pressure yielded a mixture shown by infrared analysis to consist of approximately 50% unchanged IV, 25% *cis-p*-menthane and 25% *trans-p*-menthane when only enough hydrogen was absorbed to correspond to one double bond. When IV was fully saturated with hydrogen, the product was a mixture of *cis-* and *trans-p*-menthanes in about equal parts. The hydrogen required for complete saturation was 2.0 moles per mole of IV.

Isomerization of 1(7),8-*p*-Menthadiene (IV). (A) With Rosin.—A mixture of 75% by weight gum rosin and 25% IV was heated at reflux, about 195–205°, for nine hours. The volatile oil was then steam distilled and infrared analysis showed it to consist of 54% 1,8-*p*-menthadiene, the remainder being unchanged IV.

(B) **With Clay.**—When 5 ml. of IV was heated at reflux with 50 mg. of 30/60 mesh Florex-S[5] there was obtained a mixture which was shown by infrared analysis to consist of 20% cymene, 5% dipentene, 2% 2,4(8)-menthadiene, 2 to 4% α-terpinene, 2 to 4% γ-terpinene and traces of other volatile products. The remainder consisted of high boiling polymeric material.

Conversion of nopol to 1,8-*p*-menthadiene was accomplished by heating a mixture of 350 g. of gum rosin and 166 g. nopol at 250–260° for 4 hours. The volatile oil obtained on steam distillation weighed 77 g. and infrared analysis showed that it consisted of about 80% 1,8-*p*-menthadiene and 20% alcohols. The resinous non-volatile residue possessed a softening point of 79° (Ball and Ring Method, A.S.T.M. Designation: E28-42T) and acid number 123.

Condensation of 1(7),8-*p*-menthadiene (IV) with formaldehyde was accomplished by heating equimolar quantities of IV and paraformaldehyde in a sealed tube at 175° for 4 hours. The infrared spectrum of the product could not be analyzed because of the strong blanketing influence on the spectrum of unreacted formaldehyde or its hemiformals with the alcohol formed. The product was therefore refluxed with excess aqueous 50% sodium hydroxide and ethylene glycol at 150° for one hour. Extraction of this reaction product with pentane and evaporation of the pentane produced a sample of oil free of formaldehyde which was shown by infrared analysis to consist of a mixture of 35 to 40% III and 60 to 65% unreacted IV.

1(7)-*p*-Menthene (VI) was obtained on heating 74 g. of V[1] at atmospheric pressure and 245–314° for about 8 hours a day for 10 days and employing the same type of equipment as for the preparation of IV. The decomposition of V was considerably slower than in the case of III. Aside from paraformaldehyde, there was obtained as distillate 27 g. (44% of theory) of crude VI of 90% or higher purity. It was purified by fractionation, the purest fraction as judged by infrared analysis boiled at 174° at 760 mm. pressure, and showed n^{25}_{D} 1.4575, d^{25}_{4} 0.8212. Bromine titration showed the presence of one double bond (88.6% of theory), but a crystalline bromide could not be obtained employing the same procedure as was employed for IV. Examination of the infrared spectrum shows VI to contain the characteristic $CH_2{=}C<$ absorptions at about 6.1 and 11.3 μ, but of only about one-half the optical density of those possessed by IV. Infrared absorption bands characteristic of VI include those occurring at 6.08(S), 8.98, 9.37, 9.62, 9.85, 10.07, 10.22, 11.07, 11.26(S) and 12.52 μ.

Isomerization of 1(7)-*p*-menthene (VI) was accomplished by heating about one ml. of the hydrocarbon with about 10 mg. of 30/60 mesh Florex-S[5] brand fuller's earth at reflux for 30 minutes.

Infrared analysis of the filtered, isomerized sample showed it to contain about 80% 1-*p*-menthene (VII) and 20% unchanged VI. Infrared absorption bands characteristic of VII include those occurring at 9.82(S), 10.18, 10.39, 10.50, 10.98(S), 11.66, 12.50(S), 12.73 and 13.16 μ.

Condensation of 1(7)-*p*-menthene (VI) with formaldehyde and removal of unreacted formaldehyde from the reaction product was accomplished by the same procedure outlined for synthesis of III. The formaldehyde-free reaction product was shown by infrared analysis to consist of 50 to 55% V and 45 to 55% unreacted VI.

JACKSONVILLE, FLORIDA

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[5] Floridin Company, Warren, Pennsylvania.

[CONTRIBUTION FROM THE SCIENTIFIC DEPARTMENT, ISRAELI MINISTRY OF DEFENCE]

Syntheses of Macrocyclic Compounds

BY ERNST D. BERGMANN AND ZVI PELCHOWICZ[1]

RECEIVED MARCH 16, 1953

The reaction between lithium phenyl and 2,2′-bis-(bromomethyl)-diphenylmethane and -dibenzyl leads to about equal parts of polymeric materials and 1,2,4,5,8,9,11,12-tetrabenzocyclotetradeca-1,4,8,11-tetraene and 1,2,5,6,9,10,13,14-tetrabenzocyclohexadeca-1,5,9,13-tetraene, respectively. By successive treatment of the latter with NBS and pyridine, *all-trans*-1,2,5,6,9,10,13,14-tetrabenzocyclohexadeca-1,3,5,7,9,11,13,15-octaene, a colorless hydrocarbon, was obtained. The three macrocyclic compounds are strainless but not planar. The mechanism of the synthesis is discussed. Reaction of 2-benzylbenzyl bromide with lithium phenyl gives 2,2′-dibenzyldibenzyl, reaction of 2-(*o*-methylbenzyl)-benzyl bromide with lithium phenyl 2,2′-di-(*o*-methylbenzyl)-dibenzyl. The formation of an olefin by successive treatment of an ethane with NBS and pyridine appears to be characteristic for *sym*-diarylethanes. Thus, also 2,2′-dibenzyldibenzyl is converted into 2,2′-dibenzylstilbene (*cis*-form), 1,1,2,2-tetraphenylethane into tetraphenylethylene.

The removal of the bromine atoms from 2,2′-bis-(bromomethyl)biphenyl (I) by means of lithium phenyl[2] leads to dihydrophenanthrene (II), thus to intramolecular cyclization. The question arose whether analogously 2,2′-bis-(bromomethyl)-diphenylmethane (III) or -dibenzyl (V) would permit the synthesis of seven- and eight-membered ring systems such as 1,2,4,5-dibenzocyclohepta-1,4-diene (IV) and 1,2,5,6-dibenzocycloöcta-1,5-diene (VI). This did not seem impossible in spite of the greater spatial mobility of III and V as compared with I; according to Wittig and Witt,[3] the above synthesis would proceed in the case of I *via* an organo-lithium compound of the structure VII which evidently attracts preferentially the bromine atom *in the same molecule*, an effect which could well be anticipated also in the case of the analogous derivative of III or V. Moreover, the synthesis of VI from V would be analogous to its formation from *o*-xylylene dibromide and metallic sodium.[4]

As a model experiment, the reaction of lithium phenyl with 2-benzylbenzyl bromide (X) was studied. The latter was synthesized by reduction of methyl 2-benzylbenzoate (VIII) with lithium

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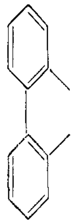
[1] Part of a Thesis submitted by Z. Pelchowicz to the Hebrew University, Jerusalem, in partial fulfillment of the requirements for the degree of Ph.D.

[2] D. M. Hall and E. E. Turner, *Nature*, **163**, 537 (1949); D. M. Hall, S. M. Lesslie and E. E. Turner, *J. Chem. Soc.*, 711 (1950); D. M. Hall and E. E. Turner, *ibid.*, 3072 (1951); E. Bergmann and J. Szmuszkowicz, THIS JOURNAL, **73**, 5153 (1951); E. Bergmann and Z. Pelchowicz, *ibid.*, **75**, in press (1953).

[3] G. Wittig and H. Witt, *Ber.*, **74**, 1474 (1941).

[4] W. Baker, R. Banks, D. R. Lyon and F. G. Mann, *J. Chem. Soc.*, 27 (1945).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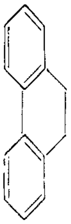
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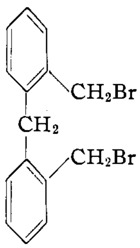
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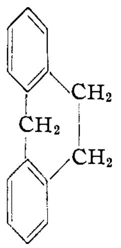
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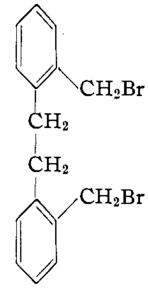
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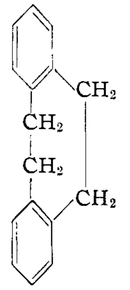
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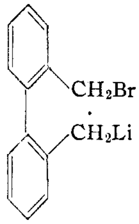
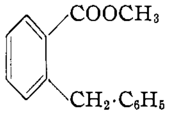
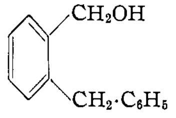

VII

aluminum hydride and treatment of the 2-benzylbenzyl alcohol (IX) so obtained with phosphorus tribromide. Reaction of X with lithium phenyl gave a hydrocarbon which had the composition and molecular weight expected of 2,2'-dibenzyldibenzyl (XI). The presence of the diphenylethane system was further proven by its dehydrogenation with NBS[5,6]; this led—expectedly—to 2,2'-dibenzylstilbene (XII) in which the double bond was identified both by the infrared and the ultraviolet spectrum. Both rather indicate that the hydrocarbon has the *cis*-configuration. The ultraviolet spectrum (Fig. 1) resembles closely that of *cis*-stilbene,[7] the decreased intensity being very probably due to the "*ortho*-effect" of the benzyl groups. In the infrared spectrum, the strong band at 965 cm.$^{-1}$, characteristic of *trans*-olefins,[8,9] is missing; at 755 and 728 cm.$^{-1}$, there appear bands which can be assigned to the phenyl and the ortho-substituted phenyl rings,[9] respectively.

The preparation of V is illustrated by Chart I.

The reduction of phthalic anhydride to stilbene 2,2'-dicarboxylic acid (XV)[10] *via* XIII[11] and XIV[10] was


VIII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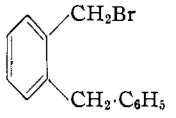
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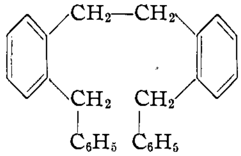
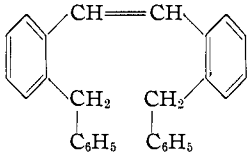
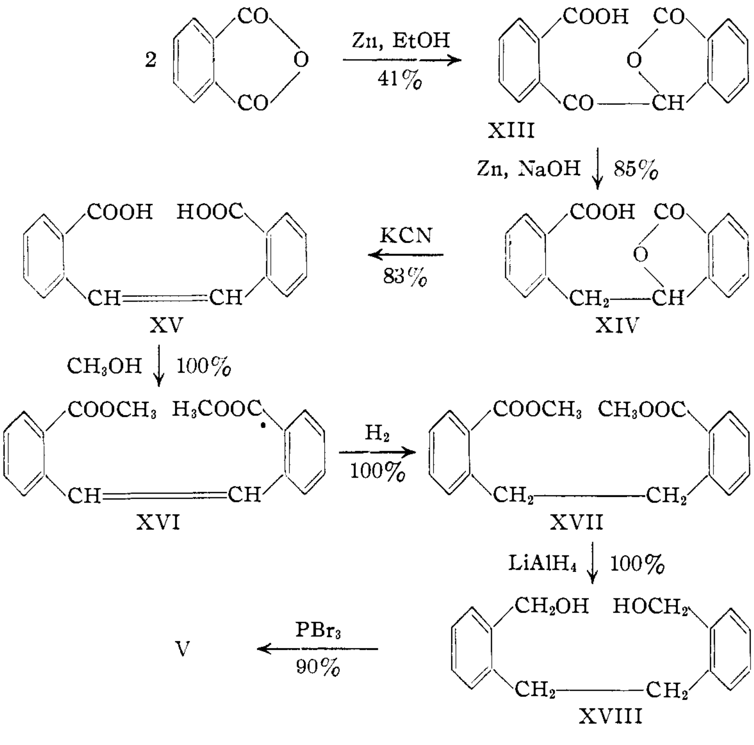

XI


XII

carried out according to the literature. The corresponding dimethyl ester XVI could easily be catalytically hydrogenated to dimethyl dibenzyl-2,2'-dicarboxylate (XVII)[12] which was reduced by means of lithium aluminum hydride. The dialcohol XVIII so obtained was converted by means of phosphorus tribromide into V. When V was treated with a solution of lithium phenyl, two products were obtained: a halogen-free polymer which was soluble in benzene and did not distil even at 300° (0.1 mm. pressure), and a crystalline hydrocarbon $C_{32}H_{32}$ of m.p. 205° which distilled *in vacuo* without decomposition. The yield of the two products was 60 and 40%, respectively.

CHART I

PREPARATION OF 2,2'-BIS-(BROMOMETHYL)-DIBENZYL (V)



For the crystalline hydrocarbon the structure of 1,2,5,6,9,10,13,14 - tetrabenzocyclohexadeca - 1,5,-9,13-tetraene (XIX) is indicated by the synthesis. It is confirmed by the formation of a tetrabromo derivative XX by means of N-bromosuccinimide and by the dehydrohalogenation of XX by means of dimethylaniline to 1,2,5,6,9,10,13,14-tetrabenzo-

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(5) *Cf.* R. A. Barnes, THIS JOURNAL, **70**, 145 (1948); E. D. Bergmann, *et al.*, *Bull. soc. chim. France*, **18**, 684 (1951); E. D. Bergmann, THIS JOURNAL, **74**, 1075 (1952); E. D. Bergmann, F. Crane and R. Fuoss, *ibid.*, **74**, 5979 (1952); the hydrogenation of XIX to XXI described in this paper.

(6) Also 1,1,2,2-tetraphenylethane is dehydrogenated by this reagent (see Exp. Part).

(7) A. Smakula and A. Wassermann, *Z. physik. Chem.*, **A155**, 353 (1931).

(8) D. Barnard, *et al.*, *J. Chem. Soc.*, 915 (1950); S. D. Brackman and P. H. Plesch, *ibid.*, 2188 (1952); B. Susz, E. Dallwigk and E. Briner, *Helv. Chim. Acta*, **35**, 345 (1952).

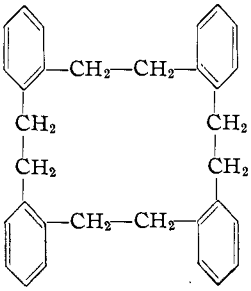
(9) H. W. Thompson, E. E. Vago, M. C. Corfield and S. F. D. Orr, *J. Chem. Soc.*, 214 (1950).

(10) P. Ruggli and R. E. Meyer, *Helv. Chim. Acta*, **5**, 28 (1922).

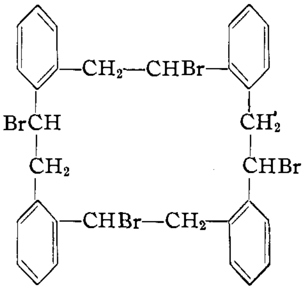
(11) A. Reissert, *Ber.*, **46**, 1487 (1913).

(12) C. Fischer and R. Wolffenstein, *ibid.*, **37**, 3215 (1904), have prepared the corresponding acid by a different method.

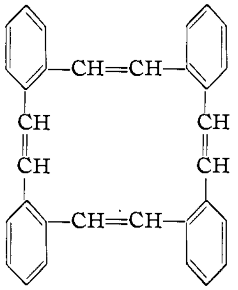
cyclohexadeca-1,3,5,7,9,11,13,15-octaene (XXI) a well-crystallized, colorless hydrocarbon of m.p. 267–268°. Its infrared spectrum (in chloroform solution) indicates the presence of the four double bonds in the peak at about 1600 cm.$^{-1}$. In addition, a very strong band at 955 cm.$^{-1}$ shows that the four stilbene double bonds have *trans*-configuration.[8,9,13]



XIX



XX[14]

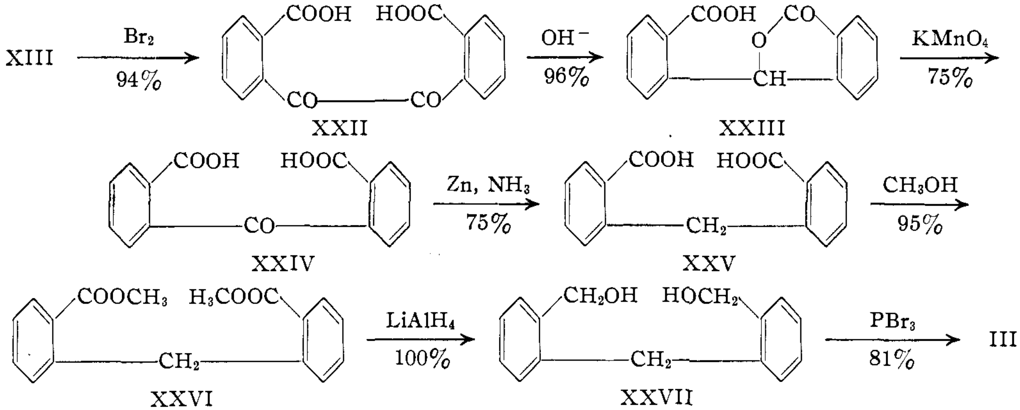


XXI

Quite analogous results have been obtained in experiments with III, the preparation of which is indicated by Chart II.

CHART II

PREPARATION OF 2,2'-BIS-(BROMOMETHYL)-DIPHENYLMETHANE (III)



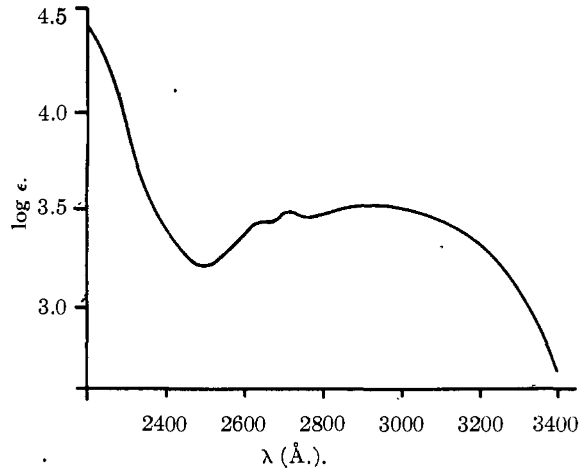


Fig. 1.—2,2'-Dibenzylstilbene (XII) in alcohol.

α-(2-Carboxybenzoyl)-phthalide (XIII) was converted *via* XXII and XXIII into benzophenone-2,2'-dicarboxylic acid (XXIV) according to Graebe and Juillard[15]; the reduction to XXV was carried out by means of activated zinc and ammonia.[16] The conversion of the corresponding dimethyl ester to III *via* the dialcohol XXVII proceeded as in the synthesis of V.

The reaction of III with lithium phenyl gave again a yield of 60% of a crystalline hydrocarbon $C_{30}H_{28}$ of m.p. 195°, for which by analogy the formula XXVIII of 1,2,4,5,8,9,11,12-tetrabenzocyclotetradeca-1,4,8,11-tetraene is suggested. In addition, two polymers were found (each in a yield of about 20%), a solid one, insoluble in benzene, which contained 2.95% of bromine and had, therefore, a molecular weight of 3000, and an oily one which was free of halogen, but could not be distilled, even at 300°, in a vacuum of 0.1 mm.

Although formula XXVIII appears reasonable enough, it was thought advisable to exclude the possibility that "dimerization" had taken place only on one side of the molecule (to XXXI) while on the other the bromomethyl radicals had simply been reduced to methyl groups, so that 2,2'-di-(*o*-methylbenzyl)-dibenzyl, $C_{30}H_{30}$, (XXIX), had formed; its analysis would be undistinguishable from XXVIII. Indeed, Baker and co-workers[17]

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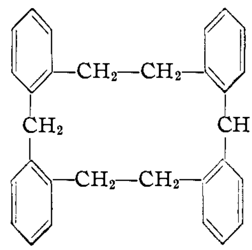
(13) (a) N. Sheppard and D. M. Simpson, *Quart. Rev.*, **6**, 1 (1952). For the infrared spectrum of *cis*-stilbene, see D. S. Brackman and P. H. Plesch, *J. Chem. Soc.*, 2188 (1952). (b) The infrared spectrum also permits one to exclude the possibility that in the dehydrobromination of XX a rearrangement ($ArCH{=}CH{\cdot}Ar \rightarrow (Ar)_2C{=}CH_2$) has taken place, as has been observed in an octadiene derivative by Cope and Fenton (THIS JOURNAL, **73**, 1673 (1951))—a possibility to which a Referee has kindly drawn our attention. The C=C and C–H frequencies of asymmetrically disubstituted ethylenes would lie at about 1650 and 890 cm.$^{-1}$, respectively (Sheppard and Simpson, ref. 13a).

(14) The relative position of the bromine atoms is, of course, arbitrary.

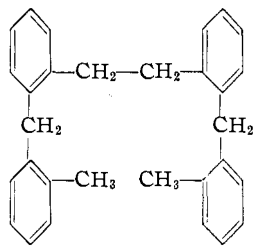
(15) C. Graebe and P. Juillard, *Ann.*, **242**, 214 (1887).

(16) Compare E. D. Bergmann and E. Loewenthal, *Bull. soc. chim. France*, **19**, 66 (1952).

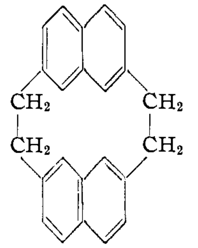
(17) W. Baker, J. F. W. McOrmie and W. K. Warburton, *J. Chem. Soc.*, 2991 (1952).



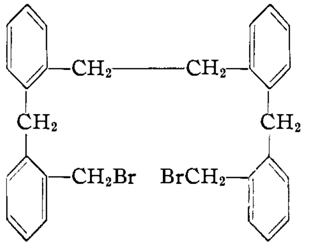
XXVIII



XXIX



XXX



XXXI

have found that the reaction of 2,7-bis-(bromomethyl)-naphthalene with sodium metal in dioxan led to significant quantities of α,β-di-(7-methyl-2-naphthyl)-ethane; however, these authors also observed that lithium phenyl failed, under the same conditions, to yield this hydrocarbon and gave, in 20% yield, "di-(naphthalene-2,7-dimethylene)" (XXX), a reaction fully analogous to the observations reported in the present paper. One will have to ascribe this difference between sodium and lithium phenyl to the fact that sodium alkyls are very much more prone than lithium alkyls to exchange the metal against hydrogen of the solvent.[18] The hydrocarbon XXIX was synthesized in analogy to XI, starting with 2-(o-methyl-benzyl)-benzoic acid. It proved different from XXVIII; its melting point (130.5–131°) is much lower than that of the latter, highly symmetrical and rigid hydrocarbon and resembles—expectedly—that of the lower homolog XI (97°).

Models[19] show that the three new macrocyclic hydrocarbons, in particular the tetrabenzocyclohexadecaoctaene (XXI) are slightly puckered, but completely strainless. This conclusion is in accord with the theoretical conclusion of Mislov[20] that the benzene homologs of the general formula C_nH_n can only be expected to be fully aromatic, *i.e.*, planar, from $C_{30}H_{30}$ upwards.

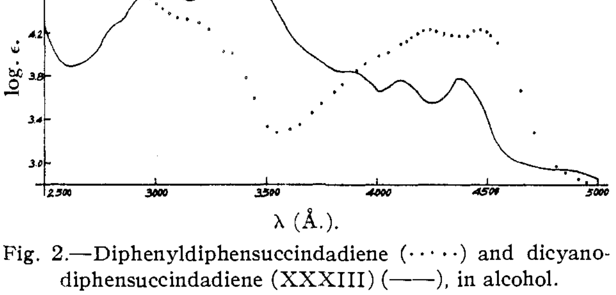
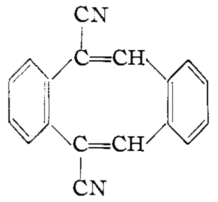
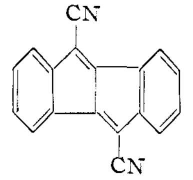


Fig. 2.—Diphenyldiphensuccindadiene (·····) and dicyanodiphensuccindadiene (XXXIII) (——), in alcohol.

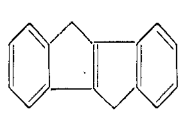
The absence of color in XXI has raised another problem. Fieser and Pechet[21] obtained in the condensation of o-phthalaldehyde and o-phenylenediacetonitrile a red by-product which appeared to have the same composition as the expected 3,8-dicyano-1,2,5,6-dibenzocycloöctatetraene, $C_{18}H_{10}N_2$ (XXXII) and was tentatively believed to contain a sixteen-membered conjugated ring system, *i.e.*, to have the double molecular weight.[22] It is suggested that the red product is dicyanodiphensuccindadiene, $C_{18}H_8N_2$, (XXXIII), formed from XXXII by isomerization and dehydrogenation.[23] A similar isomerization had already been observed by Fieser and Pechet[21] who obtained in the decarboxylation of the dicarboxylic acid corresponding to XXXII in addition to the expected hydrocarbon, also some Δ^{10}-diphensuccindene (XXXIV).



XXXII



XXXIII



XXXIV

This hypothesis is supported by the spectrum of the red substance (Fig. 2) which is similar to that of diphenyldiphensuccindadiene and the corresponding dimethyl compound[23,24]:

Diphensuccindadiene		
Dimethyl- λ_{max} (log ε)	Diphenyl- λ_{max} (log ε)	Dicyano- λ_{max} (log ε)
230 (4.23)	260 (4.72)	293 (4.63)[21,a]; 296 (4.55)
282 (4.65)	287 (4.59)	307 (4.69)[21,a]; 307 (4.59)
		335 (4.74)[21,a]; 333 (4.68)
370 (3.76)		
389 (4.05)		388 (3.83)
412 (4.09)	422 (4.23)	410 (3.74)
	446 (4.23)	438 (3.67)

[a] The log ε values are recalculated from the figures of Fieser and Pechet, using the molecular weight of XXXIII.

It has thus been shown that III and V behave differently from I; they undergo not an intramolecular, but a bimolecular cyclization.[25] This may well be due to the greater mobility of the systems III and V, as compared with I. When one bromine atom has been replaced by lithium (as in VII), the attraction for a bromine atom in a second molecule is greater than for the second bromine atom in the same molecule. The intermediary product of the type XXXI can then react intramolecularly in the same fashion; but it can also

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[18] Diethyl ether is rapidly decomposed by sodium ethyl (P. Schorigin, *Ber.*, **43**, 1931 (1910)), whilst lithium alkyls can easily be prepared in this solvent.

[19] We are most grateful to Professor K. C. Schreiber, Duquesne University, Pittsburgh, for valuable discussions on this point.

[20] K. Mislov, *J. Chem. Phys.*, **20**, 1489 (1952).

[21] L. F. Fieser and M. Pechet, THIS JOURNAL, **68**, 2577 (1946).

[22] The theoretical mol. wt. for the double molecule is 509; found, mol. wt., 400.

[23] For the physical properties, including the resonance stabilization, of the diphensuccindadiene system, see B. Pullman, A. Pullman. E. D. Bergmann, G. Berthier, E. Fischer, Y. Hirshberg and J. Pontis, *J. chim. phys.*, **49**, 24 (1952).

[24] Prof. Fieser has kindly informed us that he considers the above explanation as likely.

[25] Also in experiments carried out with very dilute solutions, no monomeric cyclization product could be detected, in contradistinction with cases as those described recently by R. Huisgen and W. Rapp, *Ber.*, **85**, 826 (1952).

continue the intermolecular process and thus give rise to the polymers observed in this investigation. Such a polymer could possess two terminal bromine atoms; but the chain could be terminated by cyclization or eventual replacement of the lithium atoms, for which the bromine atoms may be exchanged, by hydrogen or other similar processes. In these cases, a polymer of hydrocarbon nature would be formed. The relatively large yields, in which the macrocyclic compounds XIX and XXVIII have been obtained, appear, however, surprising even in the light of this reasoning, especially in view of the very low yields which Baker and his co-workers[26] have reported for similar syntheses starting from disubstituted benzene or naphthalene derivatives.

One may have to resort to the hypothesis that one molecule of the dibromide forms directly a dilithium compound which then reacts with a second dibromide molecule.

However that may be, the easy accessibility of the new macrocyclic systems described may well represent a model of the pathway by which the cell synthesizes macrocyclic systems such as the higher cycloalkanones or cyclic lactones, the porphyrins or the alkaloids of bisbenzylisoquinoline or dextro-tubocurarine type. In those cases at least in which the molecule is obviously constructed from two similar or identical halves, the cell will employ the device of simultaneous adsorption on the surface of an enzyme instead of the electrostatic attraction between lithium and bromine, which governs the reactions described in the present paper.

Experimental

Methyl 2-Benzylbenzoate (VIII).—Following Scholl and Neovius,[27] 20 g. of *o*-benzylbenzoic acid was refluxed for five hours with 200 ml. of methanol and 10 ml. of concd. sulfuric acid; b.p. 156–157° (4 mm.), yield 90%.

2-Benzylbenzyl Alcohol (IX).[28]—The preceding ester (30 g.) was added slowly to a solution of 5 g. of lithium aluminum hydride in 300 ml. of anhydrous ether; the mixture was refluxed for 30 minutes and decomposed with ice and dilute sulfuric acid. The alcohol boils at 197–199° (17 mm.), yield 95%.

2-Benzylbenzyl Bromide (X).—To a solution of 8 g. of IX in 100 ml. of benzene, containing a few drops of pyridine, there was added gradually 4.7 ml. of phosphorus tribromide. One heats for 2 hours at 60°, washes the solution with water, sodium bicarbonate solution and water and distils off the solvent. The colorless product crystallizes spontaneously; from diethyl ether needles of m.p. 43.5–44.2°; yield 90%.

Anal. Calcd. for $C_{14}H_{13}Br$: Br, 30.6. Found: Br, 30.5.

2,2'-Dibenzyldibenzyl (XI).—Twenty-four ml. of an ethereal solution of lithium phenyl, prepared from 0.255 g. of lithium and 3.75 g. of bromobenzene, was added within 20 minutes (nitrogen atmosphere) to a solution of 9 g. of X in 25 cc. of ether. The reaction mixture was stirred for one hour at room temperature and for one more hour at boiling temperature, and then decomposed with cold dilute sulfuric acid. The ethereal layer was washed with bicarbonate, dried and evaporated, and the solid residue recrystallized from petroleum ether; m.p. 97°, yield almost quantitative.

Anal. Calcd. for $C_{28}H_{26}$: C, 92.8; H, 7.2; mol. wt., 362. Found: C, 92.7; H, 7.4; mol. wt., 359 (camphor).

2,2'-Dibenzylstilbene (XII).—The mixture of 1.13 g. of 2,2'-dibenzyldibenzyl (XI), 0.60 g. of N-bromosuccinimide, a trace of benzoyl peroxide and 30 ml. of carbon tetrachloride was refluxed for four hours, filtered and concentrated *in vacuo*. As the resulting oil did not crystallize and proved to be somewhat unstable (liberation of hydrogen bromide), it was refluxed for 3 hours with 30 ml. of pyridine. The reaction mixture was poured into dilute sulfuric acid. Extraction with ether, treatment of the solution with sodium bicarbonate and water, and concentration gave an oil which solidified quickly upon trituration wtih methanol. The product was recrystallized repeatedly from methanol; m.p. 105.5–106°; yield 40%.

Anal. Calcd. for $C_{28}H_{24}$: C, 93.3; H, 6.7. Found: C, 93.3; H, 6.7.

The infrared spectrum was measured in the 10–14 μ region (0.014 g. plus 1 ml. of carbon disulfide; cell thickness, 0.5 mm.).

Stilbene-2,2'-dicarboxylic Acid (XV).—The reduction of phthalic anhydride to α-(*o*-carboxybenzoyl)-phthalide (XIII)[11] was carried out with 41.4% yield, the further reduction to α-(*o*-carboxybenzyl)-phthalide (XIV)[10] (m.p. 198.5°) with 85% and the conversion to (XV)[10] (m.p. 263–265°) with 83% yield. The **dimethyl ester (XVI)**[10] was obtained, in quantitative yield, as colorless, long needles of m.p. 101–102°.

Dimethyl Dibenzyl-2,2'-dicarboxylate (XVII).—The hydrogenation of 10 g. of XVI in 200 ml. of ethyl acetate was carried out in presence of 0.2 g. of palladium charcoal (10%), at room temperature and under a pressure of 3 atmospheres; it was complete within 30 minutes. The residue of the filtered solution was solid; from methanol, colorless needles of m.p. 103°; yield quantitative.

2,2'-Bis-(hydroxymethyl)-dibenzyl (XVIII).—In the manner described for the preparation of IX, XVIII (1 mole) was reduced with lithium aluminum hydride (1.5 moles) in anhydrous ether. Upon decomposition, the product separated between the two layers in quantitative yield. From alcohol, one obtains elongated prisms which melt at 132–136°, solidify again and then show a sharp m.p. of 151°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.4. Found: C, 80.5; H, 7.6.

2,2'-Bis-(bromomethyl)-dibenzyl (V).—Phosphorus tribromide (10 ml.) was added slowly at room temperature to a solution of (XVIII) (8 g.) in anhydrous benzene (150 ml.), which contained a few drops of pyridine. Treatment of the reaction mixture, as described above, gave a solid product which, after recrystallization from benzene, melted at 137–138°, yield 90%.

Anal. Calcd. for $C_{16}H_{16}Br_2$: Br, 43.4. Found: Br, 43.1.

For the sake of comparison, dimethyl stilbene-2,2'-dicarboxylate (XVI) was reduced with lithium aluminum hydride and the dialcohol converted into the corresponding dibromide. As expected, the C=C double bond was not attacked by the reducing agent.

2,2'-Bis-(hydroxymethyl)-stilbene.—Needles, from aqueous alcohol, m.p. 162°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7. Found: C, 80.1; H, 6.6.

2,2'-Bis-(bromomethyl)-stilbene.—Slightly yellowish needles, m.p. 180.5–181°.

Anal. Calcd. for $C_{16}H_{14}Br_2$: Br, 43.7. Found: Br, 43.6.

1,2,5,6,9,10,13,14-Tetrabenzocyclohexadeca-1,5,9,13-tetraene (XIX).—With vigorous stirring and in an atmosphere of nitrogen, a solution of lithium phenyl, prepared from 0.46 g. of lithium and 5.0 g. of bromobenzene in 45 ml. of ether, was added during 25 minutes to the solution of 8 g. of V in 100 ml. of benzene. After one hour at room temperature, the reaction mixture was refluxed for one more hour and decomposed with ice-cold dilute hydrochloric acid. The solution was washed with bicarbonate and water and subjected to steam distillation which removed together with the solvent the bromobenzene formed in the reaction, and some biphenyl. The distillation residue solidified upon cooling. It was dried and dissolved in the smallest possible quantity of warm benzene. Upon standing, colorless platelets separated, which were filtered after dilution with ether. The mother liquor was evaporated to dryness and the whole operation repeated with the residue. The crystalline product was repeatedly recrystallized from benzene and formed

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(26) W. Baker, J. F. W. McOrmie and J. M. Norman, *J. Chem. Soc.*, 1114 (1951); W. Baker, F. Glackling and J. F. W. McOrmie, *ibid.*, 1118 (1951). See also ref. 3 and 15; L. F. Fieser and M. M. Pechet, ref. 21; W. S. Rapson, R. G. Shuttleworth and J. N. van Niekerk, *J. Chem. Soc.*, 326 (1943); E. M. Davidson, *ibid.*, 30 (1945).

(27) R. Scholl and W. Neovius, *Ber.*, **44**, 1075 (1911).

(28) M. Sommelet, *Compt. rend.*, **205**, 56 (1927).

colorless, hexagonal plates of m.p. 205°; yield 1.7 g. (40%). The mother liquors contained the polymeric material, which was halogen-free.

Anal. Calcd. for $C_{32}H_{32}$: C, 92.3; H, 7.7; mol. wt., 416. Found: C, 92.3; H, 7.8; mol. wt., 430 (camphor).

A separation of the polymer from XIX is also possible by heating the crude reaction product up to 300° in a vacuum of 0.1 mm. The polymer remains; the hydrocarbon distils over; yield 40%, m.p. 205°.

Tetrabromo-1,2,5,6,9,10,13,14-tetrabenzocyclohexadeca-1,5,9,13-tetraene (XX).—A mixture of 0.55 g. of XIX, 0.93 g. of N-bromosuccinimide, a trace of benzoyl peroxide and 30 ml. of carbon tetrachloride was refluxed for four hours. After cooling, the solution was filtered and evaporated and the foamy residue triturated with methanol. From a mixture of isopropyl alcohol and a little methyl ethyl ketone, well-shaped prismatic crystals of m.p. 235° (dec.) were obtained.

Anal. Calcd. for $C_{32}H_{28}Br_4$: Br, 43.7. Found: Br, 43.0.

1,2,5,6,9,10,13,14-Tetrabenzocyclohexadeca-1,3,5,7,11,-13,15-octaene (XXI).—The foregoing substance was refluxed for three hours with an excess of dimethylaniline and the solution poured into dilute sulfuric acid. The halogen-free reaction product which precipitated, was dried and evaporatively distilled in a vacuum of 0.1 mm. A yellowish oil was thus obtained which solidified spontaneously. The hydrocarbon was purified by adsorption on active alumina and elution with benzene, and recrystallized from petroleum ether. It formed almost colorless prisms of the sharp m.p. 267–268°.

Anal. Calcd. for $C_{32}H_{24}$: C, 94.1; H, 5.9. Found: C, 94.1; H, 6.0.

Benzil-2,2′-dicarboxylic Acid (XXII).[15]—One heats 35 g. of α-(*o*-carboxybenzoyl)-phthalide (XIII) with 80 g. of ethanol on the water-bath, adds 50 g. of 33% aqueous potassium hydroxide solution and continues the heating until a clear solution results. Then 100 ml. of water, a further 50 g. of 33% potassium hydroxide solution and, with agitation, 21.5 g. of bromine are added. The slightly yellow liquid is filtered and acidified with dilute sulfuric acid. Thus 32.5 g. (94%) of XXII is obtained; colorless crystal powder of m.p. 273°.

Benzophenone-2,2′-dicarboxylic Acid (XXIV).[15]—The foregoing acid XXII was converted into XXIII according to Graebe and Juillard,[15] and the oxidation of XXIII carried out as follows: To a solution of 5 g. of anhydrous sodium carbonate and 10 g. of XXIII in 200 ml. of water, one adds a concentrated aqueous solution of 6.5 g. of potassium permanganate and heats for 3 hours at 100° with vigorous stirring. The unchanged permanganate is then destroyed with ethyl alcohol, and the solution filtered and acidified; yield 75%. As already indicated by Treibs and Klinkhammer,[29] the acid begins to melt at 185° (lactol formation), but has a final m.p. of 210°.

Diphenylmethane-2,2′-dicarboxylic Acid (XXV).—One dissolves 19 g. of the keto acid XXIV in 125 ml. of concentrated ammonia solution (28%), adds 40 ml. of water, 60 g. of zinc dust and a few crystals of cupric sulfate and heats the mixture at 100° with vigorous agitation for 20 hours. One filters, acidifies and recrystallizes the product from alcohol; colorless plates, m.p. 254.5°, yield 75%.

The **dimethyl ester XXVI** is obtained in 95% yield by esterification of XXV with methanol and concd. sulfuric acid (5 hours); m.p. 44°.

2,2′-Bis-(hydroxymethyl)-diphenylmethane (XXVII).—In the manner described before, XXVI was reduced with lithium aluminum hydride. The dialcohol precipitated in quantitative yield, when the reaction mixture was decomposed with ice-cold dilute sulfuric acid. Recrystallized from alcohol, it formed colorless needles of m.p. 158–158.5°.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.9; H, 7.0. Found: C, 78.8; H, 7.0.

2,2′-Bis-(bromomethyl)-diphenylmethane (III).—From 25 g. of XXVII in 300 ml. of benzene and 23 g. of phosphorus tribromide, there was obtained in the manner described before an 81% yield of III. After recrystallization from benzene, the compound melted at 93–94°.

Anal. Calcd. for $C_{15}H_{14}Br_2$: Br, 45.2. Found: Br, 45.1..

1,2,4,5,8,9,11,12-Tetrabenzocyclotetradeca-1,4,8,11-tetraene (XXVIII).—The reaction between 6 g. of III in 100 ml. of benzene and a lithium phenyl solution, prepared from 0.36 g. of lithium and 4.0 g. of bromobenzene in 36 ml. of anhydrous ether, was brought about at room temperature and was completed by refluxing for one hour (nitrogen atmosphere). Decomposition of the reaction mixture with ice and dilute sulfuric acid gave a solid precipitate (0.7 g.) at the interface of the two layers. This *polymer* was an amorphous, colorless powder which was insoluble in all organic solvents tested, liquefied slowly between 180–210° and contained 2.95% bromine. The molecular weight was determined in camphor and found to be 5000–6000, while from the bromine content a value of about 3000 is calculated. The filtered *organic layer* was washed with bicarbonate and water and distilled with steam. The residue was taken up in benzene, and the solution dried and evaporated; it left a semi-solid mass (2.7 g.), which was triturated with 10 ml. of ether. Thus, a crystalline powder was obtained which was recrystallized from benzene and formed colorless needles (1.6 g.) of m.p. 195°. The ethereal mother liquor was concentrated and the residue heated under a pressure of 0.1 mm. After a small head fraction of biphenyl, the hydrocarbon distilled at about 230° as an oil which crystallized spontaneously; thus, another 0.3 g. of m.p. 195° was obtained (total yield 1.9 g., 60%). The residue, which did not distil even at 300°, was an oily halogen-free polymer, yield 0.6 g. (19%).

Anal. Calcd. for $C_{30}H_{28}$: C, 92.8; H, 7.2; mol. wt., 388. Found: C, 92.5; H, 7.4; mol. wt., 397 (camphor).

2-(*o*-Methylbenzyl)-benzyl Alcohol.—To a solution of 3 g. of lithium aluminum hydride in 250 ml. of anhydrous ether, there was added within 30 minutes, 4 g. of 2-(*o*-methylbenzyl)-benzoic acid,[16] dissolved in 30 ml. of ether. The mixture was refluxed for one hour and decomposed with ice-cold dilute sulfuric acid. From the neutralized and dried ethereal solution, the product crystallized on concentration; from petroleum ether, colorless needles, m.p. 94.2–94.7°.

Anal. Calcd. for $C_{15}H_{16}O$: C, 85.0; H, 7.5. Found: C, 84.8; H, 7.4.

2-(*o*-Methylbenzyl)-benzyl Bromide.—One added 6 g. of phosphorus tribromide to a solution of 3.5 g. of the foregoing substance in 200 ml. of benzene, which contained some pyridine, and heated the mixture for two hours at 60°. The reaction product was washed with water and sodium bicarbonate solution, dried and concentrated. The residual oil solidified, when it was triturated with a little cold alcohol; yield 4.1 g. (90%); from a mixture of isopropyl alcohol and ether, large prisms of m.p. 51–51.7°.

Anal. Calcd. for $C_{15}H_{15}Br$: Br, 29.1. Found: Br, 29.6.

2,2′-Di-(*o*-methylbenzyl)-dibenzyl (XXIX).—To a solution of lithium phenyl, prepared from 0.1 g. of lithium and 1.1 g. of bromobenzene in 10 ml. of ether, there was added 3 g. of 2-(*o*-methylbenzyl)-benzyl bromide, dissolved in 50 ml. of anhydrous ether. The mixture was stirred at room temperature for 15 minutes and at boiling temperature for 45 minutes and worked up as usual. The residue crystallized spontaneously; yield 2.1 g. (quantitative); from a mixture of benzene and alcohol, m.p. 130.5–131°.

Anal. Calcd. for $C_{30}H_{30}$: C, 92.3; H, 7.7. Found: C, 92.1; H, 7.9.

Dehydrogenation of 1,1,2,2-Tetraphenylethane.—The solution of 5.15 g. of tetraphenylethane[30] and 0.1 g. of benzoyl peroxide in 200 ml. of carbon tetrachloride was refluxed with 2.2 g. of N-bromosuccinimide for 90 minutes. Filtration and evaporation of the solvent gave a solid which was refluxed with 10 cc. of pyridine for 90 minutes. The solution was poured into dilute hydrochloric acid and the solid precipitate dried and recrystallized successively from methylcyclohexane and butyl alcohol; m.p. and mixed m.p. with an authentic specimen of tetraphenylethylene, 221°, yield 2 g.

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(29) W. Treibs and H. J. Klinkhammer, *Ber.*, **84**, 671 (1951).

(30) J. F. Norris, L. Thomas and B. M. Brown, *Ber.*, **43**, 2939 (1910).