propyl chloride with thionyl chloride, and reduction of the chloride with lithium aluminum hydride yielded 1-n-propylbenzocyclobutene as a colorless oil, n_D^{25} 1·5098 (Found: C, 90·07; H, 9·63; $C_{11}H_{14}$ requires: C, 90·35; H, 9·65). The I.R. spectrum of this material showed a band at 1003 cm^{-1} which is stated to be characteristic of the benzocyclobutene system.[35]

Synthesis of o-*tolylbutenes.* (A) 1-(o-*Tolyl*)-*butene*-1 was prepared from *o*-tolylaldehyde and n-propylmagnesium followed by dehydration of the resulting alcohol with phosphorus pentoxide and was obtained as a colorless oil, homogeneous in the vpc. The C and H analysis of this material was consistently low in carbon. That the compound possessed the assigned structure, however, seems certain in view of its conversion on ozonolysis to *o*-tolylaldehyde. (B) 1-(o-*Tolyl*)-*butene*-2 was prepared from *o*-tolylmagnesium bromide and 1-bromobutene-2 (from crotonaldehyde by lithium aluminum hydride reduction and treatment with phosphorus tribromide); the crude product was fractionated through a 14″ glass helix-packed column to yield the pure hydrocarbon, b.p. 98–99° (22 mm), n_D^{25} 1·5135. It was necessary to analyze the compound soon after distillation to avoid low carbon values, presumably to be attributed to air oxidation of the material (Found: C, 89·98; H, 9·71; $C_{11}H_{14}$ requires: C, 90·35; H, 9·65%). Ozonolysis of this olefin yielded *o*-methylphenylacetaldehyde. (C) 1-(o-*tolyl*)-*butene*-3 was prepared by lithium aluminum hydride reduction of γ-(*o*-tolyl)-butyric acid, conversion to the acetate and pyrolysis of the acetate through a tube heated to 415°. However, only enough material for a vpc determination was obtained.

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[54] M. S. Newman and P. F. Beal, *J. Amer. Chem. Soc.* **72,** 5163 (1950).