

[COMMUNICATION NO. 846 FROM THE KODAK RESEARCH LABORATORIES]

The Chemistry of *o*-Terphenyl (*o*-Diphenylbenzene). I. The General Reactivity, Basal Structure and Rearrangements of the Hydrocarbon

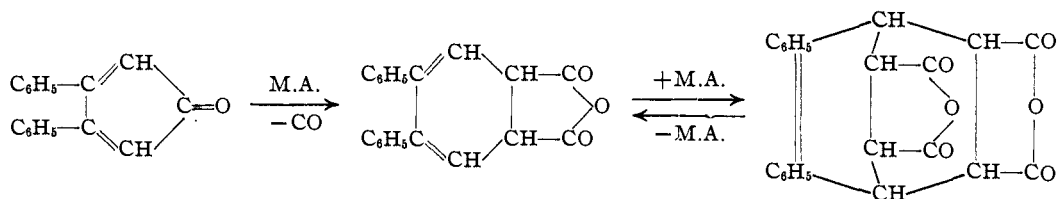
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Introduction

Up to the present, no systematic study on the chemistry of *o*-terphenyl has been published. The inaccessibility of this interesting hydrocarbon, its elusiveness and tendency to form oily and sirupy derivatives has discouraged research; an attempt to investigate it has been announced but

absent; this refers particularly to biphenyl, isomeric terphenyls and triphenylene.

We have found that the decarboxylation of the maleic anhydride adducts of 3,4-diphenylcyclopentadienone² in the presence of barium hydroxide affords *o*-terphenyl in yields comparable with those of the Wurtz-Fittig reaction. Although



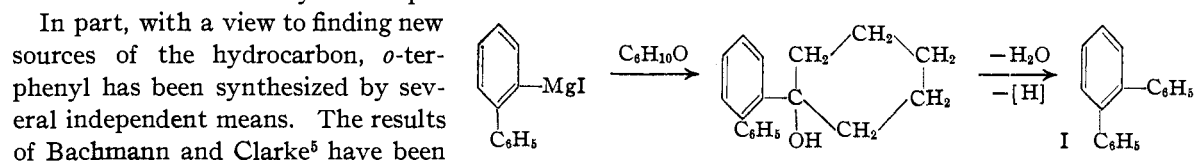
has not materialized.¹ More recently,² *o*-terphenyl has been encountered as the end-product in a series of degradations of a highly complex molecule; in this connection, several derivatives were synthesized,³ indirectly, from components not originally containing the triaryl nucleus.

About fifty years ago, while studying the Wurtz-Fittig reaction, Weiler⁴ isolated several hydrocarbons from the high-boiling fractions, but it remained for Bachmann and Clarke⁵ to identify three of them, among which was *o*-terphenyl (*o*-diphenylbenzene). Although the yield was low, the action of sodium on bromobenzene was the only known source of the hydrocarbon. The congruous reaction on chlorobenzene and the Ullmann synthesis of the *o*-terphenyl⁵ led to similar mixtures of closely related products.

In part, with a view to finding new sources of the hydrocarbon, *o*-terphenyl has been synthesized by several independent means. The results of Bachmann and Clarke⁵ have been confirmed. The oily fractions were fractionated carefully as described in the experimental part. Particular care has been taken to ensure that any appreciable amounts of contaminants were wholly

more expensive for this hydrocarbon, it appears to be adaptable to the preparation of homologs which are otherwise inaccessible. It is a valuable method for synthesizing the *o*-terphenyl ring system, and the material is free from related contaminants. Since the dienone is derived from benzil and acetone, in which arylation is not involved, the *ortho*-attachment of the phenyls is indubitable. This is an important point, in view of the catalytic isomerizations discussed below.

The reaction of phenylmagnesium halides and cyclohexanone,⁶ followed by dehydration and dehydrogenation with chloranil⁷ gives a 20% yield of *o*-terphenyl, but offers no particular advantages. Unsatisfactory Grignard reactions are listed in the experimental part; they lead to intractable oils.



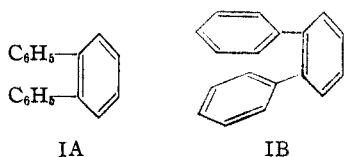
On searching the literature for other unrecognized isolations of the hydrocarbon, it was found that *o*-terphenyl had also been in the hands of Doebner⁸ as early as 1902. It appeared among the decarboxylation products of cinnamal malonic acid. For reasons best known to him, it was assigned the structure of a 1,2-diphenylbicyclo-

- (1) Reddelien, *J. prakt. Chem.*, **91**, 213 (1915), esp. p. 232.
- (2) Allen and Spanagel, *Can. J. Res.*, **8**, 414 (1933); *THIS JOURNAL*, **55**, 3773 (1933).
- (3) Allen, Eliot and Bell, *Can. J. Res.*, **B17**, 75 (1939); Allen, Bell, Bell and Van Allan, *THIS JOURNAL*, **62**, 656 (1940); Allen and Van Allan, *ibid.*, **64**, 1260 (1942).
- (4) Weiler, *Ber.*, **29**, 115 (1896); cf. also Schultz, *Ann.*, **174**, 228 (1874).
- (5) Bachmann and Clarke, *THIS JOURNAL*, **49**, 2089 (1927).

- (6) Bradsher, *ibid.*, **61**, 3131 (1939).
- (7) Arnold, Collins and Zenk, *ibid.*, **62**, 983 (1940).
- (8) Doebner and Staudinger, *Ber.*, **35**, 2129 (1902); Doebner and Schmidt, *ibid.*, **40**, 148 (1907).

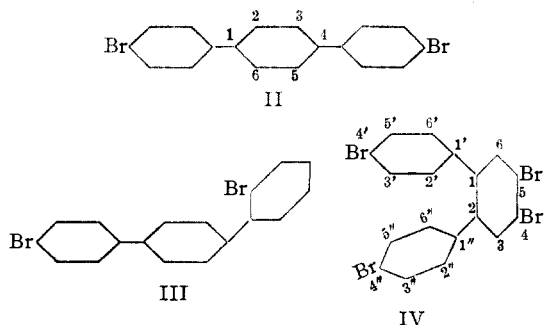
hexane. The reactions described in his papers do not furnish a suitable source of *o*-terphenyl. A discussion of this work will follow later; it is an early example of the Diels-Alder reaction.

Nomenclature.—The hydrocarbon has been variously named in the literature,⁹ but the name *o*-terphenyl seems best in accord with modern usage, and, as will shortly become evident, *with the chemical behavior*. In the usual substitution reactions it does not act like a diphenylated benzene (IA) but, rather, like two molecules of benzene connected by a relatively inert central nucleus (IB). As a general rule, centrally substituted derivatives must be prepared indirectly,



e. g., by the diene synthesis.^{2,3} This behavior is not confined to the *ortho* isomer; on the contrary, it is shared with the *meta*- and *para*-terphenyls. Moreover, their interrelation is far more intimate than would have been previously assumed.

Since the terphenyls contain three benzene rings which may be substituted in a number of positions, it is necessary to differentiate arbitrarily in each series between isomers substituted on the two terminal rings or in the central ring. It seems to us that this is best accomplished by designating the isomeric series as *ortho*-, *meta*- and *para*-terphenyls, respectively; the isomers within a given series are then distinguished by analogous sets of numbers, with the provision that the unprimed numeral is always assigned to the central nucleus. For example, II is to be designated as 4',4''-dibromo-*p*-terphenyl, III is 2',4''-dibromo-*m*-terphenyl and IV is 4,5,4',4''-tetrabromo-*o*-terphenyl.

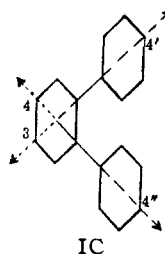


This system offers the added advantage that

(9) *o*-Diphenylbenzene, *o*-terphenyl, *o*-phenylbiphenyl, *o*-phenyl-diphenyl, *o*-xenylbenzene.

analogously constituted serial isomers and their family relationships are recognizable at a glance.

The General Reactivity of the Hydrocarbon.—Aside from the classical reactions of the triaryl group, *o*-terphenyl is capable of rearrangement and polynuclear condensations. In such aromatic substitutions (halogenation, nitration, etc.) which *do not disrupt the framework* of the polyaryl, the focus of primary attack resides at the prong ends of the forked structure. Formula IC represents diagrammatically the main chemical axes of the molecule. The heavily dashed arrows show the



most reactive positions (4',4''), the dotted arrows the points of secondary activity (4,5). The conjugation¹⁰ and resonance coupling¹¹ in *o*-terphenyl results in the activation in the 4'- and 4''-positions. In substitution reactions, a difference in behavior between bromine and nitric acid is noticed. Under all sorts of conditions, bromine substitutes in both the 4'- and 4''-positions, while with nitric acid it is possible to isolate a 4'-mononitro derivative (which can be further nitrated in the 4''-position). This is readily understandable for the 4''-position is essentially *para* to the 4'-, and the introduction of bromine increases the above-mentioned activation as a substituent of the first order, while the nitro group has an inverse effect. On exhaustive bromination, the 4,5,4',4''-tetrabromo-*o*-terphenyl (IV) is formed, as would be expected from the diphenyl structure indicated in the diagram. Depending upon the conditions of experiment, the centrally substituting bromines can be introduced one at a time as in diphenyl. The fact must be stressed that preferential reactivity by no means implies a fundamental difference in the aromaticity of the three nuclei. Indeed, the bulk of our evidence indicates that

(10) Clews and Lonsdale, *Proc. Roy. Soc. (London)*, **A161**, 498 (1937).

(11) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940. On page 137 there is a discussion of the extra resonance energy due to the coupling of two phenyl groups in diphenyl. There are two such "diphenyls" in *o*-terphenyl. The approximate additiveness of the energy of coupling of several phenyls to one central ring is shown by the comparison of diphenyl (8 kcal./mole) and 1,3,5-triphenylbenzene (25 kcal./mole).

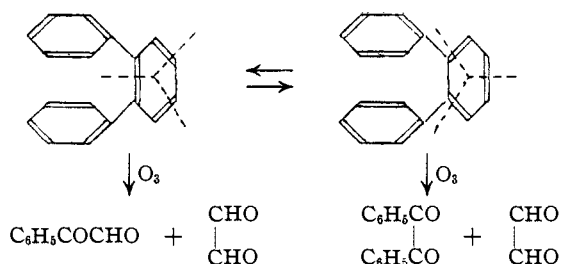
these effects comprise only differences in degree which may be quite small.

The Basal Structure of the Molecule.—The thoroughly aromatic features of those *o*-terphenyl derivatives³ which (though synthesized indirectly) contain the substituent in the central ring, dampens from the start all hope of discovering any pronounced divergence in the degree of aromaticity¹² of the bond structure. In conformance with this fact, the hydrocarbon does not give a stable picrate, if any, and hence does not possess appreciable aliphatic disproportionation so characteristic of naphthalene, phenanthrene, etc., which form stable picrates with ease.¹

A comparison of physical and chemical properties of corresponding "central" and "terminal" derivatives is remarkably devoid of startling differences. The isomeric benzoic acids and benzophenones are good examples. The substituent groups have a strong influence on, say, the melting point of the derivatives, but the actual differences between the isomers are relatively small. Thus, the isomeric *o*-terphenyl-4-carboxylic acid and *o*-terphenyl-4'-carboxylic acid melt at 218 and 202°, respectively, and the isomeric 4-benzoyl-*o*-terphenyl and 4'-benzoyl-*o*-terphenyl melt at 133 and 111°, respectively.

The hydrocarbon long ago invited theoretical speculation; it was suggested that such a molecule might permit the isolation of one of the Kekulé-structures¹ or that one of its derivatives "might show a particular shift in equilibrium on account of a preferred conjugation."¹³

On degradation with ozone, the behavior of the hydrocarbon is erratic. Minor, and for the most part unknown, changes in the condition of experiment alter the nature of the products. Though this was disconcerting, it is really what should have been expected, for if the molecule had a strongly disproportionated bond structure, say, with a partially "fixed" configuration of the Kekulé forms in the central ring,^{1,13} then the products¹⁴ of ozonization should be very definite: benzil, phenylglyoxal and glyoxal. However, this is only part of the picture. Concomitant attack of the terminal rings can yield a variety of complex aldehydic ketones, aromatic as well as aliphatic ones; only glyoxal could be a steady fragment. This is essentially what we have



found. In one fortuitous experiment, which we have been unable to reproduce, but which is, nevertheless, significant, the cleavage was effected in the central ring, and benzil was isolated. In this case, the ozonide crystallized during the reaction in fine needles instead of the usual sirup, and this removal by solidification from further attack by ozone is our only satisfactory explanation of the result. As an oxidizing agent, ozone attacked *o*-terphenyl with the formation of triphenylene and its oxidation products. This side reaction was more noticeable at room temperature.

Molecular Rearrangements.—Though anhydrous aluminum chloride is known to cleave phenylated cycloparaffins,¹⁵ with sundry subsequent recombinations of the fragments, only a few cases of phenyl migrations on ring systems have been recorded in the literature. The rearrangement of α -phenyldialin-3,4 to the β -isomer has been reported¹⁶ at elevated temperatures over silica gel, and of Bz-1-phenylbenzanthrone to Bz-2-phenylbenzanthrone in a sodium-aluminum chloride melt.¹⁷ A possible case, though not interpreted as such, has been described by Nenitzescu and Curceanu.¹⁸ Rearrangement of a phenyl group in a substituted cyclohexane has been recorded.¹⁹

Of great practical importance are the observations of Nenitzescu and Canturianu²⁰ that rigorously anhydrous, freshly resublimed aluminum chloride is ineffective, and that traces of moisture are prerequisite for the catalytic ring contraction of cyclohexane. Our observations on the migration of the phenyl group are in line with their experiences.

The action of aluminum chloride on *o*-terphenyl depends on the conditions of experiment. In anhydrous benzene solution first *m*-terphenyl and

(12) Ref. 11, pp. 139 ff.

(13) Gilman, "Organic Chemistry. An Advanced Treatise," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 71.

(14) Harries, *Ann.*, **343**, 311 (1905); cf. esp. pp. 335 ff. and 374.

(15) Corson and Ipatieff, *THIS JOURNAL*, **60**, 747 (1938).

(16) Mayer and Schiffner, *Ber.*, **67**, 67 (1934).

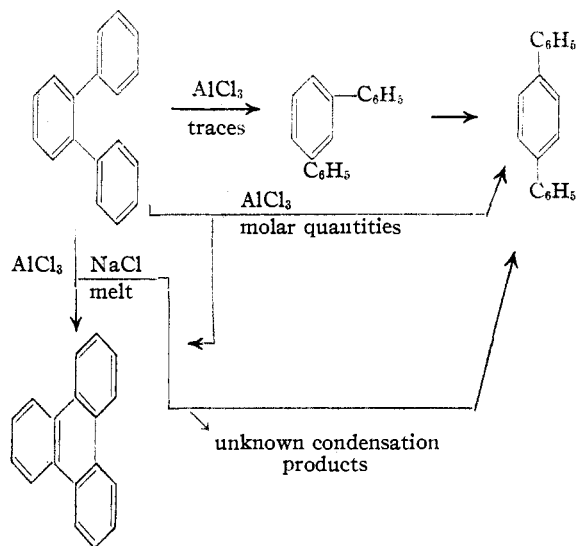
(17) German patent 491,973, *Friedl.*, **16**, 1436 (1931).

(18) Nenitzescu and Curceanu, *Ber.*, **70**, 346 (1937).

(19) LeBrazides, *Compt. rend.*, **159**, 774 (1914).

(20) Nenitzescu and Canturianu, *Ber.*, **65**, 1449 (1932); **66**, 1097 (1933).

then *p*-terphenyl is formed. With molar equivalents of the aluminum chloride the result is more drastic and leads to condensation as well as rearrangement; *p*-terphenyl and triphenylene are among the products. With increasing temperature and halide concentration the condensation products predominate.



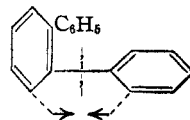
Under comparable conditions (anhydrous benzene, trace of aluminum chloride, same amounts and apparatus) the results of the rearrangement are as follows: after fifteen hours, there is 94% *meta* and 6% unchanged *ortho*-terphenyl. After seventy hours the *ortho* has entirely disappeared and a mixture of *meta* and *para* is obtained, and after eleven days only the *para* is found. Qualitatively it was also found that the pure *meta* isomer is similarly rearranged to *p*-terphenyl. Collectively, these facts indicate that the *meta* is an intermediate step in the isomerization of the *ortho* to the *para*. Not only is the rearrangement to the *meta* relatively very fast, but it is essentially quantitative.

The carefully purified Perrier double compound of benzoyl and aluminum chlorides does not bring about the rearrangement of *o*-terphenyl, but does form the phenyl ketone by substitution; that is, in the Perrier double compound the aluminum chloride is so firmly bound that it cannot accomplish the rearrangement.

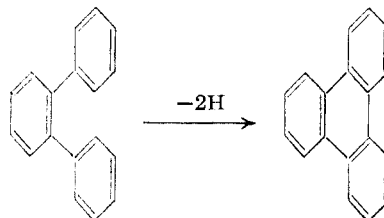
These facts suggest certain speculations about the mechanism of the Friedel-Crafts reaction, which cannot be considered here. They also indicate the necessity for carefully observing conditions of reactions, and probably account, in great

part at least, for the intractable mixtures so frequently encountered in experimental work with *o*-terphenyl.

The quantitative intermediary formation of the *meta* compound may be considered as another example of the validity of Ostwald's rule,^{20a} namely, that the less stable compound is formed on the way to the stable one. However, the cleanliness of the rearrangement with small amounts of aluminum chloride leaves little doubt that the wandering phenyl group does not leave the valence field of the molecule. This may mean that the new diphenyl bond is formed as the old one breaks, as indicated.



Condensations to Triphenylene.—The ring closure at two *ortho* positions in the terminal phenyls is a frequent side-reaction in the chemistry of *o*-terphenyl



The cyclization is concomitant with substitutions and rearrangements and is accomplished by most dehydrogenating and condensing agents such as ozone, nitric acid, bromine or aluminum chloride. Triphenylene and its derivatives are common components of the pasty and tarry residues of reactions on *o*-terphenyl. At times, this ring closure to triphenylene has been observed in reactions which "normally" would not be expected to produce it. Thus, in two runs triphenylene was isolated in substantial yields from the chloranil dehydrogenation of the Grignard reaction product described above in the synthesis of *o*-terphenyl. Why the chloranil removed the two additional hydrogens is uncertain.

Another example of ring closure was encountered when 4'-benzoyl-*o*-terphenyl in benzene solution was refluxed with sodium amide in the usual way for cleaving ketones.²¹ There was no

(20a) Eucken, "Lehrbuch der chemischen Physik," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1930, p. 605.

(21) Haller and Bauer, *Ann. phys. chim.*, [8] **16**, 145 (1909); Lucas, *ibid.*, **17**, 127 (1909).

o-terphenyl in the oily fluorescent products, but on distillation some triphenylene was obtained. It may be noted that the latter hydrocarbon is seldom found except in reactions that have taken place at an elevated temperature, so that it is advantageous to omit the customary final warming in nitrations, Friedel-Crafts reactions, and so on.

At first sight, it might appear that the phenyl migration and the triphenylene condensation are two essentially different reactions. This is not so, for they occur side by side in the aluminum chloride-sodium chloride melt. Aliquot parts of the same batch of aluminum chloride-sodium chloride melt of *o*-terphenyl yield at about 130° mainly *p*-terphenyl and at about 200° almost entirely condensation products, from which triphenylene can be isolated. Since it is known⁶ that *o*-terphenyl is unchanged on pyrolysis, the triphenylene cannot be a pyrolytic product.

Experimental

I. Preparation and Purification of *o*-Terphenyl I

A. The Products of the Wurtz-Fittig Reaction.—When the synthesis was carried out in accordance with the directions of Bachmann and Clarke,⁵ their results were confirmed within the limits of error. From 2.5 kg. of chlorobenzene and 230 g. of sodium the following high-boiling fractions were distilled at 13 mm.: (after removal of the low volatiles) up to 120°, 6 g.; 120–130°, 160 g.; 130–150°, 12 g.; 150–180°, 10 g.; 180–195°, 93 g.; 195–220°, 15 g.; 220–240°, 30 g.; residue, 178 g.; total, 504 g.

As reported,⁵ the fractions boiling above *o*-terphenyl, b. p. 180–195° (13 mm.), yielded some crystalline products, namely, *p*-terphenyl, triphenylene, and dibiphenyl. However, the bulk of the mother liquors, after these had been removed, consisted of intractable oils. These had the general composition of polyaryls, and an apparent molecular weight of about 260; this is predominantly triaryl (230).

Bachmann and Clarke used a "short column," because of the low volatility, high viscosity and bumpiness of the distilland. In order to effect a more clear-cut separation and to learn something about the nature of the intractables, fractionating columns of higher efficiency were used (though with some difficulty). These were fastened in such a manner that bumping could not damage them seriously and were heated periodically or continuously, to maintain smooth operation and prevent clogging. For mere purposes of preparation, an asbestos-covered, modified Widmer column²² was found to be quite satisfactory, but for more accurate work, a jacketed, electrically-heated, 2.5-ft. column with variable take-off head was used; it was packed with single helix copper spirals.²³

Fractionation of the "Intractable Oils."—A portion of "intractables" (150 g. comprising that portion of the prod-

ucts of the Wurtz-Fittig reaction which boiled at 15 mm. above 200°, but failed to crystallize) was fractionated in the packed column. The following cuts were taken at 2 mm.: up to 138°, 14 g.; 138–(158°), 99.5 g.; 158–160°, 14.5 g.; residue, 19 g. (including the recoverable "hold-up").

The middle fraction, b. p. 138–(158°)(2 mm.), was carefully redistilled through the same column and yielded 70 g. of *o*-terphenyl boiling at 138° (2 mm.) and melting at 58°. Further attempts to "fractionate" this *o*-terphenyl by distillation did not change its melting or boiling point.

B. The Fractional Crystallization of *o*-Terphenyl.—Though alcohol is an excellent solvent for recrystallizing *o*-terphenyl, petroleum ether excels it at low temperatures. The differential solubility of the polyaryls varies widely under these conditions and it is an easy matter, *e. g.*, to separate *o*-terphenyl from one of its persistent impurities, diphenyl, by operating in the vicinity of –20°. Crystallization from relatively dilute solutions is most desirable, but the method is workable within wide limits of concentrations and temperatures. This is particularly true of complex mixtures containing *o*-terphenyl, which often can be neatly isolated by this method. In our experience, the optimal nucleation temperature of an approximately 8% solution lies around –30°, whereas the crystallization proceeds more rapidly at about –15°.

Seventeen grams of a crude *o*-terphenyl, m. p. 52°, was dissolved in 200 cc. of low-boiling (43–48°) petroleum ether, and chilled rapidly to –35° in an acetone-dry-ice bath. Spontaneously (or upon scratching) the solution became slightly turbid. It was then removed from the bath, and allowed to warm to about –10°; at this point crystallization took place rapidly. It was filtered quickly through a Büchner funnel (chilled to about –60°); the thoroughly-cooled porcelain does not warm up readily. The yield was 12 g.; m. p. 57–58°. While a slow and gradual cooling is sometimes satisfactory, it usually produced viscous oils and sirups, even in the presence of seed. If crystallized from alcohol, *o*-terphenyl contains traces of solvent which are hard to remove.

After twelve fractional crystallizations the melting point of *o*-terphenyl was raised from 58 to 59°. The slight impurity was identified after a molecular distillation in a two-stage Hickman pump at about 3 microns; a very small amount of diphenyl sublimed on the walls of the receiver, whereas the *o*-terphenyl distilled into the alembic.

C. Pyrolysis of 7,8-Diphenylbicyclo-(2,2,2)-7-octene-2,3,5,6-tetracarboxylic Acid Dianhydride.²—A mixture of 33 g. of the anhydride and 100 g. of dry barium hydroxide monohydrate was pyrolyzed in a distilling flask. Nine grams of an oil was obtained; this was taken up in 25 cc. of boiling absolute ethanol and freed from some impurity by chilling and decanting. The hydrocarbon was then digested with boiling water and crystallized by slow evaporation of its (decolorized by Norite) alcoholic solu-

(22) "Organic Syntheses," **20**, 53 (1940).

(23) *Ibid.*, p. 96.

tion. The yield of *o*-terphenyl varied from 3–8 g. (18–50%); m. p. 56–57°.

D. Doebner's "Diphenyl-dicyclohexane."—Upon pyrolyzing the white cinnamalmalonic acid as described by Doebner and Schmidt,⁸ their data were essentially confirmed. From the fraction, b. p. 159–166° (8 mm.), comprising 7.5 g. of a light oil, 1.2 g. of *o*-terphenyl was obtained after seeding with 10 mg. of authentic specimen and allowing it to stand for three months.

Grignard Reactions.—1-(2-Xenyl)-cyclohexene-1 was prepared essentially in accordance with the directions of Bradsher⁶; the yield was increased to 44% by partially "forcing" the Grignard reaction. To 9.36 g. of the cyclohexene in xylene solution was added 19 g. of chloranil. After proceeding in a known manner,⁷ and fractionating, the yield from the reaction mixture was 4.49 g. of *o*-terphenyl; m. p. 56–57° (48%). The over-all yield of the several steps was about 20%. It should be noted that *o*-terphenyl prepared by this method contains approximately the same type of impurities as the Wurtz-Fittig reaction product, including *p*-terphenyl.

The reaction between cyclohexylcyclohexanone and phenylmagnesium bromide, with subsequent dehydration, and dehydrogenation with bromine yielded high-boiling oils from which only polybromo compounds were isolated in crystalline form. They were not investigated further. The reaction between phenylcyclohexanone and phenylmagnesium bromide gave no tractable products. Double decomposition of 2-xenylmagnesium iodide with bromobenzene at elevated temperature gave almost entirely the symmetrical products, diphenyl and *o*-dibiphenyl.

II. Ozonolysis.—The ozonization proceeds most satisfactorily at about 0°. At lower temperatures the ozonization is extremely slow and at higher temperatures oxidation becomes appreciable.

Example I.—Five grams of *o*-terphenyl was dissolved in 100 cc. of (99–100%) acetic anhydride and ozonized for eighteen hours at a temperature of about 0°. The ozonide separated out in fine rods, which coalesced to a semicrystalline sirup when the mixture was allowed to attain room temperature. The ozonide was decomposed by diluting the reaction mixture with 250 cc. of water and adding a pinch of zinc dust. The water-insoluble products crystallized out and were separated by decantation. The water-soluble products became insoluble on standing and precipitated out as a white amorphous solid (1.6 g.), which redissolved on treatment with warm aqueous phenylhydrazine acetate. The resulting reddish-brown crystals proved to be a mixture of osazones and hydrazones, melting over a wide range from about 110° on. They were separated as described below. Except for the yellowish color, the water-insoluble fraction, m. p. 55–58°, was, at first, mistaken for unchanged, slightly contaminated, *o*-terphenyl, but upon fractionating with petroleum ether (b. p. 45°, approx.) an insoluble residue (0.96 g.) was obtained. Upon purification, this proved to be benzil. The soluble portion (2.54 g.) consisted of *o*-terphenyl, slightly yellow but otherwise fairly pure.

The yield of benzil is about 84% of the theoretically possible, calculated on the basis of an equivalence of the Kekulé structures. The more easily recovered, water-soluble ketoaldehydes account quantitatively for the other

resonance form. Consequently they must consist almost exclusively of phenylglyoxal and glyoxal. That was found to be true by forming the osazones in the usual manner and separating them by fractional precipitation of their warm alcoholic solutions with petroleum ether. The solvent was added to incipient precipitation and then the mixture was cooled sharply (dry-ice). The glyoxal osazone of m. p. 180° (after suitable recrystallization) separated out first. The next two fractions were mixtures (m. p. 110–140°). Then phenylglyoxal osazone of m. p. 149° crystallized out. The mother liquor contained a small amount of a hydrazone of m. p. 129°, presumably phenylglyoxal monohydrazone. These results are thus in accord with the results of ozonolysis of *o*-xylene, which have shown the presence of both Kekulé forms²⁴ in equal proportions.

Example II.—After ozonizing 5.0 g. of *o*-terphenyl in carbon tetrachloride solution for three hours at room temperature and decomposing the oily ozonide with 100 cc. of water containing 15 cc. of hydrogen peroxide, 4.5 g. of largely unreacted material was recovered. From this product, 25 mg. of triphenylene, m. p. 198°, was isolated and identified by comparison with an authentic specimen. The aqueous liquors contained a highly soluble acid (0.15 g. after thorough drying) which carbonized readily, gave off carbon dioxide on fusion, and melted over a range above 280°. This behavior suggests mellitic acid, but the residue was not investigated further.

Example III.—A solution of 5.0 g. of *o*-terphenyl in 100 cc. of purified petroleum ether was ozonized for twelve hours at somewhat below room temperature. (The mixture was cooled, at first by means of an ice-bath, then left to itself.) A heavy, sticky oil was formed on the bottom of the absorption vessel. The reaction mixture was decomposed in water in the presence of small amounts of zinc dust; glyoxalosazone was the only identifiable product. Intractable, pasty, highly-colored osazones were also obtained.

III. Rearrangements

A. General Procedure. (1) **Dehydration of Solvent.**—Commercial benzene was dried azeotropically, about the first half of the run being rejected. The last distillate was kept over anhydrous aluminum chloride for at least three days, during which it assumed a red color. After another distillation, the treatment was repeated and the final cut taken within a degree.

(2) **Rearrangement in Solvents.**—After a number of preliminary experiments, the following procedure was adopted: using an all-glass apparatus protected from moisture *o*-terphenyl, m. p. 58°, was dissolved in anhydrous benzene and a given amount of catalyst was added. After refluxing the mixture gently for the requisite time, it was decomposed with dilute hydrochloric acid. The benzene layer was separated, dried and concentrated. The products were recovered by fractional crystallization or other suitable means.

B. Rearrangement, ortho to meta.—Five grams of *o*-terphenyl in 125 cc. of dry benzene containing 25 mg. of anhydrous aluminum chloride catalyst was refluxed for fifteen hours. The recovered solid melted at 84° with slight previous partial melting. The supernatant liquor of the incipient melt was adsorbed on filter paper and the

(24) Levine and Cole, *THIS JOURNAL*, **54**, 338 (1932); Haayman and Wibaut, *Rec. trav. chim.*, **60**, 842 (1941).

bulk of the mass was crystallized from absolute ethanol; yield 4.7 g. (94%) of a *m*-terphenyl of m. p. 86–87°. The small amount of adsorbed material contained unchanged *o*-terphenyl.

C. Rearrangement, ortho to a Mixture of meta and para.—One gram of *o*-terphenyl in 80 cc. of dry benzene containing 50 mg. of catalyst was refluxed for seventy hours. The product contained a mixture of *m*- and *p*-terphenyl, in a yield of 0.16 and 0.58 g., respectively. No attempt was made at a tedious quantitative separation. Traces (6 mg.) of diphenyl were found.

D. Rearrangement, ortho to para.—To 1 g. of *o*-terphenyl in 85 cc. of solvent was added 50 mg. of the catalyst. After refluxing for two hundred and sixty-four hours, 0.82 g. of *p*-terphenyl was obtained after crystallization from absolute ethanol.

As there are known polymeric condensation products of *m*-terphenyl which melt in a similar range as *p*-terphenyl, it was thought desirable to check the approximate molecular weight of the product.

Anal. Calcd. for $C_{18}H_{14}$: mol. wt., 230. Found: mol. wt., 244, in boiling benzene.

Rearrangements with larger amounts of anhydrous aluminum chloride, especially in molar quantities, have been studied, but the reactions are complicated by tars and are of no particular interest in this connection.

E. Aluminum-Sodium Chloride Melts.—The effect of these on *o*-terphenyl was only studied in a qualitative way,

for very complex mixtures resulted; but two instances will be described. (1) To about 20 g. of a 4:1 melt at 130° was added 2 g. of *o*-terphenyl. The mixture was cooled and decomposed by iced hydrochloric acid. The decolorized and dried benzene extract of the product left a residue on evaporation, which was treated with absolute ethanol; from this *p*-terphenyl crystallized. (2) A similar run, at 200°, gave a mixture from which were separated 0.4 g. (20%) of triphenylene and 0.15 g. of *p*-terphenyl.

Summary

o-Terphenyl has been prepared in quantity. Of the available methods, the Wurtz-Fittig was found to be most suitable.

A new synthesis that may be applicable for securing derivatives is described.

Ozonolysis of *o*-terphenyl gave the products expected.

o-Terphenyl is easily rearranged by aluminum chloride. With very small amounts, *m*-terphenyl is first formed; this then further rearranges to *p*-terphenyl. Large amounts, alone or with sodium chloride, give complex mixtures from which *p*-terphenyl and triphenylene were isolated.

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A New Type of Sulfanilamide Derivative of D-Glucose. Sulfanilyl-2-amino- α -D-glucose and Certain Derivatives

BY ERNEST L. JACKSON

Within recent years sulfanilamide derivatives^{1,2} of a number of reducing sugars have been prepared by the reaction of sulfanilamide with the sugars under suitable conditions. The sulfanilamide component of these compounds is generally regarded as linked through the primary amino nitrogen atom (N^4) to carbon atom 1 of the sugar component either as a N-glycoside or an anil. Although the structure in no case has been fully established, the crystalline derivative of glucose having a specific rotation of -123° in water has been shown by Kuhn and Birkofer² to be of the N-glycosidic type (I). This N-glycoside, which is known to be unstable in 0.1 *N* hydrochloric acid

(1) Gray, Buttle and Stephenson, *Biochem. J.*, **31**, 724 (1937); Meyer and Schreiber, U. S. Patent 2,141,843 (1938); Établissements Mouneyrat et Cie., French Patent 839,711 (1939); Klingel and MacLennan, U. S. Patent 2,167,719 (1939); Vacirca, *Boll. sez. ital. Soc. intern. microbiol.*, **11**, 16 (1939); Schering, French Patent 842,726 (1939); Meyer, U. S. Patent 2,208,641 (1940); British Patent 519,661 (1940); Winthrop Chemical Co., British Patent 526,747 (1940); Weygand, *Ber.*, **73**, 1259 (1940).

(2) Kuhn and Birkofer, *ibid.*, **71**, 621 (1938).

solution² even at room temperature, may be split *in vivo* to liberate sulfanilamide. The present article pertains to a new type (II) of sulfanilamide derivative of glucose in which the sulfanilamide component is linked through the amido nitrogen atom (N^1) to carbon atom 2 of the glucose component. A relatively stable union of the sulfanilamide and glucose components was expected in this type of compound, which offered the possibility of less toxicity and greater solubility in water than sulfanilamide.

D-Glucosamine reacts readily with N-acetyl-sulfanilyl chloride in aqueous-acetone solution to yield crystalline N-acetyl-sulfanilyl-2-amino- α -D-glucose. Deacetylation of this acetyl derivative in 0.5 *N* sulfuric acid solution at 100° yielded a highly colored sirup, which could be crystallized as a hydrochloride. The hydrochloride, though impure, proved to be a convenient intermediate for the preparation of crystalline sulfanilyl-2-