[Contribution from the Chemical Laboratory of Iowa State College]

THE FORCED REACTION OF PHENYL ISOCYANATE, PHENYL ISOTHIOCYANATE AND BENZOPHENONE-ANIL WITH PHENYLMAGNESIUM BROMIDE. AN UNUSUAL TYPE OF 1,4-ADDITION TO A CONJUGATED SYSTEM THAT IS PART ALIPHATIC AND PART AROMATIC

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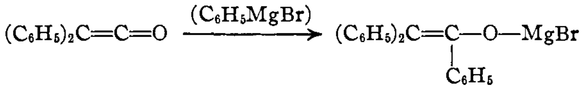
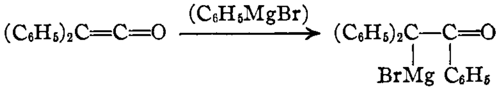
Introduction

In a study of compounds having terminal cumulated unsaturated groups, Gilman and Heckert[1] showed that phenylmagnesium bromide added to diphenylketene in the following manner



$$(C_6H_5)_2C{=}C{=}O \xrightarrow{(C_6H_5MgBr)} (C_6H_5)_2C{=}\underset{\underset{\displaystyle C_6H_5}{|}}{C}{-}O{-}MgBr \qquad (I)$$

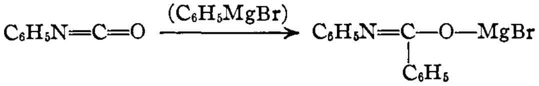
and not as follows



$$(C_6H_5)_2C{=}C{=}O \xrightarrow{(C_6H_5MgBr)} (C_6H_5)_2\underset{\underset{\displaystyle BrMg}{|}}{C}{-}\underset{\underset{\displaystyle C_6H_5}{|}}{C}{=}O \qquad (II)$$

The mode of addition represented by Reaction II is that which was currently in vogue at that time, inasmuch as the addition reactions of ketenes were then assumed to take place through a preliminary addition to the ethylenic linkage. Subsequently the earlier explanations for many addition reactions were altered to conform with that mechanism which postulates prior addition to the carbonyl group.[2]

Because of the marked similarity in many respects between ketenes and isocyanates, it might have been predicted that phenylmagnesium bromide would add to the terminal $—C{=}O$ group and not to the $—N{=}C$ group of phenyl isocyanate, in the following manner



$$C_6H_5N{=}C{=}O \xrightarrow{(C_6H_5MgBr)} C_6H_5N{=}\underset{\underset{\displaystyle C_6H_5}{|}}{C}{-}O{-}MgBr \qquad (III)$$

This reaction was studied by Gilman and Kinney[3] and although they did not get unequivocal proof for the type of addition postulated in Reaction III, they did show that addition could not have taken place at the $—N{=}C$ linkage. By analogy with the reaction of the related phenylisothiocyanate, $C_6H_5N{=}C{=}S$, and by the established relative inertness of the $—OMgX$ grouping,[4] they showed that Reaction III was undoubtedly

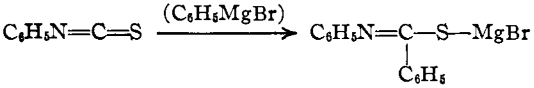
[1] Gilman and Heckert, This Journal, **42**, 1010 (1920).

[2] Staudinger, *Helv. Chim. Acta*, **5**, 87 (1922).

[3] Gilman and Kinney, This Journal, **46**, 493 (1924).

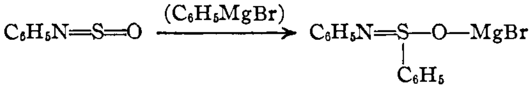
[4] Gilman and Schulze, *Rec. trav. chim.* **47**, 752 (1928).

correct. Gilman and Kinney[3] showed very definitely that phenylmagnesium bromide reacts with phenyl isothiocyanate as follows



$$C_6H_5N{=}C{=}S \xrightarrow{(C_6H_5MgBr)} C_6H_5N{=}\underset{\displaystyle C_6H_5}{\underset{|}{C}}{-}S{-}MgBr \tag{IV}$$

Subsequently Gilman and Morris[5] showed that the following reaction very probably occurs between phenylmagnesium bromide and thionylaniline



$$C_6H_5N{=}S{=}O \xrightarrow{(C_6H_5MgBr)} C_6H_5N{=}\underset{\displaystyle C_6H_5}{\underset{|}{S}}{-}O{-}MgBr \tag{V}$$

There are two marked similarities between these several reactions. First, in each case addition takes place at the ultimate unsaturated group of these types having terminal cumulated unsaturated groups. Second, the reaction stops at this unsaturated group even with a liberal excess of phenylmagnesium bromide and extended refluxing at the low temperatures given by ether as a medium. This is hardly unexpected with ketenes inasmuch as such subsequent addition would involve addition to an ethylenic linkage, and Gilman and co-workers[6] have made a good case for the non-addition of the Grignard reagent to an ethylenic linkage. We are not so certain of the —N=S group in thionylaniline, but if such a grouping has anything in common with a related —N=O group, then it is to be expected that the —N=S group should add phenylmagnesium bromide.[7]

We can speak with greater assurance and definiteness on the —N=C linkage in phenyl isocyanate and phenyl isothiocyanate. It is known that organomagnesium halides add to the —N=C— group. Accordingly, it is reasonable to expect when phenyl isocyanate (or phenyl isothiocyanate) is refluxed for an extended time and at elevated temperatures with an excess of phenylmagnesium bromide, that subsequent to addition to the terminal —C=O (or —C=S) group, a second molecule of Grignard reagent should add to the —N=C— linkage; this explains the primary objective of this paper.

When phenylisocyanate was refluxed in an ether–toluene mixture (70–80°) with a liberal excess (5 or 6 equivalents) of phenylmagnesium bromide for about eight hours, the chief product obtained (in yields

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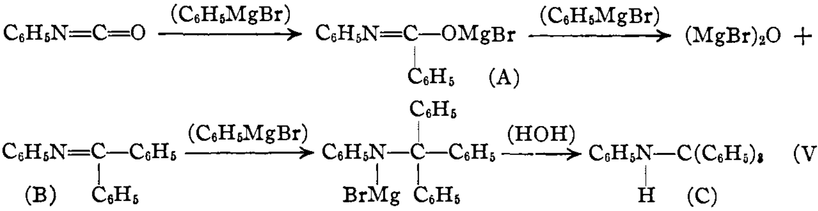
[5] Gilman and Morris, This Journal, **48**, 2399 (1926). See Footnote 6 in the paper by G. and M. on the reaction between RMgX compounds and aliphatic diazo compounds and diazo-imides.

[6] One of the more recent references to the non-addition of RMgX compounds to an ethylenic linkage is Gilman and McGlumphy, *Rec. trav. chim.*, **47**, 418 (1928). This paper contains references to earlier studies.

[7] See Gilman and McCracken, This Journal, **49**, 1052 (1927), and **51**, 821 (1929), for the reaction of the Grignard reagent with nitroso and nitro compounds.

reaching 44%) was a compound melting at 144°. The ultimate analysis and molecular weight determination showed the compound to have a molecular formula agreeing with triphenylmethylaniline. It is easy to understand, from the following reactions, how triphenylmethylaniline might have formed



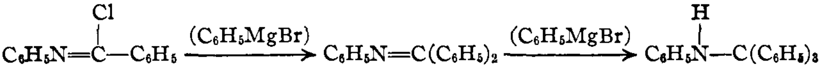
$$C_6H_5N{=}C{=}O \xrightarrow{(C_6H_5MgBr)} C_6H_5N{=}\underset{C_6H_5\ \ (A)}{C}{-}OMgBr \xrightarrow{(C_6H_5MgBr)} (MgBr)_2O +$$

$$\underset{(B)}{C_6H_5N{=}}\underset{C_6H_5}{C}{-}C_6H_5 \xrightarrow{(C_6H_5MgBr)} \underset{BrMg}{C_6H_5N}{-}\overset{C_6H_5}{\underset{C_6H_5}{C}}{-}C_6H_5 \xrightarrow{(HOH)} \underset{H\ \ (C)}{C_6H_5N}{-}C(C_6H_5)_3 \quad (VI)$$

The same product would result if prior to or simultaneous with replacement of the —OMgBr group by C_6H_5— the phenylmagnesium bromide had added to the —N=C— group in Compound (A).

The possible formation of triphenylmethylaniline, Compound (C), was rendered more reasonable when it was found that the 144° compound was obtained in equally high yields from the forced reaction not only with phenyl isocyanate but also with phenyl isothiocyanate and benzophenone-anil (Compound (B)). The formation of the same compound from the three different reactants proved that the terminal oxygen and sulfur, respectively, were replaced by two phenyl groups, and made it altogether reasonable that benzophenone-anil was an intermediate compound.

However, despite the fact that the melting point of our compound was near that of triphenylmethylaniline (147°) and that every reasonable prediction led to the expected formation of triphenylmethylaniline from the three compounds studied, the 144° compound certainly was not triphenylmethylaniline. Furthermore, the expected triphenylmethylaniline could not have been, in all probability, an intermediate. This was shown in an experiment in which triphenylmethylaniline was refluxed in an ether–toluene mixture for ten hours with five equivalents of phenylmagnesium bromide. Practically all of the triphenylmethylaniline was recovered unchanged. Our confusion was increased when we later found that Busch and Fleischmann[8a] obtained some triphenylmethylaniline from the reaction between benzanilideimidechloride and phenylmagnesium bromide. The formation of triphenylmethylaniline in their reaction is readily understandable[8b] from the following



$$C_6H_5N{=}\overset{Cl}{C}{-}C_6H_5 \xrightarrow{(C_6H_5MgBr)} C_6H_5N{=}C(C_6H_5)_2 \xrightarrow{(C_6H_5MgBr)} C_6H_5\overset{H}{N}{-}C(C_6H_5)_3 \quad (VII)$$

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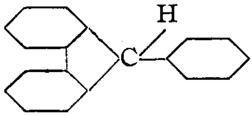
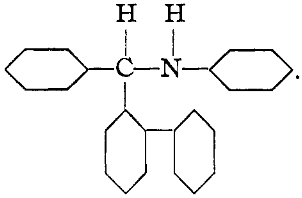
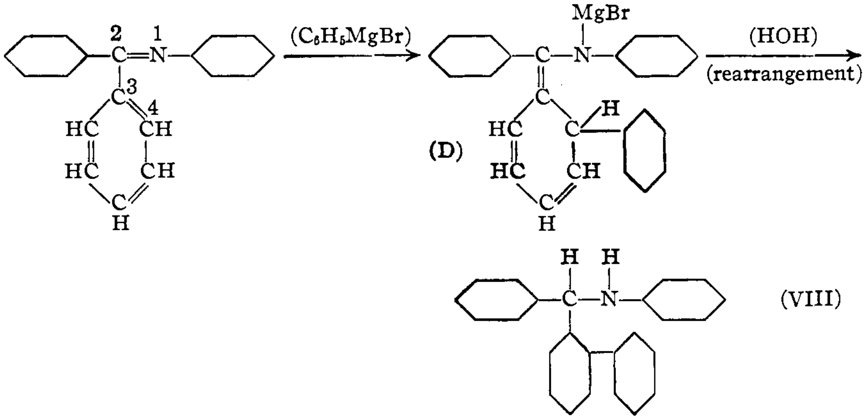
[8] (a) Busch and Fleischmann, *Ber.*, **43**, 2553 (1910). (b) The triphenylmethylaniline which they obtained might have come from reactions other than those illustrated in Reaction VII. For example, there may have been addition to the —N=C linkage prior to or simultaneous with replacement of the chlorine by a phenyl group.

It is interesting to recall their observation that they were unable to repeat this experiment. Also, their major reaction product was benzophenone-anil (Compound (B)). Although triphenylmethylaniline was not isolated in our several experiments, it would be unwise to say that it was not present, because the forced conditions of the reaction gave oily products which were not altogether tractable.

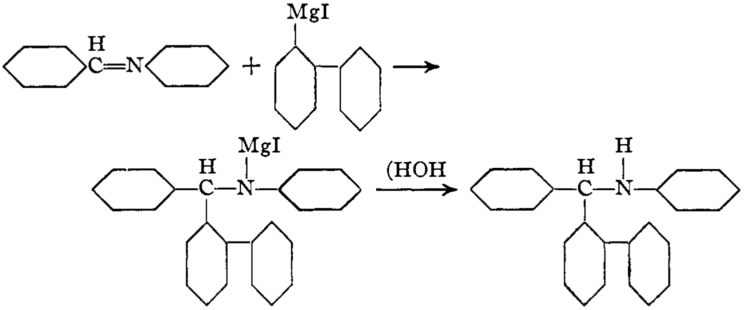
Triphenylmethylaniline hydrolyzes with ease to triphenylcarbinol and aniline. The 144° compound when hydrolyzed gave phenylfluorene, , and aniline. It was next shown that under our conditions of hydrolysis, triphenylcarbinol did not go over to phenylfluorene. The identification of phenylfluorene as a product of hydrolysis of the 144° compound was of help in suggesting several possible formulas for the 144° compound. Some critical experiments showed the impossibility of all but one of these formulas. We finally showed that the 144° compound must be *o*-phenylbenzohydrylaniline, . The idea for this compound came with the thought that inasmuch as addition of phenylmagnesium bromide probably did not take place at the —N=C— linkage (as evidenced by the absence of triphenylmethylaniline), 1,4-addition might have taken place with the conjugated system formed by the —N=C— group and a so-called ethylenic linkage in one of the phenyl groups attached to carbon, as follows



(D)

(VIII)

So far as we know, a reaction of this type has not been reported with any class of compounds. A great deal of our present knowledge on the mode of 1,4-addition to conjugated systems rests on the excellent and thorough studies of Kohler and co-workers. Their studies were carried out, in the main, with organomagnesium halides. The rearrangement postulated in Reaction VIII may or may not be correct; that remains to be determined. However, there is no doubt concerning the structure of our *o*-phenylbenzohydrylaniline. It was synthesized as follows



(IX)

Over and against this method for the proof of structure of the *o*-phenylbenzohydrylaniline, a question may properly be raised on the choice of an anil (in this case, benzalaniline) in establishing the structure of a compound which was formed in a so-called abnormal manner from an anil (namely, benzophenone-anil). But benzophenone-anil is not benzalaniline, and we have shown that benzalaniline behaves normally even *under forced conditions* with phenylmagnesium bromide. Of course, there remains the possibility of abnormal reactions with *o*-biphenylmagnesium iodide. We know of no such abnormal reactions, but to remove all doubt the *o*-phenylbenzohydrylaniline should be synthesized by a reaction not involving RMgX compounds; this we propose to do.

Additional evidence is necessary for the support of Reactions VIII and IX. When the intermediate addition compound of the forced reaction between phenyl isocyanate and phenylmagnesium bromide, namely, Compound (D), is treated with diethyl sulfate, the —NMgBr grouping should be converted to an —NC_2H_5 grouping. Diethyl sulfate and related compounds have been shown to be eminently satisfactory reagents for the characterization of the —NMgX group.[9] The product of this reaction with diethyl sulfate should be identical with that obtained from our *o*-phenylbenzohydrylaniline and diethyl sulfate. So far such identity is confined to the fact that the two products are oils, a fact which is without significance. However, the amines of this study have a marked tendency to form apparently intractable oils which crystallize slowly and with difficulty.

[9] A leading reference is that of Gilman and Heck, THIS JOURNAL, **50**, 2223 (1928).

That the 144° compound contains a secondary amine grouping is shown by the Liebermann nitroso reaction for secondary amines, the Zerewitinoff method for active hydrogen and the formation of aniline as a product of hydrolysis.

As further indicative evidence for the correctness of Reaction VIII and, in particular, for Compound (D), we should state that the reaction mixture assumes a brilliant deep red color which fades appreciably on hydrolysis. This is what one might expect in view of the quinoid structure postulated for Compound (D).

If we grant the correctness of the reactions as postulated, there remains the desirability of proposing an explanation for this unusual type of 1,4-addition to a conjugated system. The most satisfactory explanation that we offer at this time involves the phenomenon of steric hindrance. We do so with full knowledge of the traditional weakness of such an explanation for some reactions. Quite recently Gilman and Heck[10] have shown that although some reactions of organomagnesium halides can be very satisfactorily explained on this basis, other reactions of a kind that might merit such an explanation cannot be correlated with the phenomenon of steric hindrance. From the studies reported at this time we know that one equivalent of phenylmagnesium bromide reacts very smoothly with phenyl isocyanate and phenyl isothiocyanate to give benzanilide and thiobenzanilide, respectively, and that the reaction apparently stops at this stage with an excess of phenylmagnesium bromide and extended refluxing in an *ether* solution.[3] We also know that benzophenone-anil reacts decidedly slowly, if at all, under the same conditions. This resistance to addition of phenylmagnesium bromide to this particular —N=C group (a resistance which we attribute at this time to steric influences) is so marked that when the reaction is *forced* at an elevated temperature, 1,4-addition takes place with the unique conjugated system designated in Reaction VIII.

It should be possible to find an answer to this question with subsequent studies on different anils and other related compounds with a variety of Grignard reagents and other compounds. Until at least several such studies have been completed it would be wise to defer suggestive theoretical considerations on the structure of benzene and the mechanism of substitution reactions of benzene.

The Experimental Part contains brief descriptions of some of the pertinent reactions carried out in connection with other possible structures that were considered prior to the identification of our 144° compound as *o*-phenylbenzohydrylaniline.

The authors wish to thank N. J. Beaber and A. P. Hewlett for some preliminary work and for valuable suggestions.

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[10] Gilman and Heck, *Ber.*, **62**, 1379 (1929).

Experimental Part

Preparation of *o*-Phenylbenzohydrylaniline from Phenylmagnesium Bromide. (1) **Phenyl Isocyanate.**—A vigorous reaction took place with the slow addition of 16 g. (0.134 mole) of phenyl isocyanate in ether to 0.6 mole of phenylmagnesium bromide. When addition was complete, most of the ether was removed by distillation; toluene was added and the mixture was refluxed (internal temperature 70–80°) with stirring for six to eight hours. After hydrolysis by ice and hydrochloric acid, the ether–toluene layer was separated and steam distilled to remove toluene, diphenyl and other steam-distillable products. The non-volatile, sticky, reddish-brown paste that remained as a residue from the steam distillation was extracted with warm alcohol. The alcohol extractions on cooling usually deposited an oil. In some cases crystallization could be induced by rubbing with a glass stirring rod. When a little of the material solidified, it proved very effective in seeding other solutions. The compound was obtained as a yellowish powder melting between 139 and 142°. It is sparingly soluble in alcohol, and a good solvent for crystallization is a mixture of 65% alcohol and 35% toluene. When recrystallized from this mixture, the compound is obtained as glistening yellow crystals melting at 143–144°. The yield from phenyl isocyanate was generally about 30%, but in some cases yields as high as 44% were obtained.

(2) **Phenyl Isothiocyanate.**—From 25.5 g. (0.189 mole) of phenyl isothiocyanate and 0.8 mole of phenylmagnesium bromide refluxed for ten hours at 70–75° in an ether–toluene mixture, there was obtained 28.6 g. or a 45% yield of the *o*-phenylbenzohydrylaniline. In the course of hydrolysis, hydrogen sulfide was evolved. The evolution of hydrogen sulfide is indicative of the formation of $(MgBr)_2S$ (or its equivalent) in accordance with Reaction VI.

(3) **Benzophenone-anil.**—From 19.3 g. (0.075 mole) of benzophenone-anil and 0.3 mole of phenylmagnesium bromide refluxed for ten hours at 90–105° in an ether–toluene mixture, there was obtained 10.6 g. or a 42% yield of the *o*-phenylbenzohydrylaniline. The reaction mixture prior to hydrolysis was deep purple in color. In some experiments hydrolysis was also effected by means of iced ammoniacal ammonium chloride.

Analysis and Properties of *o*-Phenylbenzohydryl-aniline.—Calcd. for $C_{25}H_{21}N$: C, 89.55; H, 6.27. Found: C, 89.38, 89.75; H, 6.87, 6.53. *Mol. wt.* Calcd., 335. Found (in boiling acetone), 317, 300 and 301.

Hydrochloride.—The hydrochloride melting at 182.5° was obtained by adding hydrogen chloride to the amine dissolved in anhydrous ether. The free amine may be recovered from the salt by gently warming with dilute alcoholic potash. *Analysis.* Two samples of the hydrochloride were titrated with a standard solution of potassium hydroxide (and then back-titrated with a standard solution of hydrochloric acid). Calcd. molecular weight, 335. Found: 337 and 335.9.

Active Hydrogen by Zerewitinoff Analysis.—Two determinations by heating in xylene and amyl ether at 70° for fifteen minutes gave 0.7 and 0.69 active hydrogen. A third analysis under the same conditions with the exception of a fifty-minute period of heating at 70° gave 0.72 active hydrogen.[11] In these experiments the compound was dissolved in xylene and the methylmagnesium iodide was prepared in amyl ether. When, however, the determination was carried out with *n*-butyl ether as the solvent (both for the amine and the methylmagnesium iodide), the values obtained were 0.97 and 1.03 active hydrogen.[12]

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[11] Analyses by R. E. Fothergill.

[12] Analyses by R. J. VanderWal. It is interesting to note that triphenylmethylaniline in butyl ether reacts very slowly (eight hours at 70° for completion) with methylmagnesium iodide in butyl ether to give 1.00 and 1.01 active hydrogen. This is one of a number of striking illustrations of what appear to be cases of steric hindrance. Others

With xylene as a solvent for the amine and *n*-butyl ether as a solvent for the Grignard reagent, the value was 0.75 active hydrogen.[12]

Splitting Reactions. (1) **Concd. Hydrochloric Acid.**—When 5.0 g. of the amine was heated in a sealed tube with 75 cc. of concd. hydrochloric acid for three hours at 145°, there were obtained 3.6 g. (a 99.6% yield) of 9-phenylfluorene and aniline. That triphenylcarbinol was not an intermediate product of this hydrolysis was shown by a parallel experiment in which triphenylcarbinol was heated under like conditions. The product in this case was triphenylmethane.

(2) **Alcoholic Hydrochloric Acid.**—9-Phenylfluorene was also obtained when 5 g. of the amine was refluxed for seventeen hours with a mixture of 150 cc. of 95% alcohol and 50 cc. of concd. hydrochloric acid. Under corresponding conditions triphenylmethylaniline gave triphenylmethane. Also, triphenylcarbinol when refluxed under corresponding conditions for twenty-four hours gave a 96.8% yield of triphenylmethane.

(3) **Acetyl Chloride and Acetic Anhydride.**—In an attempt to acetylate the amine by means of acetic anhydride, an apparently intractable tar was obtained. In a subsequent experiment 9-phenylfluorene was obtained after refluxing 5 g. of the amine with a mixture of 25 cc. of acetyl chloride and 50 cc. of acetic anhydride.

The identity of every solid described in this study was confirmed by a mixed melting point determination with an authentic specimen. Synthetic 9-phenylfluorene was prepared by two different methods: first, by refluxing 10 g. of triphenylchloromethane in benzene for five hours with one g. of mossy zinc; and, second, by heating triphenylcarbinol with sirupy (85%) phosphoric acid.[13]

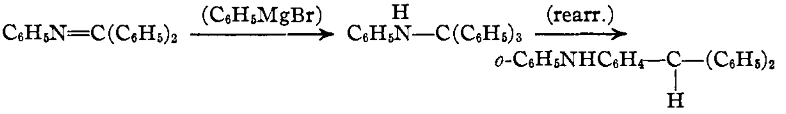
Miscellaneous.—The amine (3.9 g.) was recovered unaltered after refluxing for twelve hours in xylene. Its hydrochloride, when dry distilled, underwent considerable decomposition but gave a small quantity of 9-phenylfluorene in the distillate.

When 2 g. of the amine was refluxed for several hours with benzoyl chloride and pyridine and then worked up in the customary manner it gave a nitrogen containing compound which melted at 155–156°. However, we had no success in hydrolyzing this as yet unidentified compound to benzoic acid and the amine by means of alcoholic potash.

After refluxing 5 g. of the amine for twenty hours with 100 cc. of 20% alcoholic potash, 4.5 g. of the amine was recovered unchanged.

The yellowish color of the amine obtained from phenyl isocyanate, phenyl isothiocyanate and benzophenone-anil suggested at one time that the amine might be quinoidal in nature. Accordingly, some reduction experiments were carried out. Neither sodium and alcohol nor zinc and glacial acetic acid appeared to affect the amine. It was not until the amine was finally synthesized from benzalaniline and *o*-biphenylmagnesium iodide that we discovered the amine to be without color, or rather of a grayish-white color.

It was believed, for a time, that the amine melting at 144° was *o*-phenylaminotriphenylmethane, formed possibly by the rearrangement of triphenylmethylaniline, as follows



$$C_6H_5N{=}C(C_6H_5)_2 \xrightarrow{(C_6H_5MgBr)} C_6H_5\overset{H}{N}{-}C(C_6H_5)_3 \xrightarrow{(rearr.)} o\text{-}C_6H_5NHC_6H_4{-}\underset{H}{C}{-}(C_6H_5)_2$$

(X)

This prompted some oxidation experiments with the hope of converting the supposed

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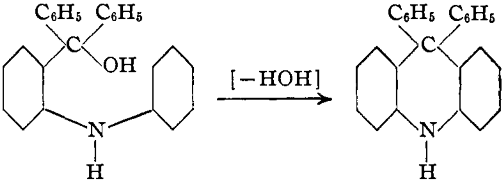
will be reported later by R. J. VanderWal. The values of triphenylmethylaniline in xylene are lower (0.81 and 0.92) after heating for fifteen hours at 70°.

[13] Kliegl, *Ber.*, 38, 287 (1905).

o-phenylaminotriphenylmethane to the known *o*-phenylaminotriphenylcarbinol, *o*-$C_6H_5NHC_6H_5—C(OH)—(C_6H_5)_2$. Mild treatment with nitric acid did not affect the amine, and gentle warming with nitric acid of sp. gr. 1.33 gave an intractable tar. Failing in this we thought we might achieve the same result by reducing the known *o*-phenylaminotriphenylcarbinol to *o*-phenylaminotriphenylmethane. However, we were equally unsuccessful in this, for when *o*-phenylaminotriphenylcarbinol was treated with alcohol and sulfuric acid,[14] formic acid,[15] glacial acetic acid and zinc dust or hydriodic acid and zinc dust, a sparingly soluble compound melting at 244–245° was obtained, and not our 144° amine. The 244–245° compound is the diphenyldihydroacridine of Baeyer and Villiger[16]



(XI)

Zinc dust and alkali, and catalytic reduction with the platinum catalyst of Adams were without effect on the *o*-phenylaminotriphenylcarbinol.

Triphenylmethylaniline and Phenylmagnesium Bromide.—After refluxing 5 g. (0.015 mole) of triphenylmethylaniline with 0.075 mole of phenylmagnesium bromide in an ether–toluene mixture at 100° for ten hours, 4 g. or 80% of the amine was recovered.

Benzalaniline and Phenylmagnesium Bromide.—A 48.5% yield of benzohydrylaniline, $(C_6H_5)_2CHNHC_6H_5$, was obtained after refluxing 18 g. (0.1 mole) of benzalaniline and 0.3 mole of phenylmagnesium bromide in an ether–toluene mixture for eight hours. No other product was isolated. In a comparable experiment with 14 g. (0.077 mole) of benzaniline, 0.1 mole of phenylmagnesium bromide and refluxing at 106° for eleven hours, the yield of benzohydrylaniline was 65%. This amine was identified as the hydrochloride melting at 194–195° and the nitrate melting at 158.5°.[17]

Some orienting experiments with benzanilide, $C_6H_5NHCOC_6H_5$, benzophenone-oxime, $(C_6H_5)_2C{=}NOH$, and benzophenone-oxime-*o*-methyl ether, $(C_6H_5)_2C{=}NOCH_3$, with phenylmagnesium bromide under forced conditions have not as yet yielded any of the expected *o*-phenylbenzohydrylaniline. The high recovery (69%) of benzophenone-oxime methyl ether might have been predicted from related experiments of Busch and Hobein[18] with oxime-ethers.

Preparation of *o*-Biphenylmagnesium Iodide.—The 2-nitrodiphenyl was prepared according to the directions of Bell, Kenyon and Robinson,[19] and then reduced to 2-aminodiphenyl by the method of Scarborough and Waters.[20]

Forty-three and one-half g. (0.21 mole) of 2-aminodiphenyl hydrochloride was diazotized in iced dilute hydrochloric acid by means of a solution of 14.5 g. (0.21 mole) of sodium nitrite. Then 100 g. of potassium iodide in 150 cc. of water was added slowly with continuous stirring. A heavy paste separated and after standing for

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[14] Schmidlin and Banús, *Ber.*, **45**, 3188 (1912).

[15] Kaufmann and Pannwitz, *ibid.*, **45**, 769 (1912).

[16] Baeyer and Villiger, *ibid.*, **37**, 3202 (1904).

[17] Bigelow and Eatnough, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 22.

[18] Busch and Hobein, *Ber.*, **40**, 2097 (1907).

[19] Bell, Kenyon and Robinson, *J. Chem. Soc.*, 1239 (1926).

[20] Scarborough and Waters, *ibid.*, 89, (1927).

one and one-half hours the mixture was warmed gently to expel nitrogen; a few crystals of sodium thiosulfate were added to remove free iodine and the almost black oil was extracted with toluene. The toluene solution was washed with water, dried over calcium chloride and then distilled in a vacuum. The yield of *o*-iododiphenyl boiling at 158° (6 mm.) was 30.4 g. or 51.7%; d_{25}^{25}, 1.6038. The iodide was strongly resistant to nitric acid decomposition in the Carius analysis.

Anal. Calcd. for $C_{12}H_9I$: I, 45.3. Found: I, 44.6.

There was no difficulty in getting a Grignard reagent from 21.1 g. of the *o*-iododiphenyl and 1.82 g. of magnesium turnings. The reaction was started with the activated 12³/₄% copper–magnesium alloy of Gilman, Peterson and Schulze.[21] The Grignard reagent gave the color test of Gilman and Schulze,[22] and when an aliquot was treated with carbon dioxide in the customary manner[23] *o*-diphenylcarboxylic acid[24] was obtained.

Preparation of *o*-Phenylbenzohydrylaniline from Benzalaniline and *o*-Biphenylmagnesium Iodide.—A toluene solution of 13.6 g. (0.075 mole) of benzalaniline was added to the 0.075 mole of Grignard reagent. Since there was no evidence of reaction the ether was partially replaced by toluene until the boiling point of the mixture was 95°. Immediately on increasing the reaction temperature, a deep red color set in. This was the only evidence of reaction, although refluxing was continued for eight hours. Occasional color tests[22] were made during the heating and in every case a deep green color was obtained. It was discovered on hydrolysis that this green color might not have been due to any unused Grignard reagent. After hydrolysis, about 0.5 g. of solid was removed by filtration from the deep red toluene layer. All of the hydrolysis mixture was steam distilled without separating the layers. The acid hydrolysis mixture immediately assumed a deep green color when steam was passed into it. Some benzaldehyde distilled over; this may have been due to unaltered benzalaniline. The residual heavy, deep green tar was taken up in 250 cc. of an alcohol–toluene mixture containing about 25% of toluene. On standing for three to four hours, crystals started to separate. After about twenty-four hours the crystals were filtered off and washed thrice with alcohol. The yield was 9 g. or 35.8% of *o*-phenylbenzohydrylaniline, and very probably more of the amine was formed as it is a compound that is affected (at least colorimetrically) by atmospheric exposure in a way to impede crystallization. The compound showed no depression in a mixed melting point determination with the amine obtained from phenyl isocyanate and phenylmagnesium bromide.

Summary

The forced reaction of phenyl isocyanate, phenyl isothiocyanate and benzophenone-anil with an excess of phenylmagnesium bromide gives *o*-phenylbenzohydrylaniline. The formation of this amine is unique in the sense that it undoubtedly takes place as a result of a 1,4-addition to the —C=N group in the side chain and one of the so-called ethylenic linkages in a benzene ring.

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[21] Gilman, Peterson and Schulze, *Rec. trav. chim.*, **47**, 19 (1928).

[22] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925); *Bull. soc. chim.*, **41**, 479 (1927).

[23] Gilman and Parker, THIS JOURNAL, **46**, 2816 (1924).

[24] Schmitz, *Ann.*, **193**, 115 (1878); Pictet and Ankersmit, *ibid.*, **266**, 143 (1891).