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Abnormal Benzo Substituent Effect on Free Radical Formation Process. A Local Symmetry Effect

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Relative stabilities of 1-bicyclo[2.2.2]octyl (**9**), 1-benzobicyclo[2.2.2]-octenyl (**10**), 1-dibenzobicyclo[2.2.2]octadienyl (**11**), and 1-tribenzobicyclo[2.2.2]octatrienyl(**12**) radicals were obtained by means of the relative rates of the free radical bromine abstraction from the corresponding bridgehead bromides by a silyl radical. It was found that **9** and **12** were more stable than expected. The observed order of stability **9**> **10**> **12**> **11** can not be explained by the usual concepts alone. The extra stabilization of **9** or **12** (or destabilization of **10** or **11**) was interpreted in terms of the local symmetry (or local asymmetry) of these radicals.

In the course of studies on factors influencing radical stability, much attention has been given to the stability of a strained radical in connection with the stable conformation of a free radical.[1] A preferred planar or nearly planar geometry of a simple, unrestricted alkyl radical has been generally accepted from vacuum ultraviolet[2] and electron spin resonance[3] spectroscopy, formation of a racemized product from from an optically active substrate[4] as well as theoretical calculations.[5] The direct kinetic investigation of the decomposition of a series of bridgehead peresters[6] (or azo derivatives[7])) having different bridgehead planarities such as adamantyl, bicyclo[2.2.2]octyl, and bicyclo[2.2.1]heptyl has shown that the decomposition rates were depressed with increasing bridgehead nonplanarity but not so dramatically as in solvolysis reactions. The instability of a strained bridgehead radical was further demonstrated by decarbonylation of a similar series of bridgehead aldehydes[8] and also by unsuccessful bridgehead hydrogen abstraction from strained bicyclo-[2.2.1]heptane[9] or bicyclo[2.1.1]hexane[10] in contrast to the ready abstraction of the bridgehead hydrogen of less strained adamantane[11] or bicyclo[2.2.2]octane.[12] All the results seem to suggest that strain, particularly angle strain, is the determining factor of the bridgehead radical stability. It has also been reported[13] that the relative rates of hydrogen abstraction from a series of aliphatic polycyclic hydrocarbons by the trichloromethyl radical were correlated with a computer analysis of the change in strain energy in going from the ground state to the radical. In this connection, a curious observation was reported by Wiberg and coworkers, who were able to show the synthetic utility of the free radical bridgehead substitution on bicyclo-[1.1.1]pentane *via* the 1-bicyclo[1.1.1]pentyl radical having the greatest deviation from planarity ever known.[14]

For these highly strained substrates for which no direct kinetic data are available, the bridgehead-to-bridge reactivity ratios in the free radical substitutions (halogenation, chlorocarbonylation, *etc.*) on the parent hydrocarbons (Table I) might be measure of the bridgehead radical stability. As illustrated in the relative reactivities of some polycyclic hydrocarbons toward autoxidation,[15] bridgehead reactivities are generally more sensitive to a structural change than bridge reactivities, presumably because of the ease with which the bridge radical (compared with the bridgehead) takes planarity or near planarity. The variation in the ratios of the bridgehead-to-bridge reactivity (Table 1) is not fully understood from the consideration of the bridgehead angle strain alone but can be interpreted by taking the geometrical symmetry of the bridgehead also into consideration. Of the compounds (Table I) only those which yield symmetrical radicals such as adamantane, bicyclo[2.2.2]octane and bicyclo[1.1.1]-pentane or those which yield radicals of similar symmetry only with respect to the vicinal carbons (this might be called "local symmetry") such as bicyclo-[3.3.0]octane, have appreciable bridgehead reactivities. This might be called local symmetry effect. An experimental evidence of this hypothesis of a local symmetry effect is presented in this paper.

TABLE 1. BRIDGEHEAD-TO-BRIDGE REACTIVITY RATIOS OF SOME POLYCYCLIC HYDROCARBONS IN FREE RADICAL SUBSTITUTIONS[a)]

Substrate	Mode of substitution	Reactivity ratio	Ref.
Adamantane	chlorination bromination	3—5	11a
	clorocarbonylation	3.7	b
Bicyclo[2.2.2]octane	chlorination	6.9	12
Bicyclo[3.3.0]octane	chlorocarbonylation	2.9	c
Bicyclo[2.2.1]heptane	chlorination	0	9
	chlorocarbonylation	0	c
Nortricyclane	chlorination	0	d
Bicyclo[2.1.1]hexane	chlorination	0	10
Tricyclo[3.3.0.$0^{2,6}$]-octane	chlorination	0	e
Bicyclo[3.1.0]hexane	chlorination	0	f
Bicyclo[1.1.1]pentane	chlorination	7	14b
	chlorocarbonylation	17	14b

a) The ratios are statistically corrected for numbers of hydrogens. b) I. Tabushi, J. Hamuro, and R. Oda, *J. Org. Chem.*, **33**, 2108 (1968). c) I. Tabushi, T. Okada, and R. Oda, *Tetrahedron Lett.*, **1969** 1605. d) M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 4293 (1965). e) J. Meinwald and B. E. Kaplan, *ibid.*, **89**, 2611 (1967). f) P. K. Freeman, F. A. Raymond, J. C. Sutton, and W. R. Kindley, *J. Org. Chem.*, **33**, 1448 (1968).

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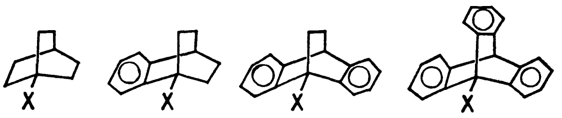
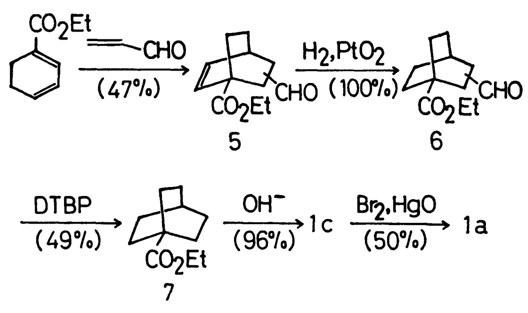
Results

A series of bridgehead bromides (**1a**, **2a**, **3a**, or **4a**) containing the bicyclo[2.2.2]octane framework was prepared. **1a** was prepared (Scheme 1) by the Hunsdiecker reaction of the corresponding acid (**1c**)[16] obtained by a slight modification of the procedure of Doering *et al.*[17]

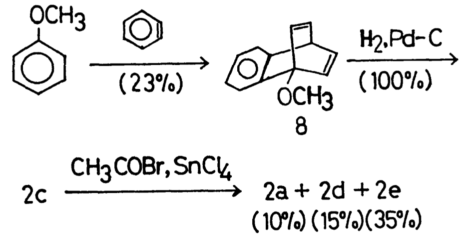


1a X=Br 2a X=Br 3a X=Br 4a X=Br
b X=H b X=H b X=H b X=H
c X=CO_2H c X=OCH_3
d X=Cl
e X=$OCOCH_3$



Scheme 1.

The procedure of Suzuki and Morita for converting 1-methoxybicyclo[2.2.2]octanes into 1-halobicyclo[2.2.2]octanes[18] was applied to the synthesis of **2a**. Thus, the 1,4-adduct of benzyne to anisole was, after hydrogenation, converted into **2a** on treatment with acetyl bromide-stannic chloride or stannic bromide (Scheme 2).



Scheme 2.

The 1,4-addition of 9-bromoanthracene with ethylene[19] or benzyne[20] gave **3a** or **4a**, respectively, in moderate yields.

The reductive debromination of a bromide (**1a**, **2a**, **3a**, or **4a**) with methyldichlorosilane in cyclohexane was carried out in a degassed, sealed tube in the presence of a catalytic amount of di-*tert*-butyl peroxide (DTBP) at 120 °C. The reaction proceeded at an appreciable rate even in the case of **4a**. The only detectable product, besides those from silanes, was the corresponding hydrocarbon (**1b**,[17] **2b**,[21] **3b**,[21] or **4b**[20]).

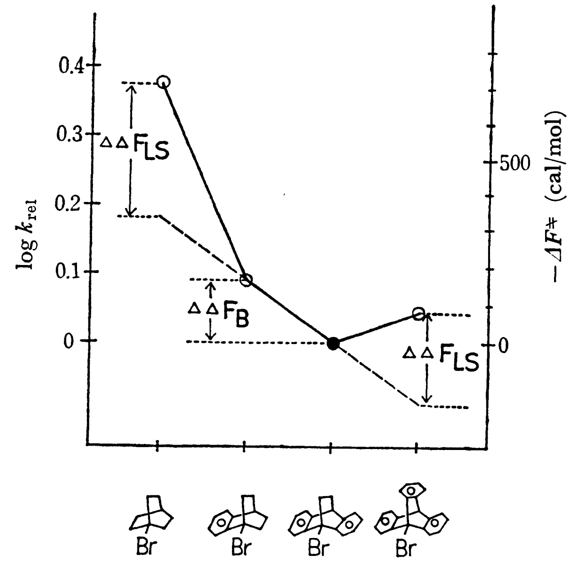


Fig. 1. Logarithmic relative rates of the bromine abstraction from **1a**, **2a**, **3a**, and **4a** by methyldichlorosilyl radical.

That the yield of the reaction was always nearly quantitative indicates that no appreciable side reaction took place.

In order to obtain the relative reactivity of a bromide, a competitive reaction was carried out, in which a bromide (**1a**, **2a**, or **4a**) competed with **3a** (standard) for the attack of the silyl radical. Relative reactivities thus obtained were **1a** (2.36±0.06), **2a** (1.24±0.04), **3a**(1, standard), and **4a** (1.11±0.04). The logarithms of the relative rates (or the relative free energies of activation) are shown in Fig. 1.

Discussion

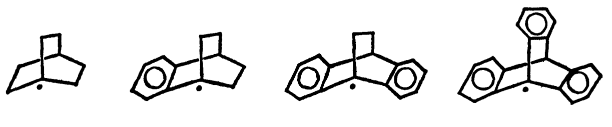
Ready Formation of Strained Radicals. As already given in many examples,[22] the present reductive debromination can be understood in terms of a radical chain mechanism involving the bromine abstraction from **1a**, **2a**, **3a**, or **4a** by the methyldichlorosilyl radical followed by the hydrogen transfer to the bridgehead radical thus formed (**9**, **10**, **11**, or **12**) from the parent hydrosilane. It is remarkable that the strained radicals **10**, **11**, or **12** can be generated with a rate not much differing from that of **9**, although the triptycyl radical (**12**) is believed to be very unstable in spite of its apparent structural similarity to the stable trityl radical.[23] An attempt to obtain **12** *via* bridgehead hydrogen abstraction of triptycene was unsuccessful.[23a] The instability of **12** was further demonstrated by the observa-

$$(tert\text{-}C_4H_9O)_2 \rightarrow tert\text{-}C_4H_9O\cdot$$

$$tert\text{-}C_4H_9O\cdot + HSiCl_2CH_3 \rightarrow tert\text{-}C_4H_9OH + \cdot SiCl_2CH_3$$

$$\cdot SiCl_2CH_3 + RBr \rightarrow BrSiCl_2CH_3 + R\cdot$$

$$R\cdot + HSiCl_2CH_3 \rightarrow RH + \cdot SiCl_2CH_3$$



9 **10** **11** **12**

tion that **12** generated by thermolysis of triptoyl peroxide readily abstracted hydrogen even from benzene.[23b] The results show the potentiality of the silyl radical method in ready formation of a strained bridgehead radical which is, otherwise, less accessible. A report was given of a similar ready formation of the strained 1-norbornyl radical from 1-bromonorbornane *via* the bromine abstraction by an organotin radical.[24] A significant exothermicity of the bromine abstraction by a silyl radical[25] might be the principal cause of the reduction in the activation energy, which, in turn, necessarily gives a small structural effect on the rate of abstraction. The electroneutral or weakly nucleophilic character of a silyl radical[26] should also be taken into account. The bridgehead carbon is thus almost electroneutral in the transition state of the bromine abstraction. Destabilization might diminish, which originates from steric (strain) or inductive effect on a carbonium ion-like transition state encountered in a usual hydrogen abstraction[27] or a perester decomposition.[28]

Relative Reactivities. It is noteworthy that the change in the reactivities is not monotonic in going from **1a** to **4a** (Fig. 1). The differences are small but they exceed experimental errors as judged from the reproducibility of the relative rates and accuracy of the glpc analysis. Although the stepwise introduction of a benzo substituent into bicyclo[2.2.2]octane framework lowers the reactivity at first, **4a** has equal or even higher reactivity than **3a**. A benzo substituent would be expected to reduce the bridgehead reactivity because of possible increase in steric crowding around the bridgehead and in the bridgehead strain. On the contrary, an electronegative inductive effect of a benzo substituent might accelerate the reaction by dispersing a possible negative charge developing in the transition state due to the nucleophilic character of a silyl radical,[26] although its nucleophilicity is extremely small. Effects of successive benzo substitution (steric, strain, or inductive) should be additive, and the overall benzo effects cumulative. If no particular effect is caused by a benzo substituent, the reactivity should monotonously decrease or increase in going from **1a** to **4a**. but this is not the case (Fig. 1). Decreasing rates with increasing benzo substituents show that strain and/or steric decelerating effect surpass the inductive accelerating effect. If the reactivity difference between **2a** and **3a**, 170 cal mol^{-1}, is taken to be inherent decelerating benzo effects ($\Delta\Delta F_{\mathrm{B}}$), the present abnormal benzo effects are characterized by the unexpectedly high reactivities of symmetrical **1a** and **4a**. Asymmetrical **2a** or **3a** suffers from abnormal destabilizing effect due to its lack of local symmetry. It should be concluded that an extra stabilization contributes to radicals **9** and **12** (or destabilization to **10** and **11**), which might be correlated with the geometrical symmetry of **9** and **12**. The gap between observed and predicted (from additivity of $\Delta\Delta F_{\mathrm{B}}$, dashed line in Fig. 1) reactivities of **1a** and **4a** ($\Delta\Delta F_{\mathrm{LS}}$), *ca.* 300 cal mol^{-1}, is thus ascribed to the local symmetry effect. Introduction of a benzo substituent into symmetrical bicyclo[2.2.2]octane is an appreciable perturbation to the geometry (one bond is shortened and three C–C–C angles at the bridgehead position become nonequivalent) and the local symmetry effect might disappear (or the local asymmetry destabilization appears). Removal of methylene from bicyclo[2.2.2]octane to give bicyclo[2.2.1]heptane would cause a much greater disturbance. The very low reactivity of the bicyclo[2.2.1]heptane bridgehead[9] might, in part, be attributed to the very asymmetrical nature of the 1-bicyclo[2.2.1]heptyl radical; the main reason is the increase in angle strain of this radical.[13] On the other hand, it is highly plausible that the local symmetry makes the bicyclo[1.1.1]pentyl[14] or cubyl[29] radical "stable" for its appreciable angle strain.

Although the theoretical interpretation of a local symmetry effect has not been accomplished* the origin of the effect would be related to the mode of the rehybridization of a radical in such a way that the hybridization energy is sensitive to local symmetry. The present effect should be considered in light of the nonplanarity of some strained secondary (*e.g.* cyclopropyl[30]) radicals with an electronegative α substituent (*e.g.* fluorine[31]). The contributing factors to the geometry of a radical might be: (1) hybridization energies, (2) repulsions of the bonding electrons, and (3) nonbonded interactions between the groups at the ends of the bonds. A planar geometry would be preferable from the viewpoint of minimization of repulsions between bonding electrons and between groups. Since the radical is in the middle of the sp^2 hybridized planar carbonium ion and the sp^3 hybridized tetrahedral carbanion, the hybridization energy of the radical would be less sensitive to planarity[32] than the carbonium ion or carbanion. The energy difference between planar and pyramidal structures should be reduced as is usually the case.[6–8] Factors other than planarity such as symmetry might contribute significantly to the hybridization energy of the radical of a given structure. At the sacrifice of some unfavorable increase in repulsions between bonds the cyclopropyl radical may prefer a nonplanar geometry because of a compensating stabilizing hybridization in a pyramidal or more symmetrical structure with respect to the three angles around the radical center. The enhanced configurational stability of α-fluorocyclopropyl radical[31] may be interpreted on similar grounds. The electron withdrawal by a fluorine substituent reduces the importance of repulsion between bonding electrons, making the hybridization energy the determining factor of the structure. A refined molecular orbital calculation may support the present arguments. It has been shown that the hypothetically strained methyl radical took

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* The C_1—C_4 rear-lobe interaction is not important in the present system. The unimportance of the rear-lobe effect has been suggested by the ESR spectrum of the 1-bicyclo[2.2.2]octyl radical see, P. J. Krusic, T. A. Rettig, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 995 (1972). An Extended Hückel calculation has also shown that the C_1—C_4 atomic bond population in the 1-bicyclo[2.2.2]octyl cation was negative, showing antibonding, see T. Yonezawa, K. Shimizu, H. Morimoto, and H. Kato, *Nippon Kagaku Zasshi*, **90**, 142 (1969).

a pyramidal structure.[33]

It is anticipated that both the nonplanarity of a strained (nonbridgehead) radical and the local symmetry stabilizing effect on a strained bridgehead radical have the same principle.

Experimental

Materials and Analysis. Melting points were uncorrected. IR spectra were obtained with a Hitachi 215 spectrophotometer. NMR spectra were taken in CDCl$_3$ with TMS as a standard and were recorded with a Varian T-60 spectrometer. Mass spectra were obtained with a Hitachi mass spectrometer. Glpc analyses were performed with a Yanagimoto 550T gas chromatograph using a poly(ethylene glycol) or silicone DC 550 column. Cyclohexane was shaken with concentrated sulfuric acid and distilled over sodium after repeated washing with water. Methyldichlorosilane was distilled prior to use. DTBP was used as received.

*1-Bromobicyclo[2.2.2]octane (**1a**).* A mixture of 30 g of 1-carbethoxy-1,3-cyclohexadiene[34] and 80 g of acrolein was heated at 150 °C under reflux for 90 hr. Distillation at 100—110 °C/1.5 mmHg afforded 19 g (47%) of the Diels-Alder adduct **5**, which was hydrogenated in an equal volume of acetic acid at atmospheric pressure in the presence of platinum oxide. After removal of the catalyst and most of the solvent, 15 g of DTBP was added (in three portions) and the mixture was heated at 130 °C for 20 hr under dry, oxygen free nitrogen. Distillation at 98—100 °C/10 mmHg (lit. 96—98 °C/12 mmHg,[34] 75—76 °C/3 mmHg[35]) afforded 8.1 g 49%) of the decarbonylated ester **7**, which was hydrolyzed[34] to give **1c** in a 96% yield. **1a** was prepared in *ca.* 50% yield by the Hunsdiecker reaction of **1c**[16]; mp 61—62 °C (lit. 58.8—59.5 °C,[16] 66—68 °C[34]); IR(KBr): 1453, 968, and 815 cm^{-1}; NMR: τ 7.53—8.00 (6H, m, methylene vicinal to Br) and 8.00—8.35 (7H, m, other methylene and bridgehead); Mass: *m/e* 190 and 188 (M$^+$, relative intensity 5.6), 109 (100), and 81 (40).

*1-Bromobenzobicyclo[2.2.2]octene (**2a**).* A mixture of benzenediazonium-2-carboxylate (from 10 g of anthranilic acid and 20 ml of iso-amyl nitrite[36]) and 200 ml of sodium dry anisole was heated at 70 °C for 15 hr. The anisole was expelled and the residue was distilled. A fraction boiling at 104—105 °C/6 mmHg was collected (4.3 g), and was found to be a mixture[37] of the 1,4-adduct **8** and benzobicyclo[2.2.2]-octadien-2-one[38] (approximately 6 : 1[37]). The mixture was hydrogenated in methanol under atmospheric pressure in the presence of palladium charcoal. The catalyst was removed by filtration and a calculated amount of tosylhydrazine was added. The mixture was refluxed for 15 hr to convert the undesired ketone into hydrazone and then passed through a silica gel column. After removal of methanol, the residue was distilled at 107 °C/2.7 mmHg to give 2.9 g of **8**; IR (neat): 1330, 1163, 1123, 1102, 1070, 1060, and 746 cm^{-1}; NMR: τ 2.30—2.95 (4H, m, aromatic), 6.45 (3H, s, methyl), 7.05 (1H, broad s, bridgehead), and 7.80—8.75 (6H, m with peaks at 7.97, 8.13, 8.42, and 8.57, methylene). To an ice-cooled mixture of 500 mg (2.6 mmol) of **8** and 640 mg (5.2 mmol) of acetyl bromide was added ten drops of anhydrous stannic chloride. The mixture was stirred at room temperature for 3 hr and at 80 °C for 15 hr, poured on ice and extracted with methylene chloride. The methylene chloride was distilled off and the residue was chromatographed on a silica gel column. Elution with petroleum ether gave 140 mg (25%) of a mixture of the bromide **2a** and the chloride **2d** (1 : 1.5). Further elution with petroleum ether-methylene chloride (1 : 1) afforded 220 mg (37%) of the acetate **2e**. Pure **2a** was obtained by means of a preparative glpc after the column chromatographic separation of **2e**. When stannic bromide was used instead of stannic chloride, **2a** and **2e** were obtained in a 1 : 3 ratio but in much lower total yield.

2a had mp 83.5—84.5 °C; IR(KBr): 962, 898, 860, 747 cm^{-1}; NMR: τ 2.17—2.47 (1H, m, aromatic (peri)), 2.53—2.97 (3H, m, other aromatic), 6.95 (1H, broad s, bridgehead), and 7.20—8.83 (8H, m with major peaks at 8.02 and 8.22, methylene); Mass: *m/e* 238 and 236 (M$^+$, 6.0), 210 and 208 (40), 157 (46.7), and 129 (100).

2d had IR(neat): 1035, 970, 913, 872, 755, 737, and 697 cm^{-1}; NMR: τ 2.20—2.60 (1H, m, aromatic (peri)), 2.60—3.00 (3H, m, other aromatic), 7.00 (1H, broad s, bridgehead), and 7.40—8.80 (8H, m, methylene); Mass: m/e 194 (M$^+$, 26), 192 (M$^+$, 73), 166 (32), 165 (49), 164 (64), 163 (67), 129 (100), 128 (76), and 127 (53).

2e had IR(neat): 1740, 1248, 1092, 1040, and 750 cm^{-1}; NMR: τ 2.55—3.00 (4H, m, aromatic), 7.02(1H, broad s, bridgehead), 7.78 (3H, s, methyl), and 7.30—8.65 (8H, m with peaks at 7.45, 7.90, 8.06 and 8.28); Mass: m/e 216 (18), 174 (100), 146 (84), and 145 (76).

*1-Bromodibenzobicyclo[2.2.2.]octadiene (**3a**).* To a solution of 5 g of 9-bromoanthracene and 50 mg of 2,5-di-*tert*-butylhydroquinone in 150 ml of chlorobenzene in an autoclave was introduced ethylene to a pressure of 60 atm. The mixture was heated at 150 °C for 40 hr under stirring (maximal pressure was 110 atm). After distillation of most of the chlorobenzene the residue was chromatographed on a silica gel column. **3a** was obtained by elution with petroleum ether. Recrystallization three times from petroleum ether gave *ca.* 2 g of pure **3a** in white powder; mp 137.5—138 °C; IR(KBr): 1457, 1300, 1160, 1140, 1030, 915, 823, 755, and 738 cm^{-1}; NMR: τ 2.10—2.50 (2H, m, aromatic (peri)), 2.57—3.05 (6H, m, other aromatic), 5.67 (1H, broad s, bridgehead), 7.55—7.95 (2H, m, methylene vicinal to Br), and 7.95—8.35 (2H, m, other methylene); Mass: *m/e* 286 and 284 (M$^+$, 6.1), 258 and 256 (100), 205 (3.8), 204 (7.0), 203 (10), 202 (12), 177 (25), and 176 (32).

*1-Bromotribenzobicyclo[2.2.2]octatriene (1-Bromotriptycene **4a**).* A mixture of 3 g of 9-bromoanthracene and benzenediazonium-2-carboxylate (from 8.2 g of anthranilic acid and 16 ml of iso-amyl nitrite) in 240 ml of ethylene chloride was heated at 70 °C for 15 hr. Evaporation of the solvent gave a tarry material, which was chromatographed on a silica gel column. Crude **4a** eluted with benzene was repeatedly washed with petroleum ether to remove unchanged 9-bromoanthracene. Pure **4a** (1 g) was obtained as white powder by recrystallization from benzene; mp 253—254.7 °C (lit,[39] 246—248 °C); IR(KBr): 1450, 1290, 1155, 1033, 925, 850, 840, 820, and 738 cm^{-1}; NMR: τ 2.10—2.35 (3H, m, aromatic (peri)), 2.45—3.15 (9H, m, other aromatic), and 4.53 (1H, s, bridgehead); Mass: *m/e* 334 and 332 (M$^+$, 37) and 253 (100).

Reductive Debromination. A solution of *ca.* 30 mg of a bromide (**1a**, **2a**, **3a**, or **4a**), *ca.* 300 mg of methyldichlorosilane and a catalytic amount of DTBP in 3 ml of cyclohexane was degassed and sealed. The mixture was heated at 120 °C for 1—3 hr. The crude reaction mixture was then analyzed by glpc. Identification of the product (**1b**, **2b**, **3b**, or **4b**) was made on the basis of the glpc retention time and IR spectrum. Authentic **1b** was obtained by the procedure of Doering *et al.*[17] All the other authentic hydrocarbons (**2b**, **3b**, and **4b**) were prepared by the addition of benzyne to benzene,[21] naphthalene,[21] and anthracene,[20] respectively, followed by hydrogenation when necessary (in the case of **2b** and **3b**). Controlled experiment showed that the reaction did not take place at all in the absence of DTBP.

The relative disappearance rates were measured by glpc analysis of competitive reactions between a bromide (**1a**, **2a**, or **4a**) and **3a** (standard) by means of appropriate standards. The relative rates obtained were average values of several runs in which the conversion ranged from 30—50%. The accuracy of the glpc analysis was carefully checked. It was found that the analytical errors were small enough compared with the differences in reactivities of the bromides.

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References

1) (a) W. A. Pryor, "Free Radicals," McGraw Hill, New York, N. Y. (1966), p. 29—43. (b) C. Rüchardt, *Angew. Chem.*, **82**, 845 (1970).

2) (a) G. Herzberg and J. Shoosmith, *Can. J. Phys.*, **34**, 523 (1956). (b) G. Herzberg, *Proc. Roy. Soc. Ser. A*, **262**, 291 (1961).

3) (a) H. M. McConnel and R. W. Fessenden, *J. Chem. Phys.*, **31**, 1658 (1959). (b) M. Kaplus and G. K. Fraenkel, *ibid.*, **35**, 1312 (1961). (c) M. C. R. Symons, *Nature*, **198**, 1196 (1963).

4) H. C. Brown, M. S. Kharasch, and T. H. Chao, *J. Amer. Chem. Soc.*, **62**, 3435 (1940).

5) (a) K. Morokuma, L. Pedersen, and M. Kaplus, *J. Chem. Phys.*, **48**, 4801 (1968). (b) T. A. Claxton and N. A. Smith, *ibid.*, **52**, 4317 (1970). S. Y. Chang, E. R. Davidson, and G. Wincow, *ibid.*, **52**, 5596 (1970).

6) (a) J. P. Lorand, S. D. Chodroff, and R. W. Wallace, *J. Amer. Chem. Soc.*, **90**, 5266 (1968). (b) R. C. Fort, Jr., and R. E. Franklin, *ibid.*, **90**, 5267 (1968). (c) L. B. Humphrey, B. Hodgson, and R. E. Pincock, *Can. J. Chem.*, **46**, 3099 (1968).

7) A. Oberlinner and C. Rüchardt, *Tetrahedron Lett.*, **1969**, 4685.

8) D. E. Applequist and K. Kaplan, *J. Amer. Chem. Soc.*, **87**, 2194 (1965).

9) E. C. Kooyman and G. E. Vegter, *Tetrahedron*, **4**, 382 (1958).

10) R. Srinivasan and F. I. Sonntag, *J. Amer. Chem. Soc.*, **89**, 407 (1967).

11) (a) I. Tabushi, J. Hamuro, and R. Oda, *ibid.*, **89**, 7127 (1967). (b) I. Tabushi, Y. Aoyama, S. Kojo, J. Hamuro, and Z. Yoshida, *ibid.*, **94**, 1177 (1972).

12) A. F. Bickel, J. Krotnerus, E. C. Kooyman, and G. C. Vegter, *Tetrahedron*, **9**, 230 (1960).

13) V. R. Koch and G. J. Gleicher, *J. Amer. Chem. Soc.*, **93**, 1657 (1971).

14) (a) K. B. Wiberg and D. S. Connor, *ibid.*, **88**, 4437 (1966). (b) K. B. Wiberg and V. Z. Williams, *J. Org. Chem.*, **35**, 369 (1970).

15) S. Ohishi, S. Ichihara, and O. Simamura, presented at the 23th Annual Meeting of the Chemical Society of Japan, Tokyo, 1970, Abstracts, Vol. 3, p. 1416.

16) F. W. Baker, H. D. Holtz, and L. M. Stock, *J. Org. Chem.*, **28**, 514 (1963).

17) W. von E. Doering, M. Farber, M. Sprecher, and K. B. Wiberg, *J. Amer. Chem. Soc.*, **74**, 3000 (1952).

18) Z. Suzuki and K. Morita, *J. Org. Chem.*, **32**, 31 (1967).

19) F. W. Baker, R. C. Parish, and L. M. Stock, *J. Amer. Chem. Soc.*, **89**, 5677 (1967).

20) B. H. Klanderman and T. R. Criawell, *J. Org. Chem.*, **34**, 3426 (1969).

21) R. G. Miller and M. Stiles, *J. Amer. Chem. Soc.*, **85**, 1798 (1963).

22) (a) J. Curtice, H. Gilman, and G. S. Hammond, *ibid.*, **79**, 4754 (1957). (b) Y. Nagai, N. Kobori, and M. Migita, *Nippon Kagaku Zasshi*, **88**, 793 (1967). (c) R. N. Haszeldine and J. C. Young, *J. Chem. Soc.*, **1960**, 4503. (d) J. A. Kerr, B. J. A. Smith, A. F. Trotman-Dickenson, and N. C. Young, *Chem. Commun.*, **1966**, 157. (e) J. A. Kerr, B. J. A. Smith, A. F. Trotman-Dickenson, and N. C. Young, *J. Chem. Soc. A*, **1968**, 510.

23) (a) P. D. Bartlett, M. J. Pyan, and S. G. Cohen, *J. Amer. Chem. Soc.*, **64**, 2649 (1942). (b) P. D. Bartlett and F. D. Greene, *ibid.*, **76**, 1088 (1954).

24) E. J. Kupchik and R. J. Kiesel, *Chem. Ind.*, **1962**, 1654.

25) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, New York, N. Y. (1940), Japanese Translation by M. Koizumi, Kyoritsu Publishing Co. (1950), p. 57.

26) Y. Nagai, I. Shiojima, and T. Migita, presented at the 21th Annual Meeting of the Chemical Society of Japan, Osaka, 1968, Abstracts, Vol. 3, p. 2073.

27) (a) P. J. Owens, J. G. Gleicher, and L. M. Smith, Jr., *J. Amer. Chem. Soc.*, **90**, 4122 (1968). (b) G. J. Gleicher, J. L. Jackson, P. H. Owens, and J. D. Unruh, *Tetrahedron Lett.*, **1969**, 833.

28) P. D. Bartlett and C. Rüchardt, *J. Amer. Chem. Soc.*, **82**, 1576 (1960).

29) R. E. Eaton and T. W. Cole, Jr., *ibid.*, **86**, 962 (1964).

30) (a) H. W. Warborsky and C-J. Chen, *ibid.*, **89**, 5499 (1967). (b) J. L. Altman and D. W. Nelson, *ibid.*, 5163 (1969). (c) M. L. S. Dewar and J. M. Harris, *ibid.*, **91**, 3652 (1969). (d) R. E. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963). (e) H. W. Warborsky and J-C. Chen, *J. Amer. Chem. Soc.*, **93**, 671 (1971).

31) (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965). (b) G. A. Carlson and G. C. Pimentel, *ibid.*, **44**, 4053 (1966). (c) D. E. Milligan, M. E. Jacox, and J. J. Comeford, *ibid.*, **44**, 4058 (1966). (d) T. Ando, F. Namigata, H. Yamanaka, and W. Funasaka, *J. Amer. Chem. Soc.*, **89**, 5719 (1967). (e) J. Cooper, A. Hudson, and R. A. Jackson, *Mol. Phys.*, **23**, 209 (1972). (f) T. Kawamura, T. Koyama, and T. Yonezawa, *J. Amer. Chem. Soc.*, **95**, 3220 (1973).

32) R. C. Fort, Jr., and P. von R. Schleyer in "Advances in Alicyclic Chemistry," H. Hart and J. Karabatsos, Ed., Academic Press, New York, N. Y. (1966), p. 337—352.

33) P. von R. Schleyer, private communication.

34) C. A. Grob, M. Ohta, E. Penk, and A. Weiss, *Helv. Chim. Acta.*, **41**, 1191 (1958).

35) J. D. Roberts, W. T. Moreland, and W. Frazer, *J. Amer. Chem. Soc.*, **75**, 637 (1953).

36) L. Friedman, *ibid.*, **89**, 3071 (1969).

37) I. Tabushi and H. Yamada (unpublished).

38) K. Kitahonoki and Y. Takano, *Tetrahedron Lett.*, **1963**, 1597.

39) R. D. Bartlett, S. G. Cohen, J. D. Cotman, Jr., N. Kornblum, J. R. Landry, and E. S. Lewis, *J. Amer. Chem. Soc.*, **72**, 1003 (1950).