Chemistry of Bivalent Carbon Intermediates. V. Intramolecular Carbon–Hydrogen Insertion Reactions in Bridged Ring Systems Carrying Phenylcarbene Moieties[1]

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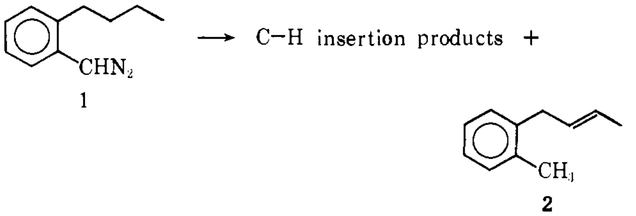
Abstract: The products obtained from 2-(*o*-methylenephenyl)bicyclo[2.2.1]heptane (**8**), produced by photolysis of 2-(*o*-diazomethylphenyl)bicyclo[2.2.1]heptane (**5d**) or by the base-induced decomposition at elevated temperature of the *p*-toluenesulfonylhydrazones of 2-(*o*-formylphenyl)bicyclo[2.2.1]heptane, have been found to be mixtures of C–H insertion products devoid of the olefin **9** that had been anticipated on the basis of earlier experiments. The major low-boiling constituent in the mixture formed from the carbene **8** is compound **15**, the result of insertion into the exo C–H bond at C-3. This result is interpreted in support of the Doering–Skell postulate which asserts that a triangular transition state is involved in the carbene C–H insertion process and in refutation of the Benson–DeMore postulate which asserts that the attack by the carbene is on the hydrogen. To accommodate the present results to the Doering–Skell postulate, however, a corollary is added which stipulates that the preferred pathway of attack on the C–H bond is perpendicular to the axis of that bond at its midpoint.

The decomposition of 2-*n*-butylphenyldiazomethane (**1**) has been shown to yield, presumably *via* a carbene intermediate, the C–H insertion products 2-*n*-propylbenzocyclobutene, 2-ethylindan, 2-methyltetralin, and benzosuberan.[3] In addition, a small amount of another product identified as 1-(*o*-tolyl)-2-butene (**2**) was isolated. With the intention of studying in more detail this unusual process whereby two hydrogen atoms are transferred to a carbene center, a compound was sought in which a phenylcarbene moiety is positioned in a semiflexible structure such that a pair of adjacent hydrogen atoms can be brought simultaneously within bonding distance of the carbene center. A system that appears to allow this possibility is the bicyclo[2.2.1]heptyl framework carrying a phenylcarbenyl moiety at the 2 position; an investigation of this compound was, accordingly, undertaken. Unfortunately, the results from this study gave little additional insight into the double hydrogen transfer process; they have, however, provided further detail to the mechanism of the C–H carbene insertion reaction.



Synthesis of 2-(*o*-Diazomethylphenyl)bicyclo[2.2.1]heptane (5d). Reaction of 2-formylstyrene (**3**)[4] with cyclopentadiene provided 2-(*o*-formylphenyl)bicyclo[2.2.1]hept-5-ene (**4a**) in 44–57% yield. To permit the selective reduction of the double bond, the aldehyde **4a** was converted to the acetal **4b**, and this was treated with hydrogen in the presence of a palladium on charcoal catalyst to yield **5a**. Acid-catalyzed hydrolysis of **5a** regenerated the free aldehyde **5b**, obtained in 65–75% overall yield from **4a**. Treatment of the aldehyde with hydrazine produced the hydrazone **5c** which was oxidized with mercuric oxide in the presence of base[5] or with silver oxide to furnish 30–75% yields (as estimated by the benzoic acid assay[6]) of 2-(*o*-diazomethylphenyl)bicyclo[2.2.1]heptane (**5d**).

Compounds **5a–5d** can exist in endo and exo forms. The endo form was required for the present investigation, and it was necessary, therefore, to determine the stereochemistry of the products obtained. This was achieved by converting the aldehyde **5b** to the corresponding methyl compound **5e** *via* a Huang–Minlon reduction[7] and subjecting **5e** to prolonged ozonolysis to remove the phenyl ring. The resulting 2-carboxybicyclo[2.2.1]heptanes were converted to the methyl esters **6** and **7** by treatment with diazomethane, and the composition of the mixture of esters was determined (by quantitative ir analysis) to be between 4:1 and 9:1, *i.e.* 80–90% endo. Thus, the compounds **5a–5d** are predominately, although not exclusively, in the desired endo form.

Decomposition of 2-(*o*-Diazomethylphenyl)bicyclo[2.2.1]heptane (5d). Irradiation of a solution of **5d** in cyclohexane yielded a complex mixture which was first separated into a higher boiling fraction (above 140° (5 mm)) and a lower boiling fraction (below 140° (5 mm)). The higher boiling fraction, containing the aldehyde **5b**, the azine of **5b**, and other substances, and accounting for 70% of the products, was not studied in detail. The lower boiling fraction, containing at least nine components and accounting for 30% of the products, was separated into three fractions by chromatography on alumina. The two smaller fractions were identified as bicyclohexyl and the azine of **5b**; the largest

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[1] Presented, in part, at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 5–9, 1965.

[2] Postdoctoral Research Associate, 1968–1969.

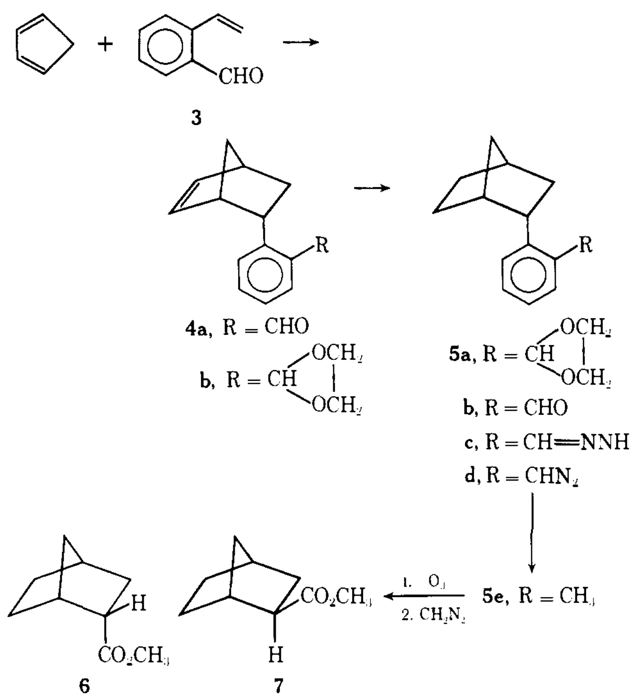
[3] (a) C. D. Gutsche, G. L. Bachman, and R. S. Coffey, *Tetrahedron*, **18**, 617 (1962); (b) T. A. Baer and C. D. Gutsche, *J. Amer. Chem. Soc.*, **93**, 5180 (1971).

[4] W. J. Dale, L. Starr, and C. W. Strobel, *J. Org. Chem.*, **26**, 2225 (1961).

[5] (a) H. Staudinger and A. Gaule, *Chem. Ber.*, **49**, 1897 (1916); (b) C. D. Nenitzescu and E. Solominica, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 495.

[6] See F. Arndt in ref 5b, p 166.

[7] Huang-Minlon, *J. Amer. Chem. Soc.*, **68**, 2487 (1946).



fraction was subjected to further separation by means of gas–liquid phase chromatography (glc) which yielded five components, designated as α (22%), β (8%), γ (12%), δ (50%), and ε (8%). To test the possibility that the product ratio might be influenced by traces of mercury introduced from the mercuric oxide oxidation of the hydrazone,[8] a comparable photolysis was performed with diazo compound prepared by the action of sodium methoxide in pyridine[9] on the *p*-toluenesulfonylhydrazone of the aldehyde **5b**. Essentially the same product ratio was obtained, however, indicating that mercury sensitization plays no part in the photolysis. As an alternative to photolytic decomposition, the base-induced decomposition of the *p*-toluenesulfonylhydrazone of **5b** (a process thought to involve diazo compounds and carbenes as intermediates[10]) was explored and found to yield the same product mixture although in somewhat altered ratios, *viz.* α (8%), β (36%), γ (5%), δ (45%), and ε (6%).

The components α–ε were indicated, on the basis of elemental analysis and/or nmr spectral determinations, to be $C_{14}H_{16}$ hydrocarbons. That the mixture contained none of the expected olefin **9**, however, was suggested by its failure to absorb hydrogen; the absence of **9** was substantiated by comparison with an authentic sample, prepared by reduction of the unsaturated aldehyde **4a**. The saturated analog **10**, which could result from the intermolecular hydrogen transfer from solvent (bicyclohexyl is a reaction product) to the carbene center, was also synthesized and shown to be absent from the photolysis mixture. Still another possibility, the tricyclic compound **11** which might arise by isomerization of **9**,[11] was synthesized and found not to be a constituent of the photolysis mixture. All of the products appear, instead, to be those of C–H insertion, two of which (β and γ) were readily characterized as the endo and exo isomers of *cis*-1,4-methano-1,2,3,4,4a,9a-hexahydrofluorene (**14** and **18**) by comparison with authentic samples prepared by hydrogenation of the Diels–Alder adduct[12] of cyclopentadiene and indene. The specification of which isomer is endo and which is exo is not entirely certain, but the presence of a one-proton multiplet at δ 0.75 ppm in the nmr spectrum of component β is indicative of an endo structure.[13] Component α, discernible on glc columns as a pair of compounds present in a ratio of 3:8, could not be separated into its subcomponents in sufficient quantity for spectral determinations. On the basis of the ir spectrum of the mixture (weak bands at 995 and 1020 cm^{-1}), the nmr spectrum (eight-proton resonance at δ 0.8–2 ppm, a four-proton resonance at δ 2.3–2.8 ppm, a four-proton resonance at δ 7.0 ppm) and the uv spectrum (a 266-nm band with a very high extinction coefficient; see following section for structural implications of these spectral data), the components in α are tentatively assigned the structures **12** and **13**. The nmr spectrum of component ε shows a six-proton envelope at δ 0.8–2.0 ppm, a six-proton envelope at δ 2.0–2.8 ppm, and a four-proton resonance at δ 7.0 ppm, commensurate with several structures including **16**, **17**, and **18**. Component δ, the major constituent of the mixture, is believed, on the basis of the evidence discussed below, to be the compound **15**.

Structure of Major C–H Insertion Product from 5d. One of the striking characteristics of component δ is its tendency to isomerize to **18** when heated or to undergo conversion to the fluorenone corresponding to **14** (or **18**?) when oxidized with dichromate or ozone.[16] The C–H insertion products most likely to manifest these properties are **12**, **13**, and **15** and the choice among these for the structural assignment to component δ is based on the combined evidence from nmr, ir, and uv spectra.

Simple benzocyclobutenes generally possess an ir band of medium intensity near 1000 cm^{-1},[17] whereas the absorption at this position in indans and tetralins is at 1020 cm^{-1} and of very low intensity.[18] The ir spectrum of component δ shows virtually no absorption at 1000 cm^{-1} but weak bands at 990 and 1020 cm^{-1}, thereby providing evidence, albeit negative, against structure **13**. Evidence against **13** is also seen in the tendency of component δ to isomerize rather than polymerize, the latter behavior being characteristic of benzocyclobutene[19] and *n*-propylbenzocyclobutene.[3]

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(8) Mercury-sensitized photolyses are well known in a variety of systems (*e.g.*, see J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 116) including those involving carbenes (see, for instance, H. M. Frey and R. Walsh, *Chem. Commun.*, 158 (1969)).

(9) D. G. Farnum, *J. Org. Chem.*, **28**, 870 (1963).

(10) L. Friedman and H. Shechter, *J. Amer. Chem. Soc.*, **81**, 5512 (1959); J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959).

(11) P. von R. Schleyer, *J. Amer. Chem. Soc.*, **80**, 1700 (1958).

(12) K. Alder and H. F. Rickert, *Chem. Ber.*, **71**, 379 (1938).

(13) In the endo isomer **14** the endo hydrogen at C-6 is much closer to the face of the benzene ring (z = 1.82, p = 1.12)[14] than in the exo isomer **18** (z = 0, p = 4.3). Using the procedure of Johnson and Bovey[15] it can be calculated that the position of the resonance from the endo hydrogen at C-6 in **14** should be shifted *ca.* 1.5 ppm upfield from that in **18**. The endo hydrogen at C-5 in **14** (z = 1.82, p = 2.24) is farther from the face of the benzene ring and is calculated to fall 1.2 ppm downfield from the endo hydrogen at C-6.

(14) See Appendix B in J. W. Emsley, J. Feeny, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Elmsford, N. Y., 1965, p 595, for a table of values.

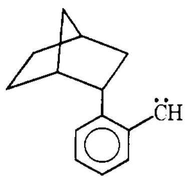
(15) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(16) The same ketone is obtained when a mixture containing **14** and **18** is similarly oxidized; that no skeletal rearrangement occurred during the oxidation was shown by reducing the ketone back to the original hydrocarbon.

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

(18) See "Catalog of Ultraviolet and Infrared Spectral Data," American Petroleum Institute Research Project 44, National Bureau of Standards.

5d →



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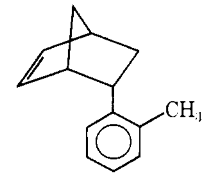

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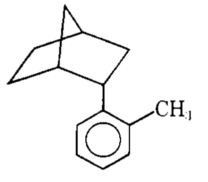

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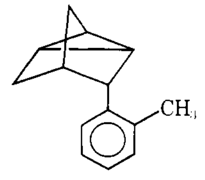

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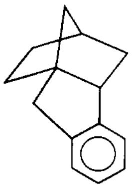

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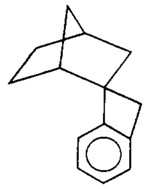

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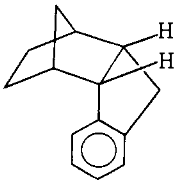

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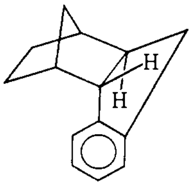

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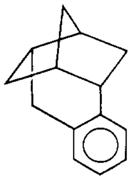

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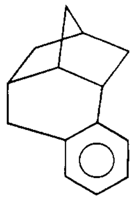

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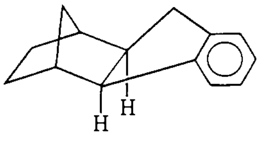

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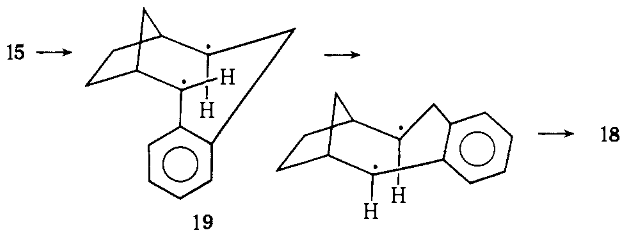
Benzenoid compounds possess uv absorption bands in the 260–280-nm region, the intensity of these moderately weak bands often being quite sensitive to the nature of the substitution on the benzene ring. As the "in-plane strain" on the benzene ring increases, the extinction coefficient generally increases as, for instance, in the following series: *o*-xylene (ϵ 256), tetralin (ϵ 622), indan (ϵ 1260), benzocyclobutene (ϵ 1868), compounds **14** and **18** (ϵ 1830). Conversely, as the "skew strain" on the benzene ring increases, the extinction coefficient appears to decrease as, for instance, in the pair of compounds, 1,2,4-triisopropylbenzene (ϵ 420) and 1,2,4-tri-*tert*-butylbenzene (ϵ 220).[20] The extinction coefficient for the most intense band in the 260–280-nm region from component δ is only 1120, suggesting that "skew strain" is being exerted on the benzene ring. Compound **13** would impose only "in-plane strain" and would be expected to have an extinction coefficient similar to or greater than that of benzocyclobutene; compound **12** would impose, at most, a small amount of "skew-strain." Compound **15**, however, because of the torsional strain resulting from the trans ring fusion, would be expected to impose a considerable amount of "skew strain." The uv spectral data, thus, are in closer accord with structure **15** than with structures **12** or **13**.

The nmr spectrum of component δ was studied in some detail, and as an aid to its analysis the nmr spectra of **14** and two of its deuterated analogs were also obtained. On the basis of this analysis, the details of which are given in the Appendix, it was concluded that the nmr spectrum of component δ is more readily accommodated to structure **15** than to structures **13** or **14**. The ir, uv, and nmr spectral data, thus, indicate that the major component of C–H insertion is *trans*-1,4-methano-1,2,3,4,4a,9a-hexahydrofluorene (**15**). Of the structures under consideration, **15** also provides the most rational explanation for (a) the thermal isomerization of component δ to **18**, a conversion which is viewed as involving homolysis of the "twisted bond" between C-2 and C-3[21] to yield the biradical **19** which, after inversion of configuration at C-2 to **20**, undergoes radical pairing to yield **18** and (b) the oxidative conversion of component δ to the fluorenone corresponding to **14**, a reaction which can be rationalized as involving inversion of configuration, *via* an intermediate enol, at C-3.[21]



15 → **19** → **20** → 18

Discussion of Results

The carbene C–H insertion reaction, known to chemists for at least a quarter of a century,[22] has provided the basis for numerous studies over the last decade and a half,[23] some of which have provided insight into the mechanistic details of this process.

Of particular note in this respect are the experiments of Doering and Prinzbach[24] and Skell and Woodworth[25] out of which came the postulate (hereafter referred to as the "Doering-Skell postulate") that the carbene C–H insertion process involves a triangular transi-

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[19] K. Alder and M. Fremery, *Tetrahedron*, 14, 190 (1961).

[20] J. Dale, *Chem. Ber.*, 94, 2821 (1961).

[21] For easy reference to the precursor carbene, the numbering scheme of the bicycloheptyl system is used in discussing the C–H insertion products, although the systematic names for these compounds assign different numbers.

[22] H. Meerwein, H. Rathjen, and H. Werner, *Chem. Ber.*, 75, 1610 (1942).

[23] For a literature survey see: (a) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; (b) D. Bethell, *Advan. Phys. Org. Chem.*, 7, 153 (1969).

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

[25] P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, 78, 4496 (1956).

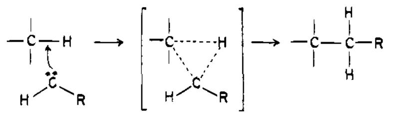

Figure 1. The Doering-Skell postulate for the carbene C–H insertion reaction.

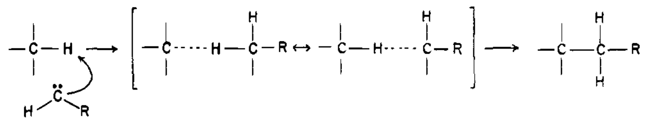

Figure 2. The Benson–DeMore postulate for the carbene C–H insertion reaction.

tion state as depicted in Figure 1. An alternative mechanism has been advanced by Benson and DeMore[26] who state 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, since the latter process should have a very small *A* factor and a fairly high activation energy." This view, hereafter referred to as the "Benson–DeMore postulate," asserts the transition state depicted in Figure 2.

Although the results from the present investigation do not make possible a definitive choice between the Doering–Skell and Benson–DeMore postulates, it is felt that they do provide added reasons for preferring the former. 2-(*o*-Methylenephenyl)bicyclo[2.2.1]heptane (**8**), the carbene generated from the diazo compound **5d**, has the potentiality of undergoing intramolecular insertion into a variety of C–H bonds in the system, only a few of the possible products being precluded because of excessive strain. The various hydrogens are not equivalently situated with respect to the carbene center, however, and, depending on the geometric requirements of the insertion reaction, might be expected to show differential reactivities. If the Benson–DeMore mechanism were operative, it would be anticipated that the hydrogens that can be brought closest to the carbene center should be the ones to preferentially migrate. In **8**, these are located at endo C-3, endo C-5, and endo C-6, insertion at these positions leading to compounds **14**, **16**, and **17**. The product mixture from **8**, containing *ca.* 50% **15**, 16% **12**, 12% **18**, 8% **14**, and 6% **13**, includes compound **14** only as a minor component and contains little, if any, of compounds **16** and **17**. Factors other than simple proximity of the migrating hydrogen to the carbene center, then, must control the course of the reaction. If, to the Doering–Skell postulate, the corollary is added that the *preferred pathway of attack is midway between the C and H atoms and perpendicular to the C–H bond* (hereafter referred to as the "perpendicular pathway"), the products formed from **8** can rationalized. Using Dreiding models[27] as well as CENCO–Petersen models (product of Central Scientific Co., Chicago, Ill.) in conjuction with several sets of human eyes and hands, some less prejudiced than others, measurements were made of the distance of closest encounter of the carbene carbon on the perpendicular pathway of the various C–H bonds in **8**. The results of these measurements are shown in Table I and Figure 3. The interesting fact emerges from inspection of this table that, although the hydrogen at endo C-3 can be brought within easy bonding distance of the carbene at C-8, the perpendicular pathway is particularly unfavorable. Conversely, although the hydrogen at exo C-3 cannot be brought within easy bonding distance of the carbene at C-8, the perpendicular pathway is more favorable than that for the endo hydrogen at C-3. Carbenes are unstable, energetic species, and the reactions in which they engage are quite strongly exothermic.[28] In accordance with the Hammond postulate[29] it would be expected, therefore, that the activated complex for C–H insertion should be relatively insensitive to the structure and stability of the product and that the facility of its formation should be governed by other factors such as the angle distortion required for the system to assume the geometry of an isosceles triangle (*i.e.* the activated complex resulting from the perpendicular pathway approach at midpoint on the C–H bond). The formation of **15** in preference to **14** thus is explainable in terms of a modified Doering–Skell postulate but incommensurate with the Benson–DeMore postulate. If the differences in the distance at which the carbene encounters the perpendicular pathway for insertion at various C–H bonds were the sole explanation for the product distribution, **12** and **16** would be predicted to form in greater amounts than **15**, and **13** should form in amounts comparable to **15**. The formation of **15** in preference to **13** may, however, be ascribed to differ-

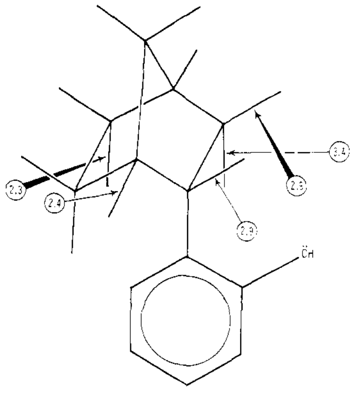

Figure 3. Perpendicular pathway approaches to C–H bonds in 2-(*o*-methylenephenyl)bicyclo[2.2.1]heptane (**8**).

Table I. Closest Approach Distances between the Carbene Center and the Carbon–Hydrogen Centers in 2-(*o*-Methylenephenyl)bicyclo[2.2.1]heptane (**8**)

C–H bond position	Attack on H, Å	Perpendicular pathway attack on C–H, Å
C-1	2.6	2.4
C-2	2.4	2.9
Endo C-3	1.3	3.4
Exo C-3	2.8	2.9
C-5	1.3	2.3
C-6	0.3	Not possible without twisting the system

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

(27) A. S. Dreiding, *Helv. Chim. Acta*, **42**, 1339 (1959).

(28) H. M. Frey in ref 23a, p 217.

(29) G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955).

ences in bond angle strain which to a small but finite extent must be present in the activated complex. Although **15** is, indeed, a strained molecule as its convertibility to **18** indicates, isomerization of the pure material requires heating at 275° for an extended period (whereas benzocyclobutene[19] polymerizes at 200° and suggests that **13** would be even more strained). Although molecular models are an uncertain guide in this respect, it appears that the strain in **13** is more localized than the strain in **15** wherein it can be distributed throughout most of the system. Nonbonding strain factors may also be important in product determination. For the carbene center to engage the perpendicular pathway for insertion at the endo C-5 position, for instance, it is necessary for C-8 to be "underneath" the bicycloheptyl system where severe nonbonding interactions are encountered.[30] Similarly, engagement of the perpendicular pathway for insertion at C-1 brings the carbene center into proximity with the endo hydrogen at C-6. As a consequence, **16** (insertion at C-5) is not formed at all, and **12** (insertion at C-1) is present, at most, in only moderate amount.

On the basis of the results of this investigation the modified Doering–Skell mechanism for the carbene C–H insertion reaction is viewed as more probable than the Benson–DeMore mechanism.[31] These experimental results, however, are contrary to the theoretical predictions obtained by extended Hückel calculations on the potential energy surface for the concerted insertion of singlet methylene into a C–H bond of methane.[33] The resolution of this subtle problem must, therefore, await an experimental approach that is more clever and sensitive than the one herein reported.

Experimental Section[34]

2-(*o*-Formylphenyl)bicyclo[2.2.1]heptane (5b). Following literature procedures,[4] *N*-β-phenylethylformamide[35] was converted to 3,4-dihydroisoquinoline by treatment with polyphosphoric acid at 166° for 3 hr. The distilled product, obtained in 60–90% yield (bp 69–72° (2 mm)), was treated with dimethyl sulfate and sodium hydroxide solution[4] to yield 50–70% of *o*-formylstyrene (**3**) as a colorless oil, bp 142–145° (5 mm), 65–68° (2 mm), 51–53° (0.1 mm). A mixture of 21.0 g (0.16 mol) of **3**, 21 g (0.32 mol) of freshly distilled cyclopentadiene, and 0.2 g of hydroquinone was heated in a mechanically shaken pressure bomb at 155° for 5 hr to yield, after distillation through a 6-in. Vigreux column, 18 g (57%) of 2-(*o*-formylphenyl)bicyclo[2.2.1]hept-5-ene (**4a**) as a colorless oil: bp 126–130° (2 mm); nmr (CCl_4) δ 1.5 (m, 3, CH_2), 2.2 (t, 1, exo H at C-3[36]), 3.0 (m, 2, bridgehead C–H), 4.3 (q, 1, benzyl C–H), 5.6 (q, 1, C=C*H*), 6.2 (q, 1, C=C*H*), 7.5 (m, 4, Ar–*H*), 10.3 ppm (s, 1, C*H*O). A mixture of 20.4 g (0.10 mol) of **4a**, 6.8 g (0.11 mol) of ethylene glycol, 1 g of *p*-toluenesulfonic acid, and 100 ml of dry, thiophene-free benzene was refluxed for 9–10 hr in an apparatus fitted with a water separator. The crude ethylene ketal **4b** was dissolved in 50 ml of absolute ethanol, treated with 250 mg of 10% palladium on charcoal, and hydrogenated at atmospheric pressure. When no more hydrogen was absorbed, the catalyst and ethanol were removed, and the residue was treated with 50 ml of dilute (1:25) sulfuric acid along with sufficient glacial acetic acid to render the mixture homogeneous. After standing at room temperature for 8–12 hr, the mixture was poured into 250 ml of saturated salt solution and thoroughly extracted with chloroform. The chloroform solution, after washing with 10% potassium carbonate solution and water, was concentrated and the residue was distilled through a 4-in. Vigreux column to give 13.4 g (67%) of 2-(*o*-formylphenyl)bicyclo[2.2.1]heptane (**5b**) as a colorless oil: bp 154–155° (5 mm); nmr (CCl_4) δ 1.4 (broad m, 8, CH_2), 2.3 (m, 2, bridgehead C–H), 4.1 (m, 1, benzyl C–H[37]), 7.4 (m, 4, Ar–*H*), 10.3 ppm (s, 1, C*H*O).

The **2,4-dinitrophenylhydrazone of 5b** was obtained, after three recrystallizations from 95% ethanol, as red needles, mp 196–197°.

Anal. Calcd for $C_{20}H_{20}N_4O_4$: C, 63.15; H, 5.30. Found: C, 62.99; H, 5.10.

The ***p*-toluenesulfonylhydrazone of 5b** was prepared by refluxing a 3-g sample of **5b** with 3 g of *p*-toluenesulfonylhydrazine in 30 ml of absolute ethanol for 30 min. The product, obtained in 54% yield, was recrystallized three times from absolute ethanol to yield colorless plates, mp 152–153°.

Anal. Calcd for $C_{21}H_{24}N_2O_2S$: C, 68.50; H, 6.53. Found: C, 68.50; H, 6.62.

A solution of 0.9 g (0.0048 mol) of 2-(*o*-tolyl)bicyclo[2.2.1]heptane (**6**) (*cf.* below) in 50 ml of methylene chloride was treated with ozone for 24 hr at −70°. The resulting ozonide was refluxed for 30 min with 10.5 ml of formic acid containing 5.1 ml of 30% hydrogen peroxide, the cooled mixture was extracted with five 10-ml portions of petroleum ether (bp 63–69°), and the petroleum ether was extracted with three 20-ml portions of potassium bicarbonate solution from which 0.100 g of acid material was obtained. The crude acid was esterified with ethereal diazomethane, and quantitative comparisons of the ir spectrum of this material in the 1070-cm^{-1} region with mixtures containing known amounts of the endo and exo isomers of 2-carbomethoxybicyclo[2.2.1]heptane[38] indicated that the ozonolysis product contained 80–90% of the endo isomer.

2-(*o*-Diazomethylphenyl)bicyclo[2.2.1]heptane (5d). (a) *Via* **Mercuric Oxide Oxidation.** A 5.0-g (0.025 mol) sample of the aldehyde **5b** was dissolved in 70 ml of anhydrous ether and slowly added to a stirred mixture of 5 ml of anhydrous hydrazine in 40 ml of ethyl ether. The mixture was stirred at room temperature for 6–8 hr, the hydrazine layer was separated and extracted with two 5-ml portions of ether, and the ethereal solution was washed with water and dried over sodium sulfate. To this solution was added 15 g of anhydrous sodium sulfate and *ca.* 30 drops of a saturated solution of potassium hydroxide. It was cooled to 0–5° and treated, over a period of *ca.* 20 min, with 10 g of yellow mercuric oxide. The mixture was then allowed to warm to room temperature

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(30) Whether the failure to observe any olefin, *i.e.* **9** from **5d**, is the result of nonbonded interactions alone or is the result of other factors as well is not known. Further details of the olefin-forming reaction are discussed in the accompanying paper.[3b]

(31) The formation of highly strained compounds is not without precedent in carbene chemistry, and numerous syntheses of cyclopropane compounds *via* intramolecular C–H insertion are known. Typical examples include the conversion of cyclopentylmethylene to bicyclo[3.1.0]hexane, cyclohexylmethylene to bicyclo[4.1.0]heptane, and norbornan-7-ylidene to tricyclo[$3.2.0.0^{2,7}$]heptane,[32] the products in all cases being accompanied by isomeric olefins. It is interesting to note that whereas the hydrocarbon olefin ratio is 2.6 in the case of cyclopentylmethylene, it is only 0.09 in the case of cyclohexylmethylene. Measurements on Dreiding models indicate that the perpendicular pathway distance is 2.4 Å for the 1,3 insertion process in cyclopentylmethylene and, assuming the methylene group to be in the equatorial position, 2.6 Å in cyclohexylmethylene, a difference which may account for the reduced tendency of the latter to undergo 1,3 insertion.

(32) W. Kirmse and G. Wachtershauser, *Tetrahedron*, **22**, 63 (1966); R. A. Moss and J. R. Whittle, *Chem. Commun.*, 341 (1969).

(33) R. C. Dobson, D. M. Hayes, and R. Hoffmann, *J. Amer. Chem. Soc.*, in press.

(34) All melting points are corrected; all boiling points are uncorrected. The infrared spectra were measured on a Perkin-Elmer Infracord instrument. The ultraviolet spectra were measured on Cary Models 11 and 14 spectrometers; the nuclear magnetic resonance spectra were recorded on Varian HR-60, A-60, A-100, and HR-220 spectrometers. The nmr resonances are reported as parts per million downfield shift from tetramethylsilane, used as an internal reference. Microanalyses were performed by Dr. Josef Zak, Mikroanalytisches Laboratorium, Vienna, Austria. Gas–liquid phase chromatographic (glc) analyses were performed on units containing thermistor detectors and using the following columns: column 1, a $^1/_4$ in. × 6 ft column packed with 5% by weight of Dow-Corning no. 710 Silicone oil on 30–60 mesh firebrick; column 2, a $^1/_4$ in. × 6 ft column packed with 20% by weight Carbowax 20-M on 30–60 mesh firebrick; column 3, a $^1/_4$ in. × 10 ft column packed with 5% silicone gum rubber XE-60 on 60–80 mesh Gaschrom-P; column 4, a $^1/_4$ in. × 10 ft column packed with 5% Carbowax 4000 on 60–80 mesh Gaschrom-A.

(35) H. Decker, *Justus Liebigs Ann. Chem.*, **395**, 282 (1913).

(36) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

(37) It has been observed that a double bond at $C_{5,6}$ exerts a downfield shift on the exo hydrogens at C-2 as compared with the saturated analog.[36] Thus, the shift in the position of the benzyl hydrogen resonance from δ 4.3 ppm in **4a** to δ 4.1 ppm in **5b** provides further proof that the compounds are predominately the endo isomers.

(38) H. Bode, *Chem. Ber.*, **70**, 1167 (1937).

and was stirred an additional 4 hr. The solids were removed by filtration, the ether was removed by evaporation, and the residue was dissolved in cyclohexane. The yield of diazo compound, based on the benzoic acid assay,[6] was 30–40%.

(b) *Via* **Silver Oxide Oxidation.** A 42-g sample of anhydrous hydrazine was heated to reflux, treated, with stirring, with 14.0 g (0.07 mol) of **5b**, and the mixture was refluxed for 2–3 hr. To the cooled solution 100 ml of cyclohexane was added, the cyclohexane and hydrazine layers were separated, and the cyclohexane was filtered to remove traces of the azine of **5b**. The cyclohexane solution was then added, with stirring, to a suspension of 30 g of anhydrous sodium sulfate and 23.2 g (0.1 mol) of silver oxide in 150 ml of cyclohexane at 0°. After 1.5 hr the reaction mixture was filtered to yield a red solution which contained, based on the benzoic acid assay,[6] 77% of the diazo compound **5d**.

(c) *Via* **the *p*-Toluenesulfonylhydrazone.** Following a procedure of Farnum,[9] a stirred mixture containing 3.0 g (0.0082 mol) of the *p*-toluenesulfonylhydrazone of **5b**, 0.44 g (0.0082 mol) of sodium methoxide, and 25 ml of pyridine was held at 60–65° for 1 hr. The mixture was poured into 100 ml of ice and water and extracted with four 40-ml portions of cyclohexane. The cyclohexane solution was washed with four 25-ml portions of water, dried over anhydrous sodium sulfate, and subjected to photolysis (see below).

Decomposition of 2-(*o*-Diazomethylphenyl)bicyclo[2.2.1]heptane (5d). (a) *Via* **Photolysis.** A 15-g sample of crude diazo compound **5d** was dissolved in 200 ml of cyclohexane, and the solution was irradiated for 18 hr either in a water-cooled quartz well containing a 100-W mercury lamp (manufactured by the Hanovia Division of Englehard Industries, Newark, N. J.) or in a Rayonet Photochemical Reactor (manufactured by the Southern New England Ultraviolet Co.) with a light source emitting 2537- or 3550-Å light; the results in all cases were comparable. After evaporation of the cyclohexane, the residue was distilled through a short-path apparatus, and the fraction boiling up to 140° (5 mm), amounting to 5 g (30%) of the starting aldehyde, was collected. Separation of this lower boiling fraction into five components, designated as α (21%), β (15%), γ (11%), δ (49%), and ε (4%) was effected on glc column 1 or 2. On column 4 component α was shown to actually contain two materials, designated as α_1 and α_2. Alternatively, the crude photolysis mixture was subjected to column chromatography on neutral alumina. Elution with cyclohexane yielded bicyclohexyl, elution with benzene yielded the aldehyde **5b** and a hydrocarbon mixture, and elution with methylene chloride yielded the azine of **5b**. Analysis of the hydrocarbon–aldehyde fraction by glc on column 4 showed that it contained, in addition to the aldehyde, components α_1 (6%), α_2 (16%), β (8%), γ (12%), δ (50%), and ε (8%).

(b) *Via* **Thermolysis.** A mixture of 2.0 g (0.0054 mol) of the ***p*-toluenesulfonylhydrazone of 5b**, 30 ml of diethyleneglycol dimethyl ether (freshly distilled from sodium hydride), and 1 g (0.019 mol) of sodium methoxide was heated at 160–165° for 15 min. The crude product was dissolved in ether, the solution was filtered, the solvents were removed by distillation, and the residue was distilled through a short-path apparatus. The fraction boiling up to 140° (5 mm) accounted for 24% of the product and contained, on the basis of glc analysis on column 1, components α (8%), β (36%), γ (5%), δ (45%), and ε (6%).

(c) **Analysis. Component** α (actually an unresolved mixture of α_1 and α_2) was obtained as a colorless oil: uv max (95% EtOH) 260 (ε 2200), 266 (ε 2400), 273 nm (ε 2120); ir (liq) 1020 (indan?), 1000 (benzocyclobutene?), 715, 732, 748, 757 (1,2-disubstituted benzene[39]), 1000 (weak), 1020 cm^{-1} (very weak); nmr (CCl_4) δ 0.8–2 (m, 8, CH_2 at C-3, C-5, C-6, C-7), 2.28 (symmetrical multiplet, 2, H at C-8 and C-8′), 2.80 (s, 1, H at C-4), 2.80 (*q*, 1, *J* = 5.2 and 13 Hz), 7.0 ppm (s, 4, Ar*H*).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 90.90; H, 8.82.

Component β was identified as *endo-cis*-1,4-methano-1,2,3,4,4a,-9a-hexahydrofluorene (**14**) by comparison of its glc, ir, and nmr characteristics with those of an authentic sample (see below): ir (liq) 710, 715, 734, 750, 1020 cm^{-1} (very weak).

Component γ was identified as *exo-cis*-1,2,3,4,4a,9a-hexahydrofluorene (**18**) by comparison of its glc, ir, and nmr characteristics with those of an authentic sample (see below): ir (liq) 705 (broad), 734, 749, 1020 cm^{-1} (weak).

Component δ, identified as *trans*-1,4-methano-1,2,3,4,4a,9a-hexahydrofluorene (**15**), was obtained as a colorless oil: uv max (95% EtOH) 260 (ε 750), 226 (ε 1050), 273 nm (ε 1140); ir (liq) 705, 742, 773, 782 (1,2-disubstituted benzene[39]), 990 (weak), 1019 cm^{-1} (weak); nmr (CCl_4) 1.0–1.37 (m, 2, H at C-5 and/or C-6), 1.48 (doubled doublet, 1, *J* = 12 and 14 Hz, H at C-3), 1.49 (d, 1, *J* = 9 Hz, H at C-7), 1.64 (doubled multiplet, 1, *J* = ~1 and 9 Hz, H at C-7), 1.37–1.65 (m, 2, H at C-5 and/or C-6), 2.25 (s, 1, H at C-4), 2.26 (t, 1, *J* = 12 Hz, H at C-8), 2.51 (doubled doublet, 1, *J* = 1 and 14 Hz, H at C-2), 2.58 (doubled multiplet, 1, *J* = ~1 and 5 Hz, H at C-1), 2.66 (doubled doublet, 1, *J* = 5 and 12 Hz, H at C-8′), 6.86 ppm (m, 4, Ar*H*).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 90.98; H, 8.99.

Synthesis of Hydrocarbons for Structural Comparison. (a) **2-(*o*-Tolyl)bicyclo[2.2.1]hept-5-ene (9)** was prepared by a Huang-Minlon reduction[7] of a 3-g sample of 2-(*o*-formylphenyl)bicyclo-[2.2.1]hept-5-ene (**4a**) using 2 g of potassium hydroxide, 15 ml of 85% hydrazine hydrate, and 15 ml of triethylene glycol. The crude product was placed on a column of alumina (Woelm, activity grade 1) and eluted with petroleum ether (bp 63–69°), and the eluate was distilled through a short-path apparatus to give 1 g (37%) of **9** as a colorless oil.

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 90.91; H, 8.92.

(b) **2-(*o*-Tolyl)bicyclo[2.2.1]heptane (10)** was prepared by hydrogenation of a 1-g sample of **9**, described above and obtained in 88% yield as a colorless oil after distillation through a short-path apparatus.

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.24; H, 9.93.

(c) **3-(*o*-Tolyl)tricyclo[2.2.1.0^{2,6}]heptane (11).** To a stirred and cooled (10–15°) mixture of 31 g (0.26 mol) of *o*-tolualdehyde, 16 g (0.26 mol) of nitromethane, and 52 ml of methanol, a solution of 11 g of sodium hydroxide in 26 ml of water was added dropwise. The white semisolid that formed was dissolved by the addition of 52 ml of concentrated hydrochloric acid and 78 ml of water. The resulting yellow oil was extracted into chloroform, the chloroform was evaporated, and the residue was distilled through a 4-in. Vigreux column to yield 32 g (86%) of ***o*-methyl-β-nitrostyrene** as a yellow oil, bp 101–103° (0.2 mm).

Anal. Calcd for $C_9H_9NO_2$: C, 66.30; H, 5.50. Found: C, 66.62; H, 5.94.

A 29-g sample of *o*-methyl-β-nitrostyrene and 30 g of cyclopentadiene was heated at reflux for 3 hr. The excess cyclopentadiene was evaporated at reduced pressure, and the residue was distilled to give 26.4 g (64%) of the Diels–Alder adduct as a yellow oil, bp 133–134° (0.5 mm). A 22.6-g sample of this material was dissolved in 100 ml of absolute ethanol, treated with palladium on charcoal catalyst, and hydrogenated at atmospheric pressure to give, after distillation of the crude product, 18.1 g (78%) of **2-(*o*-tolyl)-3-nitrobicyclo[2.2.1]heptane** as a yellow oil, bp 133–134° (0.5 mm).

Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81. Found: C, 73.14; H, 7.39.

A 16.9-g sample of 2-(*o*-tolyl)-3-nitrobicyclo[2.2.1]heptane was dissolved in 120 ml of ethanol and treated with sodium ethoxide, prepared from 3.36 g of sodium in 120 ml of ethanol. This solution was then added, over a 10-min period, to a well-stirred solution of 97 ml of concentrated hydrochloric acid, 1620 ml of water, and 970 ml of ethanol at 0° in a nitrogen atmosphere. The reaction mixture was stirred at 0° for 1 hr, at room temperature for 5 hr, and at reflux for 1 hr. Distillation of the crude product yielded 7.8 g (54%) of 2-(*o*-tolyl)bicyclo[2.2.1]heptan-3-one as a colorless oil, bp 146–149° (0.5 mm). The 2,4-dinitrophenylhydrazone was obtained, after two recrystallizations from 95% ethanol, as orange needles, mp 189–190°.

Anal. Calcd for $C_{20}H_{20}N_4O_4$: C, 63.15; H, 5.30. Found: C, 62.79; H, 5.36.

The *p*-toluenesulfonylhydrazone of 2-(*o*-tolyl)bicyclo[2.2.1]heptan-3-one, prepared as described above from 2 g of the ketone, was mixed with sodioacetamide prepared from 39 g of acetamide and 1 g of sodium, and the mixture was heated to 170° until nitrogen evolution ceased (15 min). The product was worked up to give, after distillation through a short-path apparatus, 0.5 g (27%) of **11** as a colorless oil: ir (liq) 815 cm^{-1} (tricyclene[40]); nmr (CCl_4) δ

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(39) R. N. Jones and C. Sandorfy, "Technique of Organic Chemistry," Vol. IX, A. Weissberger, Ed., Interscience, New York, N. Y., 1956, p 387.

(40) D. C. Kleinfelter and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **83**, 2329 (1961).

0.9–1.5 (m, 7, H at C-1, C-2, C-5, C-6, C-7), 1.8 (broad singlet, 1, H at C-4), 2.2 (s, 3, ArCH_3), 2.7 (broad singlet, 1, H at C-3), 7.0 ppm (m, 4, Ar*H*).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 90.99; H, 9.15.

(d) **1,4-Methano-1,2,3,4,4a,9a-hexahydrofluorene (14 and 18).** A mixture of 23 g (0.2 mol) of indene and 2 g (0.3 mol) of cyclopentadiene was heated for 16 hr at 190° in a pressure bomb. The product consisted of 14.1 g (39%) of a colorless oil, bp 134–136° (11 mm) (lit.[12] 135–136° (11 mm)). This material was dissolved in 100 ml of absolute ethanol, treated with 250 mg of 5% palladium on charcoal catalyst, and hydrogenated at atmospheric pressure to yield 12 g (85%) of a 1:1 mixture of **14** and **18** as a colorless oil: bp 121–122° (5 mm); uv max (95% EtOH) 261 (ϵ 920), 268 (ϵ 1440), 274 nm (ϵ 1830).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 90.88; H, 8.41.

When the reaction of cyclopentadiene and indene was carried out at 150–155° for 9 hr a 33% yield of product was obtained which appeared, on the basis of glc, to be the pure endo isomer **14** but which was shown by nmr analysis to contain *ca.* 20% of the exo isomer. Reduction yielded a 4:1 mixture of **14** and **18** from which the nmr of the endo isomer could be deduced: δ 0.78 (m, 1, endo H at C-6), 1.00–1.26 (m, 3, CH_2 at C-5 and exo H at C-6), 1.47 (d, 1, J = 10 Hz, H at C-7), 2.21 (broad singlet, 1, H at C-4), 2.46 (t (?), 1, H at C-1), 2.70 (m, 1, H at C-3), 2.73–2.93 (m, 2, H at C-8 and C-8′), 3.51 (doubled doublet, 1, J = 4.4 and 10 Hz, ArC*H* at C-2), 6.95 ppm (m, 4, Ar*H*). From the nmr spectrum of a mixture of **12** and **13**, taken in conjunction with the nmr spectra of the C-2 deuterio and C-2, C-8, C-8′ trideuterio analogs of **12**, the nmr spectrum of **13** could, in part, be deduced: δ 2.55 (d, 1, J = 4 Hz), 3.03 (d, 1, J = 8 Hz, H at C-2), 3.16 (doubled doublet, 1, J = 6.4 and 10 Hz, H at C-8 or C-8′), 6.95 ppm (m, 4, Ar*H*).

(e) **Deuterio-1,4-methano-1,2,3,4,4a,9a-hexahydrofluorene.** Indanone was reduced with lithium aluminum deuteride to 1-deuterioindanol, mp 51–53°, in 88% yield. A 6.7-g sample of this material was mixed with 6 g of anhydrous magnesium sulfate and twice distilled at 20 mm pressure to yield 2.0 g (34%) of 3-deuterioindene, bp 85–87° (20 mm), shown to be greater than 95% deuterated at C-3 by means of nmr analysis. The indene was then converted to the C-2[20] *deuterio* analog of **14** by the process described above: nmr (CCl_4) identical with that of **14** but lacking the doubled doublet at δ 3.51 ppm and showing a broader, less highly resolved pattern at δ 2.70 ppm.

(f) **4a,9,9-Trideuterio-1,4-methano-1,2,3,4,4a,9a-hexahydrofluorene.** An 18.5-g sample of indene was treated with 20 g of deuterium oxide and 0.7 g of trimethylbenzylammonium deuteroxide, and the mixture was refluxed for 30 min. The product, consisting of 13.5 g (72%) of distilled material, bp 42–45° (1 mm), was carried twice again through a similar treatment to yield 8 g (43%) of 1,1,3-trideuterioindene which was shown by nmr analysis to be greater than 98% deuterated at C-1 and C-3. The indene was then converted to the C-2,C-8,C-8′ [21] trideuterio analog of **14** by the process described above: nmr (CCl_4) identical with that of **14** but lacking the doubled doublet at δ 3.51 ppm, lacking the multiplet at δ 2.73–2.93 ppm, and showing a partially resolved doublet at δ 2.67 ppm.

Dehydrogenation Experiments. When a 250-mg sample of the photolysis product from **5d** containing components α–ϵ was heated for 3 hr at 400° in the presence of 50 mg of 10% palladium on charcoal or 100 mg of 5% platinum on charcoal, component δ underwent isomerization to component γ, and component ϵ disappeared (product unidentified); otherwise, no change occurred under these conditions.

Oxidation Experiments. (a) **Component δ from Photolysis of 5d.** A stirred solution of 98 mg of component δ (*i.e.*, compound **15**) in 50 ml of methylene chloride, cooled to −78°, was treated for 12 hr with a stream containing 40 mg/l. of ozone in oxygen. The ozonide was decomposed by treatment with 5 ml of 30% hydrogen peroxide and 50 ml of 10% sodium hydroxide for 1 hr on the steam bath. The product, consisting of 36 mg of a colorless oil, was shown by glc to be a mixture of several compounds, the major component (25%) being identical in glc characteristics with 1,4-methano-1,2,3,4,4a,9a-hexahydrofluorene.

(b) **1,4-Methano-1,2,3,4,4a,9a-hexahydrofluorene (14 and 18).** Following the ozonolysis procedure described above, a 1.0-g sample of a 1:1 mixture of **14** and **18** yielded 0.5 g of a colorless oil, glc analysis of which showed the presence of one major component (90%) and two minor components (10%). Separation of the major component by glc on column 1 yielded the ketone as a colorless oil: ir (liq) 1720 and 1730 cm^{-1} (cyclopentanone carbonyl).[41]

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.77; H, 7.44.

A sample of the ketone was dissolved in ethanol containing 2 drops of 70% perchloric acid, treated with palladium on charcoal catalyst, and hydrogenated at 20 psi to yield a hydrocarbon identical with the starting material, thereby demonstrating that no skeletal rearrangement had occurred during the oxidation.

The **2,4-dinitrophenylhydrazone of 1,4-methano-1,2,3,4,4a,9a-hexahydrofluorenone** was obtained, after three recrystallizations from *n*-butyl alcohol, as red needles, mp 216–217°.

Anal. Calcd for $C_{20}H_{18}N_4O_4$: C, 63.48; H, 4.80. Found: C, 63.51; H, 4.90.

Isomerization of 1,4-Methano-1,2,3,4,4a,9a-hexahydrofluorene (15). A 10-mg sample containing 96% **15** and 4% **18** was dissolved in 1 ml of diethylene glycol dimethyl ether. A 10.0-μl aliquot of the solution was assayed by glc on column 3, and the areas under the peaks corresponding to **15** and **18** were accurately measured. The remainder of the solution was divided, and each half was sealed in a nitrogen-purged heavy-walled Pyrex vial. One of these was heated at 275° for 10 hr and the other at 275° for 72 hr, after which time they were cooled and 10.0 μl of each assayed by glc. The total areas under the peaks were the same as that before heating, but the ratio of **18/14** had changed from 4/96 to 14/86 after 10 hr and to 52/48 after 72 hr.

Acknowledgment. This work was supported, in part, by Grant No. GP-4951 from the National Science Foundation, Grant No. 1781-Al from the Petroleum Research Fund administered by the American Chemical Society, and Grant No. DA ARO(D)-31-124-G533 and DAHCO4-69-C-0066 from the U. S. Army Research Office. To these donors the authors express their gratitude.

Appendix

Nmr Spectra of 14 and the C-1 and C-1,C-8,C-8′[21] Deuterio Analogs of 14. The nmr spectra of **14** at 60, 100, and 220 MHz[42] (see Figure 4) show three regions of absorption, one centering at δ 6.95 ppm and arising from the four aromatic protons, another extending from δ 1.9 to 3.7 ppm and arising from the three benzyl protons and three bridgehead protons, and a third extending from δ 0.6 to 1.6 ppm and arising from the six methylene protons.[43] The quartet at δ 3.51 ppm that can be discerned in the 220-MHz spectrum (see Figure 4) arises from the hydrogen at C-2, for this resonance disappears in the C-2 deuterio compound. The coupling constants (J = 4.4 and 10 Hz) are in accord with those expected from interaction with the H at C-1 (θ = 45°)[44] and the H at C-3 (θ = 0°).[45] The resonances from the two benzyl hydrogens at C-8 must

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(41) P. Yates and L. L. Williams, *J. Amer. Chem. Soc.*, **80**, 5896 (1958).

(42) We are indebted to Drs. W. A. Sheppard, R. C. Ferguson, and D. R. Strobach and Messrs. F. V. Ferrari and F. W. Barney of the du Pont de Nemours Company for help in securing the 220-MHz spectra. We are particularly grateful to Mr. Barney for the extra and expert effort that he expended in this respect.

(43) In bicyclo[2.2.1]heptane itself the resonance from the hydrogen at C-1 falls at δ 2.19 ppm, while those from the hydrogens at endo C-2, C-7, and exo C-2 fall at δ 1.18, 1.18, and 1.46 ppm, respectively (E. Pretsch, H. Immer, C. Pascual, K. Schaffner, and W. Simon, *Helv. Chim. Acta*, 50, 105 (1967); see also K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Lett.*, 9 (1966)).

(44) A coupling constant of 4.4 Hz is considerably larger than that ordinarily arising from long-range coupling along the "W" path in bicycloheptyl systems; the splitting is, therefore, ascribed to interaction with the H at C-1 rather than with the exo H at C-6.

(45) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Amer. Chem. Soc.*, **85**, 2870 (1963). On the assumption that **14** is sufficiently rigid to maintain the dihedral angle between the exo hydrogens at C-2 and C-3 at 0°, the $J°$ in the Karplus equation is taken to be the observed value of 10 Hz. The Karplus curve that is thereby defined (see S. Sternhell, *Quart. Rev., Chem. Soc.*, **34**, 236 (1969)) has been used for calculating the other coupling constants for **14** and **15**.

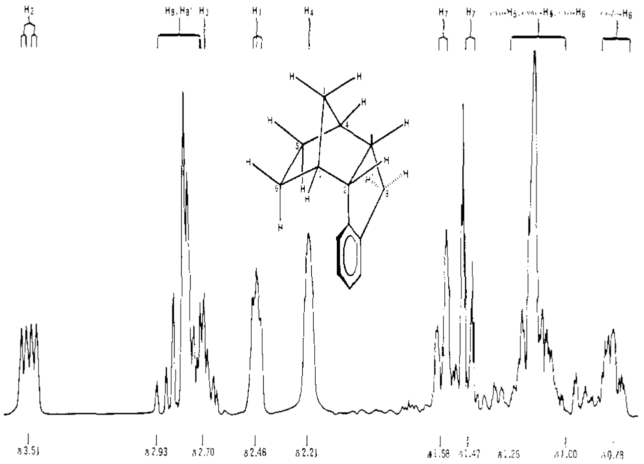

Figure 4. Upfield region of 220-MHz nmr spectrum of *endo*-1,4-methano-1,2,3,4,4a,9a-hexahydrofluorene (**14**).

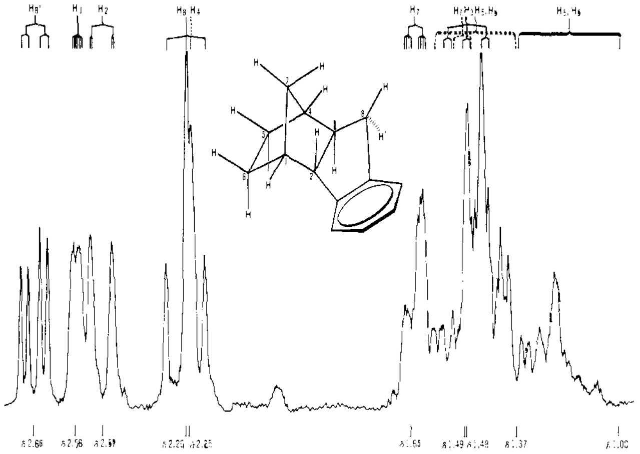

Figure 5. Upfield region of 220-MHz nmr spectrum of *trans*-1,4-methano-1,2,3,4,4a,9a-hexahydrofluorene (**15**).

fall between δ 2.5 and 2.9 ppm, for the complex splitting pattern in this region of the spectrum of the parent compound is replaced by a broad, partially resolved doublet (J = 3.4 Hz) at 2.67 ppm in the trideuterio compound. The calculated value for J_{H_1,H_2} (θ = 45°) is 4 Hz[45,46] and those for $J_{H_1,H_{6exo}}$, $J_{H_1,H_{6endo'}}$, J_{H_1,H_7}, and $J_{H_1,H_{7'}}$ are *ca.* 1.5 Hz; the resonance from the hydrogen at C-1 might, therefore, be expected to be a moderately broad multiplet. The calculated values for J_{H_3,H_2}, J_{H_3,H_4}, J_{H_3,H_8}, and $J_{H_3,H_{8'}}$ are *ca.* 10, 4, 10, and 3 Hz, respectively, and the resonance from the hydrogen at C-3 might be expected to be a better resolved multiplet. Accordingly, the resolved multiplet at δ 2.67 ppm is assigned to the hydrogen at C-3, and the quasi triplet at δ 2.46 is assigned to the hydrogen at C-1. The bridgehead hydrogen that would be expected to appear at the highest field is the one furthest removed from the benzene ring, and the broad singlet at δ 2.21 ppm is, therefore, assigned to the hydrogen at C-4. In the portion of the spectrum above δ 2.0 ppm the one-proton doublets at δ 1.58 and 1.47 ppm (J = 10 Hz) are assigned to resonances from the C-7 hydrogens, the three-proton multiplet at δ 1.00–1.26 is assigned to resonances from the exo hydrogens at C-5 and C-6 and the endo hydrogen at C-5, and the one-proton multiplet (eight lines) centered at δ 0.78 is assigned to the endo hydrogen at C-6, shifted upfield because of its proximity to the face of the benzene ring (see previous discussion and ref 13).

Nmr Spectrum of 15. Although the nmr spectra of component δ at 60 and 100 MHz showed a somewhat indistinct separation between the two upfield resonance envelopes, the 220-MHz spectrum clearly resolved these and indicated the presence of four aromatic protons at δ 6.95 ppm, five protons in the envelope between δ 2.0 and 2.8 ppm, and seven protons in the envelope between δ 1.0 and 2.0 ppm (see Figure 5). On the assumption that benzylic protons and bridgehead protons should fall in the δ 2–3-ppm envelope and methylene protons in the δ 1–2-ppm envelope, however, none of the structures **12**, **13**, or **15** appear to be commensurate with the observed spectrum. To accommodate **15** to the spectrum, an upfield shift of a benzylic or bridgehead proton must be asserted, and to accommodate **12** or **13** to the spectrum, a downfield shift of a methylene proton must be asserted. On the contention that the other features of the spectrum are more readily interpreted in terms of structure **15** than structure **12** or **13** the resonance that is shifted is postulated to be the one arising from the hydrogen at C-3. In compound **14** the C-3 hydrogen is exo and is thought to be responsible for the resonance at δ 2.67 ppm. In structure **15** the C-3 hydrogen is endo, and it is known that the change from exo to endo can result in an upfield shift by as much as 0.7 ppm.[46] Furthermore, the hydrogen at C-3 in **15** is canted toward the face of the benzene ring, and this should result in an additional upfield shift, calculated[14,15] to be *ca.* 0.2–0.3 ppm. Thus, the resonance from the hydrogen at C-3 which in compound **12** falls in the δ 2–3-ppm envelope might be expected to fall in the δ 1–2-ppm envelope in compound **15**. It is postulated that this resonance is observed as a multiplet centered at δ 1.48 ppm, the result of coupling with the hydrogens at C-2 (calcd[45] J from θ of 165° = 12 Hz), C-8 (calcd[45] J from θ of 180° = 13 Hz), and C-8′ (calcd[45] J from θ of 50° = 4 Hz). In the δ 2–3-ppm envelope the doublet of doublets centered at δ 2.66 ppm is assigned to the hydrogens at C-8′ on the basis of the coupling constants (J = 5 and 12 Hz) which are reasonably close to those expected from coupling with the geminal hydrogen at C-8 (*ca.* 12 Hz[47]) and the vicinal hydrogen (calcd[45] from θ of 50° = 4 Hz) at C-3; the doublet of multiplets centering at δ 2.58 ppm is assigned to the hydrogen at C-1 on the basis of the coupling constants (J = 5 and *ca.* 1 Hz) arising from interaction with hydrogens at C-6$_{exo}$ (calcd[45] J from θ 35° = 6 Hz), C-6$_{endo'}$ (calcd[45] J from θ of 85° $\simeq$ 0), and C-2, C-7, and C-7′ (calcd[45] J from θ of 60° = 2 Hz); the doublet of doublets centering at δ 2.51 ppm is assigned to the hydrogen at C-2 on the basis of the coupling constants (J = 12 and *ca.* 1 Hz) arising from interaction with hydrogens at C-3 (calcd[45] J from θ of 170° = 12 Hz) and H-1 (calcd[45] J from θ of 60° = 2 Hz); the triplet centering at δ 2.26 ppm is assigned to the hydrogen at C-8 on the basis of the coupling constant (J = 12 Hz) arising from equal interaction with hydrogens at C-3 (calcd[45] J from θ of 180° = 13 Hz) and C-8 (geminal coupling $J \simeq$ 12 Hz[47]); the singlet at δ 2.25 ppm is assigned to the hydrogen at C-4 which

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(46) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).

(47) A. A. Bothner-By, *Advan. Magn. Resonance*, **1**, 195 (1965).

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