Tetrahedron, 1964, Vol. 20, pp. 195 to 209. Pergamon Press Ltd. Printed in Northern Ireland

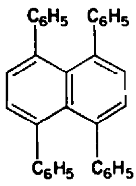
POLYPHENYLNAPHTHALENES, ESPECIALLY 1,4,5,8-TETRAPHENYLNAPHTHALENE[1]

E. D. BERGMANN, SH. BLUMBERG, P. BRACHA and SH. EPSTEIN
Department of Organic Chemistry, Hebrew University, Jerusalem

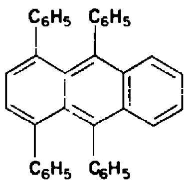
(*Received* 29 *April* 1963)

THE following diphenylnaphthalenes are known: 1,2-, 1,3-, 1,4-, 1,5-, 1,6-, 2,3-, 2,6- and 2,7-diphenylnaphthalene.[2,3]

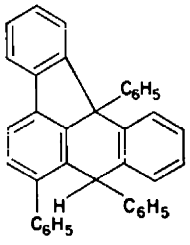
Of all the possible triphenylnaphthalenes only two, namely 1,2,3- and 1,2,4-triphenylnaphthalene have been described in the literature, and in the tetraphenylnaphthalene series only 1,2,3,4-tetraphenylnaphthalene has been reported.[4] In the present paper, a few additional phenylnaphthalenes have been described, particularly 1,4,5,8-tetraphenylnaphthalene (I), of interest as the lower homolog of rubrene



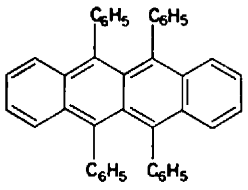
I



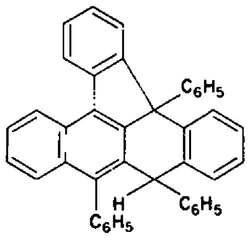
II



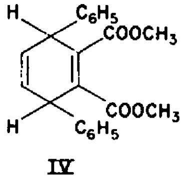
IIa



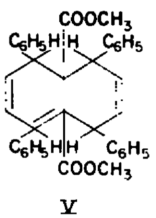
III



IIIa



IV



V

---

[1] The work on this compound was begun many years ago by one of us (E. D. B.) together with the late Dr. L. Haskelberg, see *J. Chem. Soc.* 2515 (1953).

[2] The product, m.p. 308°, obtained by A. Franssen, *Bull. Soc. Chim. Fr.*, **37**, 902 (1925) from 1,4-naphthoquinone and phenylmagnesium bromide, is obviously not 1,4-diphenylnaphthalene.

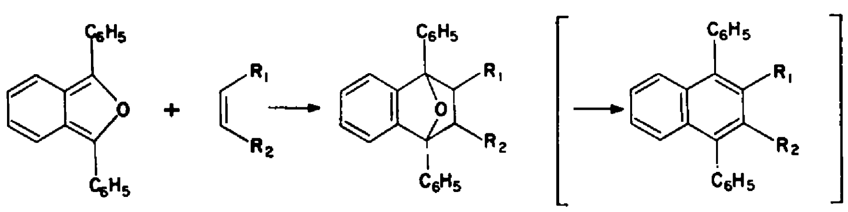
[3] K. F. Lung and H. Buffleb, *Chem. Ber.* **95**, 1049 (1962) have recently obtained by pyrolysis of a mixture of benzene and naphthalene, 2,6-diphenylnaphthalene and an isomer, m.p. 212·5–217° which may be the 1,5-compound, m.p. 220–222° (E. Buchta, H. Vates and H. Knopp, *Chem. Ber.* **91**, 228 (1958).

[4] G. Wittig, *Angew. Chem.* **72**, 213 (1960); G. Wittig and H. F. Ebel, *Ibid.* **72**, 564 (1960); G. Wittig and K. Knauss, *Chem. Ber.* **91**, 895 (1958).

(9,10,11,12-tetraphenylnaphthacene) (III),[5] and 1,4,9,10-tetraphenylanthracene (II).[6] These two compounds are characterized by their ability to isomerize under the influence of acids (to IIa and IIIa respectively) and by their very unusual absorption spectra, in which—probably for steric reasons—all fine structure has been extinguished.

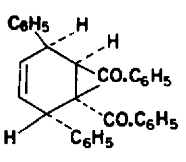
The first attempt to synthesize I was based on the diene reaction between 1,4-diphenylbutadiene and dimethyl acetylendicarboxylate in the hope that the dimethyl 3,6-diphenyl-3,6-dihydrophthalate (IV) reported by Lohaus[7] would, under more stringent conditions react with a second molecule of the diene and give V. In boiling nitrobenzene, however, IV was simply dehydrogenated to the known dimethyl 3,6-diphenylphthalate.[8]

A diene reaction, likely to give the desired result, was based on the fact that substances of the 2,7-diarylbenzoisofuran type react with dienophiles to give—potential—1,4-diarylnaphthalenes:[9]

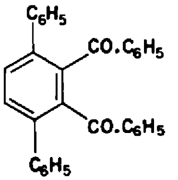


By this method, 1,4-diphenylnaphthalene was obtained.[10]

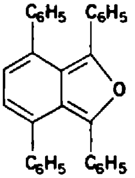
The synthesis of 2,3,6,7-tetraphenylisobenzofuran (VIII), modelled on that of the 2,7-diphenyl derivative involved the condensation of *trans*, *trans*-1,4-diphenylbutadiene



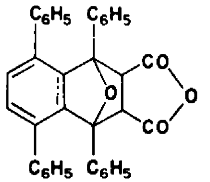
VI



VII



VIII



IX

---

[5] For a summary, see C. Dufraisse and G. Amiard, *Bull. Soc. Chim. Fr.* **12**, 1044 (1945).

[6] Ch. Weizmann, E. Bergmann and L. Haskelberg, *J. Chem. Soc.*, 391 (1939); Ch. Weizmann and E. Bergmann, *J. Chem. Soc.* 494 (1939); Y. Hirshberg and L. Haskelberg, *Trans. Faraday Soc.* **39**, 45 (1943).

[7] H. Lohaus, *Liebigs Ann.* **516**, 295 (1935).

[8] Ch. Weizmann, E. Bergmann and L. Haskelberg, ref. 6.

[9] C. Seer and D. Dischendorfer, *Monatsh.* **34**, 1493 (1913). R. Adams and A. Geissman, *J. Amer. Chem. Soc.* **61**, 2083 (1939); R. Adams and M. H. Gould, *Ibid*, **62**, 56 (1940). C. F. H. Allen and J. W. Gates, *Ibid.* **65**, 1283 (1943). R. Weiss and A. Beller, *Monatsh.* **61**, 143 (1932); R. Weiss, A. Abeles and E. Knapp, *Ibid.* **61**, 162 (1932). R. Weiss and J. Koltes, *ibid.* **65**, 361 (1935); R. Weiss and F. Mayer, *ibid.* **71**, 6 (1938). E. de Barry Barnett, *J. Chem. Soc.* 1326 (1935). C. Dufraisse and P. Compagnon, *C. R. Acad. Sci. Paris* **207**, 585 (1938), C. Dufraisse and R. Priou, *Bull. Soc. Chim. Fr.* **5**, 502 (1938). E. Bergmann, *J. Chem. Soc.* 1147 (1938). A. Etienne, *Ann. Chim.* [12] **1**, 5 (1946); A. Etienne and E. Toromanoff, *C. R. Acad. Sci. Paris* **230**, 306 (1950); A. Etienne and A. Spire, *ibid.* **230**, 2030 (1950); see also ref. 10. E. Buchta, H. Vates and H. Knopp, *Chem. Ber.* **91**, 228 (1958). G. Wittig, E. Knauss and K. Niethammer, *Liebigs Ann.* **630**, 10 (1960).

[10] A. Etienne, A. Spire and E. Toromanoff, *Bull. Soc. Chim. Fr.*, 750 (1952).

[11] Very recently, W. Ried and K. H. Boennighausen (*Liebigs Ann.*, **639**, 61 (1962)) have studied the condensation of 1,4-diphenylbutadiene with dibenzoylacetylene, which gave them under certain conditions VII, under other conditions VIII. They also described the reduction of VII to VIII.

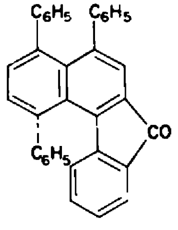
with *trans*-1,2-dibenzoylethylene[11] to give the normal adduct (VI), two isomers of which were isolated, but one in very small quantities.

The IR spectrum showed the carbonyl band at 1672 cm^{-1} and absorption at 976 cm^{-1}, indicating the disubstituted *cis*-double bond.

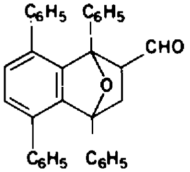
This compound is easily dehydrogenated, by treatment with two moles of bromine in boiling chloroform, to 1,2-dibenzoyl-3,6-diphenylbenzene (VII); the latter being reduced with zinc and alcoholic alkali to the desired VIII—a yellow compound exhibiting strong green fluorescence. Conversion of IX, the adduct with maleic anhydride, into I was unsatisfactory as the anhydride system is unreactive—as has been observed for the analog containing phenyl groups only in the 1,4-positions[12]—and requires prolonged boiling with alcoholic sodium hydroxide. Furthermore, at elevated temperatures IX tends—as all adducts of (VIII) do—to dissociate into its components. Heating of the calcium salt of the diacid causes dehydration to the aromatic system, but as decarboxylation did not always take place, small quantities of I were sometimes obtained, but more often, one carboxyl group was lost and the other cyclized to the fluorenone derivative (X).[13]

Consequently, another route was employed. The reaction with acrolein yields the colourless adduct (XI), which may be dehydrated by hydrochloric acid under controlled conditions to 1,4,7,8-tetraphenyl-2-naphthaldehyde(XII). The C—H frequency of the aldehyde group was observed at 2850 cm^{-1} as compared with 2838 cm^{-1} reported for 1-naphthaldehyde.[14]

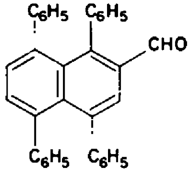
When the dehydration of XI is carried out under more stringent conditions, the aldehyde group is lost and a yellow product possessing chlorine is obtained. The analysis corresponds to a 2(?)-chloro-1,4,7,8-tetraphenylnaphthalene, and the absorption spectrum is identical with that of tetraphenylnaphthalene. The mechanism of this reaction (as well as the precise location of the chlorine atom) is unknown, but a similar reaction has been described in the 2,7-diphenylisobenzofuran series by Etienne *et al.*[10]



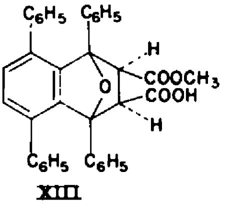
X



XI



XII



XIII

---

[12] C. Dufraisse and R. Priou, Ref. 9.

[13] Cf. R. Weiss, A. Abeles and E. Knapp, Ref. 9.

[14] R. M. Powers, J. L. Harper and H. Tai, *Analyt. Chem.* **32**, 1287 (1960). Cf. E. L. Saier, L. A. Cousins and M. R. Basila, *Ibid.* **34**, 824 (1962); *J. Phys. Chem.* **66**, 232 (1962).

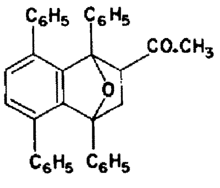
[15] see, e.g., J. O. Hawthorne and M. H. Wilt, *J. Org. Chem.* **25**, 2215 (1961).

The catalytic decarbonylation of XII with palladium[15] produced the desired 1,4,7,8-tetraphenylnaphthalene (I). This compound is practically colourless, its spectrum shows the same complete lack of fine structure (λ 248; 334 mμ) as 1,4,9,10-tetraphenylanthracene and rubrene, but it lacks the isomerizability of these two substances under the influence of acid. The reason for this difference may be due to the fact that the isomerization product would be a 1,4-dihydronaphthalene derivative which is thermodynamically less favoured than a derivative of 9,10-dihydroanthracene. The hydrocarbon (I) is strongly fluorescent and it is interesting to compare its absorption spectrum with that of terylene (XIVa) in which the 1,4,5,8-phenyl groups are forced into a coplanar position: 307, 318, 352, 365, 453, 483, 516 mμ.[16]

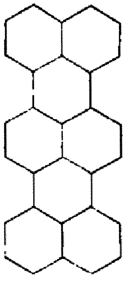
The ability of VIII to undergo Diels-Alder reactions with philodienic compounds is shown in Table 1. As all the adducts show a tendency to dissociate at elevated temperatures, in most cases it was impossible to effect aromatization by acidic dehydration. However, from the methyl acrylate adduct, methyl 1,4,5,8-tetraphenyl-2-naphthoate was obtained and the acrylonitrile adduct, first transformed into the amide, was dehydrated to 1,4,5,8-tetraphenyl-2-naphthamide. The anhydride (IX), also obtained from fumaryl chloride, due to steric hindrance gives only the mono-ester (XIII), on esterification by the method of Fischer although the diester may be prepared by treatment of XIII with diazomethane. Analogous observations have been made with the similarly hindered 3,6-dichloro,[17] tetrachloro,[18] tetrabromo[19] and tetraiodo[17] phthalic anhydrides.

In the case of the adduct (XIV) from methyl vinyl ketone and VIII, whereas gaseous hydrogen chloride in acetic acid causes only reversal of the condensation, *p*-toluenesulphonic acid in formic acid yields an isomeric compound, which does not decompose upon heating, but shows the same IR absorptions (carbonyl at 1700 cm^{-1}, epoxide at 1075 cm^{-1}) as the starting material (1700, 1083 cm^{-1}). It appears that under these conditions, IX only undergoes stereoisomerization.

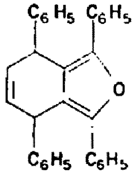
In the course of this investigation, some other interesting observations have been made. The adduct (VI), under dehydrating conditions, yields the cyclic ether (XV) of its dienol form. This is indicated by the I.R. spectrum and by the fact that treatment with bromine leads to the aromatic diketone (VII).[20] Treatment with palladium at



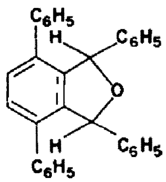
XIV



XIVa



XV



XVI

---

[16] E. Clar, *Chem. Ber.* **81**, 52 (1948).

[17] C. Graebe, *Ber. Dtsch. Chem. Ges.* **33**, 2022 (1920).

[18] V. Meyer and J. J. Sudborough, *Ber. Dtsch. Chem. Ges.* **27**, 3146 (1894). Cf. C. Graebe, *Liebigs Ann.* **238**, 322 (1888).

[19] E. Rupp, *Ber. Dtsch. Chem. Ges.* **29**, 1633 (1896).

[20] See R. Adams and ref. 9.

TABLE 1. DIENE REACTIONS OF 2,3,6,7-TETRAPHENYLISOBENZOFURAN (III); 2 g IN 20 ML BENZENE

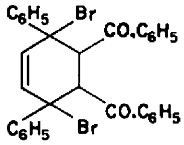
Dienophile (g)	Conditions	Product (yield)	Product m.p.	Recryst. from	C calc.	C fd.	H calc.	H fd.	I.R. Spectrum (KBr)	Remarks
Methyl acrylate (0·8)	reflux, 4 hr	$C_{36}H_{28}O_3$ (1·7 g; 70%)	187° (dec)	butyl acetate	85·0	85·0	5·5	5·6	1740 (sat. ester); 1075 (epoxide)[1]	No dehydration with acetic acid, saturated with HCl.
Crotonaldehyde (0·7)	reflux, 15 hr	$C_{36}H_{28}O_2$ (1·6 g; 60%)	104° (dec)	benzene-ethanol	87·8	87·5	5·7	5·7	1724 (sat. aldehyde); 1078 (epoxide)	As above
Methyl vinyl ketone (1·0)	reflux, 6 hr	$C_{36}H_{28}O_2$ (1·9 g; 75%)	105° (dec)	benzene-ethanol	87·8	87·8	5·7	6·1	1700 (sat. ketone); 1083 (epoxide)	See Experimental
Acrylonitrile (0·3)	reflux, 30 min	$C_{35}H_{25}NO$ (1·6 g; 55%)	230° (dec)	benzene-ethanol	88·4	88·7	5·3	5·6	2271 (nitrile); 1080 (epoxide)	N, calc., 2·9; N, fd., 2·7. No dehydration with HCl or toluenesulphonic acid. See Experimental.
Fumaryl chloride (1·0)	immediate reaction	$C_{36}H_{24}O_4$ (2 g; 72%)	267° (dec)	benzene	83·1	83·9	4·7	4·7	1785, 1869 (anhydride)[2] 1078 (epoxide)	No dehydration with HCl or HBr in acetic acid. See Experimental.
p-Benzoquinone (0·6)	reflux, 8 hr	$HC_{38}H_{26}O_3$[3] (1·6 g; 64%)	270° (dec)	insol. in benzene	86·0	86·0	4·9	5·1	1719 (sat, ketone); 1073 (epoxide)	No dehydration with acetic acid, saturated with HCl
1,4-Naphthoquinone (0·6)	reflux, 7 hr	$C_{42}H_{28}O_3$[3] (1·8 g; 67%)	275° (dec)	insol. in benzene	87·0	87·0	4·8	4·9	1725 (sat. ketone); 1075 (epoxide)	As above

[1] See E. D. Bergmann, S. Yaroslavsky and H. Weiler-Feichenfeld, *J. Amer. Chem. Soc.* **81**, 2775 (1959).

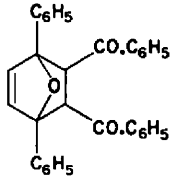
[2] See G. Stork and R. Breslow, *J. Amer. Chem. Soc.* **75**, 3291 (1953).

[3] A quantity of 5 ml benzene was used as solvent.

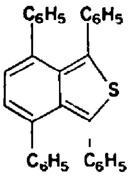
[4] In addition to this compound, a benzene-soluble isomer was formed which is not stable in solution, partly dissociates into the starting material and partly isomerizes to the stable compound.



XVII



XVIII



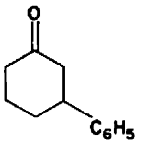
XIX

260–300° does not cause dehydrogenation, but isomerization to a product, to which formula (XVI) has been ascribed on the basis that the infrared shows a double bond absorption at 1663 cm^{-1} (which seems to be rather "aliphatic"), the dihydrofuran absorption at 1177 cm^{-1} and the phenyl peak at 1155 cm^{-1}.

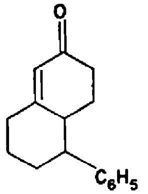
If the bromination of the adduct (VI) is carried out in glacial acetic acid containing sodium acetate instead of in boiling chloroform, a dibromosubstitution product $C_{32}H_{24}Br_2O_2$ is formed, which easily loses hydrogen bromide to give VII. This is assumed to have structure XVII, as treatment with alcoholic potassium hydroxide yields a compound $C_{32}H_{24}O_3$ which shows the typical absorption of furan[21] and, therefore, may possibly be XVIII.

The thiophen derivative (XIX) corresponding to VIII has been prepared by the action of sulphur on either XV[22] or VIII. Both XIX and VIII are sensitive to light and irradiation in the presence of oxygen brings about re-conversion to VII.[23]

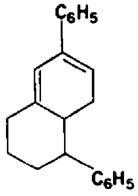
The application of the Michael reaction, occasionally used for the synthesis of arylnaphthalenes,[24–26] has resulted in a new synthesis of the known 2,7-diphenylnaphthalene[27,28] and the preparation of 1,3,6-triphenylnaphthalene (XXX). 3-Phenylcyclohexanone (XX) and methyl vinyl ketone in the presence of alcoholic potassium hydroxide yield 2-oxo-7-phenyl-2,3,4,5,6,7,8,10-octahydronaphthalene (XXI) which with phenylmagnesium bromide yields 2,7-diphenyl-4,5,6,7,8,10-hexahydronaphthalene (XXII), which easily dehydrogenates to 2,7-diphenylnaphthalene. This result



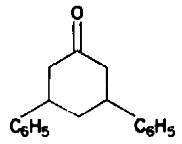
XX



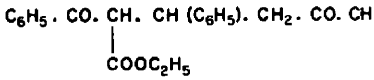
XXI



XXII



XXIII



$$C_6H_5.CO.\underset{\displaystyle COOC_2H_5}{\underset{|}{CH}}.CH(C_6H_5).CH_2.CO.CH_3$$

XXIV

---

[21] R. Manzoni-Ansidei and M. Rolla, *Atti Accad. Lincei* **27**, 410 (1938). L. W. Pickett, *J. Chem. Phys.* **10**, 660 (1942).

[22] For an analogous observation, see C. F. H. Allen and J. W. Gates, ref. 9.

[23] C. Dufraisse and L. Enderlin, *C. R. Acad. Sci., Paris* **190**, 1229 (1930); C. Dufraisse and S. Ecary, *ibid.* **223**, 735 (1946); J. Martel, *ibid.* **244**, 626 (1957); S. Ecary, *Bull. Soc. Chem. Fr.*, [12], **3**, 445 (1948).

[24] W. D. Rapson and R. Robinson, *J. Chem. Soc.* 1285 (1935).

[25] W. S. Rapson, *J. Chem. Soc.* 1626 (1936).

[26] J. R. Hawthorne and R. Robinson, *J. Chem. Soc.* 763 (1936).

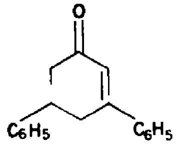
[27] D. H. Hey and S. E. Lawton, *J. Chem. Soc.* 374 (1940).

[28] N. P. Buu-Hoi and P. Cagniant, *Bull. Soc. Chim. Fr.*, [5], **11**, 127 (1944).

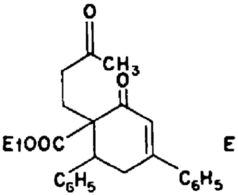
shows, that the reaction of XX with methyl vinyl ketone takes place exclusively in the 2-, and not the alternative 6-position.

For the synthesis of 3,5-diphenylcyclohexanone (XXIII), ethyl benzoylacetate was condensed with benzylideneacetone yielding ethyl 3-benzoyl-6-oxo-4-phenylheptoate (XXIV), which, when treated with alkali, undergoes cyclization, dehydration, hydrolysis and decarboxylation to 3,5-diphenylcyclohex-2-enone (XXV) which affords XXIII on hydrogenation. Unexpectedly, however, XXIII does not react with methyl vinyl ketone.

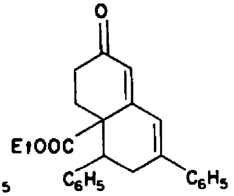
Methyl vinyl ketone condenses with ethyl 2-oxo-4,6-diphenylcyclohex-3-ene-1-carboxylate (XXVI)[29] and produces the adduct (XXVII) and its cyclization product, ethyl 7-oxo-2,4-diphenyl-3,4,5,6,7,10-hexahydronaphthalene-10-carboxylate (XXVIII). Since it proved impossible to effect hydrolysis of the ester group in XXVIII (with aqueous or alcoholic potassium hydroxide or with hydrobromic acid), the compound was subjected to an inverse Grignard reaction with phenylmagnesium bromide which attacks only the keto group and yields the tertiary alcohol (XXIX), which upon dehydrogenation loses water and the carbethoxy group producing the expected 2,4,7-triphenylnaphthalene (XXX).



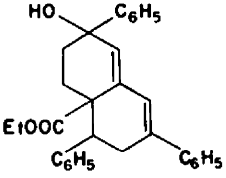
XXV



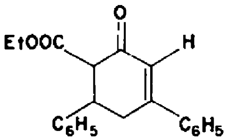
XXVII



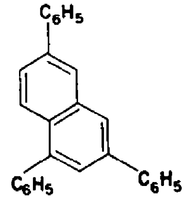
XXVIII



XXIX

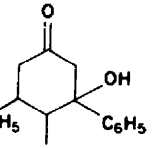


XXVI



XXX

In the course of this investigation, the resistance of the tertiary hydroxyl group in XXIX to dehydrating agents was noted. A survey of the literature shows that Walker[30] observed a similar resistance in XXXI and ascribed it to the equatorial position of the hydroxyl in this compound which in his opinion contains the phenyl and carbethoxy groups *cis* to each other. Also in the conversion of XXIV to XXV it



XXXI

---

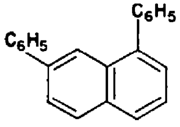
[29] R. Connor and D. B. Andrews, *J. Amer. Chem. Soc.* **56**, 2713 (1934).

[30] G. N. Walker, *J. Amer. Chem. Soc.* **77**, 3664 (1955).

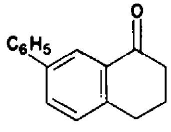
was found that the primary product is an *isomer* of XXIV which shows in the infrared an hydroxyl absorption (3367 cm^{-1}) and the band of a non-conjugated carbonyl group (1715 cm^{-1}), so that formula XXXI is indicated. Compound XXXI is gradually converted into XXV by boiling with alkali.

For the synthesis of 1,7-diphenylnaphthalene (XXXII), the reaction of 7-phenyltetralone (XXXIII, which is easily available[31,32] from biphenyl and succinic anhydride) with phenylmagnesium bromide led *via* the tertiary alcohol to 3,4-dihydro-1,7-diphenylnaphthalene which absorbs at 231 mμ as biphenyl, but with a fairly high extinction (log 4·40), probably due to the conjugation of the biphenyl with the exocyclic double bond. Dehydrogenation gave the desired XXXII[30a].

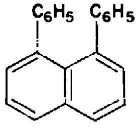
In an attempt to prepare the one remaining diphenylnaphthalene, the 1,8-compound (XXXIV), the reaction between 2-phenylbenzophenone and ethyl bromoacetate in the presence of zinc to give the ester (XXXV) failed and the synthesis of 3-(2-biphenyloyl)-propionic acid (XXXVI) either by the reaction of 2-biphenyl lithium[33] and succinic anhydride[34] or of 2-biphenylyl cadmium and 3-carbomethoxypropionyl chloride[35] gave such small yields that the attempt was abandoned.



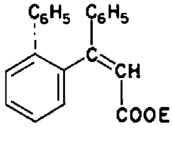
XXXII



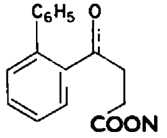
XXXIII



XXXIV



XXXV



XXXVI

An analysis of the spectra of the phenylated naphthalenes (Table 2) shows that the *E* region[36] (β-region) of the naphthalene spectrum suffers a very small bathochromic shift upon phenylation at position 1 and a fairly pronounced bathochromic shift upon phenylation at position 2. This difference may be due to the much larger difficulties impeding a coplanar arrangement of the phenyl in 1-position.[37] In naphthalenes substituted by more than one phenyl group, the bathochromic effect is approximately the sum of the shifts caused by each of the phenyl groups alone. The only exception is 2,7-diphenylnaphthalene, where the shift is smaller than expected for two β-phenyl groups.

[30a] This compound as well as the last missing diphenylnapthalene, namely, the 1,8-compound, has very recently been described by H. O. House, R. M. Magin and H. W. Thompson, *J. Org. Chem.* **28**, 2403 (1963).

[31] M. Weizmann, E. Bergmann and E. Bograchov, *Chem. & Ind.* 402 (1940).

[32] D. H. Hey and R. Wilkinson, *J. Chem. Soc.* 1030 (1940).

[33] H. Gilman and K. Oita, *J. Org. Chem.* **20**, 862 (1955).

[34] Ch. Weizmann, E. Bergmann and F. Bergmann, *J. Chem. Soc.* 1367 (1935).

[35] *Organic Syntheses* Coll. Vol. III; p. 601.

[36] E. A. Braude, *Ann. Reports Progress Chem.* **42**, 105 (1945).

[37] For another explanation, see E. Clar, *Tetrahedron* **16**, 113 (1961).

In the E_2 region (*para*-region) of the spectrum, the shift caused by phenylation is not large, but about equal for the substitution in 1- and 2-position. Here, too apparently, the effect is additive, the only exception being 1,4,5,8-tetraphenylnaphthalene (I), for which the shift is very much larger than for the di- and triphenylnaphthalenes.

TABLE 2. SPECTRA OF PHENYLATED NAPHTHALENE DERIVATIVES λ [mμ] (LOG ε)

Phenyl in position	Solvent	E_1 region	shift[a]	E_2 region	shift[a]
none[b]	ethanol	221 (5·00)	—	275 (3·80)	—
				285 (3·62)	—
1[c]	cyclohexane	226 (4·80)	+5	288 (4·03)	+3
2[d]	ethanol	250 (4·70)	+29	285 (4·06)	0
1,4[e]	ethanol	230 (4·70)	+9	300 (4·20)	+15
1,6[f]	ethanol	258 (4·73)	+37	300 (4·00)	+15
1,7[g]	chloroform	256 (4·54)	+35	302 (4·05)	+17
2,6[h]	ethanol	263 (4·48)	+42	318 (4·44)	+33
2,7[g]	ethanol	268 (4·30)	+47	300 (4·20)	+15
1,3,6[g]	ethanol	270 (4·75)	+49	301 (4·20)	+16
1,4,5,8[g]	cyclohexane	248 (4·50)	+27	334 (4·18)	+54

[a] compared with naphthalene.
[b] E. Clar and D. G. Stewart, *J. Amer. Chem. Soc.* **75**, 2667 (1953).
[c] M. P. Cava and J. F. Stucker, *J. Amer. Chem. Soc.* **77**, 6022 (1955).
[d] R. A. Friedel, M. Orchin and L. Reggel, *J. Amer. Chem. Soc.* **70**, 199 (1948).
[e] A. Etienne, A. Spire and E. Toromanoff, ref. 10.
[f] Y. Hirshberg and R. N. Jones, *Canad. J. Research*, **27B**, 437 (1949).
[g] This paper.
[h] E. Clar, ref. 37.

EXPERIMENTAL

Condensation of 1,4-*diphenylbutadiene and dimethyl acetylenedicarboxylate*

When 2 g 1,4-diphenylbutadiene and 1·8 g (or an excess) of the acetylenic ester were heated at 140° for 5 hr, a 70% yield of dimethyl 3,6-diphenyl-3,6-dihydrophthalate (IV)[7] m.p. 101° (from methanol) was obtained. Also in nitrobenzene (100°) 24 hr only 1 : 1 addition takes place yielding 3,6-diphenylphthalate[6] as white needles which were recrystallized from ethanol, m.p. 188°.

1,2-*Dibenzoyl*-3,6-*diphenylcyclohex*-4-*ene* (VI)

When 20·6 g *trans-trans*-1,4-diphenylbutadiene and 23·6 g *trans*-1,2-dibenzoylethylene[38] were refluxed in 350 ml isopropyl alcohol for 8 hr, the adduct crystallized upon cooling and was recrystallized from glacial acetic acid or butyl acetate in colourless needles, m.p. 179–180°; yield 23 g (52%). $\lambda_{\mathrm{max}}^{\mathrm{Chlf}}$ 250 (4·30); 282 (3·28), 308 mμ (2·23). $\bar{\nu}_{\mathrm{max}}^{\mathrm{KBr}}$ 1667 (phenylketone), 1595 (aromatic double bond) (Found: C, 86·6; H, 5·7. $C_{32}H_{26}O_2$ requires: C, 86·8; H, 5·9%). From the acetic acid mother-liquor, by precipitation with water, an *isomer* was obtained which was recrystallized first from ethyl alcohol and then from ethyl acetate, m.p. 120°. (Found: C, 87·0; H, 6·0. $C_{32}H_{26}O_2$ requires: C, 86·8; H, 5·9%). When the above reaction was carried out in 100 ml boiling butanol (8 hr), the product, m.p. 175° (38 g) which crystallized upon cooling, was not homogeneous. When 10 g of this product was refluxed with 150 ml glacial acetic acid and the hot solution filtered, the filtrate yielded, upon cooling, 5 g of VI, m.p. 178–179° after recrystallization from butyl acetate. The fraction insoluble in hot glacial acetic acid (4 g) recrystallized from butyl acetate in colourless crystals m.p. 245° which according to the analysis had structure XV. (Found: C, 91·1; H, 5·6. $C_{32}H_{24}O$ requires: C, 90·5; H, 5·7%).

---

[38] *Organic Syntheses* Coll. Vol. III; 248 (1955).

1,2-*Dibenzoyl*-3,6-*diphenylbenzene* (VII)

A solution of 4·3 ml bromine in 90 ml chloroform was added to 18·5 g VI in 130 ml boiling chloroform. The mixture was refluxed for 20 min, evaporated to dryness, and the residue triturated with alcohol and recrystallized from butyl acetate and xylene, yield 16 g (86%); m.p. 212°. λ_{max}^{Chlf} 254 mμ (4·50). (Found: C, 88·0; H, 4·8. $C_{32}H_{22}O_2$ requires: C, 87·7; H, 5·0%).

2,3,6,7-*Tetraphenylisobenzofuran* (VIII)

To a solution of 3 g 1,2-dibenzoyl-3,6-diphenyl-benzene (VII) and 3 g sodium hydroxide in 75 ml boiling ethyl alcohol, 3 g zinc dust (activated by short treatment with dil sodium hydroxide, followed by washing with water and alcohol) was added. The mixture was refluxed until the liquid was yellow and filtered into 75 ml acetic acid. Upon addition of 10 ml water, 2·1 g VIII (72%) precipitated and the product crystallized from benzene, yellow needles, m.p. 258–259°, exhibiting an intense green fluorescence (520 mμ); λ_{max}^{Chlf} 324 (3·40); 410 mμ (4·04). (Found C, 91·0; H, 5·1. $C_{32}H_{22}O$ requires; C, 91·0; H, 5·2%).

1,4-*Oxido*-1,4,5,8-*tetraphenyl*-1,2,3,4-*tetrahydronaphthalene*-1,2-*dicarboxylic acid anhydride* (IX)

A mixture of 0·6 g maleic anhydride and 2·1 g VIII was heated for 2 hr at 160° and the product recrystallized successively from glacial acetic acid and a mixture of benzene and light petroleum forming rods m.p. 251°; yield 95%. The same product was obtained in 90% yield, when the components were refluxed in benzene for 5 min. (Found: C, 83·3; H, 4·3. $C_{36}H_{24}O_4$ requires: C, 83·1; H, 4·6%).

The substance was not attacked by glacial acetic acid, saturated with hydrogen bromide (3 days at room temp), or by syrupy phosphoric acid in boiling glacial acetic acid.

The corresponding *dicarboxylic acid* could be isolated, when the anhydride (IX; 1·4 g) was refluxed for 3 hr with 20 ml 0·5 N methanolic sodium hydroxide solution and acidified with dil hydrochloric acid. The acid melted at 170°, after recrystallization from methanol, but the melt solidified again and melted at 251° (anhydride). Also boiling acetic anhydride reconverted the acid into the anhydride. When the diacid was distilled quickly in a high vacuum, dissociation took place, and from the distillate the isobenzofuran derivative (VIII) was recovered by trituration with methanol.

2-*Phenyl*-3,4-(3′,6′-*diphenylbenzo*)-*fluorenone* (X)

When the calcium salt of the above acid was heated quickly, a deep red substance sublimed which was purified by sublimation *in vacuo* (165–170°/0·1 mm) and subsequently recrystallized from glacial acetic acid, m.p. 240°. The analysis as well as the colour indicate formula X. (Found: C, 91·6; H, 4·9. $C_{35}H_{22}O$ requires: C, 91·7; H, 4·8%).

Methyl 1,4,5,8-*tetraphenyl*-2-*naphthoate*

When 2 g of the methyl acrylate adduct of VIII was added to a solution of 1 g *p*-toluenesulphonic acid in 25 ml acetic acid, most of the adduct dissolved immediately, and a red solution resulted. Upon standing, a certain quantity of VIII which is insoluble in glacial acetic acid, separated, due to dissociation of the adduct. After 12 hr the filtered solution was evaporated almost to dryness *in vacuo* and the residue after neutralization with bicarbonate recrystallized from butyl acetate, m.p. 205°; yield 0·5 g (45%), λ_{max}^{Chlf} 255 (4·49); 335 mμ (4·14); $\bar{\nu}_{max}^{KBr}$ 1700 (aromatic ester) (Found: C, 88·1; H, 5·5. $C_{36}H_{26}O_2$ requires: C, 88·1; H, 5·3%).

Stereoisomer (?) *of* (1,4-*oxido*-1,4,5,8-*tetraphenyl*-1,2,3,4-*tetrahydro*-2-*naphthyl*) *methyl ketone* (XIV)

When 2 g of the adduct, m.p. 105° (dec) obtained from VIII and methyl vinyl ketone, was kept for 12 hr in a solution of 1 g *p*-toluenesulphonic acid in 25 ml anhydrous formic acid, a small amount of VIII crystallized out. The filtered solution was worked up as in the previous experiment and the product recrystallized from methanol, m.p. 180° (without dec) $\bar{\nu}_{max}^{KBr}$ 1700 (carbonyl), 1075 (epoxide). (Found: C, 87·7; H, 5·9. $C_{36}H_{28}O_2$ requires: C, 87·8; H, 5·7%).

1,4-*Oxido*-1,4,5,8-*tetraphenyl*-1,2,3,4-*tetrahydro*-2-*naphthamide*

A mixture of 1 g of the acrylonitrile adduct of VIII and 20 ml glacial acetic acid, saturated with gaseous hydrogen bromide, was kept for 12 hr and the precipitate consisting of a mixture of VIII, formed by dissociation of the adduct, and the above amide was washed with benzene until it was colourless, VIII being soluble in benzene. A second crop of the colourless amide was secured by evaporation of the acetic acid mother liquor. The product (0·65 g; 65%) was recrystallized from methanol, m.p. 170°. $\bar{\nu}_{\max}^{\mathrm{KBr}}$ 1660 (amide), 1080 (1,4-oxide) (Found: C, 84·9; H, 5·6; N, 2·8. $C_{36}H_{27}NO_2$ requires: C, 85·2; H, 5·5; N, 2·8%).

Methyl hydrogen 1,4-*oxido*-1,4,5,8-*tetraphenyl*-1,2,3,4-*tetrahydronaphthalene*-2,3-*dicarboxylate* (XIII)

A mixture of 2 g IX, 30 ml methanol and 0·2 ml conc sulphuric acid was refluxed with stirring, for 7 hr, and the solution concentrated. The product (1·4 g; 64%) was recrystallized from methanol, m.p. 190° (dec) $\bar{\nu}_{\max}^{\mathrm{KBr}}$ 1725 (carboxyl), 1080 cm^{-1} (1,4-oxide). (Found: C, 79·5; H, 5·5; OCH_3, 5·8. $C_{38}H_{30}O_5$ requires: C, 80·5; H, 5·3; OCH_3, 5·6%).

Dimethyl 1,4-*oxido*-1,4,5,8-*tetraphenyl*-1,2,3,4-*tetrahydronaphthalene*-2,3-*dicarboxylate*

An ethereal solution of diazomethane was added to 1 g XIII in 15 ml ether, until the yellow colour remained stable. The product crystallized out at once. The excess reagent was destroyed with a few drops glacial acetic acid and the product filtered off; a second crop was secured by evaporation of the mother liquor. Recrystallization from butyl acetate gave 0·8 g (79%) m.p. 238° (dec) $\bar{\nu}_{\max}^{\mathrm{KBr}}$ 1748 (saturated ester); 1073 (1,4-oxide). (Found: C, 80·4; H, 5·3; OCH_3, 10·5. $C_{39}H_{32}O_5$ requires: C, 80·7; H, 5·6; OCH_3, 10·9%).

Compound (XV). A solution of 22·1 g VI and 1 g syrupy phosphoric acid in 200 ml acetic anhydride was refluxed for 3 hr. The cooled solution gave 20 g (90%) of the product (XV), which was recrystallized from butyl acetate m.p. 246°. (Found: C, 91·0; H, 5·7. $C_{32}H_{24}O$ requires: C, 90·5; H, 5·7%).

The substance did not react with maleic anhydride.

Compound (XVI). When XV was heated at 260–300° with a 10% palladium charcoal for 1 hr, an isomer was formed which was recrystallized successively from acetic acid and ethyl acetate, m.p. 176°. (Found: C, 91·0; H, 5·7. $C_{32}H_{24}O$ requires: C, 90·5; H, 5·7%). The substance, heated gently with conc sulphuric acid, gives an intense wine-red colour reaction with a bluish tinge.

1,2-*Dibenzoyl*-3,6-*dibromo*-3,6-*diphenylcyclohex*-4-*ene* (XVII)

To a boiling solution of 17·6 g 3,6-diphenyl-1,2-dibenzoyl-4-cyclohexane (V) and 20 g anhydrous sodium acetate in 20 ml *glacial acetic acid*, a solution of 12·8 bromine in 80 ml of the same solvent was added. The reaction product, which crystallized spontaneously, was recrystallized from benzene in needles, m.p. 223–224° (dec) yield, 82%. (Found: Br, 27·0. $C_{32}H_{24}Br_2O_2$ requires: Br, 27·0%). When this compound was recrystallized from boiling xylene, it lost hydrogen bromide and gave the aromatic diketone (VII) in quantitative yield.

3,6-*Diphenyl*-3,6-*oxido*-1,2-*dibenzoyl*-4-*cyclohexene* (XVIII)

When 3 g XVII was refluxed for 30 min with excess 2 N alcoholic potassium hydroxide solution, a halogen-free reaction product crystallized out. It was washed with water and recrystallized from ethyl alcohol in silky needles, m.p. 204°; yield, 84% $\bar{\nu}_{\max}^{\mathrm{Chlf}}$ 1180 (furan); no hydroxyl absorption. Also Zerewitinoff analysis showed the absence of hydroxyl groups. (Found: C, 83·6; H, 5·0. $C_{32}H_{24}O_2$ requires: C, 84·2; H, 5·3%).

2,3,6,7-*Tetraphenylisobenzothiophen* (XIX)

A mixture of 4·4 g VI and 0·8 g sulphur was heated at 220° for 20 min and the solid product triturated with acetone and recrystallized from a large volume of benzene yielding yellow crystals, m.p. 283°, which exhibited an intense green fluorescence. (Found: C, 88·0; H, 4·7; S, 7·2. $C_{32}H_{22}S$ requires: C, 87·6; H, 5·0; S, 7·3%).

(b) A mixture of 2·2 g XV and 0·2 g sulphur reacted at 160° with evolution of hydrogen sulphide. The product was triturated with benzene and recrystallized from butyl acetate, m.p. and mixed m.p. 281°.

Photo-oxidation of the isobenzothiophene derivative (XIX)

A solution of 1 g XIX in 30 ml chloroform was exposed to bright sunlight in a quartz flask. After 48 hr, the solution, completely decolourized, was evaporated to dryness and the residue recrystallized from ethanol in broad needles of 3,6-diphenyl-1,2-dibenzoylbenzene, m.p. 215°; yield, 0·78 g.

The same observations were made with the corresponding isobenzofuran derivative (VIII).

Adduct (XI) *from* (VIII) *and acrolein*

A benzene (45 ml) solution of 5·45 g VII and 2·6 ml freshly distilled acrolein was refluxed for 30 min in presence of a trace of hydroquinone. A clear colourless solution resulted, from which the adduct separated upon cooling and crystallized from isopropyl alcohol as rods, m.p. 179–180°; yield 5·0 g (91%). At the m.p., the substance dissociates (yellow colour) and in conc sulphuric acid it dissolves with a deep red colour. $\lambda_{\max}^{\mathrm{EtOH}}$ 244 mμ (4·20; shoulder) $\tilde{\nu}_{\mathrm{Max}}^{\mathrm{KBr}}$ 1725. (Found: C, 88·1; H, 5·8. $C_{35}H_{26}O_2$ requires: C, 87·8; H, 5·5%).

2,4-*Dinitrophenylhydrazone*, yellow crystals of m.p. 226–227°, after recrystallization from a mixture of ethyl acetate and ethanol. (Found: C, 75·3; H, 5·0; N, 8·1. $C_{41}H_{30}N_4O_5$ requires: C, 74·8; H, 4·6; N, 8·5%).

1,4,5,8-*Tetraphenyl-2-naphthaldehyde* (XII)

When 3 g (XI) in 23 ml glacial acetic acid was saturated with hydrogen chloride in the cold, the compound dissolved, and a reddish solution formed. This was stirred for 1 hr at room temp, whereupon 1·7 g (58%) of XVII precipitated as yellow crystals. Recrystallization from acetic acid or xylene raised the m.p. to 245° which was not changed by chromatography of a chloroform solution on alumina. $\lambda_{\max}^{\mathrm{Chlf}}$ 280 (4·45); 330 (4·06); 384 mμ (3·72). (Found: C, 91·4; H, 5·4. $C_{35}H_{24}O$ requires: C, 91·3; H, 5·3%).

x-Chloro-1,4,5,8-*tetraphenylnaphthalene*

The adduct XI (2 g) was suspended in anhydrous alcohol (100 ml) and saturated at 0° with gaseous hydrogen chloride. After 24 hr, the brown-red solution was evaporated to dryness (*in vacuo*) and the residue recrystallized from butyl acetate, as yellow prisms m.p. 221° (dec). (Found: C, 88·0; H, 5·0; Cl, 7·0. $C_{34}H_{23}Cl$ requires: C, 87·6; H, 5·0; Cl, 7·4%).

1,4,5,8-*Tetraphenylnaphthalene* (I)

A mixture of 1·1 g XII and 0·1 g 10% palladium charcoal was heated for 5 hr at 270–300°. The reaction product was powdered and extracted with boiling benzene. From the chilled solution, yellow-brownish needles (0·6 g; 58%) precipitated on cooling. Two recrystallizations from benzene gave practically colourless crystals, m.p. 266°, which show an intense violet-blue fluorescence in benzene or cyclohexane solution (437 mμ). $\lambda_{\max}^{\mathrm{cyclohexane}}$ 248 (4·50); 334 mμ (4·18). (Found: C, 94·4; H, 5·7. $C_{34}H_{24}$ requires: C, 94·4; H, 5·6%).

Boiling formic acid or cold 80% sulfuric acid did not cause any isomerization of the hydrocarbon, which was recovered quantitatively unchanged.

Ethyl 3-*benzoyl*-6-*oxo*-4-*phenylheptoate* (XXIV)

A mixture of 19·2 g ethyl benzoylacetate, 14·6 g benzylideneacetone, 250 ml anhydrous ether and a solution of 0·75 g sodium in 5 ml anhydrous ethanol was kept at room temp for 24 hr (during which time part of the product crystallized) and poured into 250 ml of water, containing 3 g acetic acid. The aqueous layer was extracted with ether, and the combined ethereal solutions were dried and concentrated and the residue recrystallized from methanol, m.p. 98–99°; yield, 18 g (54%). $\lambda_{\max}^{\mathrm{EtOH}}$ 248 (4·25); 285 mμ (3·22) $\tilde{\nu}_{\max}^{\mathrm{KBr}}$ 1724 (carbonyl). (Found: C, 74·8; H, 6·0. $C_{21}H_{22}O_4$ requires: C, 74·5; H, 6·5%). The yellow 2,4-*dinitrophenylhydrazone* was recrystallized from ethanol; m.p. 162°. $\lambda_{\max}^{\mathrm{CHCl_3}}$ 367·5 (4·26). (Found: C, 62·6; H, 4·8. $C_{27}H_{26}N_4O_7$ requires: C, 62·5; H, 5·1%).

Ethyl 3-*hydroxy*-4-*oxo*-3,5-*diphenylcyclohexanecarboxylate* (XXXI)

When 500 ml aqueous (5%) sodium hydroxide was added to a solution of 20 g of the preceding compound in 50 ml ethanol, the reaction product crystallized immediately and after recrystallization from n-amyl alcohol melted at 215°. $\lambda_{\max}^{\mathrm{EtOH}}$ 258 mμ (very insoluble); $\tilde{\nu}_{\max}^{\mathrm{KBr}}$ 1715 (carbonyl), 3367 cm^{-1} (hydroxyl). (Found: C, 75·1; H, 6·7. $C_{21}H_{22}O_4$ requires: C, 74·5; H, 6·5%).

3,5-*Diphenylcyclohex*-2-*enone* (XXV)

The foregoing experiment was repeated and the mixture refluxed for 7 hr. The product was extracted with ether and the extract washed with water, dried and concentrated. The residue distilled at 185–187° (0·2 mm) and the viscous distillate was triturated with methanol. Recrystallization from the same solvent gave 10 g (68%) m.p. 83–84°. λ_{max}^{EtOH} mμ (4·25); $\tilde{\nu}_{max}^{KBr}$ 1665 cm⁻¹ (conjugated carbonyl). (Found: C, 87·0; H, 6·6. $C_{18}H_{16}O$ requires: C, 87·1; N, 6·5%).

3,5-*Diphenylcyclohexanone* (XXIII)

Hydrogenation of the preceding compound (with 10% palladium charcoal in ethyl acetate) was slow. The crude, viscous product was purified by distillation (b.p. 180–182° (0·003 mm)) and recrystallized from methanol, in colourless prisms m.p. 140°. The yellow *D.N.P.* formed needles m.p. 174–176° after recrystallization from isobutanol. (Found: C, 66·8; H, 5·0. $C_{24}H_{22}N_4O_4$ requires: C, 66·7; H, 5·1%). The *semicarbazone*, recrystallized from methanol, m.p. 200°.

3-*Phenylcyclohex-2-enone*

(a) This ketone was prepared according to the method of Walker[30] with the following modifications: The condensation of ethyl benzoylacetate (23 g) and methyl vinyl ketone (8·2 g) in t-butanol (30 ml), catalysed by 45% aqueous potassium hydroxide (12 ml), was exothermic (60–70°). After 1 hr, the mixture was diluted with water and acetic acid (7 ml) and extracted with a mixture of ether and ethyl acetate. The extract was washed with 5% sodium hydrogen carbonate, dried and concentrated and the residue triturated with ether which dissolved unchanged ethyl benzoylacetate (2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 166–167°). The ether-insoluble product (14 g, 44%) m.p. 128–130° after recrystallization from methanol, was identified as ethyl 3-hydroxy-4-oxo-phenylcyclohexanecarboxylate, by its yellow 2,4-dinitrophenylhydrazone, m.p. 206–207° (from ethyl acetate).

This compound was hydrolysed, decarboxylated and dehydrated to give 3-phenylcyclohex-2-enone, from pet ether, m.p. 64–65°, in 95% yield, as described by Walker[30]. The red 2,4-dinitrophenylhydrazone melted at 226–228° (from ethyl acetate).

(b) Another method applied to this synthesis was the Michael reaction between 3-dimethylaminopropiophenone and ethyl acetoacetate, similar to the route described by Novello *et al.*[29] To a solution of 30 g sodium in 3 l t-butanol, 213 g 3-dimethylaminopropiophenone hydrochloride and 130 g ethyl acetoacetate was added and the mixture refluxed, with stirring, for 20 hr. The mixture was acidified with acetic acid and the solvent removed by distillation *in vacuo*. The oily residue was extracted with ether, the extract washed with 5% sodium hydroxide solution and water, dried and concentrated, and the residue refluxed for 4 hr with 2 l 10% sodium hydroxide solution. The product was extracted with ether and distilled at 135–137° (1 mm); yield, 115 g (66%), m.p. 64–65°.

3-*Phenylcyclohexanone* (XX)

The hydrogenation of 1 g of the foregoing compound in 20 ml ethyl acetate in the presence of 0·2 g 10% palladium charcoal required 4 hr at normal temp and press. The product, an oil, b.p. 131–132° (3 mm) gave a yellow 2,4-dinitrophenylhydrazone, from alcohol, m.p. 167°, and a colourless semicarbazone from alcohol, m.p. 167°.

2-*Oxo*-7-*phenyl*-2,3,4,5,6,7,8,10-*octahydronaphthalene* (XXI)

When 2·5 ml 2 N alcoholic potassium hydroxide was added to a mixture of 32 g 3-phenylcyclohexanone and 4·2 g methyl vinyl ketone, an exothermic reaction ensued which was checked by cooling with ice water. After 15 min, the product was acidified with dil hydrochloric acid, diluted with cold water and extracted with ether. Treatment with 5% sodium carbonate solution and distillation gave a small quantity of unchanged 3-phenylcyclohexanone and 9 g (75%) XXI, a very viscous oil b.p. 165–166° (0·02 mm). The analysis and the spectrum showed that the product contained small quantities of 2-oxo-7-phenyl-9-decalol which, however, did not interfere with the next step of the synthesis. λ_{max}^{EtOH} 241 mμ (4·08); $\tilde{\nu}_{max}^{liq}$ 3450 (hydroxyl), 1725 (unconjugated C═O), 1684 (conjugated C═O). (Found: C, 83·8; H, 8·0. $C_{16}H_{18}O$ requires: C, 84·9; H, 8·0%).

2,7-*Diphenyl*-4,5,6,7,8,10-*hexahydronaphthalene* (XXII)

A Grignard solution prepared from 6·28 g bromobenzene and 0·98 g magnesium was added to 5 g of the foregoing ketone in ether and the mixture gently refluxed for 2 hr. The product was decomposed with ice and sulphuric acid and the aqueous layer extracted with ether. From the combined ethereal layers, the solvent was distilled off and the residue dissolved in benzene and subjected

---

[29] F. C. Novello, M. E. Christy and J. M. Spragne, *J. Amer. Chem. Soc.* **75**, 1330 (1953).

to azeotropic distillation in the presence of 1·5 g anhydrous oxalic acid. After 4 hr when no more water collected, the benzene was removed and the residue which formed upon cooling, recrystallized from boiling methanol as glistening platelets m.p. 94°, yield, 3·6 g (55%). $\lambda_{\max}^{\mathrm{EtOH}}$ 286 mμ (4·30). (Found: C, 92·1; H, 8·1. $C_{22}H_{22}$ requires: C, 92·3; H, 7·7%).

2,7-*Diphenylnaphthalene*

A mixture of 1 g of the foregoing hydrocarbon and 0·4 g sulphur was heated at 240° (internal temp) for 4 hr. The product was extracted with ether and the ether residue in benzene was chromatographed on alumina. The product recrystallized from ethanol, m.p. 142°, in agreement with the literature.[37] $\lambda_{\max}^{\mathrm{EtOH}}$ 268 (4·60); 300 mμ (4·10).

*Ethyl-7-oxo-*2,4-*diphenyl-*3,4,5,6,7,10-*hexahydronaphthalene-*10-*carboxylate* (XXVIII) *and ethyl* 2-*oxo-*1-(3-*oxobutyl*)-4,6-*diphenylcyclohex-*3-*ene-*1-*carboxylate* (XXVII)

A solution of 5·5 g methyl vinyl ketone in 10 ml methanol and 30 ml benzene was added, slowly and with stirring, to a solution of 10 g ethyl 2-oxo-4,6-diphenylcyclohex-3-ene-1-carboxylate[29,33,40] and 0·1 g sodium methoxide in 40 ml anhydrous methanol and 60 ml benzene. After 5 hr, water was added and the benzene layer washed with dil hydrochloric acid and water and concentrated. The residue was triturated with a small amount of cold benzene, which left undissolved a white crystalline powder. This was recrystallized from glacial acetic acid and melted at 158–159°; yield, 2 g (16·5%). The analysis and the spectrum showed that the Michael condensation product had not yet cyclized. $\lambda_{\max}^{\mathrm{EtOH}}$ 292 mμ (4·25). $\tilde{\nu}_{\max}^{\mathrm{KBr}}$ 1730 (ester and unconjugated ketone), 1660 cm^{-1} (conjugated carbonyl). (Found: C, 76·4; H, 6·7. $C_{25}H_{26}O_4$ requires: C, 76·9; H, 6·7%).

The benzene solution of the crude product was chromatographed on alumina and gave in addition to small quantities of the above product 4 g (34·5%) of the expected naphthalene derivative (XXVIII). After recrystallization from methanol, it melted at 166–168°. $\lambda_{\max}^{\mathrm{EtOH}}$ 330 mμ (4·38), $\tilde{\nu}_{\max}^{\mathrm{KBr}}$ 1723 (ester), 1650 (conjugated carbonyl). (Found: C, 80·5; H, 6·7. $C_{25}H_{24}O_3$ requires: C, 80·6; H, 6·5%).

Ethyl 7-*hydroxy-*2,4,7-*triphenyl-*5,6,7,8,9,10-*hexahydronaphthalene-*10-*carboxylate* (XXIX)

A Grignard solution, prepared from 0·4 g magnesium and 2·3 g bromobenzene in 20 ml ether, was added to 5 g XXVIII, dissolved in 40 ml benzene and 10 ml ether. After 3 hr at room temp, the mass was decomposed with 100 ml ice water and 5 ml conc sulphuric acid and yielded a resin which was dissolved in benzene and chromatographed on alumina. The main product was crystallized by trituration with ethanol and recrystallized from methanol–water, yield (3·7 g; 62%); m.p. 71–72°. $\lambda_{\max}^{\mathrm{EtOH}}$ 275 (4·45); 343 mμ (4·18) $\tilde{\nu}_{\max}^{\mathrm{KBr}}$ 3440 (hydroxyl), 1724 (ester carbonyl). (Found: C, 83·1; H, 6·3. $C_{31}H_{30}O_3$ requires: C, 82·6; H, 6·7%).

1,3,6-*Triphenylnaphthalene* (XXX)

A mixture of 1 g of the foregoing substance and 0·2 g 10% palladium charcoal was heated for 8 hr at 300° in an atmosphere of nitrogen. The product was extracted repeatedly with boiling benzene and the solution concentrated and chromatographed on alumina. The product (oily) was triturated with isopropanol and recrystallized from ethanol yielding a yellowish hydrocarbon m.p. 135°, 480 mg (60%). $\lambda_{\max}^{\mathrm{EtOH}}$ 270 (4·75); 301 mμ (4·20). (Found: C, 94·2; H, 6·0. $C_{28}H_{20}$ requires: C, 94·4; H, 5·6%).

3-(4-*Biphenyloyl*)-*propionic acid*[31,32] was obtained from biphenyl and succinic anhydride in nitrobenzene in 72% yield; m.p. 181–182° (from glacial acetic acid). $\lambda_{\max}^{\mathrm{EtOH}}$ 283 mμ (4·23); $\tilde{\nu}_{\max}^{\mathrm{KBr}}$ 2700, 1685 cm^{-1}.

7-*Phenyl-*1-*tetralone* (XXXIII)

A mixture of 16 g of the foregoing acid and 320 g polyphosphoric acid was heated at 120° for 2·5 hr and poured into excess water. The product was extracted with ether and the solution washed with 5% sodium bicarbonate solution and concentrated. The residue was distilled at 180° (1 mm); 195° (3 mm) and then recrystallized from methanol, yield, 63%; m.p. 66–67° (lit. 70°) $\lambda_{\max}^{\mathrm{EtOH}}$ 245 (4·40); 314 mμ (3·16); $\tilde{\nu}_{\max}^{\mathrm{KBr}}$ 1680 cm^{-1}.

2,4-*Dinitrophenylhydrazone*, red needles from a mixture of ethyl acetate and ethanol; m.p. 253–254°. (Found: N, 13·9. $C_{22}H_{18}N_4O_4$ requires: N, 13·9%).

[40] The compound absorbs in the U.V. at 287 mμ and in the I.R. at 1670 and 1738 cm^{-1}.

1,7-*Diphenyl*-1,2,3,4-*tetrahydro*-1-*naphthol*

A solution of 5·55 g XXXIII in 50 ml ether was added to a Grignard solution, prepared from 0·68 g magnesium and 4·8 g bromobenzene in 30 ml ether. The solution was refluxed for 1 hr and after 12 hr decomposed with aqueous ammonium chloride solution. The dried ethereal layer left a solid residue (yield, 60%) which was triturated with cyclohexane and recrystallized from nitromethane, m.p. 103–104°. λ_{max}^{EtOH} 250 mμ (4·23); $\bar{\nu}_{max}^{KBr}$ 3400 cm^{-1} (Found: C, 88·2; H, 6·8. $C_{22}H_{20}O$ requires: C, 88·0; H, 6·7%).

1,7-*Diphenyl*-3,4-*dihydronaphthalene*

When in the foregoing experiment the reaction product was decomposed with dil (20%) sulphuric acid, the product was oily, but crystallized upon trituration with cyclohexane. From nitromethane, it formed colourless crystals, m.p. 132°; yield 60%. λ_{max}^{EtOH} 251 mμ (4·40). (Found: C, 93·7; H, 6·5. $C_{22}H_{18}$ requires: C, 93·6; H, 6·4%).

1,7-*Diphenylnaphthalene* (XXXII)

A mixture of 2·12 g of the foregoing substance and 0·26 g sublimed sulphur was heated at 260–280° for 4 hr and the product distilled, b.p. 185–190° (0·3 mm). The distillate (yield, 80%) crystallized immediately (m.p. 85–87°). It was purified by chromatography of its benzene solution on alumina and finally recrystallized from ethanol in needles, m.p. 92–93°. λ_{max}^{EtOH} 256 (4·54); 302 mμ (4·05). (Found: C, 94·0; H, 5·8. $C_{22}H_{16}$ requires: C, 94·2; H, 5·8%). The same product was obtained, when the dehydrogenation was carried out at 260–310° with selenium (15 hr).

2-*Phenylbenzophenone*[41]

A Grignard solution was prepared from 4·85 g magnesium and 46·6 g 2-bromobiphenyl in 200 ml ether. The solution was diluted with 50 ml benzene, and 100 ml ether was distilled off. Then a solution of 19 g benzonitrile in 220 ml benzene was added and the resulting product refluxed for 4 hr, kept at room temp for 12 hr and decomposed with ammonium chloride. The product was refluxed for 5 hr with a mixture of 37 ml acetone, 32 ml conc hydrochloric acid and 80 ml water and the resulting oil extracted with ether and washed acid-free. The ketone crystallized upon scratching; it was triturated with pet ether, to remove some biphenyl, and recrystallized from ethanol, m.p. 86° (lit.:[41] 90°); yield 50%. λ_{max}^{EtOH} 240 mμ (4·3); $\bar{\nu}_{max}^{KBr}$ 1670 cm^{-1}. (Found: C, 88·5; H, 5·8. Calc. for $C_{19}H_{14}O$: C, 88·9; H, 5·5.

The ketone did not react with ethyl bromoacetate and zinc in boiling benzene and was recovered unchanged.

3-(2-*Biphenyloyl*)-*propionic acid* (XXXVI)

(a) A solution of 2-biphenyl lithium, prepared from 2·9 g lithium and 37 g 2-bromobiphenyl, was added to a suspension of 16·6 g succinic anhydride in 100 ml boiling benzene. The reaction mixture was refluxed for 2 hr and decomposed with ice and dil sulphuric acid. The oily product was fractionated, giving at 120° (1 mm) some succinic anhydride and at 195–200° (1 mm) the desired acid, but in very poor yield. Trituration with cyclohexane gave colourless crystals, m.p. 75°. $\bar{\nu}_{max}^{KBr}$ 1685, 2700 cm^{-1}. (Found: C, 75·5; H, 5·8. $C_{16}H_{14}O_3$ requires: C, 75·6; H, 5·5%).

(b) A cadmium reagent was prepared from 7·9 g magnesium and 82·5 g 2-bromobiphenyl in 200 ml ether and 32·5 g dry cadmium chloride. Then a solution of 40·5 g 3-carbomethoxypropionyl chloride[42] in 100 ml benzene was added and the mixture refluxed for 1 hr. The usual work-up gave an oil boiling at 156–158° (0·5 mm), which contained the methyl ester of XXXVI and a number of other, unidentified compounds. The crude ester (10 g) was refluxed for 3 hr with a solution of 4·5 g sodium hydroxide in 70 ml ethanol; dil hydrochloric acid was added and the product extracted into ether. The ether solution was then treated with sodium carbonate solution and the aqueous extract acidified. The acid which separated, was extracted with ether, distilled at 195–200° (1 mm) and triturated with cyclohexane. It melted at 75°, was identical with the product described under (a) but the yield was small.

---

[41] W. Schlenk and E. Bergmann, *Ann.*, 464, 34 (1928).

[42] *Organic Syntheses* Coll. Vol. III; p. 169.