is weakly coupled to five vicinal hydrogens and would be expected to appear as a broad, ill-resolved band. In confirmation of the postulate that the resonance from the hydrogen at C-3 is shifted upfield and appears at δ 1.48 ppm, irradiation of this part of the spectrum in a double resonance experiment[42] resulted in the transformation of the triplet centered at δ 2.26 ppm to a doublet centered at that point. Thus, the nmr spectrum appears to be more readily accommodated to structure **15** than to structures **12** or **13**.

Chemistry of Bivalent Carbon Intermediates. VI. The Photolysis of 2-*n*-Butylphenyldiazomethane[1]

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Abstract: The photolysis of 2-*n*-butylphenyldiazomethane (**1**) in cyclohexane was shown in an earlier investigation to yield 2-ethylindan (**3**), 2-methyltetralin (**4**), benzosuberan (**5**), and *trans*-1-(*o*-tolyl)-2-butene (**7**). A reinvestigation of the product mixture from this reaction has revealed that, in addition to these compounds, 1-*n*-propylbenzocyclobutene (**2**), 1-*n*-butyl-2-cyclohexylmethylbenzene (**6**), and *cis*-1-(*o*-tolyl)-2-butene (**8**) are also present. The ratio of these products has been carefully measured, and it has been found that it is the same whether the irradiation is effected directly or *via* photosensitization. This unexpected result is interpreted in terms of an equilibrium between the singlet and triplet species of the arylcarbene, the rate of equilibration being more rapid than the rates of the ensuing processes leading to intramolecular C–H insertion (*i.e.* to forms **2–5**), intermolecular C–H insertion (*i.e.* to form **6**), and hydrogen migration (*i.e.* to form **7** and **8**). In an attempt to gain insight into the mechanism of formation of the olefins **7** and **8**, deuterated analogs of **1** were prepared, *viz.* the β,β-dideuterio compound (**1**-β_2), the γ,γ-dideuterio compound (**1**-γ_2), and the $\beta,\beta,\gamma,\gamma$-tetradeuterio compound (**1**-$\beta_2\gamma_2$). Analysis of the product ratios in the mixtures formed by irradiation of these compounds revealed a deuterium isotope value of 3.1–3.4 for the C–H insertion to form 2-ethylindan (**3**), a value of 1.6–1.8 for the C–H insertion to form 2-methyltetralin (**4**), a value of 3.3 for the formation of olefin from **1**-β_2, a value of 1.5 for the formation of olefin from **1**-γ_2, and a value of 7.2 for the formation of olefin from **1**-$\beta_2\gamma_2$. The close similarity of deuterium isotope effect between the formation of **3** and olefin from **1**-β_2 and **4** and olefin from **1**-γ_2, in conjunction with the fact that the product of the deuterium isotope values for olefin formation from **1**-β_2 and **1**-γ_2 is approximately equal to that for olefin formation from **1**-$\beta_2\gamma_2$, suggests an intimate mechanistic relationship between C–H insertion and olefin formation.

Experiments carried out in this laboratory several years ago showed that photolysis of 2-*n*-butylphenyldiazomethane (**1**) yields a variety of products[3] including the olefin *trans*-1-(*o*-tolyl)-2-butene (**7**). At that time an olefin-producing reaction of this type was without precedent, and no additional examples have been discovered in the intervening years. The present study is, therefore, a highly specialized one inasmuch as it deals with the mechanism of a reaction for which there is a single known example. The results, however, appear to have ramifications extending beyond this individual case.

In providing the groundwork for the present study, a careful reinvestigation of the photolysis of 2-*n*-butylphenyldiazomethane (**1**) in cyclohexane has substantiated, modified, and extended the earlier results. The presence of 2-ethylindan (**3**), 2-methyltetralin (**4**), benzosuberan (**5**), and *trans*-1-(*o*-tolyl)-2-butene (**7**) was substantiated; a compound tentatively identified in the earlier report as 2-*n*-butyltoluene has been shown instead to be 1-*n*-propylbenzocyclobutene (**2**); in addition to the trans olefin **7** some of the cis isomer **8** is also present, and in addition to the intramolecular C–H insertion products the intermolecular insertion product 1-*n*-butyl-2-cyclohexylmethylbenzene (**6**) is also formed. Shown to be absent in detectable amounts from the reaction mixture were the cis and trans isomers of 1-(*o*-tolyl)-1-butene and 1,2-di(*o*-*n*-butylphenyl)ethylene. The total yield of C–H insertion products and olefins is 78%, the remaining 22% assumed to be predominately the azine corresponding to 2-*n*-butylbenzaldehyde.

Direct *vs.* Photosensitized Decomposition. Two mechanistic possibilities for the olefin formation were entertained, *viz.* (a) a reaction involving a singlet carbene which effects an essentially simultaneous, concerted transfer of two hydrogens from the side chain to the methylene carbon and (b) a reaction involving a triplet carbene which engages in a stepwise transfer of two hydrogens from the side chain to the methylene carbon. In an attempt to distinguish between these possibilities, comparative reactions were carried out under conditions of direct irradiation and photosensitized irradiation. It is generally accepted that a carbene produced by direct irradiation is born in the singlet state, whereas a carbene produced in a photosensitized process is born in a triplet state.[4] If, then, insertion products and ole-

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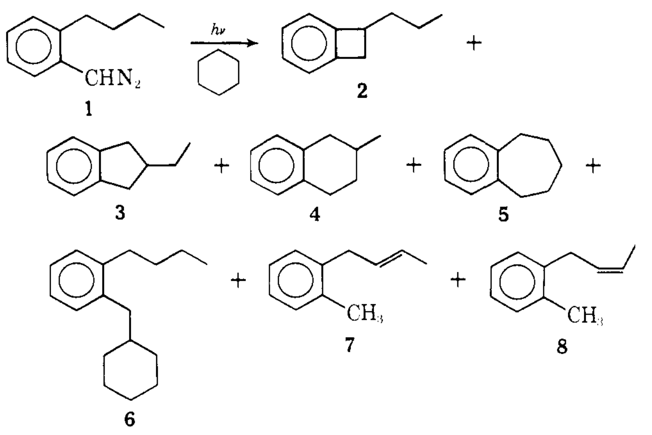
[1] Presented, in part, at the Midwest Regional Meeting of the American Chemical Society, Kansas City, Mo., Oct 29–30, 1969.

[2] NDEA Trainee, 1968–1969.

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

[4] For example, G. Herzberg (*Proc. Roy. Soc., Ser. A*, **262**, 291 (1961)) demonstrated, *via* flash photolysis techniques using direct irradiation, that diazomethane decomposes to a singlet which subsequently undergoes intersystem crossing to a triplet. Several workers have shown that the stereospecificity of addition of a carbene to an olefin



fins are formed from the same species, *i.e.* a singlet, there should be no change in product ratio between the direct and photosensitized irradiations, but if they are formed from different species, *i.e.* singlet and triplet, respectively, different product ratios would be expected. In addition to possible differences in product ratio from the direct and sensitized irradiations, differences in the product yield (particularly C–H insertion products) and differences in the stereospecificity of addition to *cis*- and *trans*-2-butene were also anticipated. It came as a surprise, therefore, to find that virtually no difference was observed in any of these respects when the direct and benzophenone-sensitized photolyses of **1** were compared (see Table I).

Table I. Product Ratios for Direct Irradiation of 2-*n*-Butylphenyldiazomethane and Its β-Dideuterio, γ-Dideuterio, and $\beta\gamma$-Tetradeuterio Analogs

Diazo compd	Products (molar product ratios)						
	2	3	4	5	6	7	8
1 (direct $h\nu$)	2.0	31.6	21.5	2.2	36.9	4.3	1.4
1 (sens $h\nu$)	1.7	36.1	20.6	2.8	32.5	4.7	1.6
1-β_2	3.2	12.8	28.2	2.9	50.5	1.8	0.6
1-γ_2	3.4	32.4	14.0	2.4	43.3	3.4	1.1
1-$\beta_2\gamma_2$	2.1	14.3	20.5	3.6	58.4	0.9	0.3

Several explanations for the identity of product yield, product ratio, and stereospecificity of olefin addition in the direct and photosensitized reactions can be advanced. It is possible that triplet carbene is being formed in both instances, the result of interaction with triplet benzophenone in the sensitized case and intersystem crossing of the excited diazoalkane singlet in the direct irradiation. Triplet carbene species, however, are thought to be rather ineffective in C–H insertion reactions,[5] particularly for such unreactive bonds as those in cyclohexane. This rationalization, therefore, seems unlikely. Conversely, it is possible that singlet carbene is being formed in both instances, the result of interaction with singlet benzophenone in the sensitized reaction and the decomposition of excited diazoalkane singlet in the direct irradiation. Transfer of energy from the short-lived excited benzophenone singlet, however, would probably require the benzophenone and diazo compound to be complexed in the ground state. No indication for such complexing was revealed by studies of the visible, ultraviolet, and nmr spectra of solutions over a wide range of concentrations. The trivial explanation that benzophenone is not acting as a sensitizer was discarded on the basis of (a) the markedly lower rate of decomposition of **1** in the absence of benzophenone at 365 nm (absorption by **1** at 365 nm is very low), (b) the mutual rate diminution in the photodecomposition of **1** and the photoisomerization of trans stilbene in mixtures containing **1**, benzophenone, and trans stilbene, and (c) the failure to observe benzopinacol formation from photolysis mixtures containing **1** and benzophenone.[6] Although the possibility for the radiationless excitation of **1** to an excited singlet *via* energy transfer from triplet benzophenone in a resonance transfer mechanism[8] cannot be entirely excluded, the molar absorptivity of **1** in the region of overlap with the phosphorescence spectrum of benzophenone is probably too low (*ca.* 35) to make this an effective process. In the face of these considerations the hypothesis that singlet species are responsible for both the direct and sensitized product mixture seems unlikely.

Even less likely is the proposition that in this particular system the singlet and triplet species behave in an identical manner. That they do not do so in other systems has been amply illustrated, and there is nothing in the structure of **1** that suggests the likelihood of such an extraordinary circumstance. On the basis of the presently available data, then, the most acceptable hypothesis asserts that an equilibrium is rapidly established between singlet and triplet species. If the rate of this equilibration is faster than any subsequent reaction, the mode of formation (*i.e.* direct or photosensitized irradiation) of the carbene (*i.e.* the set of equilibrating spin states) need not be reflected in the product mixture. Similar explanations have recently been advanced to interpret certain aspects of carbene addition and insertion reactions.[9–11]

Thus, it is suggested that direct irradiation of **1** yields the singlet species **9**, that benzophenone-sensitized irradiation of **1** yields the triplet species **10**, and that **9**

is lower when the carbene is produced by photosensitized irradiation, presumably a consequence of the formation of the triplet rather than the singlet.

(5) Whether or not triplet methylene is capable of direct C–H insertion, however, is still an unsettled issue. D. F. Ring and B. S. Rabinovitch (*Can. J. Chem.*, **46**, 2435 (1968)) have adduced evidence that at least a minor pathway in the C–H insertion of methylene (produced by photolysis of diazomethane in a large excess of inert nitrogen gas) with propane and butanes involves the triplet species. H. M. Frey and R. Walsh (*Chem. Commun.*, 158 (1969)) suggest, on the other hand, that in the mercury-sensitized photolysis of ketene in neopentane the C–H insertion products arise from singlet methylene in the system, a proposition also supported by work of D. C. Montague and F. S. Rowland (*J. Phys. Chem.*, **72**, 3705 (1968)). Frey and Walsh suggest the possibility of a collisionally induced spin inversion whereby triplet methylene changes to singlet methylene, a proposal in keeping with that suggested in explanation of the results of the present work.

(6) The photoreduction of a cyclohexane solution of benzophenone to benzopinacol and cyclohexylcyclohexane has been shown by W. M. Moore, G. S. Hammond, and R. P. Foss (*J. Amer. Chem. Soc.*, **83**, 2789 (1961)) to occur readily at 365 nm but to be curtailed in the presence of stilbene, a species known to effectively quench benzophenone triplet.[7]

(7) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and J. C. Dalton, *ibid.*, **86**, 3197 (1964).

(8) See A. F. Vaudo and D. M. Hercules (*ibid.*, **92**, 3574 (1970)) for leading references and a discussion of this phenomenon.

(9) T. W. Eder and R. W. Carr, *J. Phys. Chem.*, 73, 2074 (1969); Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, Phys 111; *J. Chem. Phys.*, **53**, 2258 (1970).

(10) G. L. Closs, *Top. Stereochem.*, **3**, 193 (1968).

(11) R. A. Moss (*Chem. Eng. News*, 47 (25), 60 (1969)) has noted the insensitivity of the reactions of phenylcarbene to the inert diluent effect which, in most other instances, gives rise to altered product ratios as the result, presumably, of changes in singlet to triplet population.

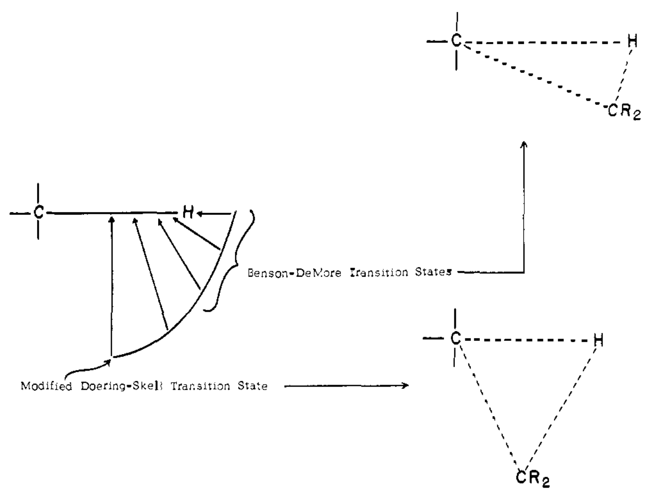
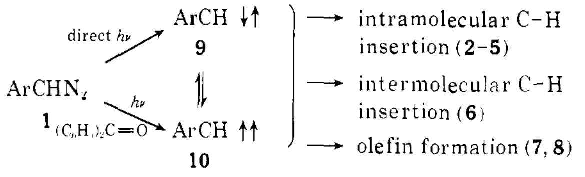


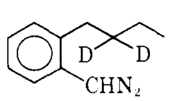
Figure 1. Comparison of Benson-DeMore and Doering-Skell transition states.

and **10** equilibrate before reacting *via* intramolecular C-H insertion, intermolecular C-H insertion, or hydrogen transfer processes. Unfortunately, this circumstance negates the original aim of using the comparison of the direct and sensitized photolyses as a means for deciding whether the various products arise from the same or different spin states.

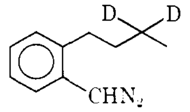


Attempts were made to substantiate the "multiplicity equilibration" hypothesis by studying the temperature dependence of the addition of the carbene from **1** (*i.e.* **9** and/or **10**) to *cis*-2-butene and by studying the effect of oxygen on the reaction. No temperature dependence of the stereoselectivity down to −72° was noted. However, if stereoselectivity of addition were to increase with diminishing temperature—a behavior, in fact, observed in the case of diphenylmethylene[10]—no significant change would be expected, since at room temperature the addition occurs with 99% retention of configuration. When **1** was decomposed by direct irradiation in the presence of oxygen the yields of products **2–8** were reduced by a factor of four, but the product ratio was essentially unaltered; an additional product, 2-*n*-butylbenzaldehyde, was formed in high yield.[12] Similarly, a benzophenone-sensitized decomposition of **1** in the presence of oxygen gave a fourfold reduction in yield but an unaltered product ratio, providing additional support for an equilibrating set of singlet and triplet species. Further work is necessary before the effect of oxygen on the reaction can be adequately interpreted, however.

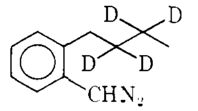
Decomposition of Deuterated Analogs of 1. Turning to another approach for discerning differences between the processes leading to insertion products and to olefins, three deuterated analogs, designated as **1**-β_2, **1**-γ_2, and **1**-$\beta_2\gamma_2$, of **1** were prepared according to the methods described in a later section. Decompositions by direct irradiation (Pyrex filter) were effected, and the results from these experiments, along with those from **1** itself, are recorded in Table I. Accepting the assumption of Kirmse and coworkers[13] that the relative yields of carbene-derived products are directly proportional to their relative rates of formation, the isotope effects were calculated by using 1-*n*-butyl-2-cyclohexylmethylbenzene (**6**) as the standard for comparison. For instance, k_H/k_D for insertion at C_β = (**3** from **1**/**6** from **1**)/(**3** from **1**-β_2/**6** from **1**-β_2) = (31.6/36.9)/(12.8/50.5) = 3.4. Alternatively, the k_H/k_D for insertion at C_β can be calculated using **1**-$\beta_2\gamma_2$ as the reference, *viz.* (**3** from 1-γ_2/**6** from 1-γ_2)/(**3** from 1-$\beta_2\gamma_2$/**6** from 1-$\beta_2\gamma_2$) = (32.4/43.3)/(14.3/58.4) = 3.1. In similar fashion, the k_H/k_D for insertion at C_γ was calculated to be 1.8 with **6** as the reference and 1.6 with **1**-$\beta_2\gamma_2$ as the reference, and the k_H/k_D for olefin formation was calculated to be 3.3 from **1**-β_2, 1.5 from **1**-γ_2, and 7.2 from **1**-$\beta_2\gamma_2$ using **6** as the reference.



1-β_2



1-γ_2



1-$\beta_2\gamma_2$

The values for k_H/k_D for C-H insertion reported in the literature[13-15] range from 1.18 (intramolecular insertion to form a cyclopropane[14]) to 1.96 (intermolecular allylic insertion[15]). None of these experiments involved an arylcarbene, however, so to provide a comparison point for the present results, the k_H/k_D for C-H insertion by phenylcarbene into cyclohexane was measured and found to be 2.1. Thus, the k_H/k_D of 1.6–1.8 for the intramolecular insertion into C_γ of **1** to form **4** is "normal," but that of 3.1–3.4 for insertion into C_β to form **3** is considerably higher than any previously recorded values. The following interpretation for this difference is advanced. According to the modified[16] Doering-Skell representation of the transition state for C-H insertion,[17] the preferred mode of approach by the carbene to the C-H bond is along a pathway perpendicular to the bond axis and midway between the carbon and hydrogen. This geometry is easily attained with respect to the C-H bond at C_γ, and the perpendicular pathway distance can be as little as 0.6 Å. For insertion at C_β, however, the minimum perpendicular pathway distance is 2.1 Å because of the inflexibility of the side chain. A "skewed" trianglular transition state, on the other hand, allows the distance between the carbene and the C-H bond to be reduced to the values indicated in Figure 1. Thus, the lowest energy transition state in this case may not be the one in which the triangle is isosceles but one in which it is less regular—*i.e.* a transition state in which the carbene is closer to the hydrogen than to the carbon. It is the more extreme examples of this situation that we assume to be what is implied by the

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[12] *Cf.* W. Kirmse, L. Horner, and H. Hoffmann (*Justus Liebigs Ann. Chem.*, **614**, 19 (1958)) who showed that diphenyldiazomethane undergoes photolysis in the presence of oxygen to form benzophenone.

[13] W. Kirmse, H.-D. v. Scholz, and H. Arold, *ibid.*, 711, 22 (1968).

[14] J. P. Chesick and M. R. Willcott, *J. Phys. Chem.*, 67, 2850 (1963).

[15] J. W. Simons and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, **85**, 1023 (1963).

[16] C. D. Gutsche, G. L. Bachman, W. Udell, and S. Bäuerlein, *ibid.*, **93**, 5172 (1971).

[17] P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956); W. von E. Doering and H. Prinzbach, *Tetrahedron*, 6, 24 (1959).

Benson–DeMore picture of the transition state for the C–H insertion process[18] for which it is stated that "the high efficiency of the insertion reaction is best explained by considering attack by methylene on the hydrogen atom rather than on the electrons of the C–H bond. . . ." The rather low values for the deuterium isotope effect in intermolecular C–H insertion reactions are commensurate with the Doering–Skell transition state in which there is a minimum of C–H bond stretching. As the geometry is skewed in the direction of a Benson–DeMore transition state, however, an increased degree of C–H bond stretching might be anticipated, and this would be reflected in a larger deuterium isotope effect. A corollary to this assertion is the prediction that the energy of activation for insertion at C_β should be greater than that for insertion at C_γ. Studies of the ratio of **3**/**4** as a function of temperature show, indeed, that this is the case, the ratio changing from 1.16 at −60° to 1.33 at 25° and 1.53 at 80°.[3]

The deuterium isotope effect for the formation of **2** from **1**-β_2 is 3.1–3.4, and that for the formation of olefins from **1**-β_2 is 3.3. The deuterium isotope effect for the formation of **3** from **1**-γ_2 is 1.6–1.8, and that for the formation of olefins from **1**-γ_2 is 1.5. The deuterium isotope effect for the formation of olefins from **1**-$\beta_2\gamma_2$ is 7.1, slightly greater than the product of the isotope effects from **1**-β_2 and **1**-γ_2. The close similarity of isotope effect for the formation of the C–H insertion products and the olefin may, of course, be fortuitous, but it suggests that there is an intimate mechanistic relationship between the two processes. Thus, on the fairly well-founded premise that the C–H insertion process involves a singlet carbene, it is postulated that the olefin-forming process also involves a singlet carbene. It is not yet known whether the latter is a truly concerted reaction in which the side chain of **1** adopts a conformation such that the hydrogens at C_β and C_γ are positioned in an unsymmetrical and symmetrical fashion, respectively, with respect to the carbene carbon as shown in Figure 2. Work is continuing in an effort to provide companions for the reaction involving the formation of olefin from **1** which, it is hoped, will provide additional insight into this type of reaction.

Preparation of Deuterated Analogs of 1. The method of choice for the preparation of **1**-β_2 and **1**-γ_2 involved the action of *n*-propylmagnesium bromide (deuterated at the α or β position) with *o*-bromobenzaldehyde to yield the alcohol **11**. Removal of the hydroxyl group by treatment with thionyl chloride followed by lithium aluminum hydride yielded the bromide **12** which was converted to the aldehyde **13** *via* the action of ethyl orthoformate on the derived Grignard reagent. The aldehyde was then transformed to the diazo compound by conversion to the hydrazone followed by oxidation with manganese oxide.

The aldehyde necessary for the preparation of **1**-$\beta_2\gamma_2$ was prepared by deuterium reduction of 1-*o*-bromo-2-propyne (**15**), obtained by the action of propynylmagnesium bromide on the tosylate of *o*-bromobenzyl alcohol (**14**). When the deuteration was carried out under homogeneous conditions using tris(triphenyl phosphine)chlororhodium as the catalyst, hydrogen exchange reactions were encountered, in agreement with other recent reports.[19] This difficulty was circumvented through the use of deuteriodiimide as the reducing agent, and the tetradeuterio compound **16** was obtained with deuterium only in the β and γ positions.

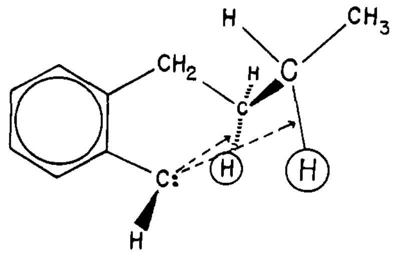
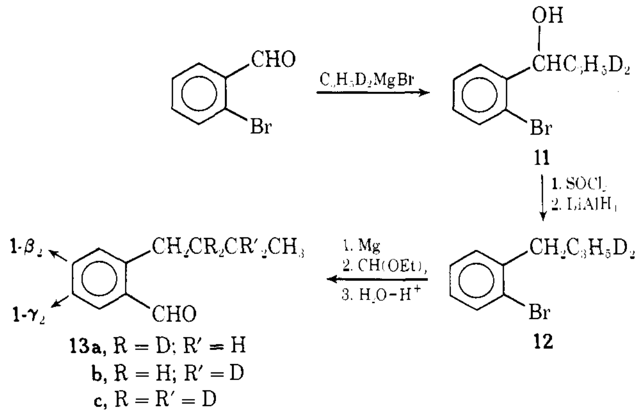
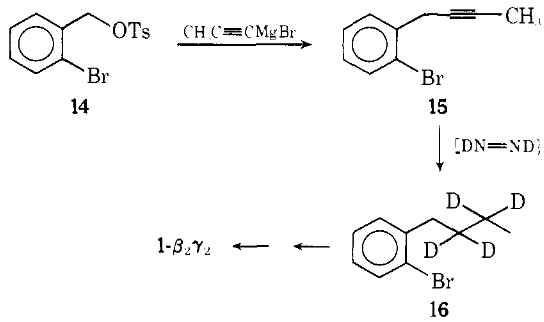


Figure 2. "Mechanism" of olefin formation.





Summary. On the basis of the data presented in this and the previous paper[16] it is postulated that: (a) the preferred pathway for C–H insertion is along an axis perpendicular to the C–H bond at its midpoint; (b) if geometric constraints are present other pathways are available but require a closer approach of the carbene and a greater C–H stretching in the activated complex; (c) the singlet and triplet states of phenylcarbenes equilibrate with each other more rapidly than they undergo the C–H insertion, C=C addition, or olefin formation; (d) the olefin-forming reaction involves a singlet carbene and is a one- rather than a two-step process.

Experimental Section[20]

Preparation of 2-*n*-Butylphenyldiazomethane (1). A 1.000-g sample (0.006 mol) of 2-*n*-butylbenzaldehyde in 15 ml of ether was

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[18] S. W. Benson and W. B. DeMore, *Advan. Photochem.*, **2**, 219 (1964).

[19] A. A. Hussey and Y. Takeuchi, *J. Amer. Chem. Soc.*, **91**, 672 (1969); W. Voelter and C. Djerassi, *Chem. Ber.*, **101**, 58 (1968).

[20] All melting points and boiling points are uncorrected. The infrared spectra were measured on a Perkin-Elmer Infracord instru-

added, all at once, to a mixture of 4 g (0.125 mol) of 95% hydrazine in 15 ml of ether at 0°. The mixture was stirred at 0° for 1 hr and at room temperature overnight. Evaporation of the ether at aspirator pressure and the excess hydrazine at vacuum pump pressure left a residue which was dissolved in 50 ml of cyclohexane and treated with 4 g of activated manganese dioxide.[21] This mixture was stirred for 4 hr at room temperature in the dark, the solid was removed by filtration, and the filtrate was diluted to a known volume of cyclohexane. The yield of diazo compound, assayed by adding a measured excess of benzoic acid and back-titrating the unused portion, generally ranged from 60 to 70%: uv (cyclohexane) 282 (ϵ 22,000), 487 nm (ϵ 35).

Photolysis of 2-*n*-Butylphenyldiazomethane (1). (a) Identification of Products. 2-*n*-Butylphenyldiazomethane, prepared in 63% yield from 0.6286 g (3.9 mmol) of 2-*n*-butylbenzaldehyde, was dissolved in 100 ml of cyclohexane and treated with 0.286 g of diphenyl ether (added as an unreactive, internal standard). One-half of this solution was photolyzed by direct irradiation (Pyrex filter) and the other half was evaporated, dissolved in methanol, and treated with a few drops of sulfuric acid. Glc analysis of the latter revealed almost no material with the retention time corresponding to 2-*n*-propylbenzocyclobutene (previously[2] thought to be 2-*n*-butyltoluene), indicating that this material is not present before photolysis. The photolysate solution was concentrated, and the residue was passed through glc column 1.[20] One of the constituents was isolated and shown to be 2-*n*-propylbenzocyclobutene (**2**) by comparison of its ir spectrum with that of an authentic sample of **2**.[2] Another of the components, previously identified as 2-ethylindan (**3**), was isolated, dissolved in methanol, treated with hydrogen and 10% palladium on charcoal, and stirred for 2 days. Glc analysis of the product revealed the presence of unchanged 2-ethylindan along with 2-*n*-butyltoluene in an amount corresponding to *ca.* one-third the amount of *trans*-1-(*o*-tolyl)-2-butene (**7**) formed in the reaction. This reducible component was identified as *cis*-1-(*o*-tolyl)-2-butene (**8**) on the basis of (a) the low uv absorption of this fraction and (b) the close similarity of the vinyl region of the nmr spectrum of this fraction with that of an authentic sample of **8**. A second fraction of somewhat longer retention time was isolated and identified as 1-*n*-butyl-2-cyclohexylmethylbenzene (**6**): ir (liq) 1600 (Ar), 1380 ($C-CH_3$), 750 cm^{-1} (1,2-disubstituted Ar); nmr (CCl_4) δ 0.70–1.95 (m, 18), 2.37–2.80 (m, 4, ArCH_2), 6.99 ppm (s, 4, Ar*H*).

Anal. Calcd for $C_{17}H_{26}$: C, 88.63; H, 11.37. Found: C, 88.62; H, 11.42.

(b) Product Ratios from Direct Irradiation. A solution of **1**, obtained in 63% yield from 0.3143 g of 2-*n*-butylbenzaldehyde, in 90 ml of cyclohexane containing 0.0143 g of diphenyl ether (as an unreactive, internal standard to permit the determination of yields) was irradiated for 1.5 hr with light from a 450-W Hanovia lamp filtered through Pyrex. The product obtained in 78% yield based on **1** was analyzed on glc column 1[20] and shown to contain 1.9 ± 0.14% **2**, 30.7 ± 0.92% **3** (containing some **8**), 20.0 ± 0.6% **4**, 2.0 ± 0.28% **5**, 41.5 ± 2.07% **6**, and 4.0 ± 0.24% **7**, the accuracies based on four replicated determinations in each case. Correcting these values for molecular weight differences and for detector responses (**3** = 100, **4** = 89, **5** = 97, **6** = 76, **7** = 102) gave the following mole percentage values: 2.0 of **2**, 33.0 of **3**, 21.5 of **4**, 2.2 of **5**, 36.9 of **6**, and 4.3 of **7**. Knowing the 2-ethylindan fraction to contain an amount of **8** equal to one-third the amount of **7** (*viz.* 1.4) changes the value of **3** to 31.6 (see Table I).

(c) Product Ratios from Photosensitized Irradiation. The 365-nm emission of a Hanovia 550-W medium-pressure mercury arc lamp was isolated by means of the combined filters: (a) 16.9-mm pathlength of cupric sulfate solution, (b) Corning glass filter 7-37 (5860), and (c) 10-mm pathlength of 0.010 g of 2,7-dimethyl-3,6-diazocyclohepta-1,6-diene perchlorate in 100 ml of water.[22] A stock solution was prepared by dissolving **1**, obtained in 65% yield from 2.2050 g of 2-*n*-butylbenzaldehyde, in 450 ml of cyclohexane. The absorbance of this solution at 487 nm was 0.790. Irradiation of a 100-ml aliquot of this solution with 365-nm light for 22 hr resulted in a decrease in absorbance to 0.624. A 22-hr irradiation with 365-nm light of another 100-ml aliquot to which 2.85 g of benzophenone had been added resulted in a decrease in absorbance to 0.049, and an additional 4.5 hr of irradiation reduced this to 0.021. A product assay as described above for the direct irradiation of **1** yielded the results recorded in Table I.

Photolysis of 2-*n*-Butylphenyldiazomethane in the Presence of 2-Butenes. (a) Addition of *trans*-2-Butene *via* Direct Irradiation. A solution containing **1** from 1.55 g of 2-*n*-butylbenzaldehyde in 260 ml of cyclohexane and 25 ml of petroleum ether (bp 63–69°, added to depress the melting point of the mixture) was deaerated with nitrogen, cooled to −7°, treated with 78 ml of *trans*-2-butene, and irradiated for 18 hr with a 100-W Hanovia medium-pressure mercury arc lamp suspended in a Pyrex well. Glc assay of the product showed that, in addition to compounds **2–8**, *trans*-1,2-dimethyl-3-(2-*n*-butylphenyl)cyclopropane was formed, but no *syn*- or *anti*-*cis*-1,2-dimethyl-3-(2-*n*-butylphenyl)cyclopropane could be detected.

(b) Addition to *cis*-2-Butene *via* Direct Irradiation. In similar fashion, a reaction of **1** with *cis*-2-butene was shown to yield compounds **2–8**, and a mixture of *syn*- and *anti*-*cis*-1,2-dimethyl-3-(2-*n*-butylphenyl)cyclopropane accompanied by the trans isomer in an amount corresponding to 1% of the cis isomers.

(c) Addition to *cis*- and *trans*-2-Butene *via* Photosensitized Irradiation. Using 365-nm light, obtained as described above, photolysis was carried out on a cooled solution of **1**, obtained in 64% yield from 0.4454 g of 2-*n*-butylbenzaldehyde, in 70 ml of cyclohexane and 7 ml of petroleum ether (bp 63–69°) to which 1.70 g of benzophenone and 23 ml of *trans*-2-butene were added. After a 53-hr irradiation the product was assayed and found to contain compounds **2–8** and *trans*-1,2-dimethyl-3-(2-*n*-butylphenyl)cyclopropane but none of the corresponding syn or anti-cis isomers. In similar fashion an experiment using *cis*-2-butene was carried out, and the product was shown to contain compounds **2–8**, the *syn*- and *anti*-*cis*-1,2-dimethyl-3-(2-*n*-butylphenyl)cyclopropanes, and the trans isomer in an amount corresponding to 2% of the cis isomers.

Photolyses in the Presence of Oxygen. A stock solution of **1**, prepared from 2.4473 g of 2-*n*-butylbenzaldehyde, in 800 ml of cyclohexane containing 0.61009 g of diphenyl ether was divided into several portions which were treated in the following manner. Passage of oxygen through a solution in the dark resulted in no decrease in the concentration of **1**, as measured by the absorption intensity at 487 nm. Passage of purified nitrogen[23] through an irradiated solution showed a decrease in absorptivity from 0.460 to 0.044 in 480 min. Passage of oxygen through an irradiated solution showed a decrease in absorptivity from 0.460 to 0.030 in 285 min. Comparison of the products from these reactions with those from a reaction in which oxygen was passed through a solution containing benzophenone and irradiated with 365 nm light gave the following results.

Product	Direct:N_2	Direct:O_2	Photo-sensitized: O_2
2-Ethylindan (**3**)	0.80	0.23	0.18
2-*n*-Butylbenzaldehyde	0.12	0.99	1.43
Diphenyl ether	1.00	1.00	1.00

Photolysis of Deuterated 2-*n*-Butylphenyldiazomethanes (1-β_2, 1-γ_2, 1-$\beta_2\gamma_2$). The photolyses of the deuterated analogs of **1** were carried out as described above for **1** itself. For instance, a solution of 2-(2,2-dideuterio-*n*-butyl)phenyldiazomethane (**1**-β_2), prepared in 50% yield from 0.6810 g of the corresponding aldehyde in 200 ml of cyclohexane, was placed in the photolysis apparatus, deaerated with nitrogen, and irradiated (Pyrex filter) at 25° for 1 hr. The cyclohexane was removed by slow distillation through a 6-in. Vigreux column, 0.0619 g of diphenyl ether was added to the residue, and the product was analyzed by glc on column 1[20] to give product ratios which were corrected for molecular weight differences and detector response differences, as described above. In similar fashion 2-(3,3-dideuterio-*n*-butyl)phenyldiazomethane (**1**-γ_2) and

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ment. The nmr spectra were measured on a Varian A-60A spectrometer; the resonances are expressed in parts per million downfield shift from tetramethylsilane, present as an internal reference. Glc analyses employed (a) column 1 consisting of a 20.5 ft × 0.25 in. column packed with 15% w/w neopentylglycol sebacate polymer on 40–50 mesh ABS Anakrom; (b) column 2 consisting of a 9 ft × 0.5 in. column packed with 20% w/w Carbowax 1540 on 45–50 mesh RZ Gaschrom. Mass spectral analyses were carried out on a Varian M-66 instrument. Microanalyses were performed by Dr. Josef Zak, Mikroanalytisches Laboratorium, Vienna, Austria. All photolyses, unless otherwise noted, were performed under nitrogen at atmospheric pressure in a thoroughly deaerated system.

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2-(2,2,3,3-tetradeuterio-*n*-butyl)phenyldiazomethane (**1-$\beta_2\gamma_2$**) were photolyzed. The results from these runs are recorded in Table I.

Photolysis of Phenyldiazomethane. (a) In Cyclohexane–Cyclopentane. A solution was prepared containing phenyldiazomethane, obtained in 59% yield from 0.5452 g of redistilled benzaldehyde by manganese oxide oxidation of the corresponding hydrazone, in 50 ml of cyclopentane. A 14.44-g sample of this solution was mixed with 8.74 g (0.104 mol) of cyclohexane, and the solution was deaerated with nitrogen and then irradiated for 4 hr with a Hanovia 550-W medium-pressure mercury arc lamp. Analysis of the product showed that the ratio of benzylcyclohexane to benzylcyclopentane was 0.601 ± 0.002.

(b) In Perdeuteriocyclohexane–Cyclopentane. A 14.44-g sample of the solution described above was mixed with 9.99 g (0.104 mol) of cyclohexane-d_{12} and irradiated under identical conditions to give a product in which the ratio of benzylcyclohexane to benzylcyclopentane was 0.286 ± 0.011. The value of k_H/k_D for insertion into cyclohexane is 0.601/0.286 = 2.1.

Preparation of 2-(2,2-Dideuterio-*n*-butyl)benzaldehyde (13a). Following, with modifications, a published procedure,[24] an 8.4-g (0.064 mol) sample of propionic anhydride was reduced with 3.0 g (0.071 mol) of lithium aluminum deuteride in 150 ml of ether. After the addition of a solution of 5 ml of concentrated sulfuric acid in 70 ml of water, the white, aqueous mixture (pH 3) was continuously extracted for 45 hr to give a product which, after distillation through a 12-in. Vigreux column, yielded 6.9 g (86%) of pure product: bp 91–93° (760 mm); nmr (CCl_4) δ 0.88 (t, 3, J = 7.1 Hz, CH_3), 1.51 (q, 2, J = 7.1 Hz, CH_2), 4.71 ppm (s, 1, OH). A 6.3-g sample was treated with phosphorus tribromide, and 9.2 g (72%) of 1-bromo-1,1-dideuteriopropane was collected after distillation: nmr (CCl_4) δ 1.03 (t, 3, J = 7.1 Hz, CH_3), 1.88 ppm (q, 2, J = 7.1 Hz, CH_2); mass spectrum 97.0% d_2, 3.0% d_1. An 8.7-g sample of the bromide was converted to the Grignard reagent which was treated with 13.0 g of 2-bromobenzaldehyde. Distillation of the crude product yielded 1.4 g with bp 52–76° (0.09 mm), consisting of 2-bromobenzaldehyde, and 10.42 g with bp 76–82° (0.10 mm) containing 66 mol % 1-(2-bromophenyl)-2,2-dideuterio-1-butanol (46% yield) and 34 mol % 2-bromobenzyl alcohol. A 5.06-g sample of this mixture was treated with 3.8 g of thionyl chloride, 2.3 g of pyridine, and 30 ml of benzene to form the corresponding chloro compound, and this was then mixed with 3.5 g of lithium aluminum hydride in 60 ml of tetrahydrofuran. The mixture was heated just below reflux temperature for 1.25 hr, stirred at room temperature for 45 min, and worked up to give, after distillation, 2.07 g with bp 100–120° from which a pure sample of 1-(2-bromophenyl)-2,2-dideuteriobutane was obtained by glc separation on column no. 2[20]: ir (liq) 2200, 2110 (C-D), 1595 (Ar), 1380 (C-CH_3), 752 cm^{-1} (1,2-disubstituted Ar); nmr (CCl_4) δ 0.93 (t, 3, J = 7.1 Hz, CH_3), 1.40 (q, 2, J = 7.1 Hz, CH_2), 2.69 (s, 2, ArCH_2), 6.66–7.58 ppm (m, 4, ArH). A solution containing 2.12 g of the pure bromo compound and 1.4 g of ethyl bromide in 10 ml of ether was added to a mixture containing 0.995 g of magnesium, 1.8 g of ethyl bromide, 1 crystal of iodine, and 65 ml of ether. After the mixture had refluxed under nitrogen for 21 hr, 13.5 g of triethylorthoformate was added, and refluxing was continued until it turned white (*ca.* 58 hr). Water was added, the organic material was extracted into ether, the ether was evaporated, and the residue was dissolved in 5 ml of dioxane and 35 ml of water containing 3 ml of sulfuric acid. This mixture was heated in an atmosphere of nitrogen for 10 hr just below reflux temperature. The product was worked up to yield 1.35 g (83%) of 2-(2,2-dideuterio-*n*-butyl)-benzaldehyde (**13a**): bp 86–87° (17 mm); ir (liq) 2790 (aldehyde C-H), 2210, 2120 (C-D), 1700 (C=O), 1600 (Ar), 1380 (C-CH_3), 757 cm^{-1} (1,2-disubstituted Ar); nmr (CCl_4) δ 0.88 (t, 3, J = 7.0 Hz, CH_3), 1.37 (q, 2, J = 7.0 Hz, CH_2), 2.95 (s, 2, ArCH_2), 7.00–7.88 (m, 4, ArH), 10.10 ppm (s, 1, CHO).

Preparation of 2-(3,3-Dideuterio-*n*-butyl)benzaldehyde (13b). Following a literature procedure,[25] methylmalonic acid was repeatedly washed with deuterium oxide–dioxane. The deuterated material was pyrolyzed to yield 2,2-dideuteriopropionic acid which was reduced with lithium aluminum hydride to 2,2-dideuterio-1-propanol, obtained in 67% overall yield. Conversion to the bromide (mass spectrum 97% d_2 and 3% d_1) and then to **13b** following the sequence described above, gave a colorless liquid: bp 73–74° (1.4 mm); ir (liq) 2790 (aldehyde C-H), 2200, 2120 (C-D), 1700 (C=O), 1600 (Ar), 1380 (C-CH_3), 757 cm^{-1} (1,2-disubstituted Ar); nmr (CCl_4) δ 0.89 (s, 3, CH_3), 1.51 (t, 2, J = 7.1 Hz, CH_2), 2.78–3.13 (m, 2, ArCH_2), 6.91–7.73 (m, 4, ArH), 9.99 (s, 1, CHO).

Preparation of 2-(2,2,3,3-Tetradeuterio-*n*-butyl)benzaldehyde (13c). Following a literature procedure,[26] 2-bromobenzyl alcohol[27] was treated with *p*-toluenesulfonyl chloride and powdered potassium hydroxide in ether at −8° to yield 91.5% of a white solid, mp 72–81°, which was crystallized from petroleum ether (bp 79–81°)–benzene (3:1) to give material with mp 79–81° (lit.[28] 80.5–81.5°). To a solution of propynylmagnesium bromide, prepared from 15 g of propyne, a solution of 136.5 g (0.400 mol) of 2-bromobenzyl tosylate in 400 ml of tetrahydrofuran was added dropwise. The mixture was then refluxed overnight and worked up by hydrolysis and distillation to yield 76.6 g of a fraction containing 34 mol % 1-(2-bromophenyl)-2-butyne (**15**) and 66 mol % 2-bromobenzyl bromide. The latter was separated by refluxing the mixture with pyridine for 24 hr and dissolving the 2-bromobenzylpyridinium bromide in water. The residue was distilled to yield 22.4 g (97%) of **15**: bp 146–148° (29 mm); ir (liq) 1600 (Ar), 750 cm^{-1} (1,2-disubstituted Ar); nmr (CCl_4) δ 1.79 (t, 3, J = 2.6 Hz, CH_3), 3.53 (q, 2, J = 2.6 Hz, CH_2), 6.72–7.64 ppm (m, 4, ArH).

Anal. Calcd for $C_{10}H_9Br$: C, 57.44; H, 4.34; Br, 38.22. Found: C, 57.35; H, 4.17; Br, 38.27.

A 234-g sample (1.26 mol) of *p*-toluenesulfonylhydrazine in 4 l. of toluene, distilled from lithium aluminum hydride, was placed in a 5-l. round-bottomed flask equipped with an addition funnel and a Dean–Stark trap, and the temperature was increased until the mixture became homogeneous (*ca.* 80°). The system was flushed with nitrogen and 100 g of deuterium oxide was added. The mixture was then maintained at reflux temperature until all of the H_2O-D_2O had collected in the Dean–Stark trap. This procedure was repeated four additional times to ensure the complete replacement of all of the hydrogens of the *p*-toluenesulfonylhydrazine by deuterium. To this solution 65.9 g (0.315 mol) of 1-(2-bromophenyl)-2-butyne was added; the resulting solution was refluxed 18 hr (nitrogen evolution subsided after 9 hr). After most of the toluene had been removed by distillation at atmospheric pressure, the residue was taken up in water and extracted with benzene. The combined extracts were washed with 5% sodium bicarbonate solution and dried over magnesium sulfate. Removal of the drying agent and the benzene and distillation of the residue yielded a 46.8-g fraction, bp 123–129° (19 mm), consisting of 13.4 g of 1-(2-bromophenyl)-2,2,3,3-tetradeuteriobutane (**16**), 17.5 g of a cis,trans mixture of 1-(2-bromophenyl)-2,3-dideuterio-2-butene,[29] and 15.8 g of starting material. A sample of the pure tetradeuterio compound was obtained by glc separation of column 2[20] as a colorless oil: bp 108° (13.2 mm); ir (liq) 2205, 2120 (C-D), 1600 (Ar), 1380 (C-CH_3), 750 cm^{-1} (1,2-disubstituted Ar); mass spectrum 97% d_4. The tetradeuterioaldehyde **13c** was prepared from **16** by the procedure described above and obtained as a colorless oil: bp 89° (2.7 mm); ir (liq) 2780 (aldehyde C-H), 2200, 2120 (C-D), 1700 (C=O), 1600 (Ar), 752 cm^{-1} (1,2-disubstituted Ar); nmr (CCl_4) δ 0.92 (s, 3, CH_3), 3.00 (s, 2, CH_2), 7.08–7.89 (m, 4, ArH), 10.13 ppm (s, 1, CHO).

Preparation of Comparison Compounds. (a) *trans*-2,2′-Di-*n*-butylstilbene. A solution of **1**, prepared from 2.1 g of 2-*n*-butylbenzaldehyde, in 180 ml of cyclohexane was treated with 0.34 g of copper powder and heated at reflux for 4 hr. The major product, isolated by glc on column 1,[20] was a colorless oil: ir (liq) 1600 (Ar), 1380 (C-CH_3), 963 (*trans*-CH=CH), 755 cm^{-1} (1,2-disubstituted Ar); nmr (CCl_4) δ 0.70–1.83 (m, 14, $CH_2CH_2CH_3$), 2.70 (t, 4, J = 7.0 Hz, ArCH_2), 6.85–7.20 (m, 8, ArH), 7.21–7.60 ppm (m, 2, =CH).

Anal. Calcd for $C_{22}H_{28}$: C, 90.35; H, 9.65. Found: C, 90.59; H, 9.74.

(b) 1-(*o*-Tolyl)-1-butene. A mixture of 26 g (0.058 mol) of α-*o*-xylenetriphenylphosphonium bromide in 400 ml of ether was added to 60 ml of a 1.1 *M* solution of *n*-butyllithium (0.066 mol) in hexane, heated at reflux for 1 hr, cooled to −30°, and treated,

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[25] V. J. Shiner, Jr., and M. L. Smith, *ibid.*, **80**, 4095 (1958).

[26] J. R. Johnson, T. L. Jacobs, and A. M. Schwartz, *ibid.*, **60**, 1885 (1938).

[27] C. Mettler, *Chem. Ber.*, **39**, 2933 (1906).

[28] A. D. Mease, M. J. Strauss, I. Horman, L. J. Andrews, and R. M. Kaefer, *J. Amer. Chem. Soc.*, **90**, 1797 (1968).

[29] The formation of a trans olefin by diimide reduction of an alkyne has not been previously reported. Additional experiments (see T. A. Baer, Ph.D. Dissertation, Washington University, 1970) showed that it arises as the result of isomerization of the initially formed cis olefin.

dropwise, with 7 g (0.013 mol) of propionaldehyde in 25 ml of ether. The mixture was stirred overnight at room temperature and then worked up to give 3.2 g (38%), bp 87–91° (12.5 mm), consisting of a mixture of cis and trans isomers. The trans isomer of 1-(*o*-tolyl)-1-butene was separated by glc on column 1[20] and obtained as a colorless liquid: ir (liq) 1650 (C=C), 1600 (Ar), 1380 (C-CH_3), 964 (*trans*-CH=CH), 744 cm^{-1} (1,2-disubstituted Ar); nmr (CCl_4) δ 1.10 (t, 3, J = 7.1 Hz, CH_3), 2.55 (quintet-doublet of quartets, 2, J = 7.0 Hz, CH_2), 2.28 (s, 3, ArCH_3), 5.75–6.75 (m, 2, =CH), 6.95–7.45 (m, 4, Ar*H*).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.69; H, 9.56.

(c) ***trans*-1-(*o*-Tolyl)-2-butene (7).** 1-(*o*-Tolyl)-2-butyne was prepared in 58% yield by the action of *o*-tolylmagnesium bromide on 1-bromo-2-butyne and was obtained as a colorless liquid: ir (liq) 1600 (Ar), 1380 (C-CH_3), 743 cm^{-1} (1,2-disubstituted Ar); nmr (CCl_4) δ 1.79 (t, 3, J = 2.5 Hz, ≡C-CH_3), 2.24 (s, 3, ArCH_3), 3.36 (q, 2, J = 2.5 Hz, CH_2), 6.92–7.49 ppm (m, 4, Ar*H*).

Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.34; H, 8.24.

A 7.2-g sample of this material was dissolved in 50 ml of ether and added to a solution of 3.55 g of sodium in 150 ml of liquid ammonia. The mixture was stirred for 1.75 hr at the reflux temperature of ammonia, ammonium nitrate was added until the blue color disappeared, and the mixture was worked up to give a middle distillation fraction consisting of 2.9 g of almost pure *trans*-1-(*o*-tolyl)-2-butene (7). A pure sample was obtained by glc separation on column 1[20] as a colorless liquid: ir (liq) 1600 (Ar), 1380 (C-CH_3), 968 (*trans*-CH=CH), 745 cm^{-1} (1,2-disubstituted Ar); nmr (CCl_4) δ 1.65 (d, 2, J = 4.6 Hz, =CCH_3), 2.24 (s, 3, ArCH_2), 3.22 (d, 2, J = 4.6 Hz, CH_2), 5.25–5.62 (m, 2, =C*H*), 7.00 ppm (s, 4, Ar*H*).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.63; H, 9.46.

(d) ***cis*-1-(*o*-Tolyl)-2-butene (8).** Following a literature procedure,[30] a 1.135-g sample of 1-(*o*-tolyl)-2-butyne was dissolved in 25 ml of anhydrous methanol, treated with 0.133 g of 10% palladium on charcoal and 4 drops of quinoline, and hydrogenated at 20 psi. After 7 min the amount of hydrogen corresponding to 1 mol equiv of hydrogen had been absorbed, and the product was worked up to give virtually pure *cis*-1-(*o*-tolyl)-2-butene as a colorless liquid: ir (liq) 1660 (Ar), 1600 (Ar), 744 (1,2-disubstituted Ar), 690 cm^{-1} (*cis*-CH=CH); nmr (CCl_4) δ 1.62–1.80 (m, 3, =CCH_3), 2.23 (s, 3, ArCH_3), 3.20–3.44 (m, 2, CH_2), 5.17–5.83 (m, 2, =C*H*), 7.00 ppm (s, 4, Ar*H*).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.42; H, 9.44.

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Halogen Abstraction Studies. III. Free-Radical Abstraction of Iodine from Bridgehead Iodides[1,2]

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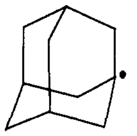
Abstract: The rate of abstraction of iodine from 1-iodoadamantane, 1-iodobicyclo[2.2.2]octane, 1-iodobicyclo[2.2.1]heptane, and *tert*-butyl iodide by the phenyl radical is reported relative to the rate of abstraction of bromine from bromotrichloromethane. All three bridgehead compounds are less reactive than *tert*-butyl iodide. The ease of formation of the adamantyl-1 radical is between that of a typical secondary radical and the *tert*-butyl radical, while the bicyclo[2.2.1]heptyl-1 radical parallels the methyl radical in stability. The intermediate bicyclo[2.2.2]octyl-1 radical resembles the adamantyl species more closely than it does the bicycloheptyl radical. A correction of the relative rates for the slight inductive effect of substituents allows a determination of the bond dissociation energies *D*(R–H) and *D*(R–I) for the bridgehead compounds.

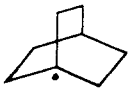
It is well established that the most stable configuration of carbonium ions is a planar, sp^2 hybridized form, while the most favorable geometry of unconjugated carbanions is generally accepted to be a rapidly inverting, pyramidal sp^3 form.[4] The unique position of free radicals, being electronically situated between these two species, has prompted considerable interest in recent years in determining the ease of formation and relative stabilities of the bridgehead free radicals **2**–**4**.[5–12]

$(CH_3)_3C\cdot$

1



2



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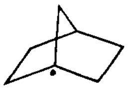

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From a study of the rate of bridgehead aldehyde decarbonylation Applequist and Kaplan[11] had con-

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