TABLE II

REACTION OF 2-CHLORO-1,1-DIPHENYLETHYLENE (XII) WITH
BUTYLLITHIUM[a]

Time, hr.	Concn. of XII, mmoles/l	Amt. of XII, mmoles	XII recovd., %	Chloride exchange, %	Rearrange-ment, %
Butyllithium prepared from butyl chloride					
2	80	4	0	0	80
2	154	8	0	0	89
Butyllithium prepared from butyl bromide					
2	56	5	54	0	34
Butyllithium prepared from butyl chloride but with an equiv. amt. of lithium bromide added					
2	154	8	35	0	55

[a] Reactions carried out at $-35 \pm 1°$ and completed by carbonation by pouring onto Dry Ice. A 10 mole % excess of butyllithium was employed.

After being dried over anhydrous calcium chloride the neutral fraction was obtained by distillation of the diethyl ether. The residue (0.17 g.) was shown by a comparison of the infrared spectrum with those of the authentic products to contain approximately 10% of butyl 2,2-diphenylvinyl ketone (absorption at 1668 cm.$^{-1}$) and not more than 13% of diphenylacetylene (absorption at 915 cm.$^{-1}$) based on iodide XIII employed in the reaction.

Reaction of the Ditolyl Bromide XIV with Butyllithium.— To 1.00 g. (3.5 mmoles) of the vinyl bromide XIV in 29 ml. of anhydrous diethyl ether at $-35°$ was added a 10% excess of titrated butyllithium (in 5.5 ml. of ether). After standing at $-35°$ for 0.5 hr. the reaction mixture was poured onto Dry Ice. Extraction of the acidic fraction with 25 ml. of 5% potassium hydroxide and acidification of the aqueous extract with several drops of hydrochloric acid gave 60 mg. (7%) of crude di-(p-tolyl)-acrylic acid, m. p. 155–160° (lit. 174°,[31a] 168–170[31b]).

The neutral fraction after drying and removal of the diethyl ether under reduced pressure appeared as a residue

(0.85 g.). The infrared spectrum indicated that it contained 74% of unreacted XIV (absorption at 1215 cm.$^{-1}$) and approximately 12% of di-(p-tolyl)-acetylene.

Reaction of the Di-(p-chlorophenyl) Bromide (XV) with Butyllithium.— Reaction of 1.00 g. (3.00 mmoles) of XV in 20 ml. of anhydrous diethyl ether with a 10% excess of butyllithium (in 4.8 ml.) at $-35°$ under nitrogen gave after carbonation after 0.5 hr. and extraction of the acidic fraction with potassium hydroxide solution 0.56 g. (65%) of di-(p-chlorophenyl)-acrylic acid, m.p. 176–179° (lit.[31a,32] 174°, 176–178°). After drying over calcium chloride and removal of the ether under reduced pressure the neutral fraction remained as 250 mg. of a semi-solid. It was estimated from the infrared spectrum to contain 25% of di-(p-chlorophenyl)-acetylene and approximately 10% of butyl 2,2-di-p-chlorophenylvinyl ketone (based on XV employed). There was no evidence of unreacted starting material.

Reaction of the Tetrachloro Vinyl Bromide XVI with Butyllithium.— The reaction carried out for 0.5 hr. at $-35°$ as before gave from 1.00 g. (2.52 mmoles) of XVI 600 mg. of an acid, m. p. 181–183° (66% based on the assumption that it is the expected diaryl acrylic acid), and a neutral residue of 270 mg., estimated from its infrared absorption to contain 33% of the bis-(3,4-dichlorophenyl)-acetylene and approximately 1% of butyl diarylvinyl ketone. There was no evidence of unreacted starting material.

Reaction of 2-Bromo-1,1-diphenylethylene-1-d-with Butyllithium.— The reaction of 1.46 g. (5.22 mmoles) of the vinyl bromide in 29 ml. of anhydrous diethyl ether with 1 equivalent (4.8 ml.) of titrated ether solution of butyllithium prepared from butyl chloride was carried out for 2 hr. at $-35 \pm 1°$. Carbonation and extraction as above failed to yield any acidic product. The infrared absorption spectrum of the neutral fraction showed it to consist of 40% of starting material (absorption at 990 cm.$^{-1}$), 35% of diphenylacetylene (absorption at 915 cm.$^{-1}$) and approximately 25% of butyl 2,2-diphenylvinyl ketone-d (absorption at 1668 cm.$^{-1}$) based on starting vinyl bromide employed. Although the lack of a sample of pure ketone makes the estimate of its amount uncertain it is in agreement with the result anticipated that the replacement of hydrogen by deuterium leaves the rate of halogen replacement little changed.

(31) (a) F. Bergmann, M. Weizmann, E. Dimant, J. Patai and J. Szmuszkowicz. THIS JOURNAL, **70**, 1612 (1948); (b) E. Bergmann, H. Hoffman and H. Meyer, J. prakt. Chem., [2] **135**, 245 (1910).

(32) J. F. Freeman and E. D. Amstutz, THIS JOURNAL, **72**, 1522 (1950).

URBANA, ILL.

The Reactions of Exocyclic Vinyl Halides with Phenyllithium[1–3]

BY DAVID Y. CURTIN AND WILLIAM H. RICHARDSON[4]

When phenyllithium in ether is added to 9-bromomethylenefluorene (VI) the only product found is 1,4-dibiphenylenebutatriene (VII) (in 55% yield) together with some 50% of unreacted starting material. Phenyllithium added to the analogous chloride V also gives the triene VII accompanied by 9-benzylidenefluorene (VIII). Evidence is advanced that these reactions proceed by way of the carbene XI. The related vinyl halide, 9-chloromethylene-9,10-dihydro-10,10-di-n-propylanthracene (XV), on treatment with phenyllithium behaves in a manner similar to the chloride V. The 7 membered analog, 1-chloromethylene-2,3,6,7-dibenz-2,6-cycloheptadiene (XXI), however, undergoes rearrangement with ring expansion to give as the major product 1-phenyl-2,3,6,7-dibenz-2,6,8-cyclooctatriene (XXIII), probably by way of the dibenzcyclooctyne XXII. It is noted also that in the reactions of 2-bromo- and 2-iodo-1,1-diphenylethylene phenyllithium shows a considerably greater preference for hydrogen exchange leading to diphenylacetylene than does butyllithium.

2,2-Diarylvinyl bromides or chlorides (I) have been found to undergo a rapid reaction even at $-35°$ in diethyl ether solution to form, in addition to the normal product of lithium–halogen exchange,
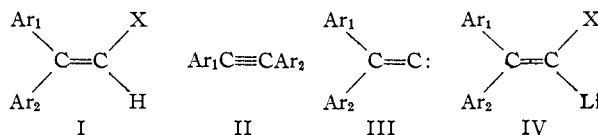
the diarylacetylene II.[5] It has been suggested[5b] that the reaction involves a lithium–hydrogen exchange followed (or accompanied) by rearrange-

ment of an aryl group and loss of lithium halide. The carbene III has been shown not to be an intermediate in the major reaction pathway.[5a] Since the rearrangement step appeared to be fast relative to the initial hydrogen exchange in the reaction of I, it was of interest to modify the structure of the vinyl halide with the objective of slowing or stopping the rearrangement and allowing the accumulation of intermediates such as the carbene III or the bromolithium compound IV during the reaction.

For this purpose 9-chloro- (V) and 9-bromomethylenefluorene (VI) were chosen for study.

V, X = Cl
VI, X = Br

VII

VIII

IXa

IXb
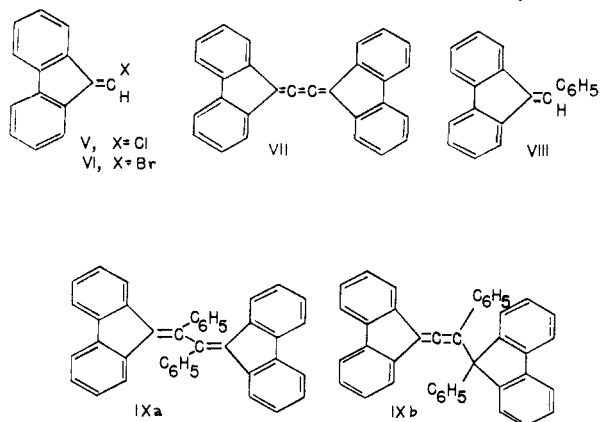
Although the previous reactions of 2-halo-1,1-diarylethylenes (I) had been carried out with butyllithium[5] it was discovered in the course of the present work that phenyllithium was more satisfactory since it showed a much greater preference as compared to butyllithium for hydrogen exchange leading to diphenylacetylene than for halogen exchange leading to a stable vinyllithium compound. Thus, butyllithium prepared from butyl chloride was allowed to react with 2-bromo-1,1-diphenylethylene and found to give a ratio of hydrogen to halogen exchange of 2.1, in good agreement with the values previously reported[5b] of 1.9 and 2.1. Phenyllithium, on the other hand, when allowed to react with the same vinyl bromide gave almost completely diphenylacetylene. Rough estimates of the ratio of rearrangement to halogen exchange gave values of 18 and 30 compared with the value of 2 obtained with butyllithium. A further demonstration of the strong preference of phenyllithium for hydrogen rather than halogen exchange was discovered in the reaction with 2-iodo-1,1-diphenylethylene which had been found previously to undergo largely halogen–lithium exchange with butyllithium[5b] (the ratio of rearrangement to halogen exchange was about 0.2).[5b] Phenyllithium, however, reacted with the iodide under similar conditions to give principally hydrogen exchange leading to rearrangement. (The ratio of rearrangement to halogen exchange was estimated to be 2.) The conclusion that phenyllithium is less reactive in general than butyllithium is well established.[6] Consequently, as predicted by the prin-

ciple stated by Hammond,[7] butyllithium would be expected to be less discriminating. There are other differences between the two reagents which may be important, however. For example, the state of aggregation has been studied by Wittig, Meyer and Lange[8] who found phenyllithium to be largely a dimer and butyllithium a pentamer in diethyl ether solution. It is also possible that steric differences are important.

When a 10 mole % excess of phenyllithium was added to the bromomethylenefluorene VI at −35° over a period of 40 minutes and the reaction mixture allowed to stand for 2.5 hours longer and then poured onto Dry Ice, the major product was 1,4-dibiphenylenebutatriene (VII) formed in 55% yield. Infrared examination of the remaining neutral fraction indicated that about 50% of the starting bromide VI was unreacted. Only 3% of an acid fraction was obtained. After this part of the work had been completed it was reported by Hauser and Lednicer[9] that treatment of the bromide I with potassium amide in liquid ammonia also leads to the triene VII. When phenyllithium was added to the chloro compound V over a 45-minute period at 0° and the reaction was allowed to continue for 6.5 hours longer at 0° and terminated by addition to water the triene, VII was again formed but only in 18% yield together with 9-benzylidenefluorene (VIII) in 19% yield and a 5% yield of a bright orange hydrocarbon, m.p. 244°, tentatively assigned the structure IXa. The basis for the structural assignment is as follows. The absence of absorption maxima in the infrared spectrum in the region 2900–3000 cm.$^{-1}$ and also in the region in the n.m.r. characteristic of aliphatic hydrogen atoms suggests that there is no hydrogen bound to a saturated carbon atom. The ultraviolet spectrum showed a broad maximum from 350 to 450 mμ (λ_{max} 414 mμ, ϵ 9600). Such absorption clearly indicates that at least one of the fluorene units is in conjugation with additional double bonds and leaves structures IXa and IXb as the most likely possibilities. 1,4-Dibiphenylenebutadiene has strong absorption in the region from 400 to 450 mμ (λ_{max} 415, 442 mμ; ϵ 49,000, 45,000). Although 1,4-diphenylbutadiene is not a good model substance because of alterations in the conjugated system in IXa both by the increased conjugation and by the introduction of some steric inhibition of resonance, it suggests that structure IXa is not in unreasonable agreement with the ultraviolet spectrum. It seems likely that the diphenyl diene IXa is formed by addition of phenyllithium to the triene VII. The triene has been found to undergo analogous 2,3-additions with lithium aluminum hydride[10] and with butyllithium[2] to give 1,4-dilithio-1,4-dibiphenylene-2-butene and 2,3-dibutyl-1,4-dilithio-1,4-dibiphenylene-2-butene, respectively. The dilithio intermediate must then undergo oxidation to the diene IXa either by air during hydrolysis or by exchange of one lithium atom with some proton source (such as the chloride V)

(6) See, for example, R. G. Jones and H. Gilman, "Organic Reactions," Vol. 6, R. Adams Editor-in-chief, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 339 ff.; H. Gilman and J. W. Morton, Jr., "Organic Reactions," Vol. 8, R. Adams, Editor-in-chief, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 258 ff.

(7) G. S. Hammond, THIS JOURNAL, 77, 334 (1955).

(8) G. Wittig, F. J. Meyer and G. Lange, Ann. Chem., 571, 167 (1951).

(9) C. R. Hauser and D. Lednicer, J. Org. Chem., 22, 1248 (1957).

(10) D. Lavie and E. D. Bergmann, ibid., 18, 367 (1953).

and loss of lithium hydride, a process which has been previously observed in the reaction of 1,4-diphenyl-2-butene with phenyllithium.[11]

A "yellowish-red" substance, m.p. 369.3°, has previously been prepared by the condensation of benzil with fluorene in the presence of ethanolic potassium hydroxide[12,13] and assigned structure IXa. It is possible that this product and that with m.p. 244° obtained in the present study are different crystalline forms of the same compound. However, structure IXb has not been rigorously excluded for the isomer m.p. 244°. Since this isomer is a minor product, the general conclusions to be drawn do not depend significantly on the structural assignment for this compound.

A comparison of the amounts of unreacted starting materials after a given time in the reactions of the bromide VI and 2-bromo-1,1-diphenylethylene with phenyllithium at −35° indicated that the reaction rate of the biphenylene bromide VI is not retarded by a factor of more than 5–6 even though the joining of the phenyl rings has prevented the phenyl migration in the reaction of VI. This implies that there is little kinetic driving force due to phenyl participation in the rearrangement of 2-bromo-1,1-diphenylethylene as was concluded previously.[5b]

An attractive interpretation of the reaction of the halides V and VI is that hydrogen–lithium exchange proceeds as before to give the halolithium intermediate X. Since X is unable to rearrange it rapidly loses lithium halide to give the carbene XI. Although XI could form the triene VII by a simple dimerization it seems likely that it may also react with the bromolithium intermediate X to give an adduct which would be expected to lose
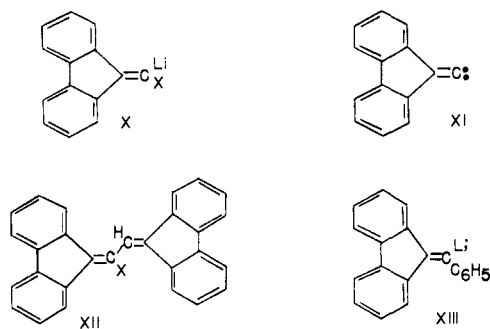
lithium halide rapidly to give triene VII.[14a] It seems probable that the benzylidenefluorene VIII formed from the chloride V comes from a competing addition–elimination mechanism although it could also arise, in part, from addition to the

(11) H. Gilman and C. W. Bradley, This Journal, **60**, 2333 (1938).

(12) L. Krasnec and J. Heger, *Chem. Zvesti*, **8**, 333 (1954); [*C. A.*, **49**, 7530c (1955); *Chem. Zentr.*, **127**, 7798 (1956); *Referativnii Zhur. Chim.* (*USSR*), **24**, No. 18, 727 (1955)].

(13) "Chemical Abstracts" gives almost no details and gives the m.p. of this substance as 228°. Both the German and Russian abstracts have descriptions of the structure proof of the compound and of the method of synthesis and give the m.p. as 369.3°. The m.p. of the reduced derivative is given there as 228°.

(14) (a) Triene VII might also arise from the reaction of phenyllithium with the cyclopropane formed from carbene X1 and olefin V; (b) K. Ziegler, F. Crossman, H. Kleiner and O. Schaefer, *Ann.*, **473**, 1 (1929); (c) K. Ziegler and O. Schaefer, *ibid.*, **511**, 101 (1934).

carbene of phenyllithium followed by a lithium–hydrogen exchange with the starting chloride V. The addition–elimination mechanism seems reasonable since even 1,1-diphenylethylene undergoes a very rapid addition of butyllithium at room temperature in diethyl ether[14b] and phenyllithium has been shown to add[14c] to certain biphenylene ethylenes.[15]

The most reasonable alternative to a mechanism with a carbene intermediate appears to be one in which the halolithium intermediate X reacts with halide V or VI to give an intermediate XII, which could subsequently be converted to the triene VII by an elimination reaction with phenyllithium serving as the base. More detailed considerations make this second mechanism seem highly unlikely as shown by the following argument. Since the bromide VI gives only triene VII in the reaction with phenyllithium, the lithium–hydrogen exchange must be faster than the replacement of the bromine atom by a phenyl group. Furthermore, since the bromolithium intermediate X (X = Br) doesn't accumulate in the solution during reaction its disappearance by addition to the bromoölefin VI must be rapid relative to its formation by lithium–hydrogen exchange and, therefore, faster than the replacement of the bromine atom by a phenyl group of phenyllithium. But this conclusion that the lithium intermediate X reacts more rapidly with the bromoölefin VI than does phenyllithium seems quite unreasonable both on electronic and steric grounds. The most promising alternative, then, seems to be the carbene intermediate proposed above. Hauser and Lednicer[9] have proposed both a carbene mechanism and an alternative very similar to that proposed here for the reaction of the bromide VI with potassium amide to give cumulene VII but made no decision between them.

If the carbene mechanism is correct then addition of the bromide VI to the phenyllithium so that the latter is always present in excess might be expected to cause interception of the carbene by phenyllithium to give the lithium reagent XIII which, if it survived, might be converted to the corresponding carboxylic acid on carbonation. An experiment in which the bromide VI was added to 10 mole % excess of phenyllithium at −35° followed by pouring onto Dry Ice was only partially satisfactory. In addition to 40% of recovered starting material the triene VII was obtained but in only 7% yield. Only 8% of an acidic fraction was obtained and no pure products were isolated from it. Infrared examination indicated that 9-benzylidenefluorene was absent and chromatography of the neutral fraction gave no additional products. Inverse addition of the chloride V to phenyllithium again lowered the yield of triene to 0%, but the amount of 9-benzylidenefluorene (17%) was essentially unchanged from what it had been when the lithium reagent was added to the chloride. No other product could be isolated. All of these reaction mixtures were examined for the presence of derivatives of phenanthrenes which might have resulted from the 1,2-migration of a phenyl ring

(15) The details of the mechanisms of replacements of this type are discussed in the paper by W. E. Truce and R. Kassinger [This Journal, **80**, 6450 (1958)] and in the references cited therein.

and in no case was there evidence of such a rearrangement. It is concluded that there is a high degree of probability that the carbene intermediate XI is involved in certain of these reactions where aryl rearrangement is sterically impeded and further work is in progress in an attempt to intercept such an intermediate.

It was also desired to examine the effect of enlarging the central ring on the reaction with phenyllithium of vinyl halides related to V and VI and the synthesis of compounds of the type XIV was investigated.

XIV, R=CH₃
XV, R=C₃H₇

XVI, R=CH₃
XVII, R=CH₂=CHCH₂
XVIII, R=n-C₃H₇

XIX, R=n-C₃H₇   XX, R=n-C₃H₇
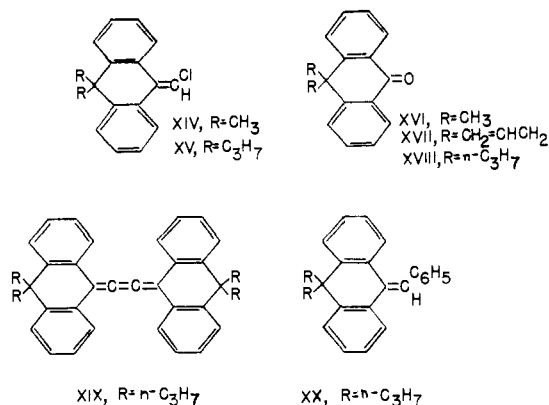
The alkylation of anthrone in aqueous potassium hydroxide had been reported[16] to yield the dimethylanthrone XVI in unspecified yield. More recently, Heymann and Trowbridge[17] have studied this reaction and obtained only a 3% yield of the desired ketone. It was hoped that the dimethyl ketone XVI might be prepared by carrying out the alkylation in a non-polar medium like toluene.[18] Since the preliminary attempts failed, the dipropyl derivative XVIII was prepared by taking advantage of the greater tendency of allyl halides to give carbon-alkylation[18] and reduction of the allyl groups of the diallyl ketone XVII.[19] The dipropyl ketone XVIII was readily converted to the chloroölefin XV by the addition of methylmagnesium iodide, dehydration of the resulting alcohol, chlorination of the olefin so obtained and dehydrohalogenation, a sequence of reactions similar to that used previously for the preparation of 2-halo-1,1-diphenylethylenes.[20] The structure of the chloroölefin XV was confirmed by oxidation to the dipropyl ketone XVIII.

When a 5 mole % excess of phenyllithium was added slowly to an ether solution of the chloride XV at 0° and the reaction was terminated by pouring onto solid carbon dioxide the major products were di-(9,10-dihydro-10,10-di-n-propyl-9-anthracenylidene)-ethylene (XIX) obtained in 15% yield and 9-benzylidene-9,10-dihydro-10,10-di-n-propylanthracene (XX) in 19% yield. The acidic frac-

(16) F. Hallgarten, Ber., 21, 2508 (1888).

(17) H. Heymann and L. Trowbridge, THIS JOURNAL, 72, 84 (1950).

(18) See D. Y. Curtin and R. R. Fraser, ibid., 80, 6016 (1958), for references to similar carbon-alkylations of salts of phenol and its 2,6-dimethyl derivative.

(19) Since this part of the work was completed it has been possible to dimethylate the lithium salt of anthrone in toluene containing a few drops of t-butyl alcohol in 70% yield [R. Tuites, Ph.D. Thesis, University of Illinois, 1959].

(20) See ref. 5b for previous literature.

tion amounted to only 0.23% by weight and 22% of the starting material was recovered. It will be recognized that these products are very similar to those obtained from the analogous fluorene derivative V and their formation is probably to be explained in a similar way. The structure of the triene XIX was established by similarity of the ultraviolet-visible spectrum to that of the triene VII and by the demonstration that on reduction it reacted with 3 moles of hydrogen to give a hexahydro derivative. The structure of XX was confirmed by the similarity of the ultraviolet spectrum to that of the fluorene analog VIII and by ozonolysis to the dipropylanthrone (XVIII) and benzoic acid. The similarity of the products of these two reactions gives added support to the suggestion that a carbene intermediate is involved.

The apparently great instability of vinylidene halolithium compounds such as X as indicated by their failure to be detected in these reactions makes the reported preparation of vinylidene fluoromagnesium compounds[21] of particular interest.

The last member of the series to be studied was 1-chloromethylene-2,3,6,7-dibenz-2,6-cycloheptadiene (XXI) which was readily prepared from the parent hydrocarbon, 1-methylene-2,3,6,7-dibenz-2,6-cycloheptadiene,[22] by treatment with chlorine. In this case the major product, obtained

XXI   XXII   XXIII

XXV   XXIV   XXVI
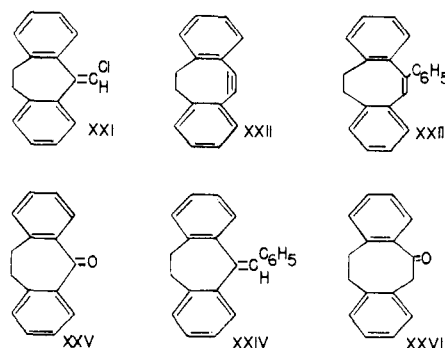
in 23% yield, was a solid, m.p. 84°, shown to be the cyclooctene derivative XXIII. In addition an acidic fraction (14% by weight based on the starting material) XXI was obtained together with lesser amounts of at least two other solid products and an estimated 11% of unreacted starting material XXI. Although no other products could be identified, the ultraviolet spectra of the crude product provided evidence for the absence of a cumulene analogous to those (VII and XIX) obtained with the smaller cycles VI and XV. The cyclooctene derivative XXIII is of particular interest. The most probable path for its formation would appear to involve a lithium–hydrogen exchange of the vinyl chloride XXI with phenyllithium followed by loss of lithium chloride and rearrangement (possibly concerted) to the acetylene XXII. The smallest ring containing a triple bond in a compound which has been isolable is the eight-

(21) J. D. Park, R. J. Seffi and J. R. Lacher, THIS JOURNAL, 78, 59 (1956); 1. L. Knunyants, R. H. Sterlin, R. D. Yatsenko and L. N. Tinkina, Isvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk, 1345 (1958).

(22) (a) W. Treibs and H. Klinkhammer, Chem. Ber., 83, 367 (1950); (b) A. C. Cope and S. W. Fenton, THIS JOURNAL, 73, 1673 (1951).

membered ring in cyclooctyne, prepared by Blomquist and Liu.[23] Even in this case both inspection of molecular models and the great reactivity of the compound suggest that there is considerable ring strain. Cyclohexyne and even cyclopentyne have been postulated as reaction intermediates by Favorskii[24] and recently Roberts and Scardiglia[25] have obtained more direct evidence for cyclohexyne by using carbon-fourteen as a tracer. It seems reasonable that the eight-membered acetylene derivative XXII should undergo a rapid addition of phenyllithium and that the resulting aromatic lithium reagent, like phenyllithium, can undergo a hydrogen–lithium exchange with the starting chloride XXI to give XXIII. Apparently, then, with a vinyl halide grouping exocyclic to rings of eight members or larger the major course of reaction with phenyllithium is the rearrangement characteristic of the diaryl acyclic vinyl halides.

The structure proof of the dibenzcyclooctene XXIII requires discussion. The n.m.r. showed the presence of a vinyl hydrogen atom (singlet at −79 c.p.s., 40 Mc., rel. to water) and the infrared showed absorption characteristic of a monosubstituted phenyl ring at 690 cm.$^{-1}$. The particular problem which arose was the distinction between XXIII and the isomer formed without ring expansion, XXIV. No benzoic acid was obtained from ozonolysis or oxidation with osmium tetraoxide followed by treatment with lead tetraacetate, but the acidic product obtained could not be isolated in pure form.

A compound assigned the seven-membered structure XXIV has been prepared by addition of benzylmagnesium chloride to the ketone XXV and dehydration of the resulting alcohol with acetyl chloride and reported to be a liquid with a maximum in the ultraviolet spectrum at 305 mμ (log ϵ 4.05 in absolute methanol).[26] The structure of this substance was not established unequivocally, however, and it had been prepared by a route which might conceivably have led to an unsuspected carbonium ion rearrangement. For this reason an independent synthesis of the eight-membered olefin XXIII was carried out by the addition of phenylmagnesium bromide to 2,3,6,7-dibenz-2,6-cycloocta-diene-1-one (XXVI) and dehydration of the resulting carbinol. The product was a solid, m.p. 84°, with an absorption maximum at 270 mμ in the ultraviolet and identical in every respect with the product of the reaction of phenyllithium with the vinyl chloride XXI. Although the dehydration of the alcohol could have led to rearrangement in this case also, it is highly unlikely that the seven-membered alcohol prepared from the ketone XXV rearranged to the eight-membered olefin and that, in addition, the eight-membered alcohol from the ketone XXVI rearranged to the seven-membered olefin.

Further confirmation of the correctness of these structural assignments is provided by a considera-

tion of the ultraviolet spectra. Jones[27] has discussed the effect of interference with the coplanarity of the phenyl rings of trans-stilbene and its derivatives. Inspection of molecular models indicates that the six-membered olefin XX can have the phenyl rings coplanar to essentially the same extent as triphenylethylene while the seven-membered olefin XXIV and the eight-membered olefin XXIII show progressively greater non-coplanarity of the phenyl rings forming the trans-stilbene type of absorbing unit. In agreement with this analysis the six-membered olefin XX has λ_{max} 305 mμ, log ϵ 4.03 which is comparable to the reported[28] λ_{max} 303 mμ, log ϵ 4.3 for triphenylethylene (both in cyclohexane as the solvent). The seven-membered olefin XXIV was reported[26] to have λ_{max} 305 mμ, log ϵ 4.05 in absolute ethanol which compares favorably with the λ_{max} 306 mμ, log ϵ 4.48 for triphenylethylene in ethanol[29] or λ_{max} 305 mμ, log ϵ 4.18 in chloroform.[30] In contrast the spectrum of the eight-membered olefin XXIII has λ_{max} 270 mμ, log ϵ 4.1 (in absolute ethanol). The shift away from the visible shown by this compound is reasonably attributed to the steric inhibition of resonance anticipated.

A final point which deserves mention is the behavior of the two dichlorides encountered in the synthetic part of this work. The seven-membered dichloride XXVII apparently loses hydrogen chloride extremely readily since the attempt to prepare it by addition of chlorine to the appropriate olefin in carbon tetrachloride at 0° followed by removal of the carbon tetrachloride under reduced pressure at room temperature led directly to the dehydrochlorination product XXI. This behavior is similar to that previously observed in the chlorination of 1,1-diphenylethylene.[31]
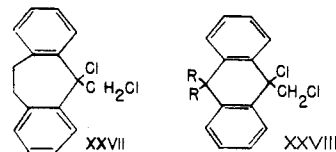
The six-membered dichloride XXVIII, however, was readily isolated under the conditions which had led to dehydrohalogenation of XXVII. When the dichloride XXVIII was treated with 10% ethanolic potassium hydroxide the major product formed in 71% yield was not the olefin but, instead, a chloro ether formed presumably by replacement of one of the chlorine atoms by an ethoxyl group. It appears likely that in this case the olefin-forming reaction is sterically retarded by a chlorine–phenyl interaction in the transition state. Such a steric interaction is less serious in the seven-membered olefin XXI and presumably also in the transition state

(23) A. T. Blomquist and L. H. Liu, THIS JOURNAL, **75**, 2153 (1953).

(24) A. E. Favorskii, M. F. Shostakovskii and N. A. Domnin, *J. Gen. Chem. (U.S.S.R.)*, **6**, 720 (1936).

(25) F. Scardiglia and J. D. Roberts, *Tetrahedron*, **1**, 343 (1957).

(26) E. D. Bergmann, E. Fischer, D. Ginsburg, Y. Hirshberg, D. Lavie, M. Mayot, M. A. Pullman and B. Pullman, *Bull. soc. chim. France*, 684 (1951).

(27) R. N. Jones, THIS JOURNAL, **65**, 1818 (1943)

(28) V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172 (1952).

(29) P. Rumpf and M. Gillois, *Bull. soc. chim. France*, 1348 (1955).

(30) B. Arends, *Ber.*, **64**, 1938 (1931). There appears to be an error in ref. 26 with respect to the absorption of triphenylethylene. In their Table IV the authors give λ_{max} 2980 Å. (solvent unspecified) but neither of the curves shown for triphenylethylene in heptane and ethanol has a maximum at this wave length. The maximum in the curve shown for triphenylethylene in ethanol, λ_{max} 283, furthermore, is in disagreement with the value reported by Rumpf and Gillois.[29] In addition to this, the spectrum of triphenylethylene reproduced in Fig. 4 of ref. 27 appears to have the wave length scale incorrectly located.

(31) E. Hepp, *ibid.*, **7**, 1410 (1874); see also ref. 5b.

leading to it so that the elimination reaction is apparently nearly as easy as in the diphenylethylene system.

Experimental[32]

Reaction of 2-Bromo-1,1-diphenylethylene with Phenyllithium.—Addition of 15.0 ml. (9.00 × 10⁻³ mole) of phenyllithium solution to a solution of 2.09 g. (7.96 × 10⁻³ mole) of 2-bromo-1,1-diphenylethylene in 35 ml. of dry ether was made in a nitrogen atmosphere over a 2-min. period at −35°. Stirring was continued for 0.5 hr. at −35° and the reaction mixture was poured onto Dry Ice. After the addition of more ether the mixture was extracted with aqueous 0.5 N potassium hydroxide solution and then with water. The ethereal extract, dried over magnesium sulfate, was concentrated to give an oil (1.96 g.), shown by its infrared spectrum to contain a 51% yield of diphenylacetylene (using the intensity at 915 cm.⁻¹), a 0.7% yield of phenyl 2,2-diphenylvinyl ketone (1665 cm.⁻¹) and 54% of the total amount of starting vinyl bromide (1225 cm.⁻¹) which had not reacted. The yield of ketone was estimated by assuming that its extinction coefficient is the same as that of butyl 2,2-diphenylvinyl ketone.[5b] Acidification of the aqueous fraction with concentrated hydrochloric acid and extraction with ether gave 0.65 g. of light tan solid, m.p. 110–112°, which was added to 15 ml. of boiling water and filtered hot. The residual material (5 mg.) had m. p. 201–204° and after recrystallization from 50% aqueous ethanol amounted to 3 mg. (0.1%) of what is believed to be triphenylacrylic acid, m.p. 216–217.5° (lit.[33] 213°). From the filtrate was obtained 0.29 g. of benzoic acid, m.p. 121–122°. A mixed m. p. with an authentic sample showed no depression. The solubility of triphenylacrylic acid was found to be approximately 2.8 mg./ml. in boiling water. Thus, a maximum of about 2% yield could have escaped detection. Repetition of the experiment with the exception that the reaction mixture was stirred at −35° for 2.5 hr. gave a neutral fraction of 1.77 g. shown by infrared examination to contain a 74% yield of diphenylacetylene, 0.9% of phenyl 2,2-diphenylvinyl ketone and 22% of starting material. Removal of benzoic acid from the acid fraction as before gave a residue which on sublimation at 185° and 0.2 mm. gave 6 mg. (0.3% yield) of triphenylacrylic acid, m.p. 216–217° (lit.[33] 213°). A maximum of 1.6% could have escaped detection.

Anal. Calcd. for C₂₁H₁₆O₂: C, 84.0; H, 5.4. Found: C, 84.0; H, 5.6.

For comparison the reaction of 2-bromo-1,1-diphenylethylene previously studied[5b] was repeated. To a stirred solution of 2.09 g. (7.96 × 10⁻³ mole) of bromodiphenylethylene[5b] in 35 ml. of dry ether, 16.0 ml. (8.45 × 10⁻³ mole) of n-butyllithium solution prepared from butyl chloride was added in a nitrogen atmosphere over a 35-min. period at −35°. After stirring for an additional 1.5 hr. at −35°, the reaction was terminated by pouring onto an excess of Dry Ice. The isolation was the same as in the reaction described above. The neutral fraction (1.12 g.) was shown by its infrared spectrum to contain a 53% yield of diphenylacetylene, a 2% yield of n-butyl 2,2-diphenylvinyl ketone, and no unreacted starting material. A total of 0.55 g. (39% yield) of diphenylacetylene, m.p. 60–61° (lit.[34] 58–59°), was isolated after recrystallization from 95% ethanol. A mixed m.p. with an authentic sample showed no depression. The acidic fraction weighed 0.42 g. (23.5% yield) and had m.p. 160–161° after recrystallization from 95% ethanol. A mixed m.p. with an authentic sample of triphenylacrylic acid[5b] showed no depression.

Reaction of 2-Iodo-1,1-diphenylethylene with Phenyllithium.—A solution of 1.0 ml. (7.21 × 10⁻⁴ mole) of phenyllithium in ether was added to 0.20 g. (6.56 × 10⁻⁴ mole) of

2-iodo-1,1-diphenylethylene[5b] over a period of 2 min. at −35° in a nitrogen atmosphere and then the reaction was poured onto an excess of Dry Ice and the isolation carried out as described above for the analogous bromide. The neutral oil (0.18 g.) was shown by infrared examination to contain a 32% yield of diphenylacetylene and 2% of diphenylvinyl ketone. The acidic fraction (60 mg.) on recrystallization from 95% ethanol gave 20 mg. (14% yield) of triphenylacrylic acid.

9-Chloromethylenefluorene (V).—Addition of chlorine to 100 g. (0.45 mole) of fluorenylideneacetic acid[35] in 700 ml. of carbon tetrachloride was carried out by passing chlorine gas into the stirred suspension of the acid over a period of 1.7 hr. The crude dichloride (87 g., 66%, m. p. 151–152° with dec.) was not fully characterized but was decomposed by addition to 1500 ml. of 0.5 N aqueous sodium hydroxide solution. Immediate evolution of carbon dioxide was found to occur. The reaction mixture was heated for 0.5 hr. on a steam-bath, cooled to room temperature and filtered. The filtrate was extracted with ether; the ether extract was dried over magnesium sulfate and concentrated to give a solid (44.0 g.) which was dissolved in benzene and chromatographed on 60 g. of alumina by elution with ether. The chromatography was terminated before a dark brown band came off the column. The eluate was concentrated and the residue was recrystallized from 200 ml. of 95% ethanol and enough benzene so the material did not separate as an oil. A total of 34.1 g. (55% yield) of the light yellow solid V, m.p. 73.5–74°, was obtained. The general method of Cristol and Norris[36] to effect dechlorinative decarboxylation was also used. A stirred solution of 20.2 g. (0.069 mole) of fluorenylideneacetic acid dichloride, 17.4 g. (0.207 mole) of sodium bicarbonate (dried at 120°) and 430 ml. of reagent grade acetone (dried over Drierite) was heated under reflux for 6.5 hr. The insoluble salt was filtered and the filtrate was concentrated to 13.0 g. of a yellow-brown solid which was partially dissolved in 50 ml. of hot methanol and the supernatant liquid was decanted from the residual oil. The decantate was cooled in an ice-bath, the precipitated solid was filtered and the process repeated twice to give 6.64 g. (45.5% yield) of V, m. p. 73.5–74.5°.

Anal. Calcd. for C₁₄H₉Cl: C, 79.1; H, 4.3; Cl, 16.7. Found: C, 79.0; H, 4.3; Cl, 17.0.

9-Bromomethylenefluorene (VI) was prepared by a method similar to that previously reported[35] with the exception that fluorenylideneacetic acid dibromide was treated with aqueous 0.5 N sodium hydroxide for 20 min. on a steam-bath, rather than under reflux for 30 min.

The isolation procedure was modified by passing the crude neutral fraction through an alumina column eluting with ether to give 72% yield of VI, m.p. 74.5–75.0° (lit.[35] 72.5–73.0°).

1,4-Dibiphenylenebutatriene (VII), m.p. 279–282° with dec. (lit.[9,10] 309°, 302°, uncor.), after recrystallization from nitrobenzene, was prepared from 1,4-dibiphenylenebutyn-1,4-diol, hydriodic acid (sp. gr. 1.7) and iodine in acetic acid by the method of Lavie and Bergmann[10] in 51% yield. The ultraviolet spectrum in chloroform showed maxima at 450 and 480 mμ with ε 40,000 and 75,000, respectively.

9-Benzylidenefluorene (VIII) was prepared by a method similar to that used by Bachman and Polansky[37] to prepare 9-heptylidenefluorene. To fluorenylpotassium prepared from 0.41 g. (3.60 × 10⁻² g. atom) of potassium in 55 ml. of xylene, 4.0 ml. (6.9 × 10⁻² moles of absolute ethanol and 6.0 g. (3.6 × 10⁻² mole) of sublimed fluorene was added 4.4 ml. (4.3 × 10⁻² mole) of freshly distilled benzaldehyde in 18 ml. of dry xylene. After completion of the reaction, acidification with concentrated hydrochloric acid, washing with water, drying over magnesium sulfate and concentration on a steam-bath under reduced pressure gave a yellow-orange oil which was distilled through a Holtzmann column to give 2.2 g. of fluorene, b. p. 100–110° (0.2 mm.); an intermediate fraction of 0.13 g., b.p. 125–130° (0.2 mm.) and 3.74 g. of VIII, b.p. 180–182° (0.2 mm.). Recrystallization twice from ethanol gave 2.30 g. (41% based on recovered fluorene) of purified VIII, m.p. 75.5–76.5° (lit.[38] 76°).

(32) All melting points are corrected unless otherwise indicated. All boiling points are uncorrected. Many of the spectra are available in the Ph.D. Thesis of William H. Richardson.³ Microanalyses were kindly performed by Mr. Josef Nemeth, Miss Claire Higham and Mrs. Frederick Ju of the Microanalytical Laboratory of the University of Illinois and by the Clark Microanalytical Laboratory, Urbana, Ill. The infrared spectra were determined by Mr. James Brader, Mr. P. E. McMahon, Mr. Brian Cloonan and Miss Mary DeMott. The n.m.r. spectra were determined by Mr. B. A. Shoulders. The ultraviolet spectra were provided by Mr. M. Chao and M. J. Chiu.

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(34) W. Schlenk and E. Bergmann, *Ann.,* 463, 76 (1928).

(35) D. F. DeTar, E. Broderick, G. Foster and B. D. Hilton, THIS JOURNAL, 72, 2183 (1950).

(36) S. J. Cristol and W. P. Norris, *ibid.,* 75, 2645 (1953).

(37) G. B. Bachman and S. Polansky, *J. Org. Chem.,* 16, 1690 (1951).

(38) J. Thiele, *Ber.,* 33, 851 (1900).

Reaction of 9-Bromomethylenefluorene (VI) with Phenyl-lithium. (a) **Slow Addition of Phenyllithium.**—To a stirred solution of 2.00 g. (7.80 × 10⁻³ mole) of 9-bromomethylene-fluorene in 35 ml. of anhydrous ether (dried over sodium), 17.0 ml. (8.60 × 10⁻³ mole) of phenyllithium solution was added over a 40-min. period at −35° under nitrogen.

A 5.0-ml. aliquot was removed 20 min. after the addition was completed and decomposed with solid carbon dioxide. After filtration, washing with distilled water and ether, 40 mg. (15% yield), m.p. 279–281° (dec.) of 1,4-dibiphenylene-butatriene (VII) was obtained. A mixed m.p. with an authentic sample showed no depression. The filtrate from the triene was extracted with 0.5 N potassium hydroxide solution and washed with water. The neutral ether extract was dried over magnesium sulfate and concentrated to give an oil (0.14 g.) shown by its infrared spectrum to contain 54 (from the absorption at 1255 cm.⁻¹) to 56% (from the absorption at 909 cm.⁻¹) of unreacted bromide VI. The basic aqueous phase, after acidification with concentrated hydrochloric acid and extraction with ether, gave less than 2 mg. of acid.

The remaining reaction mixture was allowed to stir for 2.5 hr. at −35° after the addition of phenyllithium was completed. The carbonation and isolation procedure was the same as for the aliquot. The red precipitate of butatriene VII, m.p. 279–281° dec., weighed 0.73 g. (55% yield) after allowance for removal of the aliquot. A mixed m.p. with an authentic sample of triene showed no depression. The acidic fraction amounted to 50 mg. of dark brown oil from which nothing could be isolated. The neutral fraction was shown by examination of its infrared spectrum to contain 52% (absorption at 1255 cm.⁻¹) of the starting material VI.

(b) **Addition of the Bromide VI to Phenyllithium.**—To a solution of 17.0 ml. (8.58 × 10⁻³ mole) of phenyllithium, 2.00 g. (7.80 × 10⁻³ mole) of VI in 35 ml. of dry ether was added over a period of 1.3 hr. at −35° in an atmosphere of nitrogen. The reaction mixture was stirred for an additional period of 2.5 hr. at −35° and was then poured onto excess solid carbon dioxide. After standing 10 hr. the mixture was treated with 30 ml. of water and the suspension was filtered. The resulting bright red solid VII, after washing with water and ether, weighed 185 mg. (6.8% yield) and had m.p. 279–282° (dec.). A mixed m.p. with an authentic sample showed no depression. The ether phase of the filtrate left from the separation of the triene VII, after separation from the aqueous phase, washing with 0.5 N aqueous potassium hydroxide and water, drying over magnesium sulfate and concentration gave 1.74 g. of a dark brown viscous oil shown by its infrared spectrum to contain 42 (915 cm.⁻¹) to 40% (absorption at 1620 cm.⁻¹) of starting material VI unreacted. The infrared spectrum showed that little if any benzylidenefluorene VIII (absorption at 1640 and 1285 cm.⁻¹) was present. The aqueous alkaline fractions from the extraction were acidified with concentrated hydrochloric acid and extracted with ether. The ether solution was dried over magnesium sulfate and concentrated to give 0.16 g. of an orange oil. Attempts to prepare benzylammonium or S-thiouronium salts from this fraction were unsuccessful.

Reaction of 9-Chloromethylenefluorene (V) with Phenyl-lithium. (a) **Slow Addition of Phenyllithium.**—To 2.22 g. (1.04 × 10⁻² mole) of 9-chloromethylenefluorene in 25 ml. of dry ether was added 7.0 ml. (1.04 × 10⁻² mole) of phenyl-lithium in 25 ml. of dry ether at 0° in a nitrogen atmosphere over a period of 45 min. with stirring which was continued for an additional 6.5 hr. after which the mixture was poured into distilled water. After standing for 10 hr. the decomposed reaction mixture was filtered and the red triene VII, m.p. 279–280° (dec.), 0.39 g. (18.4%), was collected after being washed with water and ether. A mixed m.p. with an authentic sample of VII showed no depression. The infrared and ultraviolet spectra of the product were identical with those of an authentic sample of triene VII. After washing the filtrate with water, drying over magnesium sulfate and concentrating, there was obtained 1.98 g. of brown tarry material shown by its infrared spectrum to contain about 5% of the starting material V (absorption at 840 cm.⁻¹). Acidification of the aqueous extracts gave only 3 mg. of unidentified material.

Chromatography of 1.64 g. of the 1.98 g. of crude material was carried out on 35 g. of ethyl acetate-treated alumina activated by heating at 250° under vacuum for 12 hr. Elution with n-hexane and with benzene-hexane (2.5;97.5)

and benzene–hexane (5:95) gave 0.50 g. (19% yield) of 9-benzylidenefluorene (VIII), m.p. 75.5–76.5°, after recrystallization from 95% ethanol. A mixed m.p. with an authentic sample showed no depression and the ultraviolet spectra of the two were identical. A bright orange solid presumed to be **1,4-dibiphenylene-2,3-diphenylbutadiene (IXa)** (0.14 g., 5% yield, m.p. 241.5–242.5° after recrystallization from a benzene–ethanol mixture) was isolated from the chromatography by elution with benzene–hexane (5:95) and benzene–hexane (8:92). The infrared spectrum showed no absorption in the region from 1900–2500 cm.⁻¹ attributable to a cumulene functional group.

Anal. Calcd. for C₄₀H₂₈: C, 94.5; H, 5.6. Found: C, 94.1; H, 5.4.

(b) **Inverse Addition of the Chloride V to Phenyllithium.**—A solution of 2.12 g. (1.00 × 10⁻² mole) of V in 45 ml. of dry ether was added to a stirred solution of 19 ml. (1.38 × 10⁻² mole) of phenyllithium over a 0.5-hr. period at 0° in a nitrogen atmosphere. Stirring was continued for an additional 2.0 hr. at 0° and the mixture was poured onto an excess of solid carbon dioxide. The carbonated reaction mixture was allowed to stand for 10 hr. and 100 ml. of water and 100 ml. of ether were added. The ether phase, after extraction with 0.5 N aqueous potassium hydroxide and drying over magnesium sulfate, was concentrated to give 1.75 g. of red-brown oil. The infrared absorption at 845 cm.⁻¹ indicated that about 5% of the starting material V was present. The remaining neutral fraction (1.63 g.) was chromatographed on 100 g. of ethyl acetate-treated alumina which had been activated by heating at 250° at 2 mm. for 12 hr. Elution with hexane gave 0.44 g. (17% yield) of the benzylidenefluorene VIII, m.p. 75.5–76.5°. A mixed m.p. with an authentic sample showed no depression. Further elution with hexane and with hexane–benzene (95:5) gave 0.22 g. (4% yield) of what is presumed to be 1,4-dibiphenylene-2,3-diphenylbutadiene (IXa), m.p. 242.5–243.5°. A mixed m.p. with the sample obtained above from the slow addition of phenyllithium to V showed no depression. Isolation of the acidic fraction by acidification of the above aqueous extracts with concentrated hydrochloric acid, extraction with ether and evaporation of the ether gave only 80 mg. of tan solid, m.p. 195–196° dec., from which was obtained by recrystallization from aqueous acetic acid 60 mg. of an unidentified acid, m.p. 204–205°.

10,10-Diallylanthrone (XVII).—To 77.7 g. (0.400 mole) of anthrone and 20 mg. of hydroquinone in 500 ml. of toluene dried over sodium was added a lithium methoxide solution prepared from 2.8 g. (0.405 g.-atom) of lithium and 120 ml. of absolute methanol in a nitrogen atmosphere. Immediately after addition of the lithium methoxide solution, distillation was begun and was continued for 2.5 hr. At this time the temperature rose to 110° and the distillate was observed to have an index of refraction, n²⁵D 1.4925 (distilled toluene, n²⁵D 1.4925). A yellow to red precipitate was formed, which was presumed to be the lithium salt of anthrone.

The column was set for total reflux and 350 ml. (4.00 moles) of freshly distilled allyl bromide was added over a 0.5-hr. period. After refluxing an additional 1.0 hr., the yellow to red suspension was dissolved and replaced by a white precipitate (presumably lithium bromide). Distillation was begun once again, to remove the allyl bromide. After the temperature rose to 110°, the distillate had an index of refraction n²⁵D 1.4925 and distillation was stopped. The entire procedure was then repeated in order to effect diallylation.

After the allyl bromide was distilled, 70 ml. of Claisen alkali[39] was added to the cooled reaction mixture. The precipitated material was filtered and washed with ether. The filtrate was extracted with more Claisen alkali and then with ether. The combined ether extracts were dried over magnesium sulfate and concentrated on a steam-bath under reduced pressure to give a green-brown oil which solidified on cooling; yield 93.6 g. (86% of theory) of crude product. A small sample was purified for analysis by passing through ethyl acetate-treated alumina of activity I[40] with n-hexane. Recrystallization of the concentrated product from the chromatography with 95% ethanol gave white crystals of the diallylanthrone XVII, m.p. 85–86°. The infrared

(39) L. Claisen, F. Kremers, F. Roth and E. Tietze, *Ann.*, **442**, 210 (1925).

(40) H. Brockmann and H. Schodder, *Ber.*, **74B**, 73 (1941).

spectrum showed the expected carbonyl absorption at 1662 cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{18}O$: C, 87.6; H, 6.6. Found: C, 87.8; H, 6.8.

Alkylation of the lithium salt prepared from anthrone and lithium metal was less satisfactory. Thus, when 3.88 g. (2.00×10^{-2} mole) of anthrone, 0.14 g. (2.00×10^{-2} g.-atom) of lithium, 1 mg. of hydroquinone and 40 ml. of toluene (distilled from sodium) were heated under reflux overnight under a nitrogen atmosphere and then 1.73 ml. (2.00×10^{-2} mole) of freshly distilled allyl bromide was added and the reaction mixture was stirred at room temperature for 24 hr. there was no apparent reaction. A 10-fold molar excess of allyl bromide was then added and refluxing continued for 4.5 hr. The solvent was distilled until the distillate had $n^{25}D$ 1.4925 (20 ml. of additional toluene had to be added).

The above procedure was repeated using again a 10-fold molar excess of allyl bromide to ensure diallylation. After a 4.0-hr. refluxing period the solution was filtered (precipitate water-soluble) and the filtrate extracted with Claisen alkali as in the preparation described above. The viscous yellow oil (3.94 g.) obtained was estimated by the intensity of its absorption in the infrared at 1662 cm.$^{-1}$ to contain about 33% of the diallyl ketone XVII.

10,10-Di-*n*-propylanthrone (XVIII).—Crude diallylanthrone XVII (93.0 g., 0.338 mole, obtained from the lithium methoxide procedure) in 150 ml. of ethyl acetate was hydrogenated[41] at 12.5–35.0 p.s.i. over 8.0 g. of 5% palladium-on-charcoal with an uptake of 91% of the theoretical amount of hydrogen. After filtration, the filtrate was passed through Filter-cel and concentrated on a steam-bath under vacuum to yield 88 g. of crude product which after recrystallization from 95% ethanol amounted to 75.6 g. (80.5% yield) with m.p. 125–126°. Further recrystallization gave XVIII with m.p. 125.5–126.5° (lit.[42] 124°).

Anal. Calcd. for $C_{20}H_{22}O$: C, 86.3; H, 8.0. Found: C, 86.3; H, 7.9.

9,10-Dihydro-10,10-di-*n*-propyl-9-methyleneanthracene.—To a solution of methyllithium prepared from 71.0 ml. (1.14 moles) of methyl iodide in 250 ml. of dry diethyl ether and 15.5 g. (2.24 g.-atoms) of lithium in 500 ml. of ether at −10 to −6° was added 75.0 g. (0.225 mole) of the di-*n*-propylanthrone XVIII in 100 ml. of dry benzene and 200 ml. of dry ether over a 0.5-hr. period at −5°. Stirring was continued for an additional 3 hr. at 0° and then the reaction mixture was poured onto a mixture of 1 kg. of ice and 40 g. of ammonium chloride. The ether phase was separated, washed with water, dried over magnesium sulfate and concentrated to yield 78.0 g. (98% yield) of crude solid, m.p. 92–94°. Recrystallization of a small sample gave m.p. 99–100°. The compound was not further characterized but was dehydrated as follows. A solution of 78.0 g. (0.251 mole) of crude alcohol and 0.2 g. (8.0 × 10^{-4} mole) of iodine in 300 ml. of benzene was heated on a steam-bath with slow distillation for 2.5 hr. The solvent was removed under reduced pressure first on a steam-bath and then at room temperature to yield 68.7 g. (94% yield) of a brown solid, m.p. 49–51°. A small sample was passed through ethyl acetate-treated alumina of activity 1/II[40] and was then recrystallized from absolute ethanol to give 10,10-dihydro-10,10-di-*n*-propyl-9-methyleneanthracene, m.p. 59.5–60°.

Anal. Calcd. for $C_{21}H_{24}$: C, 91.3; H, 8.8. Found: C, 91.0; H, 9.1.

9-Chloro-9-chloromethyl-9,10-dihydro-10,10-di-*n*-propylanthracene (XXVIII).—A solution of 16.9 g. (0.238 mole) of chlorine in 195 ml. of carbon tetrachloride at 0° was added to a stirred solution of 68.7 g. (0.235 mole) of crude 9,10-dihydro-10,10-di-*n*-propyl-9-methyleneanthracene, in 170 ml. of carbon tetrachloride over a period of 20 min. at −10°. Stirring was continued for an additional 1.3 hr. at −10° and then for 2 hr. at 0°.

The solution was concentrated under reduced pressure at room temperature to give 86.6 g. of crude product, m.p. 108–109.5° (with gas evolution). The crude solid was washed with ether to give 50.6 g. (60% yield) of white crystals, m.p. 120–121° (with gas evolution). A small

sample of the dichloro compound XXVIII recrystallized from cyclohexane for analysis had m.p. 122–123° (with gas evolution).

Anal. Calcd. for $C_{21}H_{24}Cl_2$: C, 72.6; H, 7.0. Found: C, 72.4; H, 7.3.

9-Chloromethylene-9,10-dihydro-10,10-di-*n*-propylanthracene (XV).—A stirred solution protected from moisture by a calcium chloride tube of 21.6 g. (6.00 × 10^{-2} mole) of dichloride XXVIII, 5.4 ml. (6.60 × 10^{-2} mole) of pyridine and 90 ml. of dry tetrahydrofuran (distilled from sodium) was refluxed for 12 hr. A voluminous, water-soluble precipitate, presumably pyridine hydrochloride, which formed was filtered and washed with dry ether. The filtrate was concentrated on a steam-bath under reduced pressure. To the residue was added 125 ml. of ether and the solution was washed with water. The ether extract was dried over magnesium sulfate and concentrated. The residual oil was distilled through a Holtzmann column and 15.45 g. (79% yield) of distillate was collected at 154–157° (0.4 mm.). After standing for two weeks, the distillate solidified and had m.p. 47.5–48.5°. Redistillation of a small portion of the distillate was carried out to obtain an analytical sample of the chloroölefin XV.

Anal. Calcd. for $C_{20}H_{23}Cl$: C, 80.4; H, 7.8. Found: C, 80.7; H, 7.5.

Oxidation of the Chloroölefin XV with Osmium Tetroxide.—A solution of 0.20 g. (6.12 × 10^{-4} mole) of XV, 0.27 g. (1.07 × 10^{-3} mole) of osmium tetroxide, 0.36 ml. (4.65 × 10^{-3} mole) of pyridine and 10 ml. of dry benzene was allowed to stand for 15 days in a stoppered flask.[43] The solution was concentrated to a black residue. A solution of 4.0 g. of anhydrous sodium sulfite in 35 ml. of distilled water and 10 ml. of tetrahydrofuran was added. The mixture was allowed to reflux for 2 hr. The black suspension was filtered through a fluted filtered paper and then through Filter-cel. The aqueous portion of the filtrate was separated and extracted with ether. The ether solution was dried over magnesium sulfate and then concentrated to give 0.17 g. (86% yield, assuming it to be 9,10-dihydro-10,10-di-*n*-propyl-9-hydroxy-9-anthracene aldehyde) of a viscous light yellow oil.

To 80 mg. (2.46 × 10^{-4} mole) of the above oil, 5 ml. of dry benzene and 200 mg. (4.60 × 10^{-4} mole) of lead tetraacetate was added. The flask was stoppered and allowed to stand for 24 hr. at 26°. The reaction mixture was decomposed at this time with 0.5 ml. of water. The brown precipitate was filtered and washed with benzene. Upon concentration of the filtrate, 95 mg. of a light brown semi-solid was obtained. Recrystallization of the semi-solid from 95% ethanol was found to give 60 mg. (83% yield), of a solid, m.p. 125–126°. A mixed m.p. with an authentic sample of di-*n*-propylanthrone XVIII showed no depression.

Reaction of the Chloromethylenedihydroanthracene XV with Phenyllithium.—To a stirred solution of 4.36 g. (1.40 × 10^{-2} mole) of chloromethylenedihydroanthracene XV in 60 ml. of dry diethyl ether, 26.0 ml. (1.47 × 10^{-2} mole) of phenyllithium solution was added over a period of 20 min. at 0° in a nitrogen atmosphere. The reaction mixture was stirred for an additional 12 hr. at 26° and decomposed by pouring onto an excess of solid carbon dioxide. After 10 hr. 30 ml. of water was added and the suspension filtered. After washing with water and ether the bright orange solid, di-(9,10-dihydro-10,10-di-*n*-propyl-9-anthracenylidene)-ethylene (XIX), m.p. 246–247°, amounted to 0.52 g. An additional 20 mg. of XIX was obtained from the chromatography of the neutral filtrate; the total was thus 0.54 g. (15% yield).

Anal. Calcd. for $C_{42}H_{44}$: C, 91.4; H, 8.1. Found: C, 91.7; H, 8.5.

After separation of the aqueous phase from the filtrate above, the ether layer was extracted with 0.5 N aqueous potassium hydroxide solution and then washed with water. The ether solution after drying over magnesium sulfate was concentrated to give 4.20 g. of a dark brown viscous oil shown by its infrared absorption at 837 cm.$^{-1}$ to contain 22% of the total starting material XV. The aqueous fraction was acidified with concentrated hydrochloric acid and then extracted with diethyl ether. The ether solution was washed with water, dried over magnesium sulfate and con-

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(42) F. Hallgarten, *Ber.*, **22**, 1069 (1889).

(43) R. Criegee, B. Marchand and H. Wannowius, *Ann.*, **550**, 99 (1942).

centrated to give 10 mg. of an oily acidic fraction. The neutral fraction (4.15 g.) was chromatographed on 212 g. of ethyl acetate-treated alumina, which was activated by heating at 250° at 3.5 mm. for 10 hours. Elution with hexane gave 0.52 g. of chloride XV as shown by the infrared spectrum. A later fraction (0.55 g.) was found to be 80% chloride XV as indicated by the absorption at 835 cm.$^{-1}$. This amounts to a total of 0.96 g. (22% recovery) of un-reacted chloride XV. Further elution with hexane gave 0.95 g. (19% yield) of white solid 9-benzylidene-9,10-dihydro-10,10-di-n-propylanthracene (XX), m.p. 121–122°, after recrystallization from a mixture of absolute ethanol and 95% ethanol. No other solid product was obtained from the chromatography.

Anal. Calcd. for $C_{27}H_{28}$: C, 92.0; H, 8.0. Found: C, 92.0; H, 8.2.

Catalytic Hydrogenation of the Triene XIX.—To a sus-pension of 9.4 mg. of prehydrogenated Adams catalyst in 20 ml. of distilled ethyl acetate was added 100 mg. (1.83 × 10^{-4} mole) of XIX and the stirred suspension was hydro-genated at 746 mm. pressure at 25° for 8 hr. The uptake of hydrogen was 13.4 ml. compared to a theoretical uptake of 13.7 ml. on the basis of three olefinic bonds.

The catalyst was filtered and washed with ethyl acetate and the concentrated filtrate gave 100 mg., m.p. 191–192° of a light yellow solid. The solid was passed through 10 g. of ethyl acetate treated alumina, which was activated by heating at 250° under high vacuum overnight. The hexane eluate gave 90 mg. (89% yield) of white di-(9,10-dihydro-10,10-di-n-propyl-9-anthracenyl)-ethane m.p. 212–213°, after recrystallization from absolute ethanol.

Anal. Calcd. for $C_{42}H_{50}$: C, 90.9; H, 9.1. Found: C, 91.3; H, 8.8.

Ozonolysis of the Benzylidenedihydroanthracene XX.—The general procedure was that of Henne and Hill.[44] Ozone was passed through a solution of 300 mg. (8.16 × 10^{-4} mole) of XX in 30 ml. of distilled methylene chloride for 6 min. at 80° with a flow rate of 0.171 mmole/min. At the end of this period the yellow-green solution was concentrated under reduced pressure at room temperature to give 0.31 g. of a yellow oil which was refluxed with 12 ml. of 30% hydrogen peroxide, 20 ml. of water, 10 ml. of acetic acid and 0.5 ml. of concentrated sulfuric acid for 2 hr. The reaction mixture was extracted with ether and the ether layer with 0.5 N aqueous potassium hydroxide and then water. It was then dried over magnesium sulfate and concentrated to give 200 mg. (84% yield) of 10,10-di-n-propylanthrone, m.p. 125–126°. A mixed m.p. with an authentic sample of this ketone showed no depression.

The aqueous phase was acidified with concentrated hydro-chloric acid and extracted with ether. The ether extracts were dried over magnesium sulfate and concentrated to 330 mg. of a liquid. Further concentration of this liquid was found to give 60 mg., m.p. 110–112°, of a solid residue from which was obtained by recrystallization from water 40 mg. (40% yield) of benzoic acid, m.p. 121–122°. A mixed m.p. with an authentic sample showed no depression.

1-Methylene-2,3,6,7-dibenz-2,6-cycloheptadiene.—A solu-tion of 37.0 g. (0.165 mole) of 2,3,6,7-dibenz-1-methyl-2,6-cycloheptadien-1-ol,[22] 50 mg. of iodine and 300 ml. of rea-gent grade benzene was refluxed for 1 hr. on a steam-bath and then the solvent was distilled under reduced pressure. The residue was dissolved in 100 ml. of ether and extracted with saturated sodium thiosulfate solution and then with water. The ether extract was dried over magnesium sulfate and concentrated to give 34.09 g. (100% yield) of a light yellow solid, m.p. 63–64° (lit.[22] 63–64°, 67–68°). A small portion recrystallized further had m.p. 63.5–64.5°.

1-Chloromethylene-2,3,6,7-dibenz-2,6-cycloheptadiene (XXI).—A solution of 12.6 g. (0.178 mole) of chlorine in 150 ml. of carbon tetrachloride at 0° was added to a stirred solution protected with a calcium chloride drying tube of 33.4 g. (0.162 mole) of 1-methylene-2,3,6,7-dibenz-2,6-cyclohepta-diene in 100 ml. of carbon tetrachloride over a 40-min. period at −10°. After the addition was completed, stirring was continued at 0° for 2.5 hr. Some hydrogen chloride evolu-tion was noted during the stirring period at 0°.

The solution was concentrated on a water-bath main-tained at 80° under reduced pressure. Under these condi-tions, the temperature of the solution was maintained below room temperature. The resulting oil crystallized to a light

tan solid, 41.96 g., m.p. 73–76°. Recrystallization from absolute alcohol gave 30.2 g. (77% yield) of chloroölefin XXI, m.p. 88–89°. A sample of crude XXI recrystallized from cyclohexane and then sublimed at 89° (0.2 mm.) had m.p. 88–89°.

Anal. Calcd. for $C_{16}H_{13}Cl$: C, 79.8; H, 5.4. Found: C, 79.6; H, 5.6.

1-Hydroxy-1-phenyl-2,3,6,7-dibenz-2,6-cycloöctadiene.—To phenylmagnesium bromide prepared from 0.44 g. (1.8 × 10^{-2} g.-atom) of magnesium turnings, 3.1 g. (1.98 × 10^{-2} mole) of bromobenzene and 5.0 ml. of ether (dried over sodium) was added a solution of 0.40 g. (1.8 × 10^{-3} mole) of 2,3,6,7-dibenz-2,6-cycloöctadien-1-one[45] in 5.0 ml. of ether and 2.0 ml. of benzene over a 5-min. period. The solution was heated under reflux for 3.0 hr. in an atmosphere of nitrogen. The reaction mixture was poured into an ice-cold solution of 0.25 g. of ammonium chloride in 5 ml. of water. The aqueous phase was separated and extracted with ether. The ether solution was dried over magnesium sulfate and concentrated to give 0.93 g. of a viscous brown oil.

An attempt was made to dehydrate the above brown oil in 60 ml. of benzene by heating it under reflux for 1.3 hr. in the presence of a small crystal of iodine. After the benzene was distilled, the residual oil was dissolved in 20 ml. of ether. The ethereal solution was extracted with 10% aqueous sodium thiosulfate solution. The ether solution was dried over magnesium sulfate and concentrated to an oil to which 3 ml. of petroleum ether (b.p. 60–90°) was added, after which a light yellow solid precipitated. After recrystallizing from petroleum ether (b.p. 60–90°) 0.30 g. (56% yield) of alcohol, m.p. 150–151°, was obtained.

Anal. Calcd. for $C_{22}H_{20}O$: C, 88.0; H, 6.7. Found: C, 87.8; H, 6.6.

1-Phenyl-2,3,6,7-dibenz-2,6,8-cycloöctatriene (XXIII).—A mixture of 0.17 g. (5.7 × 10^{-4} mole) of 1-hydroxy-1-phenyl-2,3,6,7-dibenz-2,6-cycloöctatriene in 1.0 ml. of acetic acid and 0.1 ml. of concentrated hydrochloric acid was heated on a steam-bath for 1.0 hr. To the cooled reaction mixture, 10 ml. of ether was added and the solution was washed with water. The ether phase was dried over magnesium sulfate and concentrated to give 0.14 g. of a viscous light yellow oil which could not be crystallized from methanol or n-hexane.

The oil was dissolved in n-hexane and passed through 2 g. of alumina with n-hexane. The alumina was previously treated with ethyl acetate and activated by heating at 250° under high vacuum overnight. Upon concentration of 30 ml. of the eluate 0.11 g. of a viscous, cloudy white oil was obtained. This oil was crystallized from absolute ethanol to give 0.09 g. (56% yield), m.p. 83–84°, of XXIII as a white solid.

Reaction of 1-Chloromethylene-2,3,6,7-dibenz-2,6-cyclo-heptadiene (XXI) with Phenyllithium.—To a stirred solu-tion of 3.23 g. (1.34 × 10^{-2} mole) of chloromethylene-cycloheptadiene XXI in 60 ml. of dry ether, was added 26 ml. (1.47 × 10^{-2} mole) of phenyllithium solution over 25 min. at 26° under nitrogen. The reaction mixture first turned a bright yellow color on addition of phenyllithium and then a yellow-brown color. After stirring an additional 5.5 hr. at 26°, the reaction mixture was poured onto an excess of solid carbon dioxide.

After standing 2.5 hr., 30 ml. of distilled water and 40 ml. of ether was added to the carbonated reaction mixture and the ether phase was separated and extracted with aqueous 0.5 N potassium hydroxide solution and then washed with water. After drying over magnesium sulfate, the ether extract was concentrated to give 3.13 g. of a viscous yellow-brown oil. An infrared spectrum of this neutral fraction showed it to contain 12 (absorption at 830 cm.$^{-1}$) to 14% (absorption at 905 cm.$^{-1}$) of the total starting chloride XXI.

The aqueous fraction was acidified with concentrated hydrochloric acid and then extracted with ether. The ether extracts were washed with water, dried over magnesium sulfate and concentrated to give 0.48 g. of a viscous brown oil. The oil was taken up in 30 ml. of 0.5 N aqueous potas-sium hydroxide and extracted with ether. The aqueous portion was acidified with concentrated hydrochloric acid and extracted with ether. After drying over magnesium sulfate, 0.46 g. of a viscous brown oil was obtained upon

(44) A. L. Henne and P. Hill, THIS JOURNAL, **65**, 752 (1943).

(45) Kindly provided by Professor N. J. Leonard. [N. J. Leonard, A. J. Kresge and M. Ōki, *ibid.*, **77**, 5078 (1955)].

concentration. The infrared spectrum of this oil showed absorption at 695 cm.$^{-1}$, characteristic of a monosubstituted phenyl group.[46] However, there was no evidence for benzoic acid in this acid fraction, as was seen by the infrared spectrum (1460 cm.$^{-1}$).

The neutral fraction was boiled with n-hexane and the suspension was filtered on cooling to give 0.09 g. of an unidentified tan solid, m.p. 141–146°. The remainder of the neutral fraction (3.03 g.) was chromatographed on 144 g. of ethyl acetate-treated alumina activated by heating at 300° (0.2 mm.) overnight. Elution with n-hexane gave 0.34 g. (11% recovery) of XXI, m.p. 88–89°. A mixed m.p. with an authentic sample of this chloride showed no depression. Elution with n-hexane and with benzene-hexane (5:95) gave 1-phenyl-2,3,6,7-dibenz-2,6,8-cyclo-octatriene (0.88 g., 23% yield, m.p. 83–84°). A mixed m.p. with chloromethylenedibenzcycloheptadiene XXI showed m.p. 64–80°.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.6; H, 6.4. Found: C, 93.0; H, 6.4.

An unidentified compound (0.33 g., 8.8% yield), m.p. 271–272° dec., was obtained by elution with benzene-hexane (10:90). Its molecular weight was 508 to 567 as determined by the Rast method.[47]

Anal. Calcd. for $C_{44}H_{36}$: C, 93.6; H, 6.4. Found: C, 92.5; H, 6.1.

A further unidentified product was obtained from a latter fraction eluted with benzene–hexane (10:90). A bright yellow solid, it was found to weigh 0.17 g., m.p. 150–155° dec. The visible spectrum was completely unlike those of the trienes VII and XIX.

Anal. Calcd. for $C_{18}H_{14}$: C, 93.2; H, 6.8. Found: C, 92.9; H, 6.1.

Reaction of 9-Chloro-9-chloromethyl-9,10-dihydro-10,10-di-n-propylanthracene (XXVIII) with Alcoholic Potassium Hydroxide.—A mixture of 8.15 g. (2.24 × 10^{-2} mole) of XXVIII and 50 g. of a 10% alcoholic potassium hydroxide solution was shaken for 1.5 hr. at room temperature. The mixture was filtered to give 6.2 g., m.p. 118.5–120°, of a white solid. Recrystallization of this solid from absolute ethanol was found to give 5.9 g. (71% yield), m.p. 123–

124°, of what is probably 9-chloromethyl-9-ethoxy-9,10-dihydro-10,10-di-n-propylanthracene. A product, m.p. 123–124°, which showed no m.p. depression on admixture with the sample prepared with ethanolic potassium hydroxide was also obtained when the recrystallization of the dichloride XXVIII from ethanol was attempted. The infrared spectrum showed strong absorption at 1082 and 1118 cm.$^{-1}$ and no absorption in the hydroxyl or carbonyl stretching regions. The ultraviolet spectrum showed only a modest absorption maximum at approximately 255 mμ, indicative of the presence of unconjugated phenyl rings.

Anal. Calcd. for $C_{23}H_{29}OCl$: C, 77.4; H, 8.2. Found: C, 77.6; H, 8.6.

Alkylation of the Lithium Salt of Anthrone with Methyl Iodide.—A mixture of 3.88 g. (2.00 × 10^{-2} mole) of anthrone, 0.14 g. (2.00 × 10^{-2} g.-atom) of lithium and 40 ml. of dry toluene (distilled from sodium) was allowed to reflux overnight under nitrogen. The toluene was distilled under nitrogen, after which a vacuum was applied for 5 min. The deep red colored salt was transferred to a Carius tube and 25 ml. of methyl iodide was added. The tube was swept with nitrogen, sealed and placed in an oven at 130° for 24 hr. The methyl iodide was removed and the above procedure was repeated.

To the resulting solid was added 25 ml. of ether and 20 ml. of Claisen alkali. The insoluble material was filtered and later was added to the Claisen alkali fraction. The ether phase was separated, extracted with additional Claisen alkali and then washed with water. After drying over magnesium sulfate, the ether extract was concentrated to give 1.56 g. of a deep red oil. From the infrared spectrum of this oil it was ascertained that a maximum of 23% yield of 10,10-dimethylanthrone was obtained. The estimate may be high, since the calculation was based on the carbonyl absorption (1662 cm.$^{-1}$) and higher melting compounds with carbonyl absorption of this frequency had been observed in previous attempted methylations of anthrone. Crystallization of the red oil from absolute ethanol was carried out, yielding 0.29 g. (6.5% yield from anthrone) of an orange solid, m.p. 104.5–105.5° (lit.[48] 99.5–100.5°, 102.5–103°).[3] A mixed m.p. with an authentic sample of 10,10-dimethylanthrone kindly supplied by Dr. N. J. Leonard showed no depression. No other product was isolated.

(46) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., p. 55.

(47) N. D. Cheronis, *Technique of Org. Chem.,* **6,** 211 (1944).

(48) A. J. Kresge, Ph.D. Thesis, University of Illinois, 1954.
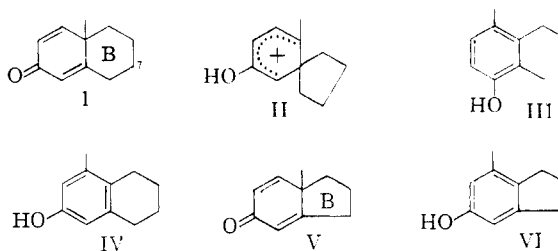
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Ring Size in the Dienone–Phenol Rearrangement

BY STANLEY M. BLOOM*

The synthesis and acid-catalyzed rearrangement under anhydrous conditions of 8-methyl-$\Delta^{4,9,6,7}$-dihydroindane (V) is reported. The *m*-phenol 7-methyl-5-indanol (VI) is obtained and the significance of this result discussed.

In the acid-catalyzed rearrangement of a number of polycyclic cyclohexadienones,[1] the formation of a *p*-phenol has been shown to proceed *via* a five-membered spiran.[2a,b] Thus 10-methyl-2-keto-$\Delta^{1,9; 3,4}$hexahydronaphthalene (I) rearranges in acidic media to 8-methyl-5-hydroxy-1,2,3,4-tetra-hydronaphthalene[1a] (III) *via* the spiran II. Compound I, on change of solvent[3] or by introduction

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(1) (a) R. B. Woodward and T. Singh, THIS JOURNAL, **72,** 494 (1950): (b) H. H. Inhoffen, *Angew. Chem.,* **63,** 297 (1951); (c) C. Herran, O. Mancera, G. Rosenkranz and C. Djerassi, *J. Org. Chem.,* **16,** 899 (1951).

(2) (a) R. B. Woodward, "Perspectives in Organic Chemistry," Interscience Publishers, Inc., New York N. Y., 1956, p. 178; (b) S. M. Bloom, THIS JOURNAL, **80,** 6280 (1958).

(3) A. S. Dreiding, W. J. Pummer and A. J. Tomasewski, *ibid.,* **75,** 3159 (1953).

of a $\Delta^{7,8}$-double bond into ring B followed by hydrogenation,[4] has been shown to rearrange *via* a simple 1,2-methyl shift to the *m*-phenol 8-methyl-6-hydroxy-1,2,3,4-tetrahydronaphthalene (IV).

(4) A. Sandoval, L. Miramontes, G. Rosenkranz and C. Djerassi, *ibid.,* **73,** 990 (1951).