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A NOVEL REACTION COURSE IN THE WOLFF-KISHNER REDUCTION OF DIBENZYLIDENE-ACETONE SEMICARBAZONE

S. VROMEN, A. MODIANO, A. MANDELBAUM and D. GINSBURG*
Department of Chemistry, Israel Institute of Technology, Haifa

and

B. HWANG[1], R. H. SCHLESSINGER and M. P. CAVA[1]
Department of Chemistry, Ohio State University, Columbus

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Abstract—The structure of a compound formed during Huang Minlon reduction of dibenzylidene-acetone was shown to be 1,4-diphenyl-2,5-di(β-phenylethyl)-benzene (I). Irradiation of 1,4-diphenyl-2,5-di(β-phenylvinyl)-benzene (III) gave a mixture of 2 stereoisomers of 3,7-diphenyl-3,4,7,8-tetrahydro-1,2,5,6-dibenzanthracene (VII and VIII). Both of these were dehydrogenated to give 3,7-diphenyl-1,2,5,6-dibenzanthracene (IX).

It is known that Wolff Kishner reduction of various derivatives of α,β-unsaturated ketones may lead not only to the net change $>C=O \rightarrow >CH_2$ but that products containing a cyclopropane ring may be obtained via intermediate pyrazole derivatives.[2,3]

We wish to report a different, novel cyclization observed when the semicarbazone of dibenzylidene-acetone was submitted to the conditions of the Huang Minlon reduction procedure. A hydrocarbon was isolated in 6% yield having an analysis in perfect agreement with the results calculated for 1,5-diphenyl-1,4-pentadiene. However, a Rast mol. wt. determination showed that a dimeric product had been produced. It was first believed that the dimer had the structure *a*. A product of similar molecular skeleton is formed in the light-sensitized dimerization of dimethyl-3-oxo-1,4-pentadiene-1,5-dicarboxylate.[4–6] Treatment of *a* with N-bromosuccinimide gave a tetrabromide which, after prolonged boiling with zinc in ethanol,[7] was quantitatively debrominated to afford an unconjugated diene which could be reduced to *a* after uptake of 2 moles of hydrogen. Such results could be rationalized on the basis of structure *a*, namely *b* for the tetrabromide and *c* for the diene.

The spectral evidence, however, ruled out the above structures. Two independent stilbene chromophores[8] were not observed in the alleged *c* and Fig. 1 which shows

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* This contribution has been dedicated to the memory of Professor H. Stephen.

[1] Present address: M.P.C., Department of Chemistry, Wayne State University, Detroit, Mich.; B.H., Smith Kline and French Laboratories, Philadelphia, Pa.

[2] D. Todd, "*Organic Reactions*" Vol. 4, p. 383, J. Wiley, N.Y. (1948).

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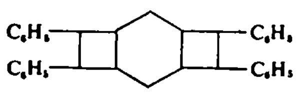
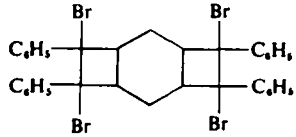


a



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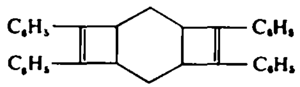
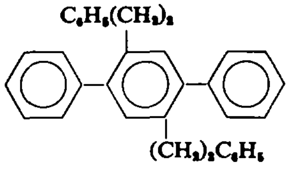
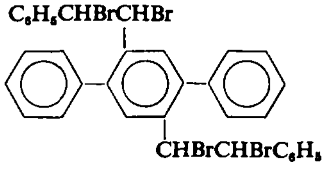


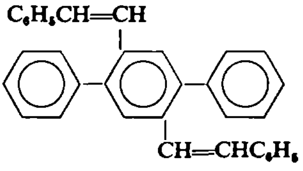
c



I



II



III

its UV absorption spectrum, indicates a higher degree of conjugation than exists in stilbene. Its NMR spectrum showed only aromatic and vinylic protons but no aliphatic protons.

The mass spectrum of I and III showed molecular peaks at *m/e* 438 and *m/e* 434, respectively, i.e. 2 mass units *less* than calculated on the basis of the structural formulae *a* and *c*, indicating that a mole of hydrogen had been lost during the dimerization–cyclization process. Compound I, therefore, corresponds to a hydrocarbon of the formula $C_{34}H_{30}$. A strong peak was found at *m/e* 347 (M-91) indicating the presence of a benzyl group. This conclusion was supported by the presence of an intense peak at *m/e* 91 ($C_7H_7^+$). An intense peak in the mass spectrum of I was at *m/e* 105. This ion can correspond only to $C_8H_9^+$ (since there is no oxygen atom present), arising from a phenethyl group in the molecule. The presence of the moiety

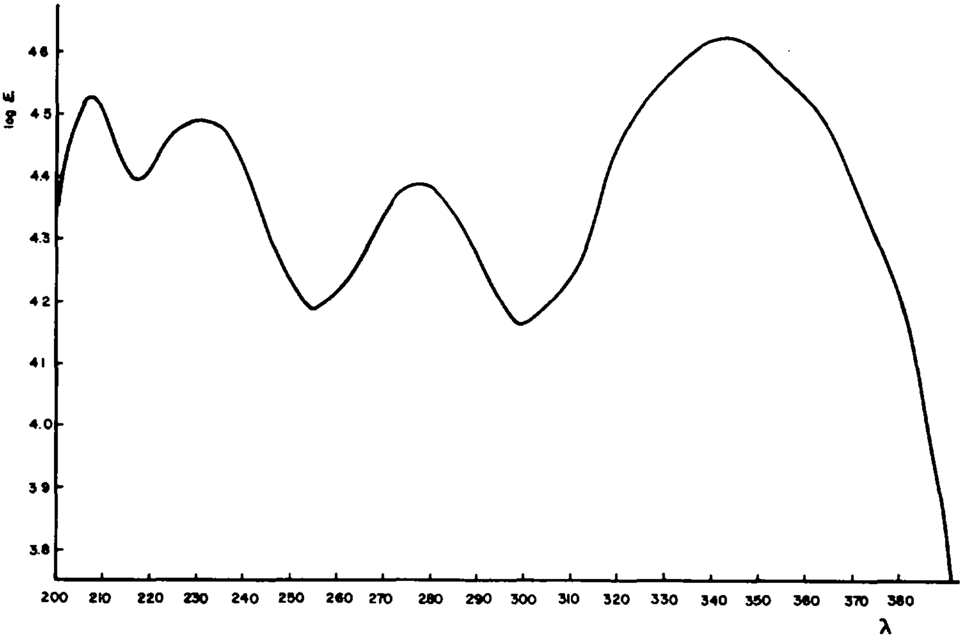
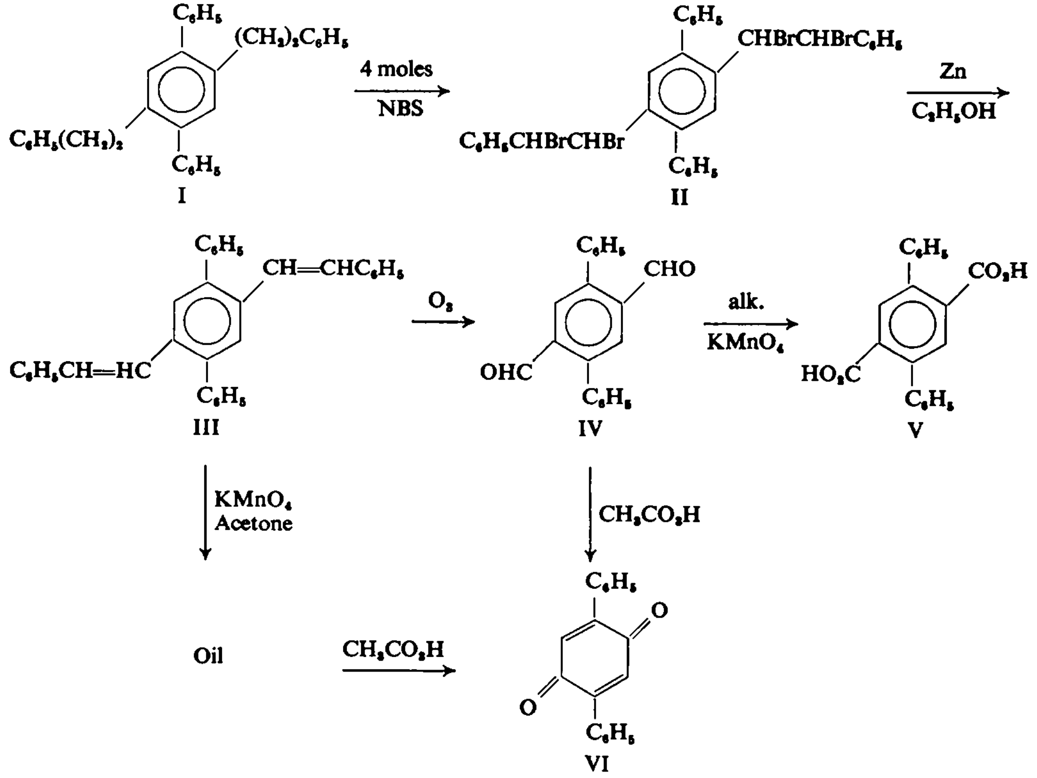


FIG. 1. UV spectrum of III, in cyclohexane.

$ArCH_2CH_2C_6H_5$ would indeed be expected to afford an abundant M—C_7H_7 ion. The NMR spectrum of I clearly showed only aromatic and benzylic protons, in the ratio of approximately 22:8. This led to the formulation $C_6H_2(C_6H_5)_2(CH_2CH_2C_6H_5)_2$ for compound I. NBS bromination attacks the four benzylic hydrogens and debromination gives III with two new double bonds. Hence III must be $C_6H_2(C_6H_5)_2(CH{=}CHC_6H_5)_2$. The mass spectrum of III shows the expected mol. wt. of 434. The molecular peak was the most intense in the spectrum and there was only a weak peak at *m*/*e* 91. The peak at *m*/*e* 105 was completely absent.

Compound I could then be either 1,4-diphenyl-2,5-di(β-phenylethyl)benzene or 1,4-diphenyl-2,3-di(β-phenethyl)benzene.

Oxidative degradation proved the first alternative to be correct. Ozonization of III led to the previously unknown 2,5-diphenyl-terephthaldehyde (IV) and to more than one equivalent of benzaldehyde (characterized as the 2,4-dinitrophenylhydrazone). Oxidation of IV with alkaline permanganate gave 2,5-diphenylterephthalic acid (V). Oxidation of IV with peracetic acid gave the known 2,5-diphenyl-*p*-benzoquinone (VI) identical in all respects with an authentic specimen prepared by a different route.[9] The same quinone was obtained when III was first oxidized with potassium permanganate in acetone and the resulting oil further treated with peracetic acid.



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[9] P. R. Shildneck and R. Adams, *J. Amer. Chem. Soc.* **53**, 2373 (1931).

UV irradiation of III gave two products, (VII and VIII), which could be fractionated by crystallization. Both products were isomers of the starting material and both exhibited a parent peak at *m/e* 434. Their mass spectra were very similar to that of III. *cis-trans* Isomerism about the side chain double bonds was excluded since the UV spectra of the products differed greatly from that of III. Figure 2 shows that except for differences in the extinction coefficients the UV spectra are practically superimposable. Further, attempted ozonolysis did not lead to a mixture of IV and benzaldehyde, showing that the $C_6H_5CH{=}CH$-groups were no longer present in the products of irradiation.

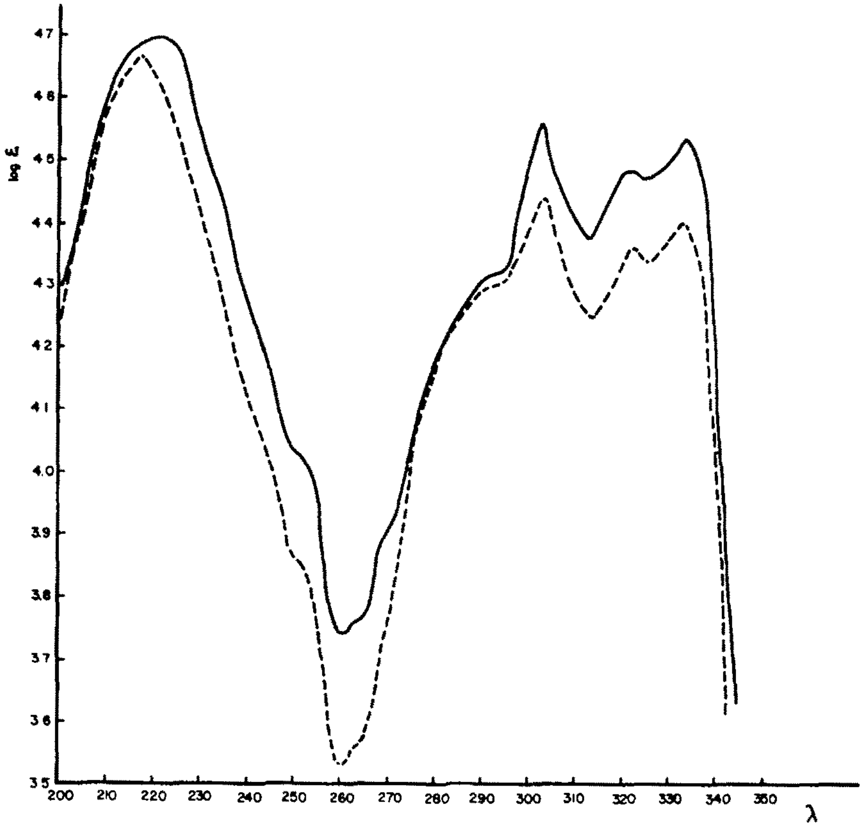
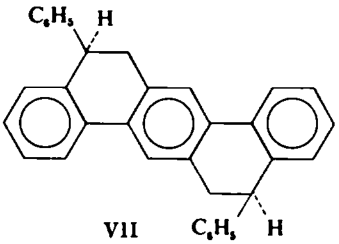


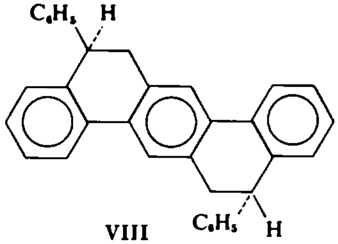
FIG. 2. UV spectra of VII (———) and VIII (– – –), in cyclohexane.

The mass spectra of VII and VIII show the presence of phenyl groups attached to six-membered hydroaromatic rings and not benzyl groups attached to five-membered hydroaromatic rings since the latter would be expected to lead to intense peaks at *m/e* M—$C_7H_7^+$ and at *m/e* 91; these were absent in the mass spectra. Furthermore, the appearance of M-2 (432) and M-4 (430) peaks in the spectrum of VII with relatively less intense analogous peaks in VIII, indicates ready aromatization of the six-membered hydroaromatic rings in these substances.

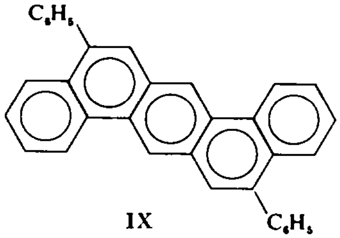
Both VII and VIII were dehydrogenated in high yield to give the same hydrocarbon, $C_{34}H_{22}$, formulated as 3,7-diphenyl-1,2,5,6-dibenzanthracene (IX) and the latter was oxidized to the corresponding 9,10-anthraquinone (X).



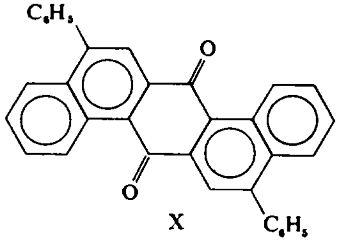
VII



VIII



IX

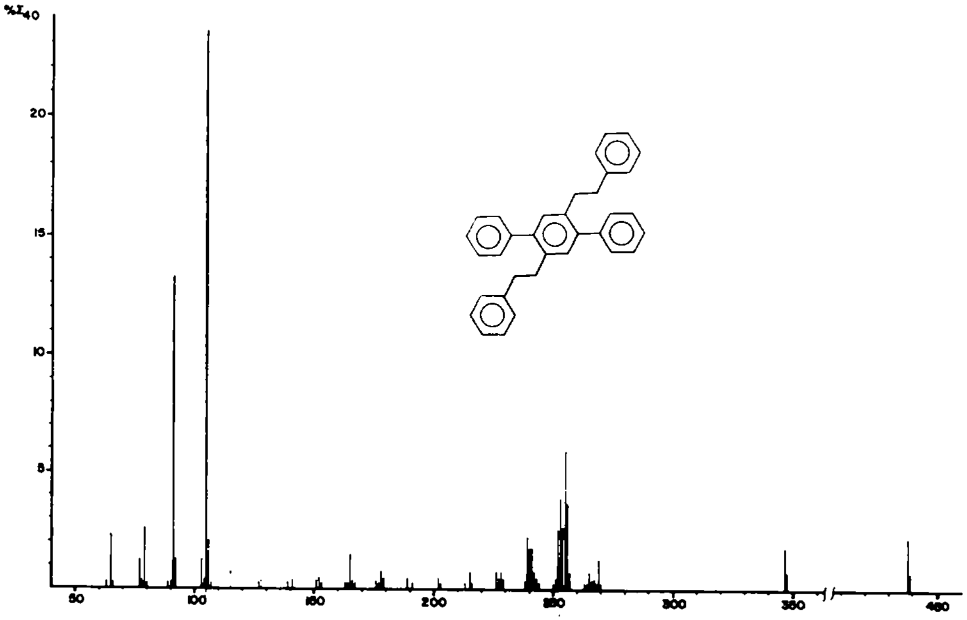


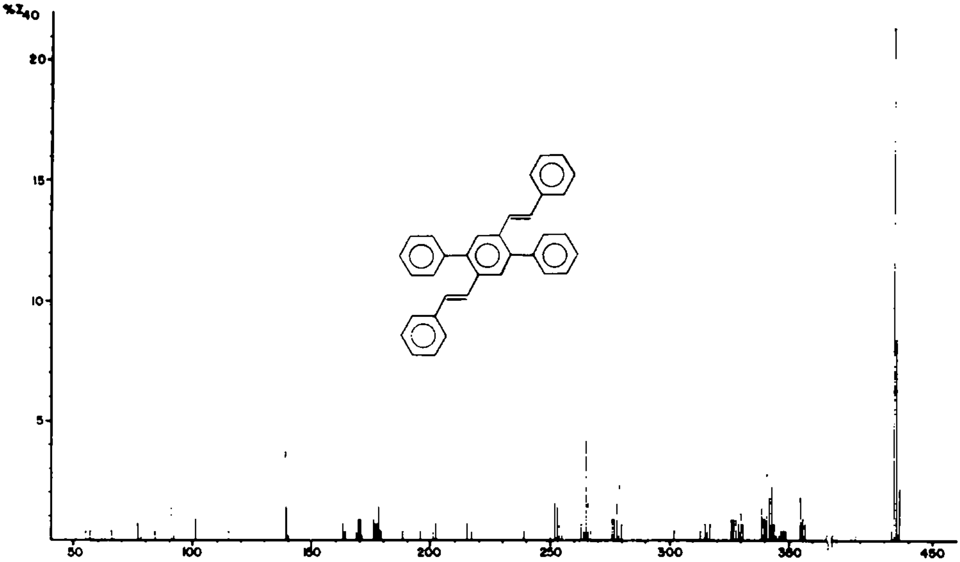
X

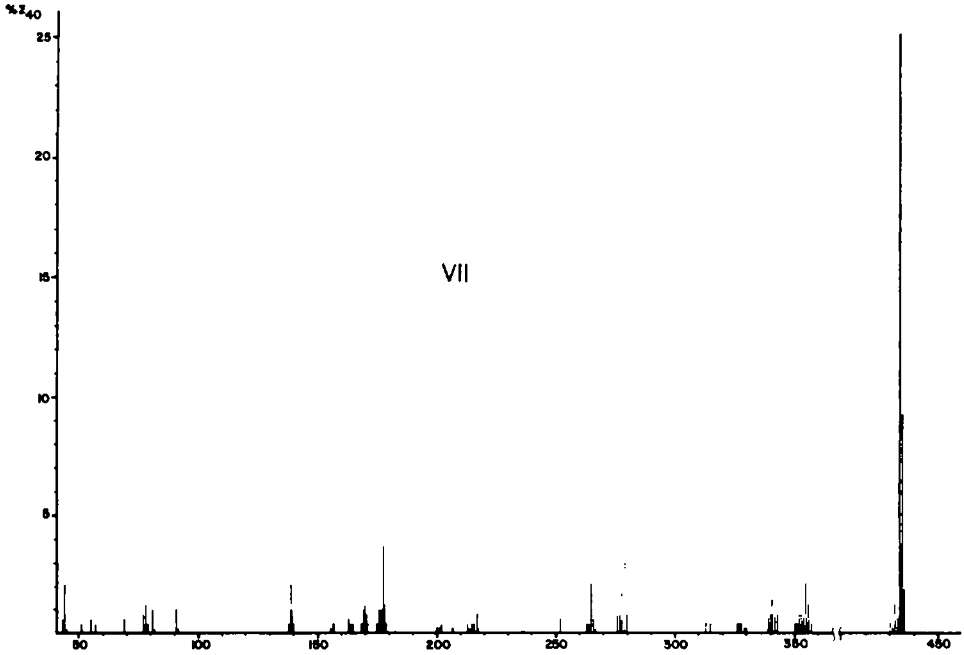
The configurations of the phenyl groups in VII and VIII are tentatively assigned on the basis of the relative abundance of certain peaks in the mass spectra of these substances. The Table summarizes the data.

	%Σ_{40}			
	M$^+$ *m/e* 434	[M—C_6H_6-1]$^+$ *m/e* 355	[M—C_6H_6]$^{2+}$ *m/e* 178	[M—2C_6H_6]$^{2+}$ *m/e* 139
(VII)	25·1	2·1	3·7	2·1
(VIII)	31·2	2·2	2·3	1·3

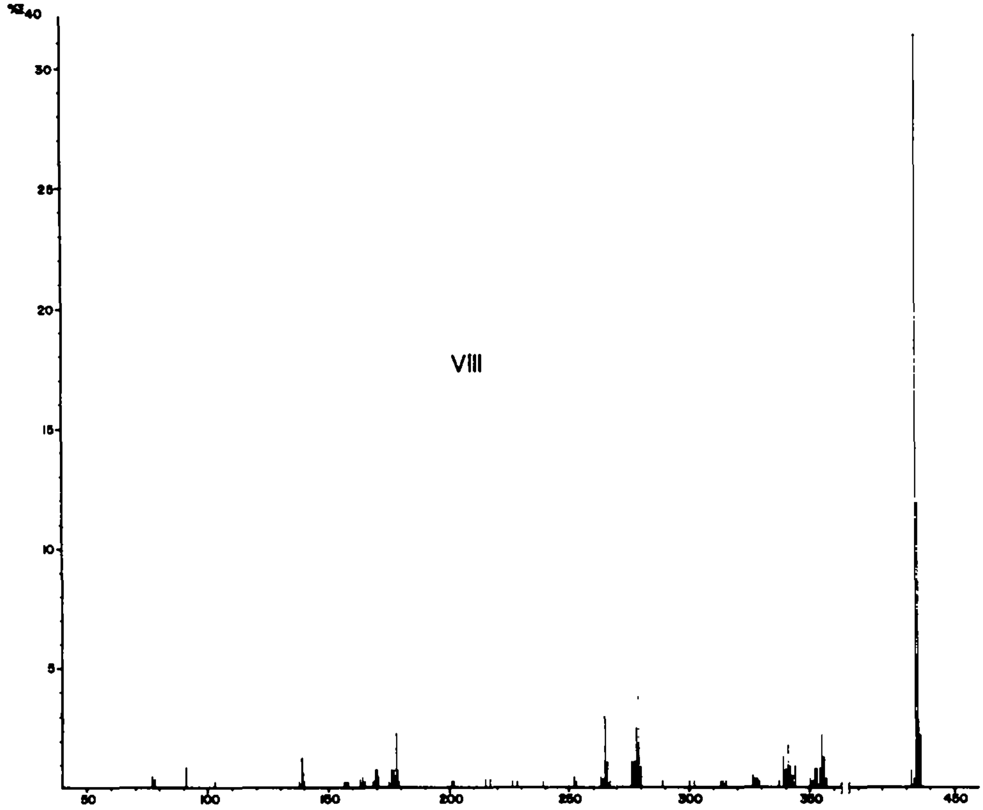
It appears from the mass spectral data that VIII is more stable than VII; its molecular ion is more abundant and its fragments less abundant than in VII. The mass spectra are shown in the corresponding figures.







It is evident, in attempting to write a mechanism for the novel formation of I through dimerization–cyclization, whether one employs a carbanion intermediate or a carbene, that several steps must be involved. The oxidation state of the central aromatic ring in the terphenyl system present in I, taken together with the presence of the two β-phenylethyl (i.e. reduced) substituents, clearly show that a deepseated disproportionation has occurred. This is evidenced also by the formation of I in



very low yield and the only way to rationalize its being formed at all is to invoke the driving force of aromatization of the central ring in the ultimate terphenyl system.

EXPERIMENTAL

Instrumentation used. NMR spectra—Varian A-60 ($CDCl_3$ with tetramethylsilane as internal standard). Mass spectra—Atlas CH4 with direct inlet system, 70 eV; 20 μA. UV spectra—Carey 14 (in cyclohexane unless otherwise stated). All m.ps are uncorrected.

1,4-*Diphenyl-2,5-di(β-phenylethyl)benzene* (I). To a solution of KOH (11 g) in anhydrous triethylene glycol (100 ml) at 200° was added portionwise with stirring, dibenzylidene-acetone semicarbazone (m.p. 180–181°; 14·2 g). Vigorous foaming took place after each portion was added and subsequent portions were added after foaming had subsided. After the addition was complete, the temp was maintained at 195–200° for 4 hr. After cooling, the mixture was poured into cold water and 7N HCl was added until the solution was neutral to litmus. The mixture was extracted with ether, the ether extract was washed with water and dried (Na_2SO_4). Evaporation of the solvent left a brown oil (12 g).

Trituration of the oil with EtOH–ether (1:1) gave crystalline material but a better procedure was to chromatograph the oil in light petroleum solution over neutral alumina (Merck) using the same solvent as eluent. Trituration of the oil remaining after evaporation of the solvent gave a colorless solid. Recrystallization gave colorless needles of *dimer*, m.p. 159·5° from EtOH–ether; 0·635 g, 6% yield. (Found: C, 92·96; H, 6·97. $C_{34}H_{30}$ requires: C, 93·11; H, 6·89%.) M.Wt. Found: (Rast) 425, 414, 430; (mass spectral) 438. $C_{34}H_{30}$ requires: 438·6.

The remaining intractable oil contained nitrogen. It was not investigated further.

1,4-*Diphenyl-2,5-di(α,β-dibromo-β-phenylethyl)benzene* (II). A mixture of I (16·5 g), N-bromosuccinimide (33·4 g), sodium acetate (15·4 g), dibenzoyl peroxide (0·75 g), acetic acid (18 ml) and

CCl_4 (350 ml) was heated under reflux for 20 hr. After cooling and filtration, the colorless precipitate was washed with warm water and dried, m.p. 248–251° (26·1 g). The CCl_4-filtrate was washed with water, dried (Na_2SO_4) and the solvent removed, yielding identical colorless rods, m.p. 248–251° (1·5 g; total yield 100%). The analytical sample of *tetrabromide* was obtained by recrystallization, m.p. 246–248° (dec) from CCl_4. (Found: C, 54·30; H, 3·64; Br, 41·92. $C_{34}H_{26}Br_4$ requires: C, 54·14; H, 3·47; Br, 42·38%.)

1,4-*Diphenyl*-2,5-*di*(β-*phenylvinyl*)*benzene* (III). A mixture of II (5 g), activated Zn dust[7] (10 g) and EtOH (4 l.) was heated under reflux for 20 hr (no hydroquinone was used). At the end of the reaction the solution displayed strong fluorescence. After filtration, the filtrate was concentrated to a volume of 100 ml, giving, after cooling, III as pale yellow fluorescent rods (2·87 g; 100%). m.p. 251–252° from EtOH. (Found: C, 93·74; H, 6·08. $C_{34}H_{26}$ requires: C, 93·97; H, 6·03%.)

Hydrogenation of III. A suspension of III (1·1 g) in methylcyclohexane (100 ml) was hydrogenated at atm press using 10% Pd-C (0·4 g). The fluorescence disappeared and the substance undergoing reduction dissolved as reduction progressed. When hydrogen uptake (126 ml; calc. 114 ml) had ceased, the catalyst was removed. Evaporation of the solvent afforded I (0·83 g), m.p. and mixed m.p. with authentic I, 159–161°.

Ozonization of III. A solution of III (0·5 g) and pyridine (0·18 g) in CH_2Cl_2 (50 ml) was ozonized at −78° until the solution turned light blue (45 min). The reaction mixture was washed with HCl (from 2 ml conc. HCl + 4 ml water), and then with water. The organic layer was dried ($MgSO_4$) and then concentrated to a volume of 2 ml. After cooling, the pale yellow 2,5-*diphenylterephthalaldehyde* (IV) crystallized and was removed by filtration. The analytical sample had m.p. 198° from benzene–ether. (Found: C, 84·29; H, 4·48. $C_{20}H_{14}O_2$ requires: C, 83·90; H, 4·93%.) *NMR*: $\tau - 0{\cdot}2(2H)$; 2·50(10H). *IR*: 5·94 μ (aromatic aldehyde).

The first mother liquor was treated in the usual way with 2,4-dinitrophenylhydrazine. The precipitated dark yellow 2,4-dinitrophenylhydrazone was recrystallized to give dark yellow needles (380 mg; 1·2 eq.), m.p. 243° from ethyl acetate. The IR spectrum was identical with that of authentic benzaldehyde 2,4-dinitrophenylhydrazone and admixture with the latter caused no m.p. depression.

Oxidation of IV *with peracetic acid.* 2,5-Diphenylterephthalaldehyde (200 mg) was dissolved in a hot mixture of acetic acid (2 ml) and peracetic acid (40% solution; 2 ml). The solution turned red on the steam bath and finally flaky orange-yellow crystals formed. After heating for 1 hr the mixture was cooled and the crystalline product was separated by filtration. Recrystallization gave the analytically pure 2,5-diphenylbenzoquinone (VI; 100 mg), m.p. 215·5° from benzene–ether. (Found: C, 82·85; H, 4·75. Calc. for $C_{18}H_{12}O_2$: C, 83·06; H, 4·65%.) *NMR*: τ 2·42(8–9H), 2·70(2H). *IR*: 6·08 μ (quinone C═O).

The product (VI) was identical in IR spectrum and showed no depression in m.p. on admixture with the authentic quinone prepared by the method of Shildneck and Adams.[9]

2,5-*Diphenylterephthalic acid* (V). A suspension of IV (200 mg), in aqueous (40 ml) alkaline (400 mg NaOH) $KMnO_4$ (300 mg) was heated under reflux with stirring for 15 hr. At this point most of the solid had dissolved. The reaction mixture was filtered and the hot filtrate was acidified with dil HCl. The colorless *diacid* (V) precipitated. The analytical sample (145 mg) had m.p 305–306° from acetone. Lit.[10] m.p. 297–298°. (Found: C, 75·29; H, 4·53. Calc. for $C_{20}H_{14}O_4$: C, 75·46; H, 4·43%.) *IR*: 3·3 and 3·4 μ; 5·9 μ (CO_2H).

Mixture of isomeric 3,7-*diphenyl*-3,4,7,8-*tetrahydro*-1,2,5,6-*dibenzanthracene* (VII and VIII). Compound III (1·5 g) was dissolved in benzene (200 ml) and was irradiated for 15 hr, with stirring, by UV from a medium pressure Hanovia lamp using a water cooled quartz probe. The resulting yellow solution was chromatographed on a column (500 mm × 30 mm) of neutral alumina (grade I). The colorless eluate was concentrated to a volume of 2 ml. Upon cooling a crystalline product (VII; 500 mg), m.p. 254–255° was separated by filtration. The mother liquor was concentrated to a volume of about 1 ml. Upon filtration, a mixture of the isomers (VII and VIII) was obtained (150 mg). Ether (3 ml) was added to the filtrate, affording needles of VIII (550 mg) m.p. 205–207°.

Compound VII formed flaky crystals from benzene and VIII formed needles from benzene–ether. The two isomers were not interconvertible by seeding with each other. Admixture caused a m.p. depression. The UV absorption spectra are shown in Fig. 2. The NMR spectra were indistinguishable. τ 6·71 (doublet, J = 7·5 c/s); 5·72 (triplet J = 7·5 c/s); 2·90 (multiplet). (Found VII: C 93·83; H, 5·96. VIII: C, 93·86; H, 6·01. $C_{34}H_{26}$ requires: C, 93·96; H, 6·03%.)

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[10] F. Ebel and W. Deuschel, *Chem. Ber.* **89**, 2794 (1956).

3,7-*Diphenyl*-1,2,5,6-*dibenzanthracene* (IX). Dehydrogenation of VII (100 mg) or VIII (100 mg) was effected by heating each with 5% Pt-C (100 mg) at 275–285° for 30 min. After cooling, benzene (8 ml) was added and the mixture heated on the steam bath for 20 min. Filtration to remove the catalyst followed by evaporation of the colorless filtrate to dryness and recrystallization from benzene afforded the same hydrocarbon (IX), m.p. 292·5° (60 mg and 65 mg, respectively). (Found: C 94·97; H, 5·35. $C_{34}H_{22}$ requires: C, 94·85; H, 5·15%.) *UV* (dioxan): 226 (4·653), 298 (4·978), 310 (5·025), 332 (4·30), 348 (4·305), 364 (4·285). *UV* (ethanol): 209 (4·544), 225 (4·655), 296 (5·016), 308 (5·035), 332 (4·390), 346 (4·377), 364 (4·360).

3,7-*Diphenyl*-1,2,5,6-*dibenz*-9,10-*anthraquinone* (X). The hydrocarbon (IX; 20 mg) was dissolved in boiling acetic acid (8 ml). To this solution was added 40% peracetic acid solution (2 ml) and the whole was heated on the steam bath for 4 hr. The mixture turned yellow and the brown crystalline product was separated by filtration. Recrystallization of the crude *quinone* gave yellow needles (10 mg) m.p. 354° from toluene. (Found: C, 88·57; H, 4·32. $C_{34}H_{20}O_2$ requires: C, 88·67; H, 4·38%.) *UV* (dioxan): 226 (4·716), 305 (4·716), 340 (4·032) (shoulder), 401 (3·957).