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Preparation and Reactions of *o*-Dilithiobenzene

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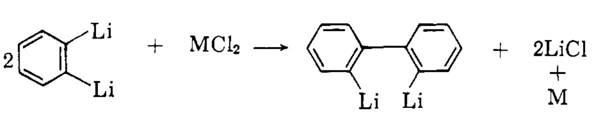
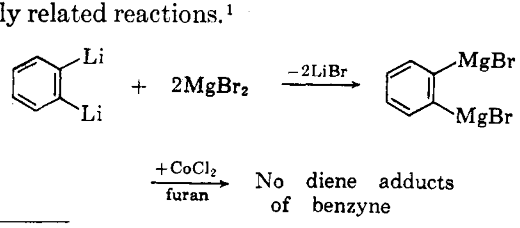
The preparation of *o*-dilithiobenzene from *o*-phenylenemercury is reported. The reactions of *o*-dilithiobenzene with chlorides of the first transition metal series leads to the formation of closed-chained *o*-phenylene compounds (diphenylene, triphenylene, tetraphenylene, etc.) and open-chained ones (diphenyl, *o*-terphenyl, *o*-quarterphenyl, etc.). The yields of these hydrocarbons vary with the transition metal used. Some characteristic properties of *o*-dilithiobenzene distinguish it from other aryllithium compounds.

The preparation of *o*-dilithiobenzene was first reported by G. Wittig and F. Bickelhaupt.[1] The reactions of *o*-dilithiobenzene with various compounds indicated that this valuable new organometallic compound contained two lithium cations bonded to the *o*-phenylene dianion, in itself remarkable since it contains two neighboring anionic carbon atoms. The compound in ether solution has a deep red color and could not be caused to crystallize from ether, but deposited red crystals from a mixed ether–tetrahydrofuran solvent. A number of transition metal chlorides were allowed to react with the new reagent and the resulting hydrocarbons separated and identified.

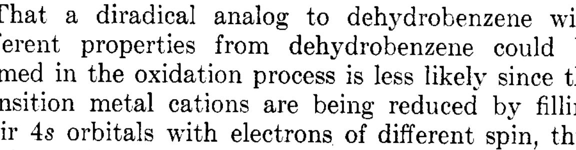
In the present study the remaining transition metal halides were brought to react with *o*-dilithiobenzene under comparable conditions. The possibility that *o*-dilithiobenzene in these reactions initially coupled to form 2,2′-dilithiobiphenyl could be excluded on basis of the very different yields of hydrocarbons obtained from the reactions of preprepared 2,2′-dilithiobiphenyl and the same transition metal halides.[2]



The intermediacy of dehydrobenzene tentatively was excluded because of the failure to isolate any dehydrobenzene adducts with the commonly used dienes[3] in closely related reactions.[1]

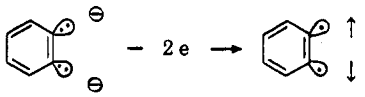


In the present work it was shown implicitly that free dehydrobenzene[4] can be excluded as a free intermediate in the reaction of *o*-dilithiobenzene with copper(I) and -(II) chlorides in the presence of 2,5-dimethylfuran or 1,3-diphenylisobenzofuran both of which have proved to be very effective dienes for capturing dehydrobenzene as intermediate. Both of these dienes are not readily



metalated by *o*-dilithiobenzene in contrast to either furan or cyclopentadiene. Copper salts were chosen for this study since only in these cases was there any isolated diphenylene.

That a diradical analog to dehydrobenzene with different properties from dehydrobenzene could be formed in the oxidation process is less likely since the transition metal cations are being reduced by filling their 4*s* orbitals with electrons of different spin, thus leaving a hypothetical nonexcited entity with paired electrons (benzyne).



The complete series of transition metal chlorides were allowed to react with *o*-dilithiobenzene in ether under comparable conditions. The reaction is stoichiometrically a redox process in which the transition metal cation acts as an oxidizing agent for the *o*-phenylene dianion.

The results of these studies are shown in Table I.

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[1] F. Bickelhaupt, Ph.D. thesis, University of Tübingen; G. Wittig and F. Bickelhaupt, *Chem. Ber.*, **91**, 883 (1958).

[2] G. Wittig and G. Lehmann, *ibid.*, **90**, 875 (1957).

[3] G. Wittig and L. Pohmer, *ibid.*, **69**, 1334 (1956).

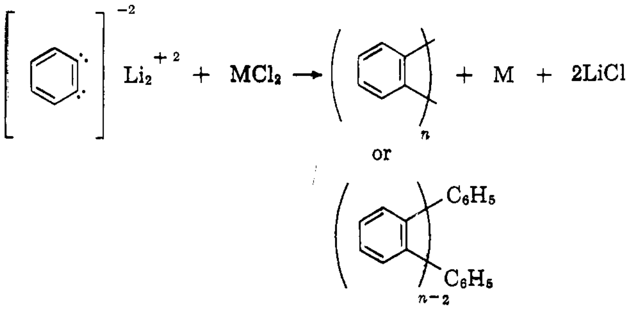
[4] Dehydrobenzene, C_6H_4, also commonly called "benzyne."

TABLE I

REACTIONS OF *o*-DILITHIOBENZENE WITH METAL CHLORIDES

Product[a]	Yields, %											
	Ti^{-4}	Ti^{+2} (1)	V^{+2}	Cr^{+3}	Mn^{+2}	Fe^{+2} (1)	Co^{-2}	Ni^{+2} (1)	Cu^{+2}	Ag^{+1} (1)	Pd^{+2}	Cu^{+1}
C_6H_6[b]	7		5		9		5		6	3	2	2
$C_6H_5C_6H_5$	8	4	15	18	13	26	7	18	2	4	14	22
$(C_6H_5)_2(o\text{-}C_6H_4)$				2		+	+[c]		4	5		7
$(C_6H_5)_2(o\text{-}C_6H_4)_2$		2	8	3		+	+		2	+		
$(C_6H_5)_2(o\text{-}C_6H_4)_4$					9	+				+		+
$(C_6H_5)_2(o\text{-}C_6H_4)_6$						+						
$(o\text{-}C_6H_4)_2$									3			
$(o\text{-}C_6H_4)_3$	18	14	2	14	15	10	26	3	24	15		12
$(o\text{-}C_6H_4)_4$			5				+	11	7	+	9	9
$(o\text{-}C_6H_4)_6$										+		+
$(o\text{-}C_6H_4)_8$							+	18		+		

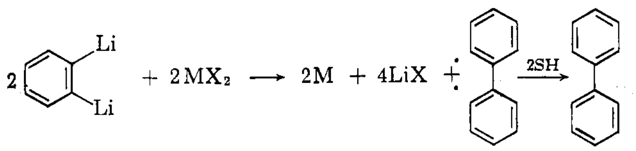
[a] Molar ratios of $n/2$, *o*-dithiobenzene to metal chloride, were used throughout unless otherwise noted (n is oxidation state of metal). [b] Benzene was not sought in all reactions; entries labeled (1) were taken over from ref. 1. [c] A yield of less than 1% is represented by +.



The following observations relative to the information contained therein were judged significant.

1. The yields of the various hydrocarbons appear to depend on the metal cation and the dependence is different from that observed from the same reactions of 2,2'-dilithiobiphenyl.[2]

2. Open-chained *o*-substituted polyphenyls containing the phenyl end groups resulted from the reactions previous to hydrolysis of corresponding organolithium reagents since the color test[5] was negative in all cases before hydrolysis was performed. This appears to be evidence for abstraction of hydrogen atoms from the solvent of an intermediate 2,2'-diphenyl diradical.



Biphenyl may partly have been the direct product from the reaction of phenyllithium, a possible impurity in the *o*-dilithiobenzene.[6] It is necessary, however, to consider the possibility that intermediate organometallic compounds, incapable of giving a positive color test, could have been formed and that these on hydrolysis give the open-chained hydrocarbons.

3. Cyclic *o*-phenylene compounds were formed in varying yields, the following being especially significant: Tetraphenylene was found in significant amounts from reactions with $NiCl_2$, $PdCl_2$, and CuCl whereas octaphenylene was the major product from the reaction with $NiCl_2$ only. Particularly high yields of biphenyl were found in reaction with $FeCl_2$ (also from 2,2'-dilithiobiphenyl). Diphenylene was detected only in the reaction with copper salts. If the relative yields of biphenyl and triphenylene are plotted for the metals Mn^{+2} ($3d^5$), Fe^{+2} ($3d^6$), Co^{+2} ($3d^7$), Ni^{+2} ($3d^8$), Cu^{+2} ($3d^9$), Cu^{+1} ($3d^{10}$), an alternating relationship appears to have been found between the number of electrons in the $3d$ level and the yields of these two hydrocarbons. However, such a relationship does not appear to hold throughout the series studied.

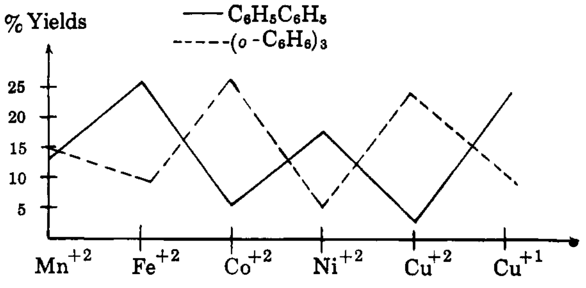


CHART 1

V^{+2} ($3d^3$) and Cr^{+3} ($3d^3$), Ni^{+2} ($3d^8$) and Pd^{+2} ($4d^8$), Cu^{+1} ($3d^{10}$) and Ag^{+1} ($4d^{10}$) show different yields, pairwise, although the number of d-electrons are alike in each pair. Hence the electronic configuration does not suffice to explain these observations. (See Chart 1.)

The formation of complexes of the ferrocene or the bisbenzene chromium type[7] was anticipated in the early study. It appears reasonable that not all the ten available electrons of the *o*-phenylene anion nor the eight electrons from the oxidized intermediate (six in the aromatic π-system and four or two in the sp^2-hybridization orbitals of the neighboring carbon atoms) can be accommodated readily in a stable sandwich compound. Counting sixteen electrons back from krypton one arrives at calcium, the chloride of which did not react with *o*-dilithiobenzene.[1] The nodal plane of the four electrons in thr sp^2-system is perpendicular to that of the aromatic system. A possible bis-*o*-phenylene anion metal complex would be difficult to visualize since the orbitals available for ligand bonding are fixed by the geometry of the benzene nucleus and not removed by two atoms, the general requirement for the formation of a chelate with a transition metal.

If a free diradical were the intermediate in these reactions, one would expect very similar results for the var-

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(5) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(6) M. S. Kharasch, D. W. Lewis, and W. B. Reynolds, *ibid.*, **65**, 498 (1943).

(7) See Chap. 7 and 8 in H. Zeiss, "Organometallic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1960.

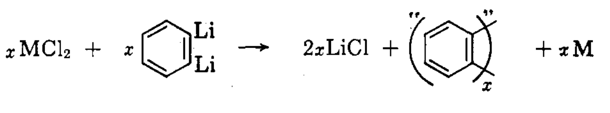
ious transition metals if it is assumed that the same steady state concentration of this intermediate is attained in these reactions. If phenyl radicals were formed to any considerable extent, then the major product would be benzene.[8] Neither of these possibilities are substantiated by the experiments.

An interpretation of these reactions is further complicated by the heterogeneity of the reaction mixture, both the salts and the metals are insoluble in ether. A local enrichment and subsequent coupling of intermediates partially bonded to the surface of the metal would be dependent on the crystalline structure of either the salt or the metal formed. A possible preference of open-chained polyphenyls can be rationalized by postulating a slow decomposition of organometallic intermediates to free radicals thus making the hydrogen atom abstraction from the solvent the chain terminating step.

A related mechanism was postulated in relating the products obtained from the reaction of 2,2′-dilithiobiphenyl with transition metal halides.[2]

The formation of tetraphenylene and octaphenylene in reaction of particular transition metal halides can be ~~considered analogous~~ to the catalytic action of certain nickel complexes in the tetramerization of acetylene to cyclooctatetraene.[8] In these reactions a coordination complex is considered intermediate to the formation of the ring compound.[9] The tempting analogy of a similarly coordinated complex of four dehydrobenzene molecules (formally containing one bent acetylenic bond each) must be considered with reservation since tetraphenylene should predominate as a product of the reaction with nickel salts, a reaction which leads predominantly to octaphenylene. The possible formation of a complex containing two central metal atoms each coordinated to four dehydrobenzene molecules as a route to octaphenylene is only speculative.

A connection between the oxidation potential of the transition metal and product distribution was sought.



The better a metal can function as a reducing agent, the poorer will be the oxidizing power of the metal cation. Thus, the lower the reduction potential of the metal cation the slower one would expect the reaction to proceed and the higher would be the probability for dissociation of intermediate complexes with the subsequent hydrogen atom abstraction from the solvent and the higher the yields of the open-chained compounds. There exists no apparent relation between the reduction potentials and the ratio of open-chained to closed-chained polyphenyls isolated. A dependence of the yields on the presence of lithium halide was observed in the reaction of 2,2′-dilithiobiphenyl with transition metal halides. The effect was studied in the comparable reactions of *o*-dilithiobenzene but no significant effect could be ascertained.

It has been observed that compounds containing organic radicals linked by σ-bonds to a metal such as chromium can be isolated if tetrahydrofuran is used as the solvent. The compounds accommodate one or several molecules of tetrahydrofuran in their coordination spheres.[7] A series of experiments was hence undertaken to attempt the isolation of a complex of the *o*-phenylene dianion coordinated to a metal and tetrahydrofuran. However, the unusual metalating powers of *o*-dilithiobenzene toward tetrahydrofuran made the preparation of *o*-dilithiobenzene in tetrahydrofuran impracticable. It was, however, possible to prepare *o*-dilithiobenzene in ether, remove the ether by distillation, and dissolve the compound in tetrahydrofuran. Reactions of the thus prepared solutions of *o*-dilithiobenzene with nickel chloride gave product distributions entirely different from that observed for the same reaction in ether; neither octaphenylene nor tetraphenylene could be found. This indicates that tetrahydrofuran contains a more strongly liganding oxygen than does ether, and it appears that the solvent molecules displace the weakly bonded *o*-phenylene dianion from the intermediate complex resulting in the much higher yields of simple lower molecular weight fragments. This effect may be coupled with the higher acidity of the α-hydrogen atoms in tetrahydrofuran.

The reactions of *o*-dilithiobenzene with *cis*-dichlorobis(triphenylphosphine)platinum(II) were performed in the hope of isolating a platinum complex of benzyne similar to the acetylene platinum complexes recently prepared by J. Chatt and co-workers.[10] Instead of the expected product there was obtained a mixture of triphenylphosphine platinum complexes.[11]

$$o\text{-C}_6\text{H}_4\text{Li}_2 + (\text{Ph}_3\text{P})_2\text{PtCl}_2 \longrightarrow (\text{Ph}_3\text{P})_n\text{Pt} + 2\text{LiCl}$$

The plausible intermediacy of benzyne was demonstrated in the reaction of *o*-dilithiobenzene with *p*-bromoanisole. The prime interest in this reaction was concerned with the estimation of the metalating power of *o*-dilithiobenzene. Unusual metalating powers were not observed, neither from the attempted metalation of *p*-bromoanisole in the position *ortho* to the methoxyl group nor in the attempted metalation of diphenylmethane. It was significant, however, to observe the new route to benzyne *via* halogen–metal interconversion. The expected products were found and are shown in Chart 2 (p. 1736).

Experimental

Preparation of *o*-Phenylenemercury.—Sodium amalgam was prepared in a 500-ml. Schlenk tube, preferably of soft glass, since in the latter type glass it was noticed that, after the reaction, the mercury separated more readily as a liquid instead of as a colloidal suspension. To the nitrogen-filled Schlenk tube was added 50 ml. of pure mercury (680 g., 3.4 g.-atoms). The Schlenk tube was heated to *ca.* 50° and 7 g. (0.305 g.-atom) of sodium, cut into pea-size cubes, was added slowly. The exothermic amalgamation procedure provided sufficient heat to proceed to completion without further external heating. The tube was allowed to cool to room temperature before 28.4 g. (0.12 mole) of *o*-dibromobenzene and 150 ml. of ether were added. The Schlenk tube was then sealed under nitrogen and shaken for 5 days. At the end of this time, the tube was opened under nitrogen and 50 ml. of water was added carefully. If on shaking the tube gently the mercury separated readily from the yellow suspension, the work-up was performed according to method 1. However, if a gray colloidal suspension resulted, then the work-up proceeded according to method 2.

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(8) W. Reppe, *et al.*, *Ann.*, **560**, 5636 (1957).

(9) T. L. Cairns, *et al.*, *J. Am. Chem. Soc.*, **74**, 5636 (1953).

(10) J. Chatt, G. A. Bowe, and A. A. Williams, *Proc. Chem. Soc.*, 208 (1957); J. Chatt, R. G. Guy, and H. R. Watson, *J. Chem. Soc.*, 2332 (1961).

(11) L. Malesta and C. Carrello, *ibid.*, 2323 (1958).

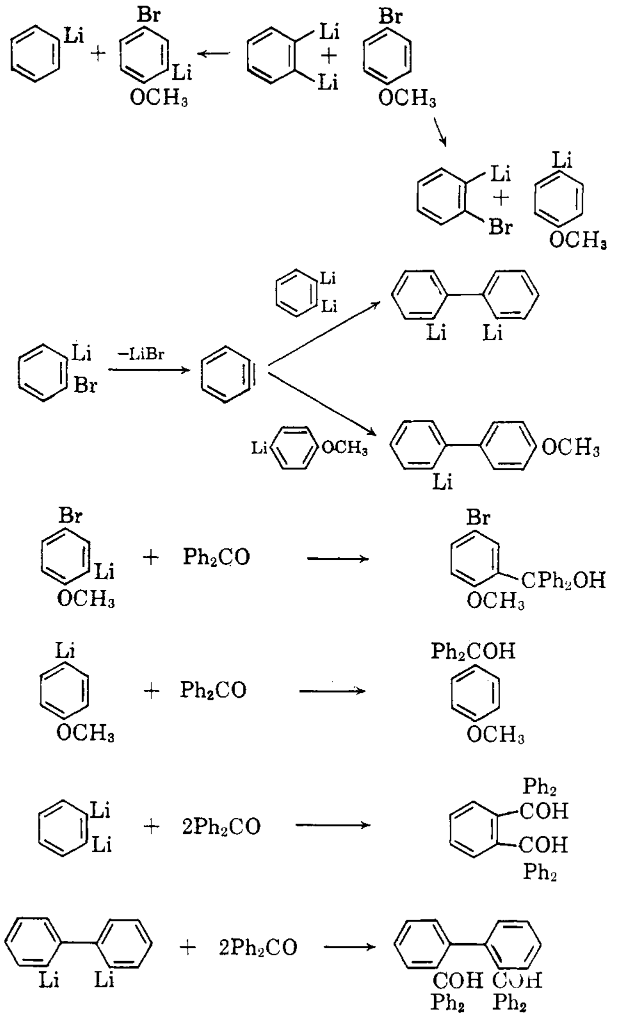

CHART 2

Method 1.—The contents of the Schlenk tube were transferred to a separatory funnel and the mercury removed. The organic and aqueous phases were filtered; solid remaining was washed with water and ether and dried at 80° for 2 hr. This solid was divided in four equal portions and each portion successively placed in 250-ml. round-bottomed flask fitted with a vibro-mixer, N-methylpyrrolidone (100 ml.) was added to the flask and the slurry extracted at 120° for 10 min. under violent agitation. The contents of the flask were decanted into a centrifuge tube and the process repeated with the other portions of crude product. The last traces of mercury were removed by centrifuging these suspensions and the red-brown mother liquors were combined and mixed slowly with 200–300 ml. of methanol, which caused the precipitation of the finely divided *o*-phenylenemercury. This was removed by filtration and the mother liquors concentrated *in vacuo*. The purer fractions thus obtained were combined and recrystallized from dimethylformamide. The product crystallized in small thin needles and was dried at 100° for 24 hr. in a slow current of air. Product melted with decomposition at 332–334°.

Anal. Calcd. for C_8H_4Hg: C, 26.04; H, 1.46. Found: C, 26.24; H, 1.79.

Method 2.—The colloidal suspension was isolated on a filter paper and dried in the air. It was transferred to a cloth which was folded around it and squeezed until no more mercury passed through it. The solid remaining was then treated as described in method 1.

Preparation of *o*-Dilithiobenzene.—Standard solutions of *o*-dilithiobenzene were prepared immediately before the organometallic compound was needed. A 200-ml. Schlenk tube was cleaned with chromic acid cleaning solution and distilled water before drying. The tube was then dried hot by evacuating and filling it three times with purified nitrogen. A few glass splinters were added and 5 g. of *o*-phenylenemercury (sufficient to yield 18 mmoles of *o*-dilithiobenzene). The tube was evacuated still another time to remove the air entrained in the fluffy precipitate. The ether to be used was heated under reflux in the presence of sodium and a trace of benzophenone until the formation of benzophenone ketyl changed the color of the solution to deep blue. The ether then was distilled and kept in the dark over freshly pressed sodium. To the tube being swept by a slow current of nitrogen was then added 50 ml. of ether and 2.6 g. (0.38 g.-atom) of freshly pressed lithium. The lithium was pressed into bands, from a heated sodium press lubricated with a few drops of mineral oil, and cut into short sections falling directly into ether. Another 60 ml. of ether was added after complete transfer of the lithium. The Schlenk tube was sealed under nitrogen and shaken for 4 days. After the elapse of 1 day a brown color was noticed and on complete reaction a deep red solution only containing suspended black mercury and lithium was obtained. It readily may be established whether unchanged *o*-phenylenemercury is present since any such compound can readily be seen as suspended crystals. The agitation should be continued if any such crystals are seen.

Such solutions were analyzed for organolithium content by the method of double titrations (using methyl iodide) according to a published procedure.[12] Agreement was found between the results found by determination of the remaining alkali and subtracting this from the total alkali obtained on simple hydrolysis and the results obtained on determination of the iodide content by the Volhard procedure. The content of *o*-dilithiobenzene was 80–90% of the theoretical not allowing for any volume changes during the formation of the solution of the organometallic compound.

Reaction of *o*-Dilithiobenzene with Transition Metal Halides. General Procedure.—The reactions were performed under comparable conditions by decanting the solution of the organometallic compound through a glass-wool plug in a short section of Teflon tubing connecting the Schlenk tube[13] in which *o*-dilithiobenzene had been prepared with the nitrogen-filled Schlenk tube in which the reaction was to take place. This tube had been dried carefully in advance and the salt (for molar ratios see *a* of Table I) had been introduced and was agitated under 10–20 ml. of dry ether by means of a magnetic stirrer. The reaction vessel was being cooled to −30° in a dry air acetone bath. The reaction usually commenced in the cold, as was evident from darkening of the precipitate and the solution. After 1 hr. at −30° the stirred reaction mixture was allowed to heat to room temperature and color test 1[5] was taken. In most cases it was positive and the tube was sealed under nitrogen and shaken for 1–3 days before the color test was negative, indicating the absence of organolithium compounds.

Work-up was performed in all cases by hydrolysis (in an atmosphere of nitrogen) with water until no more gas was liberated. The solids were removed by filtration and washed on the filter with ether and water before drying. The solids were then placed in the thimble of a Soxhlet extractor and extracted with hot benzene for 5–10 hr. The extracts were concentrated and the oil remaining sublimed *in vacuo* at various temperatures. Only in the case of copper(II) chloride were there any significant yields of hydrocarbon. The organic layer of the filtrates was separated and dried over calcium chloride. This solution was then concentrated to *ca.* 10 ml. and an equal volume of benzene-free ethanol was added. The contents were then transferred to a smaller flask and fractionally distilled to collect any benzene–ethanol azeotrope in the middle fraction. This fraction, and the other ones, for safety, were analyzed for trace amounts of benzene by vapor phase chromatography (v.p.c.). Any irregularities in experimental procedure which could have led to introduction of water would thus have been readily recognizable.

The remaining oil was then evacuated to remove traces of ethanol and triturated with petroleum ether, b.p. 60–70°, before a second removal of the solvent. The oil remaining was then extracted with petroleum ether, b.p. 60–70°, and the extracts passed through a 25-cm. column containing *ca.* 50 g. of neutral alumina. Petroleum ether, b.p. 60–70°, was used as eluent until no more movement of the adsorption bands were noticed. The substance insoluble in petroleum ether was then extracted with cyclohexane (or a mixture of cyclohexane and benzene, 9:1) and these extracts passed through the same column. The chromatogram was developed by the use of cyclohexane, cyclohexane–benzene (9:1), benzene, chloroform, ethyl acetate, and ethanol as eluents. In most cases there was obtained several fractions of triphenylene contaminated with other hydrocarbons. These fractions were extracted with petroleum ether, b.p. 60–70°, and

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(12) R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 353 (1951).

(13) See E. Müller, Houben-Weyl, "Methoden d. Org. Chem." I/2, G. Thieme, Stuttgart, 1959, p. 340.

the extracts rechromatographed, eluting with petroleum ether, cyclohexane, cyclohexane–benzene (9:1), and benzene. The pure hydrocarbons were often obtained from this procedure. *The fractions of triphenylene remaining after extraction with* petroleum ether were recrystallized from ethanol. In some cases the fractions did not dissolve completely in the solvent, and the insoluble residues were often identified as trace amounts of octaphenylene, m.p. 423–425°, presumably swept along with triphenylene.

Reaction of *o*-Dilithiobenzene with Titanium(IV) Chloride (2:1).—The general procedure was followed, no vigorous reaction occurred and the color test[5] was positive even after the reaction mixture had been allowed to heat to room temperature. The Schlenk tube was sealed and shaken. After 16 hr. of agitation the tube was opened and the color test of the black suspension found to be negative. From the ether phase of the work-up there was obtained by azeotropic distillation with ethanol a fraction which, by v.p.c. analysis, was found to contain benzene amounting to 7% of that expected for the total conversion of *o*-dilithiobenzene to benzene. The residue from the azeotropic distillation was evacuated and intermittently slurred with petroleum ether (b.p. 60–70°). Chromatography from neutral alumina yielded the compounds shown in Table I.

Part of the triphenylene was recovered as the 2,4,7-trinitrofluorenone complex.

Reaction with Vanadium(II) Chloride.—A sample of this green compound was dried by heating it under refluxing thionyl chloride for 5 hr., followed by removal of the volatile components, and by finally drying for 4 hr. at 95° and for 6 hr. at 130° *in vacuo*.[14] The reaction of 2.44 g. (20 mmoles) of this salt with *o*-dilithiobenzene (18 mmoles) was carried out under normal conditions. The color test of the reaction mixture was negative after 40 hr. However, a difference in the green color usually obtained in positive color test was observed to develop slowly on addition of the iodine in acetic acid solution. For this reason a titration of the reaction mixture was performed (using methyl iodide instead of benzyl chloride in the double titration method) and it was found that no C–Li was present. The usual work-up gave the indicated yields of aromatic hydrocarbons.

Reaction with Manganese(II) Chloride.—Manganese(II) chloride was dried under refluxing thionyl chloride and then heated *in vacuo*.[14] The dried salt was cream colored, and finely divided; 2.5 g. (20 mmoles) was allowed to react in a Schlenk tube with 18 mmoles of *o*-dilithiobenzene with 10 ml. of ether. The reaction mixture turned brown and the color test was negative after 16 hr. agitation in the closed Schlenk tube. A strong evolution of heat and/or gas was caused by the hydrolysis. The layers were filtered and the organic phase fractionated as usual with ethanol. V.p.c. analysis indicated the presence of benzene. Careful elution chromatography yielded compounds shown in Table I.

Reaction with Cobalt(II) Chloride.—The cobalt chloride to be used was prepared from cobalt(II) chloride hexahydrate which was placed in a 100-ml. round-bottomed flask into which was distilled thionyl chloride. The apparatus was protected from the atmosphere by a calcium chloride tube. When sufficient thionyl chloride had collected and the flask reached room temperature, then it was equipped with a reflux condenser and the thionyl chloride heated until it refluxed briskly. The cobalt(II) chloride was heated for 4 hr. at which time the evolution of the hydrogen chloride and sulfur dioxide has subsided. The thionyl chloride was removed by distillation and the solid remaining in the flask was dried *in vacuo* (0.1 mm.) for 4 hr. at 120°. The flask was then evacuated and filled with dry nitrogen three times to remove the last traces of thionyl chloride. The lithium chloride used was dried by heating it to 100° for 16 hr. *in vacuo*.

Molar Ratio 1:1.—The reaction was performed as described under the general procedure. An immediate blackening of the light blue suspension resulted. At room temperature there was obtained a brown solution above a black precipitate. The reaction mixture was sealed off and agitated for 3 days at which time the color test was negative. The reaction mixture was hydrolyzed and worked up as described previously. The yields obtained differed insignificantly from those obtained by Bickelhaupt.[1]

Excess Cobalt(II) Chloride.—The reaction was performed as discussed under **Molar Ratio 1:1** but 9.35 g. (72 mmoles, threefold excess) of cobalt(II) chloride was used. The color test was negative after 2 hr. at room temperature and two chromatograms gave the indicated yields(Table II).

TABLE II

Product	Yield, %	M.p., °C.
Benzene	6	
Biphenyl	8	66–67
o-Terphenyl	14	53–54
Triphenylene	15[a]	191–192

[a] This yield was increased by 3% by obtaining from the many colored and oily fractions a complex with 2,4,7-trinitrofluorenone from benzene, m.p. 230–231°. That this complex consisted of a 1:1 mixture of complexing agent and triphenylene was shown by the obtainment of the latter by chromatography.

Molar Ratio 1:1 Containing 1 Mole Lithium Chloride.—To 2.6 g. (20 mmoles) of cobalt(II) chloride was added 0.77 g. (18 mmoles) of lithium chloride and 15 ml. of ether. The suspended salts were allowed to react with *o*-dilithiobenzene under the same conditions as described previously. The results shown in Table III do not differ significantly from those reported previously.

TABLE III

Product[a]	Yield, %	M.p., °C.
Benzene	5	. . .
Biphenyl	8	68–69
Triphenylene	17	188–189
Octaphenylene	4	423–424

[a] In some cases *o*-terphenyl did not crystallize. The yields of noncrystalline *o*-terphenyl are not reported.

Reaction with Copper(I) Chloride. Ratio 2:1.—Copper(I) chloride was washed with several portions of sulfurous acid and then with glacial acetic acid until the washings were colorless. The solid was then dried in the air until the odor of acetic acid had disappeared and then *in vacuo* at 120° for 6 hr. The reaction proceeded in a manner very similar to that observed for copper(II) chloride and a negative color test was obtained after 24-hr. reaction at room temperature (Table IV).

TABLE IV

Product	Yield, %	M.p., °C.
Benzene	2	
Biphenyl	22	59–60
o-Terphenyl	7	Impure oil
o-Quarterphenyl	1	115–117
Diphenylene	2	111–112
Triphenylene	12	190–191
Tetraphenylene	9	230–231
Hexaphenylene	Trace	325–330

Reaction of Copper(II) Chloride with *o*-Dilithiobenzene (1:1).—The salt was dried as described under **Cobalt Chloride** using thionyl chloride. The reaction was performed under the usual conditions to give a light green precipitate under a brown solution. The color test was negative after 3 days of shaking. Hydrolysis yielded a precipitate of finely divided copper. The diphenylene was characterized by mixture melting point, infrared spectroscopy (superimposability of a reference spectrum), and melting point and mixture melting point of its red picrate, m.p. 116–118°.

Reaction with Silver Chloride.—Silver(I) chloride was dried at 110° for 4 hr. *in vacuo* and 5.8 g. (40 mmoles) hereof was allowed to react under standard conditions herewith (Table V).

TABLE V

Products	Yield, %	M.p., °C.
Benzene	3	. . .
Biphenyl	3	59–60
o-Terphenyl	10	53–55
Tetraphenylene	3	228–229
o-Quarterphenyl	1	110–116

Reaction with Chromium(III) Chloride.—The reaction was performed as described under general procedure using 2.5 g. (15.8 mmoles) of chromium(III) chloride and 18 mmoles of *o*-

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(14) The drying procedures were generally those recommended by G. Brauer, "Handbuch d. Präparativen Anoganischen Chemie," I and II, F. Enke, Stuttgart, 1960.

dilithiobenzene. The chromium(III) chloride was purified by heating it in concentrated hydrochloric acid until the reaction discontinued and then it was dried after washing with distilled water *in vacuo* at 200° for 6 hr. The reaction with *o*-dilithiobenzene proceeded in the cold (−30°) to give a dark brown suspension but since the color test was not negative after 1 hr., the tube was sealed and shaken for 3 days after which time the color test was negative. A gas was evolved during the hydrolysis. The following reactions were performed in addition to those shown in Table I using the same general procedure.

Reaction with Palladium(II) Chloride.—The standard reaction of 18 mmoles of *o*-dilithiobenzene with 3.5 g. (18 mmoles) of dry palladium chloride was performed. The color test was found to be negative after 3 days. A very large fraction of an unidentifiable brown oil (15% yield by weight) was obtained in addition to the compounds shown in Table VI.

TABLE VI

Product	Yield, %	M.p., °C.
Benzene	2	. . .
Biphenyl	14	59–60
Tetraphenylene	9	230–231

Reaction with Thallium(I) Chloride.—The salt was dried at 130° *in vacuo* and 9.6. g. (40 mmoles) thereof was allowed to react under the usual conditions with *o*-dilithiobenzene (18 mmoles). Color test 1 was negative after 16 hr. A voluminous precipitate was obtained. Since extraction with benzene caused some apparent decomposition noted by the separation of metallic thallium, the extraction was performed under milder conditions over a water bath. The extracts were concentrated to give a precipitate which did not dissolve in benzene after standing overnight in the air. The experiment was repeated and the precipitate, in part obtained by extraction with hot dioxane, was allowed to stand under petroleum ether, b.p. 60–70°. After repeated recrystallizations from a mixture of chloroform and ethanol (20:1), there was obtained a solid which decomposed with gas evolution at 145° and which at its point of decomposition yielded a needle-like product which itself decomposed to a brown liquid at 180–185°.

Anal. Found: C, 85.31; H, 7.61.

Reaction with Copper(II) Chloride in the Presence of 2,5-Dimethylfuran.—The reaction was performed as described previously by the addition of *o*-dilithiobenzene (18 mmoles) to a slurry of 2.8. g. (20 mmoles) copper(II) chloride in 7.5 ml. (69 mmoles) of 2,5-dimethylfuran maintained at −30° (the furan had been distilled under nitrogen from sodium directly into the reaction vessel). The reaction mixture underwent color changes similar to those observed for the same reaction in the absence of the furan. The color test was negative after 2 hr. reaction at room temperature. The usual work-up yielded the compounds shown in Table VII. None of the adduct was isolated or could be detected by its characteristic odor.

TABLE VII

Compound	Yield, %	M.p., °C.
Benzene	8	. . .
Biphenyl	10	70–72
Triphenylene	8	193–194
Tetraphenylene	17	229–230
o-Terphenyl	1	57–58
o-Quarterphenyl	1	115–117

Reaction with Copper(II) Chloride in the Presence of 1,3-Diphenylisobenzofuran.—A sample of 1,3-diphenylisobenzofuran was purified by recrystallization from cyclohexane, m.p. 131–133°. A slurry of this compound (4.86 g., 18 mmoles) and copper(II) chloride (2.8 g., 20 mmoles) in 20 ml. of ether was placed in the reaction Schlenk tube and the *o*-dilithiobenzene in ether was added to the reaction vessel cooled to −60°. The color test was negative after a reaction time of 1 hr. and heating to room temperature during a second hour. The reaction mixture was worked up essentially as before with the difference that basic alumina was used to prevent decomposition of a possible dehydrobenzene adduct. The precipitate consisting of inorganic and organic substances was filtered and washed with excess ether. The ether layer was worked up as usual by azeotropic distillation and chromatography. The precipitate from the reaction mixture was extracted with benzene, this solution was concentrated, and cyclohexane was added. The material which separated on standing for 16 hr. (1.2 g., m.p. 110–115°) was chromatographed to give 0.5 g. of diphenylisobenzofuran (m.p. 126–128°) and 0.62 g. of *o*-dibenzoylbenzene (m.p. 141–144°). The ether solution on concentration after fractionation gave a yellow substance of considerable melting range. The solid was dissolved in benzene and air was passed through it to oxidize the unchanged 1,3-diphenylisobenzofuran to *o*-dibenzoylbenzene (m.p. 141–142°). The compounds isolated are indicated in Table VIII.

TABLE VIII

Compound	Yield, %	M.p., °C.
Benzene	6	. . .
Biphenyl	6	60–62
o-Terphenyl[a]	10	. . .
o-Quarterphenyl	3	115–117
Triphenylene	9	189–190
Tetraphenylene	13	221–232
Hexaphenylene	1	336–338
o-Dibenzoylbenzene	58	141–142

[a] In some cases *o*-terphenyl did not crystallize. The yields of noncrystalline *o*-terphenyl are not reported.

Reaction of Dehydrobenzene with 1,3-Diphenylisobenzofuran.—To substantiate that the proper isolation procedure was used the reaction of dehydrobenzene, prepared by an independent route, with diphenylisobenzofuran was carried out as a control experiment. To a solution of *o*-bromofluorobenzene (1.05 g., 6 mmoles, freshly distilled, 92–94° at 70 mm., n^{20}_{D} −1.5335) and diphenylisobenzofuran (1.6 g., 6 mmoles) in 40 ml. of ether and 20 ml. of tetrahydrofuran was added predried magnesium turnings. The reaction was allowed to proceed at room temperature for 2 hr. and at the boiling point of the solution for 1 hr. After standing for 16 hr. at room temperature, 100 ml. of benzene was added. Concentration after washing with a solution of ammonium chloride (saturated) and drying gave 2.06 g. of a crude product, m.p. 187–188°. One half of this compound (1.0 g.) was dissolved in benzene and oxidized for 12 hr. in a current of air. Chromatography yielded 9,10-diphenyl-9,10-dihydroanthracene-endoxide-9,10 (0.65 g., 62%) and *o*-dibenzoylbenzene (0.24 g., 16%).

Preparation of Dichlorobis(triphenylphosphine)platinum(II).—The complex was prepared according to a published procedure[11] by agitation of a mixture of 5.2 g. of triphenylphosphine and 4.16 g. of potassium tetrachloroplatinate(II) in 100 ml. of 50% aqueous alcohol for 24 hr. The compound was purified by washing it on the filter with excess ether, to remove triphenylphosphine, and with ethanol–water to remove excess inorganic materials, and finally with ether to aid the drying process. The sample was dried *in vacuo* at 80–100° for 16 hr. A sample of this complex (m.p. 308–312° dec.) was analyzed without further purification.

Anal. Calcd. for $C_{36}H_{30}P_2PtCl_2$, $(Ph_3P)_2PtCl_2$: C, 54.68; H, 3.82. Found: C, 54.97; H, 3.85.

Reaction of Dichlorobis(triphenylphosphine)platinum(II). In Benzene–Ether I.—A solution of *o*-dilithiobenzene (prepared from 4.05 g., of *o*-phenylenemercury) in 65 ml. of benzene containing 7 ml. of ether was prepared. The reaction was followed by titrating 3-ml. aliquots by the double titration method.[12] The total solution containing 7.5 mmoles of *o*-dilithiobenzene was added to a suspension of dichlorobis(triphenylphospine)platinum(II) in benzene. The reaction mixture liberated heat and the color of the solution changed from red to brown. The color test was negative after 1 hr. but the reaction mixture was agitated for an additional 4 hr. No care was taken in this experiment to isolate the reaction products in the absence of the atmosphere. There was isolated 2.34 g. of a solid which was partly lithium chloride. The inorganic salt was removed by washing with ethanol and water. The washings were combined, diluted to volume, and aliquots were titrated for chloride content. A total of 12 out of a possible 15 mmoles of lithium chloride was found (80%). Innumerable unsuccessful attempts were made to bring this compound to crystallization. There was obtained a recovery of 1.16 g. of the dichlorobis(triphenylphosphine)platinum(II) (an excess of 1.20 g. of the platinum complex had been present). The brown residues did not yield any crystalline compounds on treatment with the common organic solvents. The amorphous powder obtained from treatment with ethanol was soluble in chlorinated solvents to give dark red solutions. The brown amorphous fractions (m.p. 120–130°) underwent no observable change on boiling with pyridine, piperidine, 5% aqueous sodium hydroxide, dilute acids, or a solution of diphenylisobenzofuran. Heating of the crude product with thiourea (which combines preferentially with any platinum chlorides present) in benzene–ethanol (1:5) gave a product of similar appearance.

Another sample (0.5 g.) of the product was heated for 2 hr. in boiling concentrated hydrochloric acid. The solid was filtered and washed with ethanol. The filtrates were combined and fractionally distilled. There was found no benzene by v.p.c. in any of the fractions collected. The gray precipitate was recrystallized to yield 0.39 g. (80% recovery) of dichlorobis(triphenylphosphine)platinum(II). The various mother liquors and the filtrate from the crude reaction mixture were evaporated to dryness *in vacuo*, slurred with benzene–cyclohexane (1:7), and chromatographed from 200 g. of alumina. There was obtained the following compounds: triphenylene (partly isolated as the trinitrofluorenone, complex), 17 mg., m.p. 195–196°; various oils, 71 mg.; and triphenylphosphine oxide, 0.90 g., m.p. 154–155°. A red lacquer, m.p. 115–120° dec., was also obtained. The infrared spectrum of the crude but dry product tentatively indicated the presence of *o*-substituted aryl groups in the 600–900-cm.$^{-1}$ region as shoulders on the two monosubstituted phenyl out-of plane deformation absorptions.

In Benzene–Ether II.—The reaction between 6 mmoles of platinum complex (recrystallized from chloroform) and a benzene solution of *o*-dilithiobenzene (analyzed to contain 5.9 mmoles) was carried out as described in I. The reaction vessel, however, was in case a double Schlenk tube containing a fine fritted glass plug between the two compartments.[13] The appearance of the reacting mixture was the same as described under I. The benzene slurry was cooled to −60° and the Schlenk tube sealed *in vacuo*. On thawing the frozen reaction mixture and cooling the second compartment it was possible to filter the solution into the other compartment. Distillation of the benzene solvent of the filtrate was accomplished and the noncrystalline residue from removal of the solvent was agitated with freshly distilled ether. The ether was removed from the dark amorphous residue and carbon monoxide was passed through a furan suspension of this residue. The reaction mixture was freed from solvents and chromatographed by preferential solution, elution chromatography. Several unidentifiable red lacquers were obtained but none of the expected 1,4-dihydronaphthalene-endoxide-1,4 could be detected.

The precipitate which had been obtained by filtration of the original reaction mixture was suspended in the benzene solvent, distilled by cooling the receiver back into the reaction vessel, filtered, and the precipitate was washed with benzene and chloroform to give a benzene- and a chloroform-soluble fraction. From the benzene washings was obtained on evaporation of the solvent and trituration with ethanol, a brown, amorphous solid (0.515 g., m.p. 168–180° dec.). Chloroform washings gave, on fractional crystallization, 3.47 g. of dichlorobis(triphenylphosphine)platinum(II), m.p. 305–307°, identified by comparison of infrared spectra between the sample thus obtained and the starting material. The precipitate from these washings consisted mainly of lithium chloride which was dissolved in ethanol–water, diluted to volume, and aliquots were analyzed to give a total liberation of 11.7 mmoles of lithium chloride (theory, 11.8 mmoles not considering the recovery of 3 mmoles platinum complex, see discussion).

In Ether III.—An ether solution of *o*-dilithiobenzene (prepared from 2.76 g., of *o*-phenylenemercury) was analyzed and part of the solution (containing 4 mmoles of *o*-dilithiobenzene) was added to 3.2 g. (4 mmoles) of dichlorobis(triphenylphosphine)platinum(II) which had been recrystallized from chloroform and heated under refluxing petroleum ether (b.p. 60–70°) for 6 hr. before drying *in vacuo* for an additional 12 hr. at 50°. The reaction did not proceed rapidly at room temperature. The Schlenk tube was sealed off and, after 14 hr. of agitation, the tube was opened and the color test found to be negative. The precipitate was collected on the filter paper under nitrogen and dried in the dark *in vacuo* after successively evacuating the desiccator and filling it with nitrogen. A sample of this solid (m.p. 162–168° dec.) was exposed to the atmosphere and the melting point observed with 24-hr. intervals; there was no significant change in decomposition point. There was found practically no lithium chloride in the ether solution from the filtration of the crude solid. From the filtrates there was obtained two fractions of solids, m.p. 152–154° and 121–123°, respectively. The precipitate (2.66 g.) was extracted with 200 ml. of hot chloroform. These extracts produced 1.03 g. (30% recovery) of unchanged platinum complex. The precipitate from the chloroform extracts yielded 5.2 mmoles of lithium chloride (65%) on extraction with ethanol–water and analysis as before. The chloroform extracts were concentrated and ether was added to give several fractions of brown amorphous solids (m.p. 150–160° dec. with gas evolution). Two of these fractions were analyzed after careful drying.

Anal. Calcd. for $C_{42}H_{34}P_2Pt$, $(Ph_3P)_2PtC_6H_4$: C, 63.38; H, 4.30. Found for sample I: C, 58.13; H, 4.35. Calcd. for $C_{54}H_{45}P_3Pt$, $(Ph_3P)_3$-Pt (m.p. 125–130° dec.): C, 66.04; H, 4.61. Found for sample II: C, 65.34; H, 4.57.

Further evaporation of the solvents and addition of ethanol (since addition of ether only produced oils) gave 0.235 g. of a product, m.p. 149–153°, triphenylphosphine oxide.

Attempted Preparation in Tetrahydrofuran.—To a dry nitrogen-filled Schlenk tube was added 2.6 g. of *o*-phenylenemercury, 1.5 g. of freshly cut lithium, some glass splinters, and 50 ml. of freshly purified tetrahydrofuran. The reaction tube was closed and shaken for 15 days. A gray suspension of lithium metal resulted. The tube was opened intermittently and aliquots analyzed for total base and C–Li content as usual (theory, C–Li 0.4 *N*). It proved impossible to duplicate the total base content of the aliquots removed because of the difference in content of lithium metal of the samples. It was concluded, however, that no or very little C–Li was present since the color test was negative. The mixture was poured on Dry Ice–ether. When the carbonation mixture had reached room temperature, methanol was added to destroy the finely divided lithium metal. Acidification produced a suspension with oily droplets floating on top. Extraction of the gray precipitate (containing drops of mercury) with dimethylformamide (50 ml.) and addition of methanol yielded no recovery of *o*-phenylenemercury. The oils were dissolved in ether and the ether solution dried over anhydrous sodium sulfate. Distillation of the oils remaining after removal of the solvent gave a slightly yellow oil (565 mg.), b.p. 158–160° (0.1 mm.), $n^{20}{}_{D}$ −1.4893. Infrared analysis showed that the compound was aliphatic and contained a carbonyl group and an ether group.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.42; H,10.27; O, 16.37; for $C_{12}H_{18}O_2$: C, 74.18; H, 9.34; O, 16.47. Found: C, 73.35; H, 9.58 (O, 17.07).

Reaction with Tetrahydrofuran.—A solution of *o*-dilithiobenzene (analysis 0.25 *N* or 70%) was prepared from 5 g. of *o*-phenylenemercury, 2 g. of lithium, and 100 ml. of ether. The dark red solution was decanted into another nitrogen-filled Schlenk tube and 20 ml. of tetrahydrofuran, freshly distilled from lithium aluminum hydride, was added. The Schlenk tube was then sealed and shaken for 6 days. A red precipitate formed which redissolved after 2 days. Analysis for organolithium compounds (by determining total base and remaining alkali after reaction with methyl iodide) indicated that the solution was 0.04 *N* or more than 80% of the organometallic reagent had decomposed. The analysis was repeated using ethylene bromide for determining the amount of remaining alkali liberated after organolithium compounds including phenyllithium had been removed as a source of alkali on hydrolysis. The solution was now found to be 0.06 *N* in C–Li by this method. The reaction mixture was then poured on Dry Ice in ether. The organic layer was extracted once more with 1 *N* sodium hydroxide and the aqueous layers combined and acidified before repetition of ether extraction. Benzoic acid, m.p. 120–121°, was found in both extracts (673 mg., 32%). The mother liquors were combined and chromatographed twice but no crystalline fractions could be obtained.

Reaction with Nickel(II) Chloride in Tetrahydrofuran.—The normal preparation of *o*-dilithiobenzene in ether was decanted into a double Schlenk tube and the tube was sealed *in vacuo*. This allowed the distillation of the solvent into the other branch. The ether was poured off and 100 ml. of freshly distilled tetrahydrofuran was added to the residue. The red solution which resulted was in one branch and 2.1 g. of nickel(II) chloride, dried as described in a previous report, was added to the other branch. The red *o*-dilithiobenzene solution was concentrated by slow removal of the solvent at room temperature into the other branch over a period of 16 hr. No crystalline products were obtained. The solution had changed appearance to a brown color. The solution was then filtered into the other branch containing the nickel(II) chloride while cooling was provided from the outside. A green solution resulted, but the color changed to a dark brown during the subsequent increase in temperature to room temperature. At this time the color test was negative. The double Schlenk tube was resealed *in vacuo* and part of the tetrahydrofuran was distilled into the other branch in the hope of isolating a crystalline product. Since none was found hydrolysis was performed and the reaction products isolated as described in a previous section. Chromatography yielded 266 mg. of biphenyl in addition to several fractions of intractable oils which on addition of trinitrofluorenone gave 21 mg. of the triphenylene complex, m.p. 230–232°. Since the solution of *o*-dilithiobenzene had been allowed to stand for 16 hr. at room temperature the reaction was repeated without storing the solution before reaction. The same color changes were noticed and there was found no octaphenylene. Chromatography yielded biphenyl, 256 mg., m.p. 64–65° (18%), and a triphenylene complex with trinitrofluorenone, m.p. 230–231°. Particular care was taken to dissolve the metal to search for octaphenylene but none was found.

Attempted Preparation of *o*-Dilithiobenzene in Ethylene Glycol Dimethyl Ether.—Ethylene glycol dimethyl ether was purified by a standard procedure, b.p. 85°, $n^{20}\text{D}$ −1.37965. A slurry of 2.5 g of *o*-phenylenemercury and 1 g. of lithium in 50 ml. of ethylene glycol dimethyl ether was shaken for 7 days. A gray-black suspension resulted. Neither the precipitate nor the solution gave a positive color test. Filtration of the slurry yielded no crystalline product on concentration of the filtrates. A small amount of lithium carbonate was found, 71 mg.

Reaction of *p*-Bromoanisole with *o*-Dilithiobenzene.—Distillation of *p*-bromoanisole under reduced pressures yielded a pure sample, $n^{20}\text{D}$ −1.509 (lit. 1.5605), b.p. 132–134° (20 mm.).

A solution containing 18 mmoles of *o*-dilithiobenzene in 100 ml. of ether was added to 3.35 g. (18 mmoles) of *p*-bromoanisole and the reaction mixture was left at room temperature for 15 min. before 6.6 g. (36 mmoles) of benzophenone was added. The color test was negative after 10 min. and hydrolysis with water was performed. The aqueous extracts of the organic phase contained 9.6 mmoles of lithium bromide (on Volhard analysis). The *p*-bromoanisole remaining was recovered by distillation, 2.3 g. (35%), and partly also by later chromatograms. Biphenyl was contained in the higher boiling fractions (estimated 150 mg.). The oils remaining from the distillation were combined and chromatographed. A fraction containing 34% biphenyl and 66% *p*-bromoanisole was obtained in addition to several oily and solid fractions. These fractions were recombined and chromatographed anew. From the second chromatogram was obtained *o*-xylyleneglycoltetraphenyl, 776 mg. (1.75 mmoles); this sample showed no depression with an authentic sample, m.p. 196–197°; 2-methoxy-5-bromotritanol, 1.13 g. (3 mmoles); *p*-methoxytritanol, 1.40 g. (3.8 mmoles). Several other fractions were obtained but none corresponding to *p*-methoxybiphenyl, bis(*p*-methoxyphenyl). A fraction, m.p. 121–122°, was assigned the structure 2-*p*-methoxyphenyltritanol on basis of spectral data and analysis. In addition there was obtained a compound, 0.5 g., m.p. 246–247°, after several recrystallizations. This compound gave no melting point depression with bis(-2-diphenyloxymethyl)diphenyl, m.p. 246–247°.

Attempted Metalation of Diphenylmethane with *o*-Dilithiobenzene.—Diphenylmethane was purified by distillation. A solution containing 18 mmoles of *o*-dilithiobenzene was added to 36 mmoles of diphenylmethane in ether (5.7 g.). The reaction mixture was left standing for 16 hr. before 6.6 g. of benzophenone was added. The color test was negative almost immediately after addition and the reaction mixture was worked up by removing 5.185 g. (91%) of diphenylmethane by distillation. From the residue left after the removal of the diphenylmethane there was obtained 2.876 g. (22%) of tetraphenyl-*o*-xylylene glycol, m.p. 196–197° (lit. reports a 15% yield). The mother liquors yielded 1.807 g. of benzophenone (27% recovery), m.p. 48–49°, on distillation and the oils now remaining were chromatographed to yield triphenylmethane, 33 mg. (probably present in the diphenylmethane as an impurity). There was found no tetraphenyl-*o*-xylylene glycol from this chromatogram, 18 mg. of tritanol, and a total of 130 mg. of tetraphenylphthalan after the various oily fractions were dehydrated with glacial acetic acid.

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Base-Catalyzed Reaction of Acetylene and Vinylacetylenes with Carbonyl Compounds in Liquid Ammonia under Pressure

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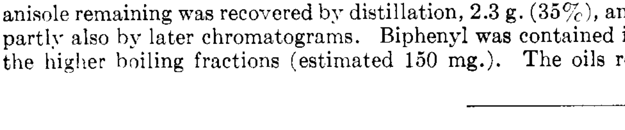
A high productivity, catalytic method for the ethynylation of aldehydes and ketones to the corresponding secondary and tertiary acetylenic carbinols is described. The method uses catalytic amounts of potassium or sodium hydroxide in liquid ammonia with acetylene, vinylacetylene, or isopropenylacetylene under pressure.

The condensation of aldehydes and ketones with acetylene at atmospheric pressure in the presence of excess, finely divided potassium hydroxide is known as the Favorskiĭ[1,2] reaction. At temperatures below 5° ethynylcarbinol (I) is formed almost exclusively, while acetylenic glycol formation predominates at higher temperatures (25–35°).



$$3R_1R_2C{=}O + 2CH{\equiv}CH \underset{}{\overset{KOH}{\rightleftarrows}} \underset{\text{I}}{R_1R_2\underset{OH}{C}{-}C{\equiv}CH} + \underset{\text{II}}{R_1R_2{-}\underset{OH}{C}{-}C{\equiv}C{-}\underset{OH}{C}R_1R_2}$$

This reaction, since its discovery, has been extensively studied[3-6] and modified.[7-10] Results of these investigations have shown that ether, acetal, or amine solvents used with stoichiometric to excess amounts of finely ground potassium hydroxide give optimum results at atmospheric pressure (Favorskiĭ conditions).

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