[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MARYLAND]

Synthesis and Ultraviolet Absorption Spectra of *m*-Di-substituted Benzenes

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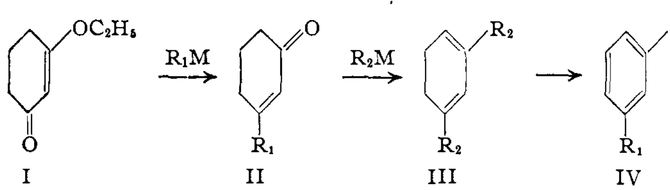
We have completed the synthesis of the series of *m*-diarylbenzenes shown in Table I. Substances



V through X were prepared earlier,[1] while substances XI through XIV have now been prepared by the series of reactions where one of the organometallic reagents was 2-xenylmagnesium bromide and the other was either phenylmagnesium bromide or the appropriate xenylmetallic reagent. The data for these substances, all of which contain the *o*-terphenyl structure, are given in Table II.

These compounds (Table I) have interested us because resonance involving the whole molecule in a hybrid structure is not possible while at the same time complete conjugation does exist. For instance, the *m*-terphenyl, quaterphenyl, and quinquephenyl molecules (V, VI and VIII) can have only two adjacent phenyl rings involved in a resonance unit. Certain other molecules (VII, IX, X and XII) contain a *p*-terphenyl structure. The remaining molecules contain an *o*-terphenyl structure. It seemed of interest therefore to see whether these variations in structure led to peculiarities in ultraviolet absorption.

The ultraviolet absorption curves of the completely *m*-polyphenyls are shown in Fig. 1. It is noted that for all these substances the absorption maxima are just below 250 mμ, and that the wave length of maximum absorption does not shift on increasing the number of ring units, while the value of the extinction coefficient increases with the number of ring units. Gillam and Hey[2] have obtained the ultraviolet absorption spectra of the *m*-polyphenyls containing 3, 9, 11, 12, 13, 14, 15, and 16 phenyl rings. These workers also noted that the wave length of maximum absorption did not appreciably shift, that the curves were free of fine structure, and that the value of the maximum extinction coefficient is a function of the number of benzene rings. We are in excellent accord with these observations, although our value for the *m*-terphenyl extinction coefficient is somewhat lower.

The ultraviolet absorption curves of those molecules containing the *p*-terphenyl unit (except for those containing the ortho linkage in addition) are given in Fig. 2. Here a pronounced bathochromic effect is observed. It would seem that the molecule VII should absorb further toward the visible than *p*-terphenyl itself. But a hypsochromic effect seems to be present since

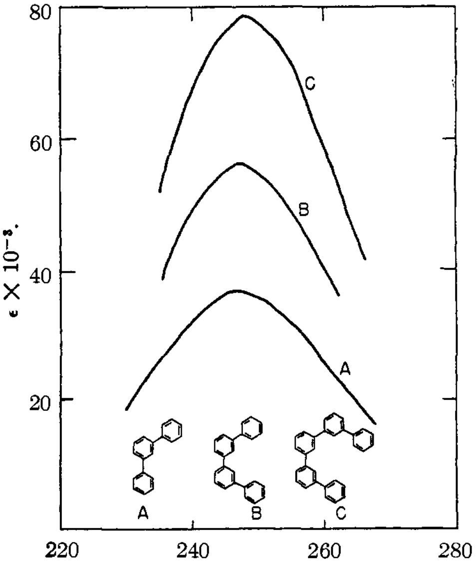


Fig. 1.

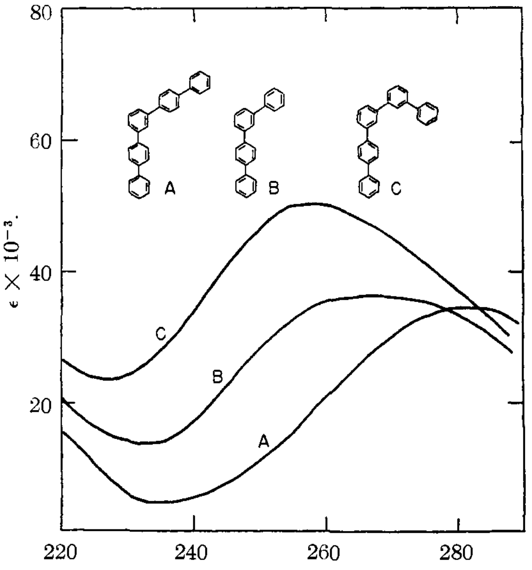


Fig. 2.

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(1) For earlier papers in this series see: (a) Woods and Tucker, THIS JOURNAL, **70**, 2174 (1948); (b) *ibid.*, **70**, 3340 (1948); (c) Woods and Reed, *ibid.*, **71**, 1348 (1949).

(2) Gillam and Hey, *J. Chem. Soc.*, 1170 (1939).

Gillam and Hey[2] report that *p*-terphenyl has a maximum absorption at 2760 Å.

Figure 3 gives the absorption spectra for these molecules which have an *ortho* structure. A powerful hypsochromic effect is observed resulting in a shift of the wave length of maximum absorption as in X (282 mμ) to 234 mμ in XIV. A more pronounced method of stating this effect is that the introduction of two more benzene rings into *m*-terphenyl, V, to yield XIV does not shift the wave length of maximum absorption toward the visible even though the *ortho* linkages would make possible a degree of resonance (if there were no steric effect), but instead represses the absorption some 15 mμ into the ultraviolet region. This phenomenon has been observed by Friedel, Orchin and Reggel.[3] These workers consider the hypsochromic shift to be the result of a steric factor which inhibits a coplanar structure in the molecule.

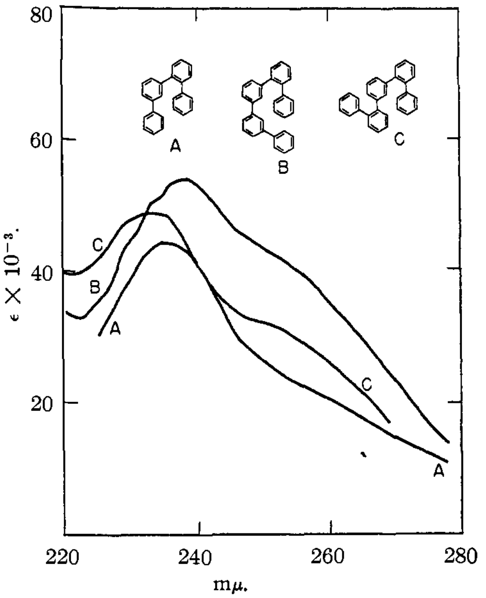
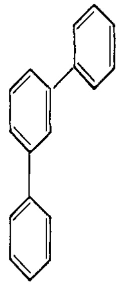
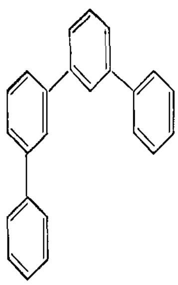


Fig. 3,

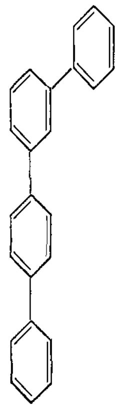
TABLE I



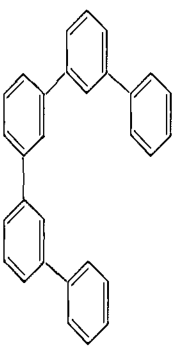
V



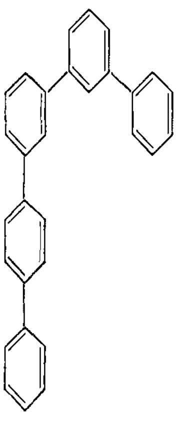
VI



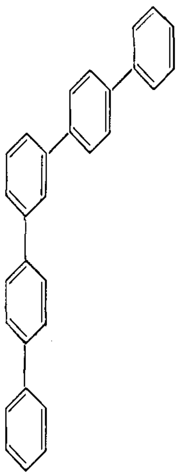
VII



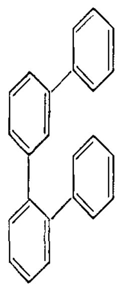
VIII



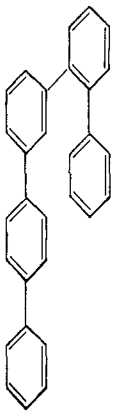
IX



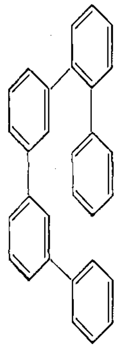
X



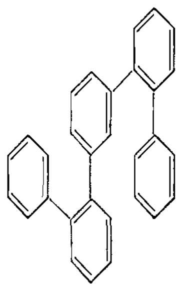
XI



XII



XIII



XIV

Figure 4 contrasts the absorption curve of XIII, which shows absorption peaks for both an *ortho* structure and a *para* structure, with those of XIV and X.

The attempts to correlate these curves with the structures involved and with the broad generalizations relating structure to spectra led to the conclusion that certain fundamental principles of light absorption by organic molecules might not be entirely correct. Jones[4] in his excellent paper on ultraviolet absorption spectra of organic

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[3] Friedel, Orchin and Reggel, THIS JOURNAL, **70**, 199 (1948).

[4] Jones, *ibid.*, **67**, 2127 (1945).

TABLE II

ARYLKETONE AND DIARYLBENZENES

	M. p., °C.	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
3-(2-Xenyl)-Δ^2-cyclohexenone[a]	104.5–105.5	$C_{18}H_{16}O$	87.06	6.50	86.56 86.86	6.66 6.83
1-Phenyl-3-(2-xenyl)-benzene (XI)[b,c]	90.5–91	$C_{24}H_{18}$	94.07	5.92	94.22 94.10	6.06 6.03
1,3-Di-(2-xenyl)-benzene (XIV)	155.5–156.6	$C_{30}H_{22}$	94.20	5.80	94.07 93.97	6.21 6.17
1-(2-Xenyl)-3-(4-xenyl)-benzene (XII)[d,e]	144.5–145.5	$C_{30}H_{22}$	94.20	5.80	94.35 94.45	5.94 5,96
1-(2-Xenyl)-3-(3-xenyl)-benzene (XIII)	113–114	$C_{30}H_{22}$	94.20	5.80	93.86 94.71	5.86 5.79

[a] Red 2,4-dinitrophenylhydrazone prepared: m. p. 220.5–221.5°. *Anal.* Calcd. for $C_{24}H_{20}O_4N_4$: C, 67.28; H, 4.71. Found: C, 67.17, 67.19; H, 4.90, 4.94. [b] Prepared from 3-(2-xenyl)-Δ^2-cyclohexanone and phenylmagnesium bromide. [c] The same compound prepared from 3-phenyl-Δ^2-cyclohexanone and 2-xenylmagnesium bromide melted at 91.0–91.5° and gave no depression on mixed melting point determination. *Anal.* Calcd. for $C_{24}H_{18}$: C, 94.07; H, 5.92. Found: C, 94.08; H, 5.98. [d] Prepared from 3-(2-xenyl)-Δ^2-cyclohexanone and 4-xenyllithium. [e] The same compound prepared from 3-(4-xenyl)-Δ^2-cyclohexanone and 2-xenylmagnesium bromide melted at 142–143° and gave no depression on mixed melting point determination. *Anal.* Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.27, 94.16; H, 6.09, 6.01.

molecules has stated certain of these broad generalizations relating structure to spectra. For instance, the bathochromic effect is defined by a small shift of a spectrum of a given molecule toward the visible region without too great an alteration of the curve with reference to the spectrum obtained from a second type of molecule (which is closely related to the former type of molecule). A conjugate effect (resonance) not only alters the shape (including the loss of fine structure) of one curve with reference to the second curve but also causes an extensive shift toward the visible region. Where steric factors seem to repress a conjugate effect the spectrum appears to revert to that of the parent hydrocarbon. An example of this is given by Jones[4] in the 9,10-dimethyl- and 9,10-diphenyl-anthracenes. It has therefore become common to read or to find implied that where resonance is present a shift in a spectrum toward the longer wave lengths occurs (*cf.* Murray and Galloway[5]).

We wish to point out that any such explanation of the relation of resonance is far too simple, and that repression of a resonance effect does not necessarily cause the spectra to revert to that of the parent compound. Yet some correlation of structure to the hypsochromic effect is possible. The difficulty in the application of the above principles is realized when one considers the facts that (1) the methylstyrenes, styrene and biphenyl all have absorption bands further into the ultraviolet region with reference to benzene and (2) that *o*-terphenyl (which is more conjugated than *m*-terphenyl) absorbs further into the ultraviolet than either *m*-terphenyl or biphenyl (*i. e.*, where a steric factor is operative the spectra of *o*-terphenyl did not revert to that of biphenyl).[6]

Jones has pointed out that the region of absorption in the ultraviolet of a molecule is a consequence of the energy *difference* between some *ground state* and *excited state*. The greater the energy difference involved here the further in the ultraviolet a compound will absorb. To state that a molecule has greater resonance energy and therefore a lower ground state implies that a molecule would absorb further into the ultraviolet *per se*, unless some statement is made which will also indicate a lowering (greater than for the ground state) of the first excited state.

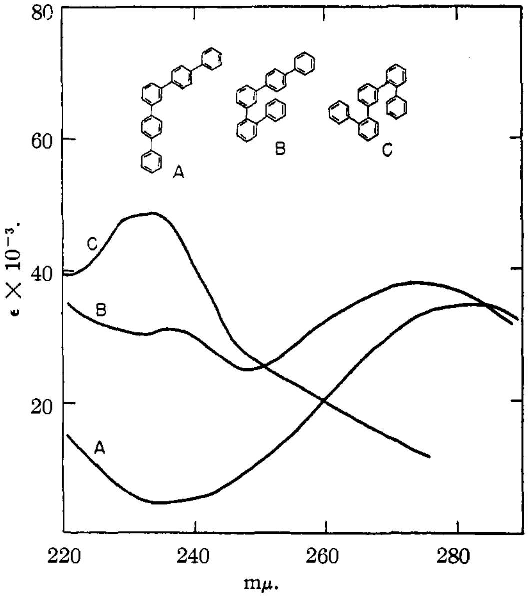

Fig. 4.

The statement of a simple conjugate effect would cause one to expect biphenyl to absorb further toward the visible than benzene (which is not the case). It has been recognized that for the benzene molecule, the ground state can be represented for a first approximation by the hybrid structure based on the Kekulé forms but *not* contributed to by the various ionic states. But it is the ionic forms which contribute to the excited state. Therefore it has been written

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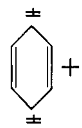
(5) Murray and Galloway, THIS JOURNAL, **70**, 3867 (1948).

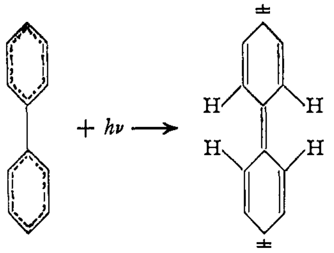
(6) As this work was being developed, it seemed that *o*-terphenyl should absorb in the region of 235 mμ. The results of Pickett, Walter and France (THIS JOURNAL, **56**, 2298 (1936)) on this substance(?) indicated no absorption band in this region. The absorption curve determined by us on a sample of *o*-terphenyl kindly furnished by Dr. C. F. H. Allen of the Eastman Kodak Co. had a maximum extinction at 233 mμ (2.9 × 10⁴). The actual curve is very similar to that of XI in our work.

Benzene (ground state) + $h\nu \longrightarrow$



+ other quinonoid forms

Then in biphenyl the ground state hybrid is roughly represented by the molecule written below to represent the hybrid of the various Kekulé forms, which upon absorption of a photon is elevated to an excited electronic state, the hybrid of which is coplanar.



To the extent that there is any repulsion between the *ortho* protons the energy of the excited state would be somewhat higher than without this repulsion (which is lacking in benzene). This effect is also concurrent with the recognized effect of the greater the separation of charges the smaller the contribution of this state to the resonance hybrid. In this manner the absorption of biphenyl at shorter wave lengths than that of benzene can be explained[7] and this argument leads to the conclusion that restricted rotation exists in biphenyl. Actually this results in a reversal of the conjugate effect. A replacement of the *ortho* hydrogen with groups more effective in preventing a coplanar structure would cause an elevation of the energy level of the first excited state resulting in absorption further into the ultraviolet. It would thus seem reasonable to expect an *o*-methyl, *o*-phenyl or any *ortho* substituted biphenyl to absorb further into the ultraviolet than biphenyl itself. A logical extension of this hypothesis is that those biphenyls showing optical activity which are markedly stable to racemization either absorb far into the ultraviolet relative to biphenyl or else some other excited form than that represented above becomes effective in absorption in the ultraviolet region.

We conclude that the simple statement that "where resonance is possible a shift of an ultraviolet spectrum toward the visible region" is insufficient or inadequate. Further qualifications must be made with reference to the ground and excited states; and that, as Mulliken has stated the requirements of the energy levels of the ground and excited states for the conjugate effects, it now is evident that certain hypsochromic shifts result from an elevation of the energy level of the first excited state, and that the spectrum in such cases does not necessarily revert to that of the "parent" hydrocarbon.[8]

While the above preparations and studies of the *m*-diarylbenzenes were in progress, another avenue of synthesis to prepare *m*-arylalkylbenzenes with the monoethyl ether of dihydroresorcinol was instituted whereby some dimethyl- and dicarboxybiphenyls were obtained.

The reaction of (I) with tolylmagnesium bromide proceeded normally and yielded the corresponding 3-tolyl-Δ^2-cyclohexenones of structure (II), the data for which are collected in Table III. The corresponding 1-tolyl-3-methylcyclohexadienes of structure (III) were obtained by the reaction of the unsaturated ketones with methylmagnesium bromide. Aromatization of these with palladium charcoal yielded the three dimethylbiphenyls of structure (IV), the data for which are contained in Table IV. In order to prove that the structures were correct and to extend the utilization of these reactions, the dimethylbiphenyls were oxidized to the corresponding and known dicarboxybiphenyls. In Table V are collected the data for the dicarboxybiphenyls.

It is thus shown that the monoethyl ether of dihydroresorcinol can be utilized in the synthesis of *m*-arylalkylbenzenes. It would seem that the results should be the same in the preparation of the three dimethylbiphenyls possible by this method regardless of the order of use of the methylmagnesium bromide or tolylmagnesium bromide. However, it had been shown that the

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[7] Mulliken, *J. Chem. Phys.*, **7**, 14, 20, 121, 339, 353, 364, 570 (1939), has clearly stated the reverse effect of this in that the lowering of energy in the excited state leads to absorption toward the visible. This accounts for the bathochromic and conjugated effects. However, O'Shaughnessy and Rodebush (THIS JOURNAL, **62**, 2906 (1940)), who recognized a factor related to the elevation of the excited states in restricted biphenyls, seem to attribute the consequences of this to a lowering of the maximum extinction coefficient rather than to a shift of the absorption band into the ultraviolet region. Calvin (*J. Org. Chem.*, **4**, 256 (1939)) assumes that if a biphenyl has a hindrance to becoming planar the absorption of the biphenyl would be double (in maximum extinction coefficient) that of two independent benzenes (substituted).

[8] These ideas have been developed fundamentally on the assumption that the absorption band at 250 mμ of biphenyl is derived from the 255 mμ band of benzene. However, a number of other theories have been presented to explain this anomalous situation of the ultraviolet absorption spectra of biphenyl and the styrenes; the most prevalent (Doub and Vandenbelt, THIS JOURNAL, **69**, 2714 (1947)) and Wheland, "Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 151) of these has been the argument given in very brief form as follows. Benzene has two known regions of absorption in the ultraviolet, one near 200 mμ and the other at 255 mμ. The absorption band of biphenyl at 250 mμ is then the 200 mμ band of benzene shifted toward the visible. The bands of biphenyl which would correspond to the 255 mμ bands of benzene have either been shifted to the visible and "washed out" or are masked within the strong envelop of the 250 mμ band of biphenyl.

Much the same situation exists for the various methyl substituted styrenes. This can be explained by the ideas expressed within this footnote or alternately by the idea of the elevation of the first excited state as expressed in this paper. But the authors wish to point out that for most of the benzenoid substances whose spectra have been obtained in the 200 mμ region, the 200 mμ band remains (Carr and Stücklen, *J. Chem. Phys.*, **4**, 764 (1936)) and has not shifted toward the visible (or disappeared) but that a new band has appeared at the expense of the 255 mμ band.

TABLE III

3-SUBSTITUTED-Δ^2-CYCLOHEXENONES AND THEIR DERIVATIVES

	Ketones							2,4-Dinitrophenylhydrazone derivatives				
				Analyses, %					Analyses, %			
				Calcd.		Found			Calcd.		Found	
	Yield, %	B. p. °C.	Mm.	C	H	C	H	M. p., °C.	C	H	C	H
o-Tolyl-	41.4	132–132.5	0.2	83.87	7.52	83.88	7.50	151–151.5	62.29	4.91	61.93	4.90
m-Tolyl-	43.5	128–128.5	.2	83.87	7.52	83.90	7.49	127–128	62.29	4.91	62.52	5.10
p-Tolyl-	51.7	154	.5	83.87	7.52	83.85	7.51	228–229	62.29	4.91	62.40	5.07

TABLE IV

DIMETHYLBIPHENYLS

					Analyses, %			
					Calcd.		Found	
	Yield, %	B. p. °C.	Mm.	n^{25}_D	C	H	C	H
3,2′-Dimethyl-[a]	92.0	81	0.2	1.5490	92.32	7.70	92.89	7.60
3,3′-Dimethyl-[b]	93.3	108 (m. p. 9)	.2	1.5922	92.32	7.70	92.41	7.68
3,4′-Dimethyl-[c]	95.3	99–100 (m. p. 16–17)	.5	1.5984	92.32	7.70	92.39	7.71

[a] Schultz (*Ber.*, **17**, 471 (1884)) reports a b. p. of 270° at 760 mm. [b] Schlenk and Brauns (*Ber.*, **48**, 666 (1914)) report a b. p. of 280° at 760 mm. Muller and Topel (*ibid.*, **72**, 286 (1939)) report a b. p. of 270–290° at 760 mm. Neither reports a melting point. [c] Hey and Jackson (*J. Chem. Soc.*, 648 (1934)) report a b. p. of 284–287°. Kruber (*Ber.*, **65**, 1390 (1932)) reports a b. p. of 288–289° at 752 mm., m. p. of 14–15°, and n^{20}_D 1.59713.

TABLE V

DICARBOXYBIPHENYLS

			Analyses, %			
			Calcd.		Found	
	Yield, %	M. p., °C.	C	H	C	H
3,2′-Dicarboxy-[a]	68.9	216–216.5	69.46	4.13	69.60	4.10
3,3′-Dicarboxy-[b]	57.7	357–358	69.46	4.13	69.52	4.11
3,4′-Dicarboxy-[c]	65.4	336–337	69.46	4.13	69.53	4.10

[a] Sieglitz and Schatskes (*Ber.*, **54**, 2070 (1921)) report a m. p. of 213–214°. [b] Ullmann and Lowenthal (*Ann.*, **332**, 72 (1903)) report a m. p. of 352–354°. [c] Weiler (*Ber.*, **32**, 1063 (1899)) reports a m. p. of 339–341°.

reaction of dihydroresorcinol monoethyl ether with methylmagnesium bromide gives poor yields, while with phenylmagnesium bromide good yields are obtained. In this investigation the tolylmagnesium bromides gave good yields.

Figure 5 shows the ultraviolet curves of the three dimethylbiphenyls and again the following observations can be made which correspond with those made for the diaryl compounds: (1) the bathochromic effect of the *p*-methyl group and (2) the marked hypsochromic effect of the *o*-methyl group.

Acknowledgment.—The authors wish to acknowledge that this work was supported in part by a contract from the Office of Naval Research.

Experimental

Preparation of 3-(2-Xenyl)-Δ^2-cyclohexenone.—A Grignard solution of 2-xenylmagnesium iodide was prepared in the usual manner from 76.0 g. (0.27 mole) of 2-xenyl iodide, 6.0 g. (0.245 mole) of magnesium, and 75 ml. of dry ether. To this was added 36.4 g. (0.26 mole) of monoethyl ether of dihydroresorcinol in 25 ml. of dry ether. After completion of the reaction, the resulting solution was hydrolyzed with 10% sulfuric acid solution and steam distilled to remove biphenyl. After no further organic material appeared in the steam distillate (5 l.), the residue was extracted with ether, washed with sodium bicarbonate solution and water and dried over magnesium sulfate. After removal of the drying agent, the ether solution was reduced in volume and crystals of 3-(2-xenyl)-Δ^2-cyclohexenone were obtained on cooling. An analytical sample was prepared by sublimation. See Table II for the analytical and physical data.

The compounds XI, XII, XIII and XIV were prepared by essentially the same procedures as described in the previous papers[1] of this series. With exception of 1,3-di-(2-xenyl)-benzene (XIV) which could be prepared by only one route, the compounds were prepared by both possible routes as has been indicated in Table II. Comparison of melting points and mixed melting points was made for those compounds obtainable through two routes. Analytical and physical data are given in Table II.

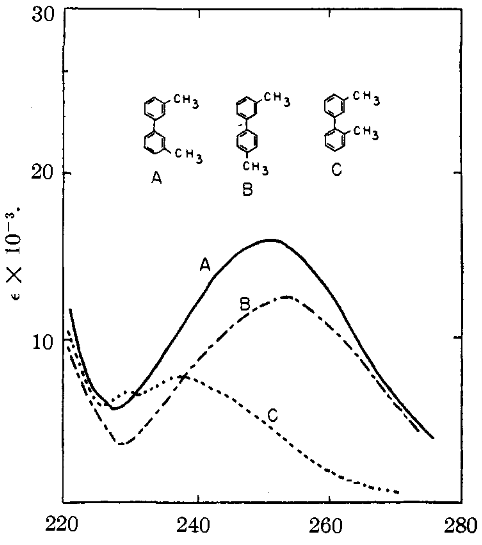

Fig. 5.

A typical procedure is the preparation of 1-(2-xenyl)-3-(4-xenyl)-benzene (XII). The organolithium derivative of 4-xenyl bromide was prepared in the usual manner from 0.5 g. of lithium, 18.5 g. of 4-xenyl bromide, and 30 ml. of dry ether. To this was added 10.0 g. of 3-(2-xenyl)-Δ^2-cyclohexenone in 10 ml. of dry ether. After completion of reaction, the resulting solution was hydrolyzed with 10% sulfuric acid and steam distilled until no further organic material appeared in the distillate. The residual material was extracted with ether, washed with sodium bicarbonate solution and water and dried over magnesium sulfate. After removal of the drying agent the ether solution was evaporated until crystals of the intermediate diene appeared on cooling. These were filtered and not purified further. Aromatization was effected by adding this compound to a refluxing mixture of 0.5 g. of 5% palladinized charcoal in 25 ml. of *p*-cymene. After refluxing two hours, as much *p*-cymene as possible was removed by distillation. A small amount of benzene (30 ml.) was added to the residue, the mixture was filtered, and the volume of solution reduced to about 15 ml. Approximately twice this volume of alcohol was added and the desired 1-(2-xenyl)-3-(4-xenyl)-benzene crystallized on cooling. The compound was recrystallized twice from a solution of alcohol and benzene. Analytical and physical data are given in Table II.

Preparation of 3-Tolyl-Δ^2-cyclohexenone.—An ethereal solution of the monoethyl ether of dihydroresorcinol was added to an ethereal solution containing an excess of the appropriate tolylmagnesium bromide. The Grignard addition complex was decomposed in the usual manner with dilute sulfuric acid and the whole subjected to steam distillation in order to remove unreacted bromotoluene and any Wurtz reaction product. Actually some loss by steam distillation of the ketone occurs in this step. The residue in the steam pot was extracted with ether, washed with water and dried over magnesium sulfate. After removal of the ether the residue was distilled under reduced pressure.

The *p*-tolyl-Δ^2-cyclohexenone is a solid and need not be distilled but may be easily crystallized from the ether solution after concentration. White crystals result on recrystallization from petroleum ether (30–60°). The analytical and physical data for the 3-tolyl-Δ^2-cyclohexenones are collected in Table III.

The 2,4-dinitrophenylhydrazones (red) of these ketones were prepared in the usual manner. See Table III for analytical and physical data.

Preparation of the Dimethylbiphenyls.—An ethereal solution of the 3-tolyl-Δ^2-cyclohexenone was added to an excess of methylmagnesium bromide in ether. The Grignard complex solution was hydrolyzed with dilute sulfuric acid. The ether layer was washed with water and dried over magnesium sulfate. After removal of the ether, the residue was distilled under reduced pressure.

cyclohexadiene-1,3	Yield, %	B. p. °C.	Mm.	n^{25}D
1-(*o*-Tolyl)-3-methyl-	83.3	85	0.06	1.5661
1-(*m*-Tolyl)-3-methyl-	87.2	100–101	.5	1.5885
1-(*p*-Tolyl)-3-methyl-	88.9	115–116	.2	1.5900

Aromatization to the dimethylbiphenyls was accomplished by refluxing the 1-tolyl-3-methylcyclohexadienes with palladium charcoal (5%) for three hours in the absence of a solvent. The aromatized product was distilled directly from the palladium–charcoal residue.

The dienes tend to polymerize; therefore, it is advantageous to aromatize as quickly as possible. It is interesting to note that these dienes and their aromatized products possess a very pleasing odor, especially *p*-tolyl-methylcyclohexadiene-1,3 and 3,4-dimethylbiphenyl. See Table IV for the analytical and physical data pertaining to the dimethylbiphenyls.

Preparation of the Dicarboxybiphenyls.—The dimethylbiphenyl was refluxed with 2% alkaline potassium permanganate solution. Mechanical stirring was used. The manganese dioxide sludge was removed by filtration, the filtrate heated to nearly boiling, and then acidified with sulfuric acid. On cooling crystalline dicarboxybiphenyl was obtained which was recrystallized from glacial acetic acid. For analytical and physical data, see Table V.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra were determined using a Beckman spectrophotometer. The solvent used was cyclohexane purified by successive extensive treatments with chlorosulfonic acid, concentrated sulfuric acid, alkaline permanganate solution, and final distillation from sodium.

Summary

1. 3-Phenyl-1-(2-xenyl)-benzene, 3-(4-xenyl)-1-(2-xenyl)-benzene, 3-(3-xenyl)-1-(2-xenyl)-benzene and 1,3-di-(2-xenyl)-benzene have been prepared.
2. The ultraviolet absorption spectra of a series of *m*-diaryl benzenes have been determined.
3. The 3,2′-, 3,3′- and 3,4′-dimethylbiphenyls and dicarboxybiphenyls have been synthesized from the monethyl ether of dihydroresorcinol. The ultraviolet absorption spectra of the above dimethylbiphenyls have been determined.
4. The theoretical significance of the ultraviolet absorption spectrum in relation to molecular structure is discussed.

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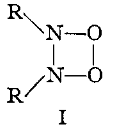
[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES]

The Crystal Structure of Dimeric Tribromonitrosobenzene

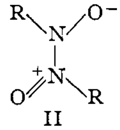
BY CHARLES P. FENIMORE

The problem of the structure of the C-nitroso dimers has not been completely solved. The presence of an N–N bond in the molecule is indicated because the N–N group occurs among the reduction products of one of the dimeric nitroso compounds (dimeric methyl-α-nitroso isopropyl ketone).[1] With this restriction, the only formulation of the molecule is[2]



I

or



II

and other resonance forms. It has been found that some nitroso dimers possess a permanent dipole moment in solution[3] and this observation has been offered as evidence against II under the assumption that II should be centro-symmetric; but since bulky R groups might forbid a center of symmetry in II, this evidence is inconclusive.

The principal cause of failure of a sure discrimination between these structures by classical chemical methods, particularly when R is aromatic, is the ready depolymerization of the dimers in solution. In their colorless crystals, however, C-nitroso compounds are always polymerized and therefore it has been possible to reach a decision by X-ray crystallography: the correct structure is II.

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(1) Aston, Menard and Mayberry, THIS JOURNAL, **54**, 1530 (1932).

(2) For a discussion of the C-nitroso dimers, see Sidgwick's "Organic Chemistry of Nitrogen," Oxford University Press, 1942, p. 213.

(3) Hammick, New and Williams, *J. Chem. Soc.*, 29 (1934).