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CARBENOID REACTION

THE REACTION OF DIBROMODIPHENYLMETHANE 9,9-DIBROMOFLUORENE AND 9,9-DICHLORO-9*H*-TRIBENZO[a.c.e] CYCLOHEPTENE WITH ALKYLLITHIUM IN THE PRESENCE OF OLEFINS

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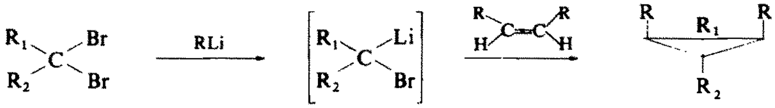
Abstract—1,1-Diphenyl-2-ethoxycyclopropane was obtained from the reaction of dibromodiphenylmethane (II) with methyllithium in the presence of ethyl vinyl ether. A cyclopropane derivative was not obtained from the reaction of 9,9-dibromofluorene (III) or 9,9-dichloro-9*H*-tribenzo[a.c.e]cycloheptene (IV) with alkyllithium in olefin but 9,9′-bifluorenylidene (IX) and 9,9′-dibromo-9,9′-bifluorenyl (XI) were produced from III and 9-methylene-9*H*-tribenzo[a.c.e]cycloheptene (XXIII) and 9*H*-tribenzo-[a.c.e]-cyclohepten-9-ol (XXIV) from IV. The mechanism of the reaction is discussed.

INTRODUCTION

Photolysis of diazoalkanes produces true divalent carbon species, which add to olefins to give cyclopropanes.[1] Although the reaction of organo alkali metal compounds with certain halides may also produce cyclopropanes when carried out in the presence of olefin (carbenoid reaction), recently it has been demonstrated that different chemical reactivities were observed concerning to the above reactions.[2] Thus diphenylmethylene obtained from the photolysis of diphenyldiazomethane adds to olefin nonstereospecifically,[3,4] or abstracts an hydrogen atom easily, and the ground state triplet was confirmed.[5] On the other hand, the reaction of dibromodiphenylmethane (II) with MeLi in the presence of 2-butene gives cyclopropane stereospecifically.[4]



I

These results suggest that the above reactions may involve different intermediates. Closs proposed that α-haloalkyllithium compound (I) may be formed, which then

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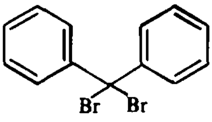
[1] For a recent review of the subject of carbene chemistry, see W. Kirmse, *Carbene Chemistry*. Academic Press, New York, N.Y. (1964).

[2] For a recent review on the mechanism of α-elimination, see W. Kirmse, *Angew. Chem.* **77**, 1 (1965).

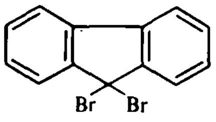
[3] R. M. Etter, H. S. Skovronek and P. S. Skell, *J. Am. Chem. Soc.* **81**, 1008 (1959).

[4] G. L. Closs and L. E. Closs, *Angew. Chem.* **74**, 431 (1962).

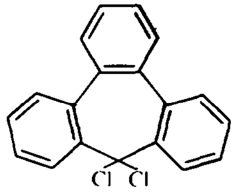
reacts with olefin through a S_N2 like transition state.[4,6] The presence of intermediate I was recently confirmed by the isolation of α-haloalkyllithium compounds.[7-9]



II



III

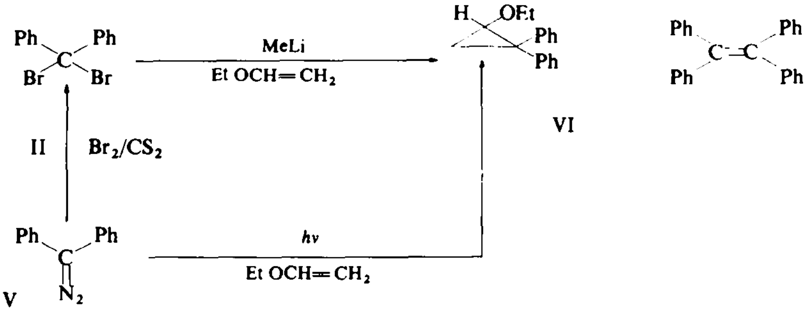


IV

Fluorenylidene adds to olefin nonstereospecifically,[10] while 9*H*-tribenzo[a.c.e]-cycloheptenylidene adds stereospecifically.[11] If Closs's hypothesis is correct, 9,9-dibromofluorene (III) and 9,9-dichloro-9*H*-tribenzo[a.c.e]cycloheptene (IV) should give cyclopropane derivatives on treatment with alkyllithium in the presence of olefins. However, it was found that the reaction of III and IV with MeLi in olefin gave instead VIII, XII, XXIII and XXIV. These results cannot be explained by Closs's hypothesis. The mechanism of this reaction is discussed on the basis of the present results.

RESULTS

The reaction of dibromodiphenylmethane (II) *with methyllithium in the presence of olefin.* Dibromodiphenylmethane (II) was obtained by bromination of diphenyldiazomethane (V). Treatment of II with 1·5 mole equivalents of MeLi in the presence of ethyl vinyl ether gave tetraphenylethylene (78 %) and 1,1-diphenyl-2-ethoxycyclopropane (VI; 4·8 %).



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[5] [a] R. W. Murray, A. M. Trozzolo, E. Wasserman and W. A. Yager, *J. Am. Chem. Soc.* **84**, 3213 (1962); [b] R. W. Brandon, G. L. Closs and C. A. Hutchison, Jr., *J. Chem. Phys.* **37**, 1878 (1962).

[6] [a] G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.* **86**, 4042 (1964); [b] G. L. Closs and J. J. Coyle, *Ibid.* **87**, 4270 (1965); [c] R. A. Moss, *J. Org. Chem.* **30**, 3261 (1965).

[7] W. T. Miller and D. M. Whalen, *J. Am. Chem. Soc.* **86**, 2089 (1964).

[8] D. F. Hoeg, D. I. Lusk and A. L. Crumbliss, *J. Am. Chem. Soc.* **87**, 4147 (1965).

[9] G. Köbrich, K. Flory and W. Drischel, *Angew. Chem.* **76**, 536 (1964); [b] G. Köbrich and H. R. Merkle, *Chem. Ber.* **99**, 1782 (1966); [c] G. Köbrich, K. Flory and R. H. Fischer, *Ibid.* **99**, 1793 (1966); [d] G. Köbrich and W. Drischel, *Tetrahedron* **22**, 2621 (1966).

[10] [a] E. Funakubo, I. Moritani, T. Nagai, S. Nishida and S. Murahashi, *Tetrahedron Letters* 1069 (1963); [b] S. Murahashi, T. Nagai and I. Moritani, *Bull. Chem. Soc. Japan* in press; [c] M. Jones, Jr., and K. R. Rettig, *J. Am. Chem. Soc.* **87**, 4013, 4015 (1965).

[11] S. Marahashi, I. Moritani and M. Nishino, *J. Am. Chem. Soc.* **89**, 1257 (1967). Photolysis of 9-diazo-9*H*-tribenzo-[a.c.e]cycloheptene in *cis*-2-butene gave 70 % yield of cyclopropane derivative stereospecifically.

Irradiation of a solution of diphenyldiazomethane (V) in ethyl vinyl ether gave VI (18·5 %) and benzophenone azine and *syn*-tetraphenylethane.

The reaction of 9,9-*dibromofluorene* (III) and 9-*bromofluorene* (XVIII) *with alkyllithium in the presence of olefin.* 9,9-Dibromofluorene (III) was obtained by bromination of 9-diazofluorene (VII). The results of the reactions of III with alkyllithium in the presence of olefins are summerized in Table 1. The reaction of bromide III with 2·8 mole equivts of MeLi in the presence of *cis*-2-butene gave 9,9′-dimethyl-9,9′-bifluorenyl (VIII; 81 %) and a small amount of bifluorenylidene (IX) and 9,9-dimethylfluorene (X). On the other hand, 9,9′-dibromo-9,9′-bifluorenyl (XI; 18 %), IX (33 %) and biphenylenephenanthrone (XII; 22 %) were obtained from the reaction with one mole equiv of MeLi.

TABLE 1. THE REACTION OF 9,9-DIBROMOFLUORENE (III) WITH ALKYLLITHIUM IN THE PRESENCE OF OLEFIN

Temp (C°)	Olefin	RLi	RLi/III	Products				
				VIII	IX	X	XI	XII
−20°	*cis*-2-butene	MeLi	1	—	33	—	18	22
−15°	*cis*-2-butene	MeLi	2·8	81	1	1	—	—
−20°	*cis*-2-butene	MeLi[a]	3	37	—	41	—	—
−20°	ethyl vinyl ether	MeLi	1[b]	—	22	—	—	31
−30°	ethyl vinyl ether	n-BuLi	2	19[c,d]	—	—	—	—
−20°	ethyl vinyl ether	MeLi	2[e]	62	2	—	—	—

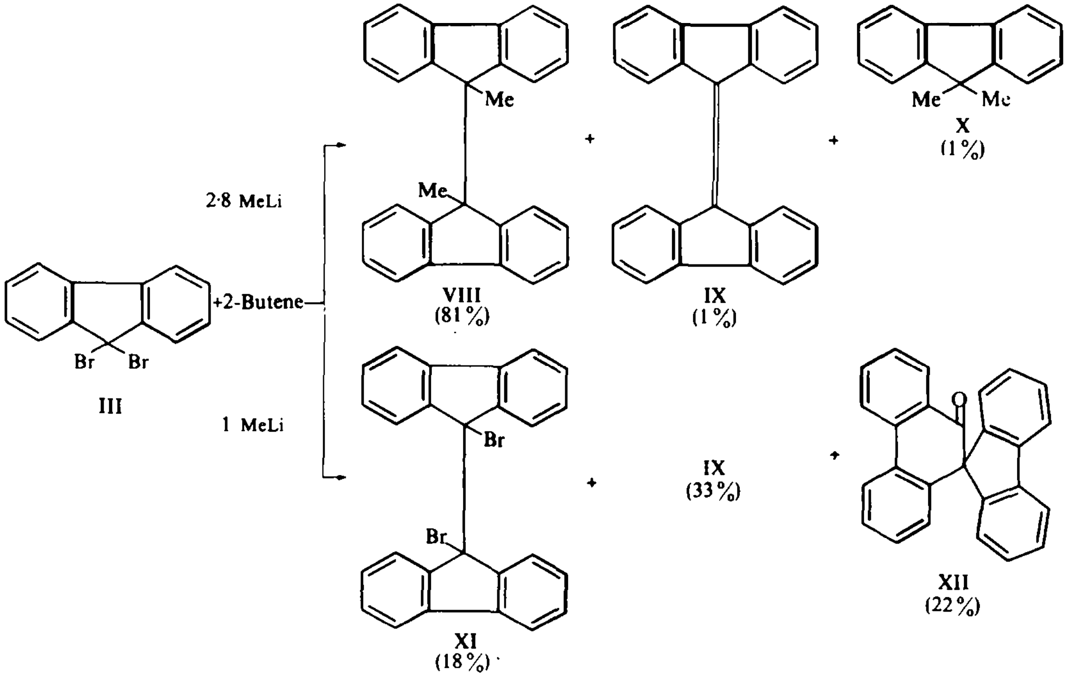
[a] To a soln of MeLi and *cis*-2-butene was added a soln of III.

[b] Fluorenone was obtained in 9 % yeild.

[c] R=n-Bu (compound XIII).

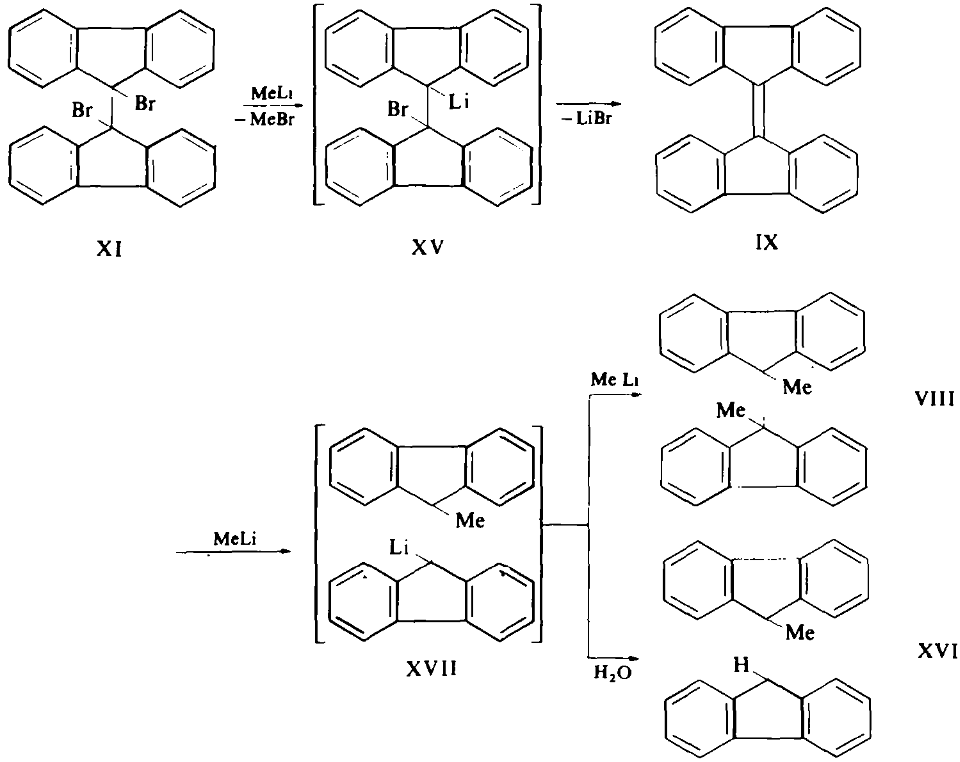
[d] Compound XIV was obtained in 31 % yield.

[e] 9,9-Dichlorofluorene was used instead of III.



Addition of III to a mixture of 3·0 mole equivs MeLi and *cis*-2-butene gave VIII (37 %) and X (40·5 %). The reaction of III with n-BuLi in ethyl vinyl ether gave 9,9′-di-n-butyl-9,9′-bifluorenyl (XIII) (19 %) and 9-n-butyl-9,9′-bifluorenyl (XIV) (31 %). Moreover, similar products were obtained from the reaction of 9,9-dichlorofluorene and MeLi. In any case, the formation of a cyclopropane derivative was not observed.[12]

In view of the fact that different products were obtained from the reaction of III with various amounts of alkyllithium, this reaction was investigated in detail. Compound XI is converted to IX by treatment with MeLi. This suggests that IX might be formed from metallation of XI to form XV followed by β-elimination.



When a solution of MeLi was added to a red solution of IX, the colour of the solution changed to orange yellow. Moreover, when a solution of methyl bromide was added to the orange yellow solution, the colour of the solution immediately disappeared and VIII was obtained. On mixing the above orange yellow solution with moist ether 9-methyl-9,9′-bifluorenyl (XVI) was obtained. These results suggest that the orange yellow solution should contain 9-lithio-9′-methyl-9,9′-bifluorenyl (XVII) which is formed by addition of MeLi to IX.[13] When n-BuLi was used, instead of MeLi, XIII (19 %) and XIV (31 %) were obtained. The mechanism leading to XII is not clear.

9-Bromofluorene (XVIII) reacts with MeLi to give 9,9′-bifluorenyl (XIX) in 98 %

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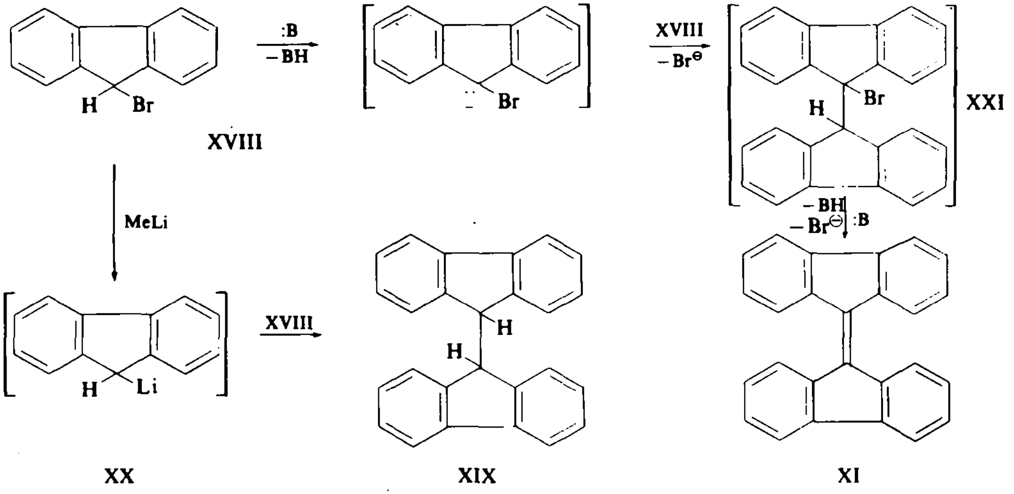
[12] The reaction mixture was subjected to alumina chromatography. The soln eluted was divided into ca. 30 fractions. After removal of soluvent the residue was checked by infrared spectrum.

[13] U. Schöllkopf and M. Eisert, *Liebigs Ann.* **664**, 76 (1963).

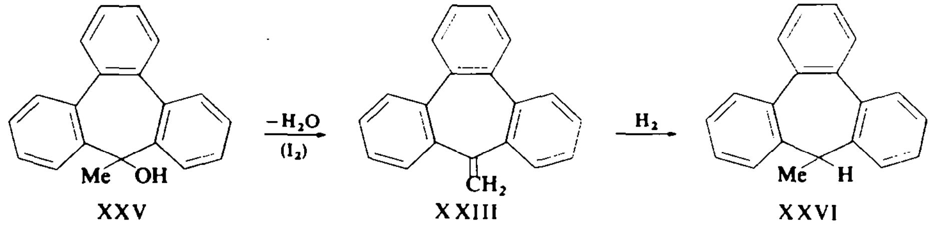
yield. Halogen metal conversion may occur preferentially, and 9-lithiofluorene (XX) formed may react easily with 9-bromofluorene. On the other hand, it is reported that XVIII reacts with t-butoxide or benzyltrimethylammonium hydroxide to give IX.[14]



:Bt-BuOK in t-BuOH
$PhCH_2$ N Me_3 (OH)

The reaction of 9,9-*dichloro*-9*H*-*tribenzo*[a.c.e]*cycloheptene with alkyllithium in the presence of olefin*. Reaction of 9*H*-tribenzo[a.c.e]cycloheptene-9-one (XXII)[15] with phosphorus pentachloride at 180° gave 9,9-dichloro-9*H*-tribenzo[a.c.e]cycloheptene (IV) in 88% yield.[16]

The reaction of dichloride IV with 1·4 mole equivts of MeLi in the presence of ethyl vinyl ether was observed to afford 9-methylene-9*H*-tribenzo[a.c.e]cycloheptene (XXIII; m.p. 157–158°, 44% yield) and 9*H*-tribenzo[a.c.e]cyclohepten-9-ol (XXIV-a; m.p. 95–96°, 11% yield). The structure of the former compound was confirmed by mixed m.p. with an authentic sample prepared by dehydration of 9-methyl-9*H*-tribenzo[a.c.e]cyclohepten-9-ol (XXV) with iodine. Moreover, hydrogenation of XXIII gave 9-methyl-9*H*-tribenzo[a.c.e]cycloheptene (XXVI).



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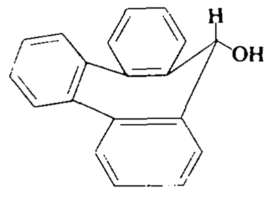
[14] D. Bethell, *J. Chem. Soc.* 666 (1963).

[15] W. Tochtermann, K. Oppenländer and U. Walter, *Chem. Ber.* 97, 1329 (1964).

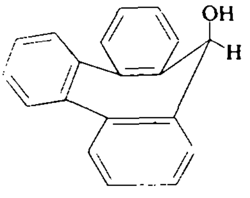
[16] 9,9-Dibromo-9*H*-tribenzo[a.c.e]cycloheptene could not be prepared from the reaction of XXII with PCl_2Br_3 or PBr_5. When the tosylhydrazone of XXII was treated with MeONa in dry pyridine, 9-diazo-9*H*-tribenzo[a.c.e]cycloheptene was obtained in 4% yield. Furthermore bromination of this diazo compound in CS_2 at −15° gave 9,9-dibromo-9*H*-tribenzo[a.c.e]cycloheptene in 5% yield. d.p. 150°. This *gem*-dibromide is very unstable in the air and easily decomposed to give XXII.

On the other hand, the NMR spectrum of the XXIV-a shows a methine proton at τ 4·59 and an OH proton at τ 7·65. The IR spectrum shows an OH band at 3180 cm^{-1} (ν, O—H) and 1048 cm^{-1} (ν, C—O). This compound was, therefore, assigned to be 9*H*-tribenzo[a.c.e]cyclohepten-9-ol. It has been reported[17] that 9*H*-tribenzo[a.c.e]-cyclohepten-9-ol (XXIV-b) (m.p. 117–118°) was obtained from sodium borohydride reduction of ketone XXII. The NMR spectrum of this compound had a methine proton at τ 4·64.

The preferred conformation of cycloheptatriene is boat-shaped.[18] Although interconversion of cycloheptatriene is rapid at room temperature,[19] optically active isomers of 9-carboxymethylene-9*H*-tribenzo[a.c.e]cycloheptene have been obtained.[20] This has been attributed to steric interaction of the *ortho* hydrogen atoms of three benzene rings in a planar transition state. Thus, the presence of conformational isomers of 9*H*-tribenzo[a.c.e]cyclohepten-9-ol should be possible. The alcohol (m.p. 117–118°) which was obtained from sodium borohydride reduction should be the axial alcohol XXIV-b,[21] while the alcohol (m.p. 95–96°) should be the equatorial alcohol XXIV-a. Compound XXIV-b was also obtained from the reduction of XXII with LAH, while XXIV-a was obtained from catalytic reduction by platinum oxide. This assignment was confirmed by IR spectrum. The O—H stretching vibration of XXIV-b (3300 cm^{-1}, ν, O—H) is higher than that of XXIV-a, since the formation of hydrogen bonding of XXIV-b is unfavorable.[22]



XXIV—a (equatorial)



XXIV—b (axial)

Thus no cyclopropane derivative was detected from the reaction of dichloride IV with MeLi. The fact that alcohol XXIV-a was obtained indicates that 9-chloro-9-lithio-9*H*-tribenzo[a.c.e]cycloheptene (XXVII) is formed as an intermediate. The equatorial chlorine atom of IV may be metalated to form XXVII by a multicentre mechanism,[23] and protonated with water followed by forming equatorial alcohol XXIV-a by nucleophilic substitution (S_N2) as shown in Scheme 1.

DISCUSSION

Although carbene and a carbenoid molecule add to olefin to give cyclopropane, significant discrepancies exist in the reactivities of both reactions. Thus, diphenyl-

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[17] M. Stiles and A. J. Libbey, *J. Org. Chem.* **22**, 1243 (1957).

[18] M. Traetterberg, *J. Am. Chem. Soc.* **86**, 4265 (1964).

[19] [a] F. A. L. Anet, *J. Am. Chem. Soc.* **86**, 458 (1964); [b] F. R. Jensen and L. A. Smith, *Ibid.* **86**, 956 (1964).

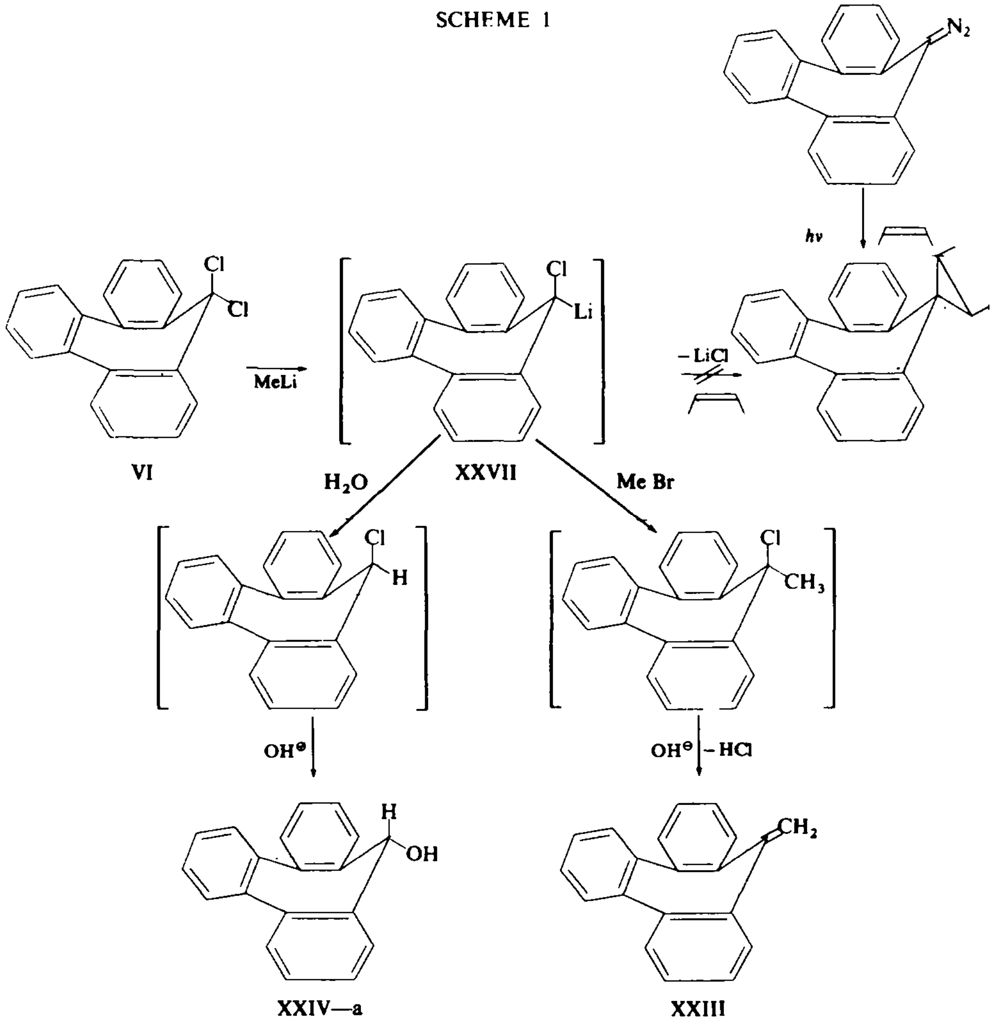
[20] W. Tochtermann and H. Küppers, *Angew. Chem.* **77**, 173 (1965).

[21] O. H. Wheeler, *The Chemistry of the Carbonyl Group* (Edited by S. Patai), p. 507. Wiley, New York (1966).

[22] L. J. Bellamy, *The Infrared Spectra of Complex Molecules* p 95. Wiley, New York (1958).

[23] E. A. Brande, *Progress in Organic Chemistry* Vol. 3, p. 193. Butterworths, London (1955).

SCHEME 1

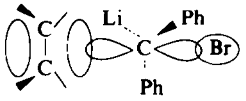


methylene adds to olefin nonstereospecifically, while the reaction of dibromodiphenylmethane with MeLi is stereospecific. The latter reaction has been explained by S_N2 like transition state. Nevertheless, no cyclopropane derivative was obtained from the reaction of III with MeLi or n-BuLi[24] in the presence of 2-butene or ethyl vinyl ether.[25, 26] In this reaction 9-bromo-9-lithio-fluorene (XXVIII) is isolated, therefore XXVIII should also give a cyclopropane derivative, since this intermediate may be easily attacked by olefin through a S_N2 like reaction as shown in XXIX.[4, 6]

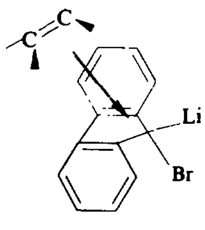
[24] n-BuLi was used to avoid Wurz type reaction caused by accompanying LiI. U. Schöllkopf, A. Lerch and J. Paust, *Chem. Ber.* **96**, 2266 (1963).

[25] Ethyl vinyl ether has enough electron density to catch weak electrophilic carbene. U. Shöllkopf and E. Wiskott, *Angew. Chem.* **75**, 725 (1963).

[26] H. D Hartzler, *J. Am. Chem. Soc.* **86**, 526 (1964).

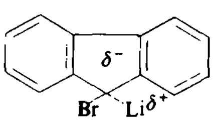


XXIX—a

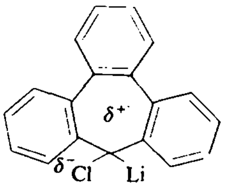


XXIX—b

Therefore the present results can not be interpreted in terms of Closs's hypothesis. For these reactions, the following two explanations may be possible. At first, α-elimination of lithium bromide may be difficult, since the bond of lithium to carbon is polarized by the stabilization of fluorenyl anion as shown in XXVIII-a. Indeed, greater difference for stabilization of carbanion between XXVIII and bromo-diphenylmethyllithium (XXX) might be expected on comparing the p*Ka* value[27] of fluorene (25) with that of diphenylmethane (35). Such an explanation has been proposed for the formation of hetaryne *via* β-elimination.[28] In the 9*H*-tribenzo[a.c.e]cycloheptene system, the stabilization of an anion can not be expected, since the p*Ka* value is large (>25). In spite of the formation of 9-lithio-9-chloro-tribenzo[a.c.e]-cycloheptene (XXVII), no cyclopropane derivative was obtained from the reaction of dichloride IV with MeLi in the presence of ethyl vinyl ether. This result reveals that anionic stability of α-haloalkyllithium compound is not a predominant factor for formation of cyclopropane.



XXVIII—a



XXVII—a

We are left with the question of whether the reactivity of IV with olefin is explicable with the stability of tribenztropylium cation as depicted in XXVII-a. However, since the pK_R value[29] of tribenztropyl alcohol (~ -15) is as small as that of benzhydrol ($-13{\cdot}3$) or 9-fluorenol (-14), the cationic stability of XXVII-a could not retarded α-elimination of lithium bromide from XXVII.

Another explanation may be as follows: According to Closs's hypothesis an olefinic double bond may attack the carbon of the reaction centre from the back side of the bromine atom of XXVIII and then give cyclopropane derivatives. Nevertheless, no cyclopropane derivatives were obtained from XXVIII. This fact suggests that another transition state such as XXXI-a may be involved. Thus, bromo-diphenylmethyllithium may hold a nearly sp like configuration at the reaction centre carbon,

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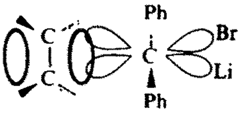
[27] D. J. Cram, *Fundamentals of Carbanion Chemistry* Chap. 1. Academic Press, New York (1965).

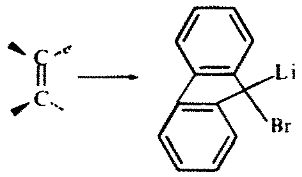
[28] Th. Kauffmann, *Angew. Chem.* 77, 557 (1965).

[29] A. Streitwieser, Jr., *Molecular Orbital Theory* Chap 12. Wiley, New York (1961).

and be attacked by olefin concertedly. On the other hand, 9-bromo-9-lithiofluorene cannot be attacked at C_9 by olefin, since the addition of an olefinic double bond to XXVIII is hindered sterically as shown in XXXI-b. This scheme can also be applied to the 9*H*-tribenzo[a.c.e]cycloheptene system. Such a transition state has been pointed out concerning the reaction of organozinc compounds with olefin.[30, 31] However, cyclopropane derivatives have been obtained from the reaction of *gem*-dihalocyclopropanes[32] or *gem*-dihalovinyl compounds[9d, 26, 33] with alkyllithium. These compounds could not proceed through a sp like transition state. It is noteworthy that the reaction of *gem*-dihalocyclopropanes with alkyllithium gave insertion products in addition to cyclopropane derivatives.[32] Since it has been pointed out that the insertion products are obtained from a carbene reaction[1] the above reaction might not proceed through carbenoid but by a carbene reaction.



XXXI—a



XXXI—b

Now, the reaction products, VIII–XIV, from the reaction f III with alkyllithium may be found to proceed according to Scheme 2. The nucleophilic displacement reaction of XXVIII may give XI[8], while electrophilic reaction[34] of XXVIII may give X.

It is concluded that nucleophilic attack by the olefinic double bond on a carbenoid molecule can be visualized to proceed through a sp like transition state as depicted schematically in XXXI.

EXPERIMENTAL

All temps were uncorrected. IR spectra were recorded with a Hitachi-S2 spectrophotometer; NMR spectra were recorded with a JNM-4H-100 spectrometer against internal TMS. Chemical shifts are given in tau-scale together with splitting patterns and relative integrated area. Electronic spectra were recorded on a Hitachi EPS-2 spectrophotometer. Petroleum ether refers to the fraction b.p. 40–60°.

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[30] [a] H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.* **80**, 5323 (1958), **81**, 4256 (1956); [b] E. P. Blanchard and H. E. Simmons, *Ibid.* **86**, 1337 (1964); [c] H. E. Simmons, E. P. Blanchard and R. D. Smith, *Ibid.* **86**, 1347 (1964).

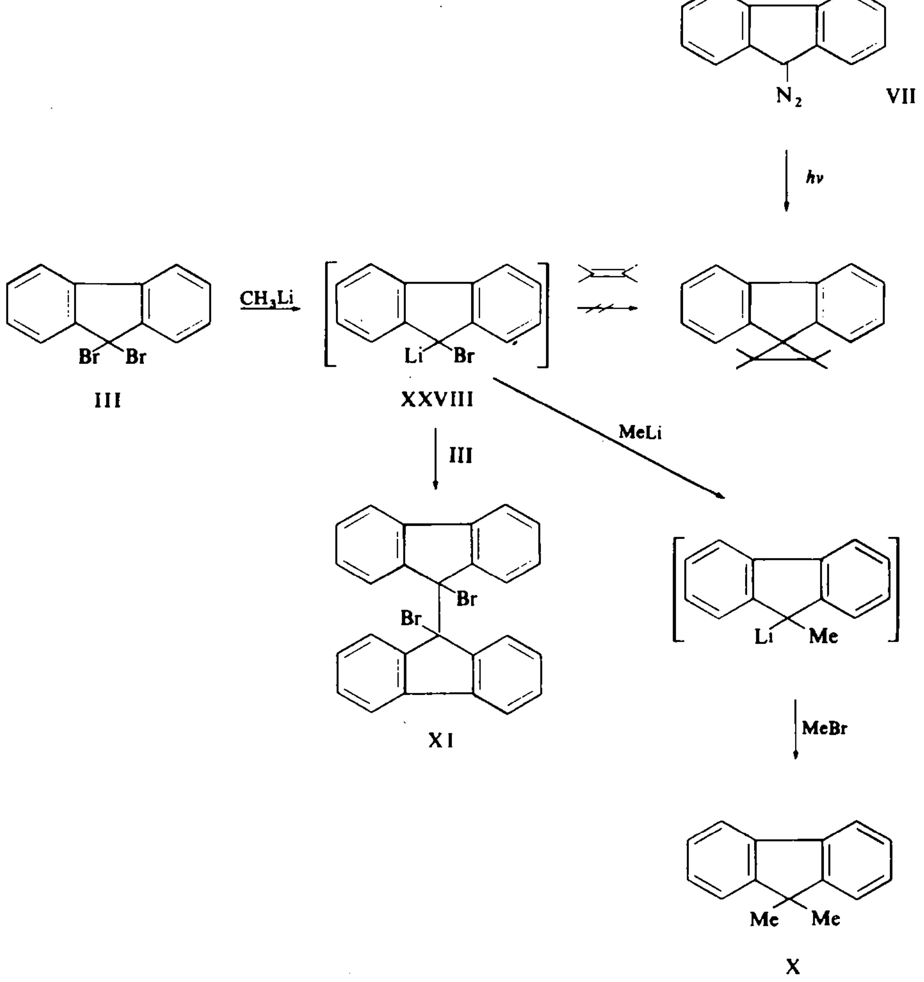
[31] [a] G. Wittig and K. Schwarzenbach, *Liebigs Ann.* **650**, 1 (1961); [b] G. Wittig and F. Wingler, *Ibid.* **656**, 18 (1962), *Chem. Ber.* **97**, 2139, 2146 (1964).

[32] [a] W. R. Moore, H. R. Ward and R. F. Merritt, *J. Am. Chem. Soc.* **83**, 2019 (1961); [b] W. R. Moore and H. R. Ward, *J. Org. Chem.* **27**, 4179 (1962); [c] L. Skattebøl, *Acta. Chem. Scand.* **17**, 1683 (1963); [d] L. Skattebøl, *J. Org. Chem.* **31**, 2789 (1966).

[33] [a] H. D. Hartzler, *J. Am. Chem. Soc.* **83**, 4990, 4997 (1961); [b] M. Tanabe and R. R. Walsh, *Ibid.* **85**, 3522 (1963); [c] R. F. Bleiholder and H. Schechter, *Ibid.* **86**, 5032 (1964); [d] G. Köbrich and H. Heinemann, *Angew. Chem.* **77**, 590 (1965).

[34] [a] G. Köbrich and H. R. Merkle, *Chem. Ber.* **99**, 1782 (1962); [b] W. Kirmse and B. G. v. Bülow, *Ibid.* **96**, 3316, 3323 (1963); [c] W. Kirmse and B. V. v. Wedel, *Liebigs Ann.* **666**, 1 (1963); [d] G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.* **81**, 4996 (1959), **82**, 5723 (1960); [e] U. Schöllkopf and M. Eisert, *Liebigs Ann.* **664**, 76 (1953).

SCHEME 2



Photolysis of diphenyldiazomethane (V) *in ethyl vinyl ether*

A soln of V(8·00 g, 0·041 mole)[35] in ethyl vinyl ether (200 ml) was photolysed by a 500-W high press Hg lamp. On standing, benzophenone azine (4·08 g) slowly separated, m.p. 163–164° (reported[36] m.p. 163–163·5°). The soln was concentrated to ca. 50 ml by distillation and then filtration gave *syn*-tetraphenylethane (0·61 g), m.p. 211–212° (reported[36] m.p. 211–212°). After removal of ethyl vinyl ether in vacuum, the residue was subjected to alumina chromatography. Elution with pet. ether gave an oil (2·22 g). Distillation in vacuum (b.p. 114°/0·3 mmHg) gave VI (1·80 g, 18·5%), n_D^{20} 1·5671. IR spectrum: 1606, 1500, 1451, 1402, 1376, 1348, 1305, 1260, 1192, 1116, 1082, 1076, 1058, 1035, 1005 cm^{-1}. UV spectrum: λ_{max} (EtOH) 274 mμ (log ε 2·51), 267 mμ (2·74), 253 mμ (2·81), 260 mμ (2·81) and 220 mμ (4·44). NMR spectrum: 9·03 (triplet, 3); 6·66 (quartet, 2) and ABX type 6·3, 8·3–8·8 (J_{AX} 7 c/s, J_{BX} 4 c/s and J_{AB} 7 c/s). (Found: C, 85·65; H, 7·62. $C_{17}H_{18}O$ requires: C, 85·67; H, 7·61 %.) Further elution with pet. ether gave benzophenone (0·90 g).

Dibromodiphenylmethane (II).

Compound V[35] (90 g, 0·46 mole) was dissolved in CS$_2$ (100 ml). The stirred soln was maintained at

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[35] *Organic Synthesis* Col. Vol. 3; p. 351. Wiley, New York (1955).

[36] W. E. Parham and W. R. Hasek, *J. Am. Chem. Soc.* **76**, 935 (1954).

$-20°$ by a Dry Ice–acetone bath and a soln of Br (74 g, 0·46 mole) in CS_2 (200 ml) was slowly added. The resulting soln was filtered and benzophenone azine, m.p. 161–162° (reported[36] m.p. 163–164°) removed. The solvent was removed by distillation and the residue was vacuum distilled. After removal of a small forerun (136–146°/0·6 mm Hg) a clear liquid (84 g) was collected at 155–159° and 0·6 mm Hg (56% yield). Dibromide II is extremely reactive toward moisture and must be stored under N and at low temp. (Found: C, 49·39; H, 3·21; Br, 47·65. $C_{13}H_{10}Br_2$ requires: C, 47·89; H, 3·10; Br, 49·02%.)[37]

The reaction of dibromodiphenylmethane (II) *with methyllithium in the presence of ethyl vinyl ether*

To dry ether (200 ml) II (33 g, 0·100 mole) and ethyl vinyl ether (50 ml) were added. The soln was cooled to $-20°$ and 0·012 mole of MeLi was added slowly over 30 min with stirring. After 30 min, the reaction was allowed to warm slowly to room temp. After addition of water the soln was extracted with benzene, washed and dried. The soln was concentrated to ca. 50 ml. On standing tetraphenylethylene (6·84 g) was obtained, m.p. 222–224°.[38] The resulting soln was subjected to alumina chromatography (400 g). Elution with benzene gave tetraphenylethylene (6·10 g, total yield 78%). Further elution with benzene gave VI (0·926 g, 4·8%) which was identified by comparison with the sample obtained from the photolysis of V in ethyl vinyl ether. Finally elution with benzene gave benzophenone (3·0 g, 16·5%).

9,9-*Dibromofluorene* (III). Dibromide III was synthesized by the bromination of VII[39] in 71% yield, m.p. 115–116° (reported[39] m.p. 114°).

The reaction of 9,9-*dibromofluorene* (III) *with methyllithium*

(a) *The reaction with one mole equivalent methyllithium.* To a mixture of III (7·3 g, 0·023 mole) and *cis*-2-butene (60 ml) in ether (100 ml) MeLi (0·025 mole) in ether (30 ml) at $-22°$ was added over a period of 60 min. After treatment as described for II, the reaction mixture was dissolved in a mixture of benzene and pet. ether (1:1) followed by chromatography on alumina. Elution with pet. ether (400 ml) gave XI (0·97 g, 18%), m.p. 237–238° (benzene), which was confirmed by comparing the IR spectrum and mixed m.p. with an authentic sample (reported[40] m.p. 235°). Elution with benzene (750 ml) gave a red substance IX (1·39 g, 33%), m.p. 188–189° (reported[41] m.p. 189–200°), which was identified by mixed m.p. Further elution with benzene (750 ml) gave a white substance (0·85 g), m.p. 256–257° (benzene); IR spectrum: 1686 cm^{-1} (ν C=O); NMR spectrum: only aromatic protons; UV spectrum: λ_{max} (EtOH) 245 mμ (log 4·9), 254 mμ (4·9), 272 mμ (4·8), 295 mμ (3·9) and 308 mμ (3·8). This material was identified as XII (reported[42] m.p. 257°). (Found: C, 90·44; H, 4·70, 314. $C_{26}H_{16}O$ (344) requires: C, 90·67; H, 4·67%.) Finally elution with benzene–alcohol gave an unidentified polymer (0·67 g).

(b) *The reaction with* 2·8 *mole equivalents of methyllithium.* To a soln of III (13·0 g, 0·040 mole) and *cis*-2-butene (30 ml) in ether (100 ml) 0·105 mole MeLi in ether (75 ml) was added. The reaction mixture was chromatographed on alumina. Elution with pet. ether (500 ml) gave VIII (5·78 g, 81%), m.p. 202–203°; UV spectrum: λ_{max} (EtOH) 270 mμ (log ε 4·5), 294 mμ (4·2) and 306 mμ (4·2). (Found: C, 93·75; H, 6·15. $C_{28}H_{22}$ requires: C, 93·81; H, 6·16%.)

(c) *The reaction with three mole equivalents of methyllithium.* A soln of III (7·3 g, 0·023 mole) in ether (150 ml) was added to a soln of *cis*-2-butene (40 ml) and 0·069 mole of MeLi in ether (60 ml) at $-22°$ over 2 hr. The oil obtained (3·9 g) was subjected to alumina chromatography. Elution with benzene (800 ml) gave X (1·79 g, 41%), m.p. 97–98° (pet. ether) (reported[43] m.p. 98°). (Found: C, 92·43; H, 7·37. $C_{15}H_{14}$ requires: C, 92·73; H, 7·27%.) NMR spectrum: τ 8·54 (singlet); UV spectrum: λ_{max} (EtOH) 221^{sh} mμ (log ε 3·8), 229 mμ (3·5), 264 mμ (4·0), 292 mμ (3·6) and 303 mμ (3·8). Further elution with benzene (600 ml) gave VIII (1·52 g, 37%), m.p. 199–201°.

9,9′-*Dimethyl*-9,9′-*bifluorenyl* (VIII)

To a soln of 9-methyl-9-fluorenol (0·80 g, 0·045 mole, m.p. 175°) (reported[44] m.p. 174–175°) in dry

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[37] Hydrolysis on handling for analysis probably explains the low Br value, since briefest exposure to air was sufficient to allow production of HBr.

[38] *Organic Synthesis*, Vol. 31; p. 104. Wiley, New York (1951).

[39] H. Staudinger and A. Gaule, *Chem. Ber.* **49**, 1955 (1916).

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[41] J. R. Sawpey and E. E. Reid, *J. Am. Chem. Soc.* **69**, 234 (1947).

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[43] P. Lebeau and M. Picon, *C. R. Acad. Sci., Paris*, **173**, 84 (1921).

[44] J. L. Kice, *J. Am. Chem. Soc.* **80**, 348 (1958).

CH_2Cl_2 (40 ml), $CaCl_2$ chloride (5 g) was suspended. The soln was cooled to 0° and 1·5 mole equivs of dry HCl gas was bubbled through. After removal of $CaCl_2$ without exposing to the air, dry benzene (40 ml) and Cu powder (2 g) were added to the filtrate, followed by evaporation of CH_2Cl_2. The reaction mixture was heated under reflux for 2 hr and the Cu powder filtered off. Evaporation of the benzene gave VIII (0·55 g, 69 %), m.p. 202–203° (pet. ether) (reported[42] m.p. 206°).

The reaction of 9,9'-dibromo-9,9'-bifluorenyl (XI) *with methyllithium*

A soln of MeLi (0·004 mole) in ether (4 ml) was added to a soln of XI (0·181 g, 0·0004 mole) in ether (50 ml) at −22°. The reaction mixture was poured into water. The organic layer was washed and dried. After filtration the solvent was evaporated, leaving IX (0·093 g, 90 %) and XI (0·0031 g).

The reaction of bifluorenylidene (IX) *with methyllithium*

To a soln of IX (4·2 g, 0·010 mole) in ether (200 ml) 0·028 mole MeI in ether (35 ml) at −10° was added during 2·5 hr. The organic yellow reaction mixture was divided into two parts. One part was poured into water. The organic layer was separated, the aqueous layer was extracted with benzene and the combined organic layers washed and dried. Evaporation of the solvent gave XVI (0·66 g, 76 %), m.p. 167–168° (pet. ether). NMR spectrum: 8·08 (singlet, 3); 5·46 (singlet, 1). (Found: C, 94·00; H, 5·93. $C_{27}H_{20}$ (Mol. wt, 344) requires: C, 94·13; H, 5·85 %. Mol. wt. 353.)

To the other part a soln of MeBr (0·005 mole) in ether (50 ml) was added. The color of the intermediate Li compound disappeared immediately. Treatment of this reaction mixture usually gave VIII (0·830 g, 95 %), m.p. 203–204°.

The reaction of 9,9-dibromofluorene (III) *with n-butyllithium in the presence of ethyl vinyl ether*

To a soln of III (7·9 g, 0·024 mole) and ethyl vinyl ether (40 ml) in ether (200 ml) 0·076 mole n-BuLi in ether (50 ml) was added at −30 ~ −35° during 30 min. The reaction product (6·27 g) was dissolved in the mixture of pet. ether–benzene (7:3) and chromatographed on alumina. Elution with benzene gave XIII (1·02 g, 19 %), m.p. 185–186°. Further elution with benzene gave white needles of XIV (1·41 g, 31 %), m.p. 150–151° (pet. ether). NMR spectrum: 9·27 (triplet, 3); 8·7–9·2 (multiplet, 4); 7·4 (multiplet, 2); 5·43 (triplet, 1). (Found: C, 93·10; H, 6·87. $C_{30}H_{26}$ requires: C, 93·22; H, 6·78 %.) Finally, elution with benzene–MeOH gave a polymer. (Found: C, 92·08; H, 5·91 %.)

9,9'-Di-n-butyl-9,9'-bifluorenyl (XIII)

To a soln of n-BuMgBr (prepared from Mg ribbon (0·95 g) and n-BuBr (4·8 g) in 100 ml ether) a soln of fluorenone (5·4 g) in ether (60 ml) was added at 0° during 30 min. Treatment of the reaction mixture gave 9-n-butyl-9-fluorenol in 82 % yield. m.p. 132 ~ 132·5° (alcohol). (Found: C, 85·45; H, 7·65. $C_{17}H_{18}O$ requires: C, 85·67; H, 7·61 %); XIII was prepared from this alcohol similar to the method for preparation of VIII in 98 % yield, m.p. 185–186° (pet. ether). (Found: C, 92·34; H, 7·74. $C_{34}H_{34}$ requires: C, 92·26; H, 7·74 %.) UV spectrum: λ_{max} (EtOH) 248 mμ (log ε 4·3), 257 mμ (4·4), 270 mμ (4·4), 295 mμ (4·1) and 306 mμ (4·2).

The reaction of 9-bromofluorene (XVIII) *with methyllithium in the presence of* cis-*2-butene*

To a soln of XVIII (4·90 g, 0·020 mole) in ether (150 ml) MeLi (0·021 mole) in ether (50 ml) was added. Immediately XIX was precipitated (3·2 g, 98 %), m.p. 245–246° (reported[40] m.p. 246°). NMR spectrum: 5·24 (doublet, 2 c/s, 2); 2·35–3·2 (4H); 2·7–3·2 (multiplet, 12). UV spectrum: λ_{max} (EtOH) 215 mμ (log ε 5·7), 268 mμ (5·4), 293 mμ (5·0) and 305 mμ (5·0).

*9,9-Dichloro-9*H*-tribenzo*[a,c,e]*cycloheptene* (IV)

A mixture of XXII (10·0 g, 0·039 mole)[15] and PCl_5 (10·0 g, 0·048 mole) was heated at 180° during 4 hr. To the reaction mixture a small amount of dry acetone was added dropwise. $POCl_3$ was evaporated *in vacuo* and the residue was recrystallized from a mixture of CH_2Cl_2 and pet. ether (1:1) (10·7 g, 88 %), m.p. 146–147°. (Found: C, 73·11; H, 3·89. $C_{19}H_{12}Cl_2$ requires: C, 73·31; H, 3·89 %.)

*The reaction of 9,9-dichloro-9*H*-tribenzo*[a,c,e]*cycloheptene* (IV) *with methyllithium in the presence of ethyl vinyl ether*

To a mixture of benzene (200 ml) and THF (100 ml) IV (4·91 g, 0·016 mole) and ethyl vinyl ether (50 ml) were added. The soln was cooled to −20°, and 0·023 mole MeLi in ether (50 ml) was added slowly during

15 min. After 2 hr the reaction was allowed to warm to room temp. After addition of water, the soln was extracted with benzene, washed with water and dried. The soln was concentrated to ca. 50 ml and subjected to alumina chromatography (130 g). Elution with n-hexane gave XXIII (2·02 g, 44%), m.p. 157–158° (pet. ether). Further elution with $CHCl_3$ gave XXIV-a (0·65 g, 11%), m.p. 95–96° (benzene). These compounds were identified by comparison of IR spectra and mixed m.p. with authentic sample.

9-*Methylene*-9H-*tribenzo*[a.c.e]*cycloheptene* (XXIII)

A mixture of XXV (1·00 g, 0·0038 mole) and I_2 (0·10 g) was heated at 160° for 30 min. The reaction mixture was cooled and benzene (30 ml) was added. The soln was washed twice with $NaHSO_3$aq and water, and dried. After evaporation of the solvent the residue was recrystallized from pet. ether (0·91 g, 94%), m.p. 157–158°. (Found: C, 94·37; H, 5·71. $C_{20}H_{14}$ (Mol. wt. 254) requires: C, 94·45; H, 5·55%.) IR spectrum: 1160, 1100, 1038, 1000, 977, 942, 900, 784, 759 and 746 cm^{-1}. UV spectrum: λ_{max} (EtOH) 232 mμ (log ε 4·65), 234 mμ (4·75).

Hydrogenation of 9-*methylene*-9H-*tribenzo*[a.c.e]*cycloheptene* (XXIII)

Hydrogenation of a mixture of XXIII (0·26 g, 0·0010 mole) and Raney Ni (0·5 g) in EtOH (70 ml) at atm press gave XXVI (0·20 g, 77%), m.p. 120–121° (pet. ether). IR spectrum: 1155, 1024, 1001, 967, 940, 795, 750, 736 cm^{-1}. NMR spectrum: 8·20 (doublet, 3); 6·24 (quartet, 7·5 c/s, 1); 2·3–2·8 (multiplet, 12) (Found: C, 93·46; H, 6·33. $C_{20}H_{16}$ requires: C, 93·71; H, 6·29%.)

9-*Methyl*-9H-*tribenzo*[a.c.e]*cycloheptene*-9-*ol* (XXV)

A soln of MeMgBr (prepared from MeI (6·4 g) and Mg ribbon (1·2 g)) in ether (100 ml) was added to a soln of XXII (6·84 g, 0·030 mole) in THF (100 ml) with heating under reflux. After 1 hr, the reaction mixture was treated in the usual manner. Recrystallization from benzene gave XXV (6·43 g, 79%), m.p. 147–148°. IR spectrum: ν_{Nujol} 3750 cm^{-1} (O—H), 1035 cm^{-1} (C—O). NMR spectrum: 8·67 (singlet, 12); 7·80 (singlet, 1); 2·05–2·85 (multiplet, 3). UV spectrum: λ_{max} (EtOH) 242 mμ (log ε 4·65), 236 mμ (4·62), 261 mμ (4·21). (Found: C, 88·10; H, 5·84. $C_{20}H_{16}O$ requires: C, 88·20; H, 5·92%.)

9H-*Tribenzo*[a.c.e]*cyclohepten*-9-*ol* (XXIV-a)

A mixture of XXII (1 g, 0·004 mole) and PtO_2 (0·2 g) in AcOH containing 10% HCl (100 ml) was hydrogenated at atm press. After treatment, recrystallization from benzene–pet. ether (1:1) gave XXIV-a, m.p. 95–96°. IR spectrum: ν_{Nujol} 3180 cm^{-1} (O—H), 1048 cm^{-1} (C—O), ν_{CCl_4} 3300 cm^{-1}, 3630 cm^{-1} (O—H). UV spectrum: λ_{max} (EtOH) 221 mμ (log ε 4·85), 238 mμ (4·40), 256 mμ (4·31). NMR spectrum: 4·59 (singlet, 1). (Found: C, 88·05; H, 5·49. $C_{19}H_{14}O$ requires: C, 88·34; H, 5·46%.)

9H-*Tribenzo*[a.c.e]*cyclohepten*-9-*ol* (XXIV-b)

To a soln of XXII (1 g, 0·004 mole) in THF (100 ml) a soln of LAH (0·2 g) in ether (50 ml) was added with heating under reflux. The mixture was poured into water The benzene extract was washed with water and dried. After removal of the solvent the residue was recrystallized from pet. ether–benzene, m.p. 117–118°. IR spectrum: ν_{Nujol} 3300 cm^{-1} (O—H), 1050 cm^{-1} (C—O), ν_{CCl_4} 3630 cm^{-1} (O—H). UV spectrum: λ_{max} (EtOH) 221 mμ (log ε 4·82), 238 mμ (4·85), 256 mμ (4.41). NMR spectrum: 4·64 (singlet, 1). (Found: C, 88·25; H, 5·49. $C_{19}H_{14}O$ requires: C, 88·34; H, 5·46%.)