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POLYANILINE COMPOUNDS—III

REACTION OF PHENYL- AND METHYLLITHIUM WITH N,N'-DIPHENYL-*p*-QUINONE DIIMINE

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Abstract—The reaction of N,N'-diphenyl-*p*-quinone diimine (I) with PhLi proceeds predominantly as 1,6-addition together with reduction. In an analogous reaction with MeLi, in addition to reduction 1,6- and 1,4-addition was found to take place probably together with 1,2-addition. The influence of metal salts on the reaction course was studied, and possible mechanisms are discussed.

In reactions of quinones with Grignard reagents, in almost all cases 1,2- and 1,4-addition has been observed in combination with a concurrent reduction.[1a–h] The occurrence of 1,6-addition is, in general, very rare (the reaction of anthraquinone with t-butylmagnesium chloride,[2] the reaction of fuchsone with phenylmagnesium bromide[3]). In analogous reactions of quinones with organolithium compounds, the 1,2-addition is more general than the 1,4-addition.[1c, f, g; 4]

In the series of *p*-quinone diimines, only reactions of N,N'-diacyl derivatives have been studied. In reactions of N,N'-dibenzoyl- and N,N'-dibenzensulphonyl-*p*-quinone diimine with Grignard reagents, only reduction takes place;[5] in the reactions of analogous derivatives of 1,4-naphthoquinone, 1,2- as well as 1,4-addition was established.[5, 6]

The actual course of these reactions has not been elucidated. Very probably, quinones or quinone imines react with organometallic compounds according to the general reaction of strong electron acceptors with bases:[7]

$$A + B^{-}M^{(+)} \rightarrow A^{-\cdot}M^{+} + B^{\cdot}$$

In this reaction, the mechanism of reduction can be explained. The reaction mechanisms of 1,4-additions may be similar to the analogous reactions of cyclic conjugated ketones.[8, 9]

Under these circumstances the reactions of N,N'-diphenyl-*p*-quinone diimine (I) with organometallic reagents have been investigated. Presumably, reactivity of this substrate toward organometallic reagents should be, governed by the fact that this compound is a weaker electron acceptor than the oxygen-containing quinones or acylated *p*-quinone-imines—a condition, which should facilitate the investigation. Moreover, a study of the reactivity of I promised to bring advancement of the synthetic procedures in the polyaniline series. In a preceding paper[10] on this topic, a synthesis of oligomers of I has been described.

It was found in preliminary experiments that only reduction was encountered in the reaction of I with phenylmagnesium bromide. However, N,N,N'-triphenyl-*p*-phenylenediamine (IIIa) was obtained as the principal product from the reaction with phenyllithium (cf. Chart 1). Thus, the reaction proceeds predominantly as 1,6-addition. In minor yields, a product (II) of reduction, and a compound substituted with two Ph groups was formed. We failed to localize the position of the substituents in the latter substance; estimation of active hydrogen and the fact that the substance was not oxidized with silver oxide to a quinone diimine indicated that one Ph group is located on one of the N atoms, whereas the other is attached to some aromatic nucleus (IV).

The first instance of 1,6-addition of organolithium compounds mentioned in 1961 involved sterically hindered aromatic ketones,[11] but the available data is insufficient.

In order to establish, whether this unusual reaction takes place also with other organolithium compounds, the reaction of I with methyllithium was investigated. Besides leuco-base II, the following compounds were isolated from the reaction: N-methyl-N,N'-diphenyl-*p*-phenylenediamine (IIIb), 2-methyl-N,N'-diphenyl-*p*-phenylenediamine (V), 2,6-dimethyl-N,N'-diphenyl-*p*-phenylenediamine (VI), 2,5-dimethyl-N,N'-diphenyl-*p*-phenylenediamine (VII), 2,5-dimethyldiphenylamine (VIII), and 3,4-dimethyldiphenylamine (IX). The structure of each compound with the exception of V was indicated by IR and NMR spectroscopy, and established by independent synthesis. The structure of V was elucidated by degradation to aniline and 2-methylhydroquinone.

In the course of the preliminary structural examination of the above compounds, NMR spectra of the quinone imines prepared from bases V–VII by oxidation with silver oxide were also studied. This gave rise to some interesting observations concerning isomerism in these compounds. A record of the spectrum with the bands corresponding to Me groups is presented in Fig. 1. 2-Methyl-*p*-quinone diimine (a) shows two bands differing from each other by 8 c/s and splitted by allylic interaction. Hence, this compound exists predominantly as a mixture of two isomers. On the other hand, the spectrum of the 2,5-dimethyl derivative (b) shows only one band splitted by allylic interaction, temperature being of no substantial influence on its width or position. It is thus probable that only one isomer predominates in this compound. In the spectrum of the 2,6-derivative, there is a very broad band with two maxima of equal intensity at a distance of 23 c/s (c) from each other at ambient temperature—a shape corresponding to a conception of a mixture of two isomers occurring in equal proportions in a mobile equilibrium. With elevated temperature, the width of this band decreases rapidly (d), which effect could be explained by an enhanced rate of transition of one isomer into the other. Since completion of this work, a paper by Layer and Carman appeared in Tetrahedron Letters, 1285 (1968), in which a similar isomerization mechanism has been described.

In the reaction of N,N'-diphenyl-*p*-quinone diimine with methyllithium reduction as well as 1,6-, 1,4-, and may be also 1,2-addition takes place. (cf. Chart 1).

Compound VI, the central ring of which is substituted in positions 2 and 6, was formed probably as a product of a chain reaction, in which an intermediate of 1,4-addition was oxidized by the unreacted starting compound I to give the corresponding quinone imine, which in turn was able to add a further molecule of the organometallic reagent.

In order to explain the formation of the diphenylamine derivatives VIII and IX, a cleavage of C—N bond probably takes place either in the course of the actual reaction or during the subsequent decomposition of intermediates with water. The cleavage is suppressed, if the reaction is conducted at a lower temperature. The closest analogy for such a reaction may be seen in the cleavage of C—N bond observed by Eisch[12] with derivatives of dimethylaniline and triphenylamine by the action of a

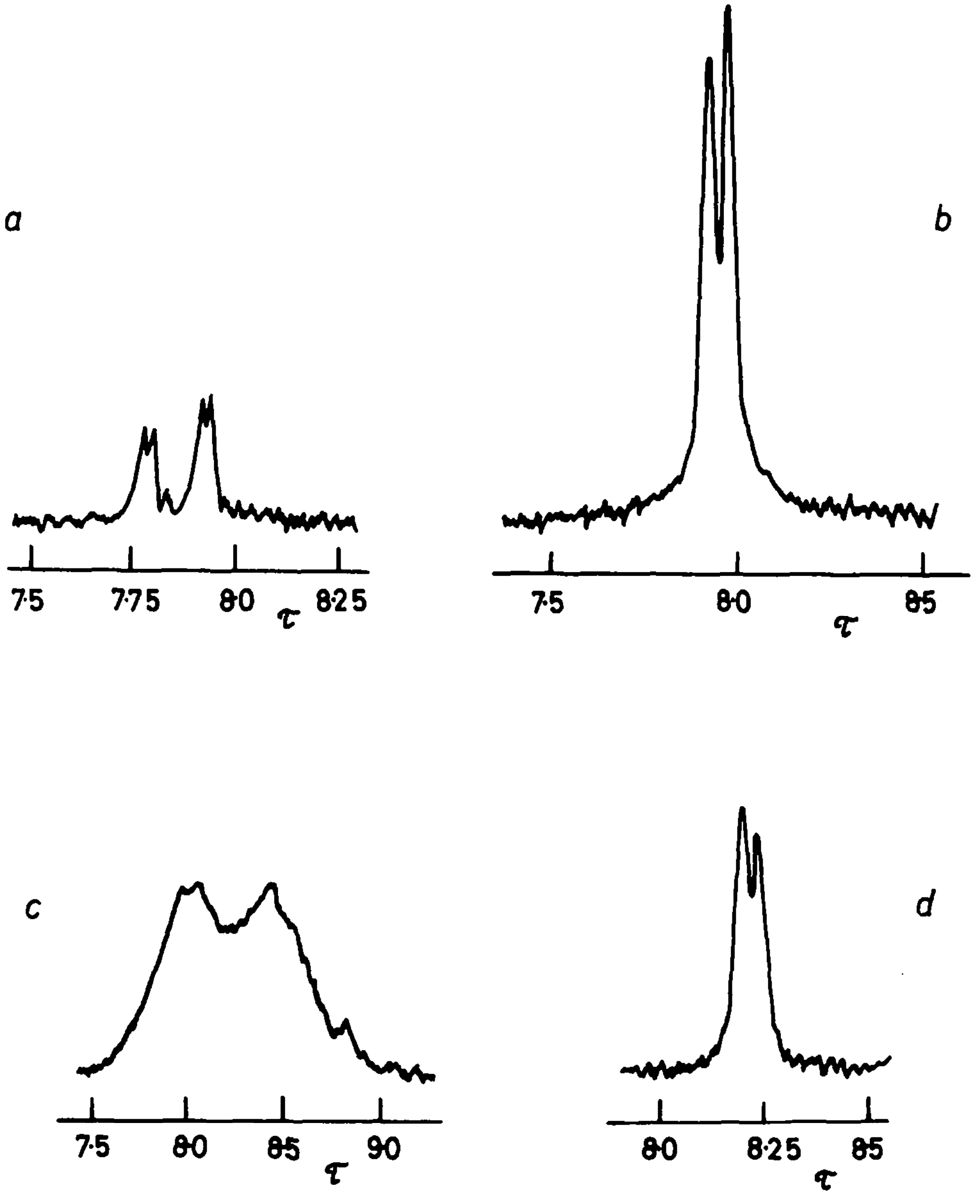
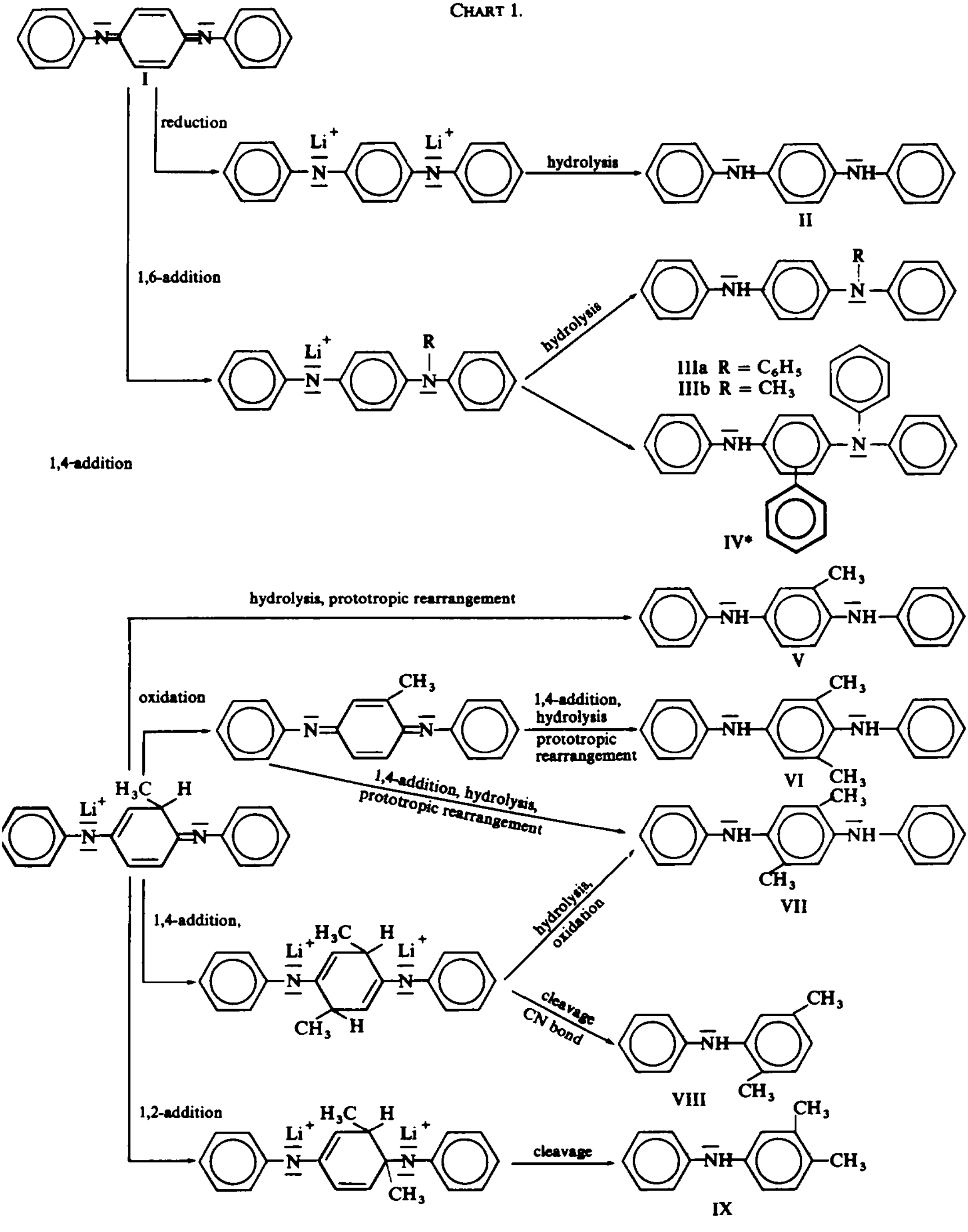


Fig. 1 (a) 2-methyl-N,N′-diphenyl-*p*-quinone diimine (measured at 70°); (b) 2,5-dimethyl-N,N′-diphenyl-*p*-quinone diimine (measured at 20° and 70°); (c) 2,6-dimethyl-N,N′-diphenyl-*p*-quinone diimine (measured at 20°); (d) 2,6-dimethyl-N,N′-diphenyl-*p*-quinone diimine (measured at 70°).

CHART 1.



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* It cannot be excluded that the phenyl group (in thick lines) is situated on one of the outer rings instead of the central one.

complex of biphenyl with lithium metal, which proceeds likewise in tetrahydrofuran. The formation of compounds IX is probably by cleavage of a product originating from 1,4- and 1,2-addition.

In order to obtain some indication regarding mechanisms, the influence of cobaltous and cuprous salts on the reaction course was followed in analogy to previous studies on the reaction of Grignard reagents with conjugated ketones[13a,b] or Schiff bases.[13c] In addition, the influence of a change in polarity of medium was studied; however, the reaction in a non-polar medium takes place only in heterogeneous phase due to insolubility of the substrate.

TABLE 1. REACTION OF N,N'-DIPHENYL-*p*-QUINONE DIIMINE (I) WITH METHYLLITHIUM

Reaction conditions	MeLi excess	Yields of substances (%) (Relative yields referred to the substance IIIb)				
		II	IIIb	V	VI + VII[c]	VIII + IX[c]
A	3·2	—	5·6	14·4	8·7	16·7
			(1·0)	(2·6)	(1·6)	(3·0)
A[a]	3·0	19·4	4·7	13·7	9·2	15·4
		(4·1)	(1·0)	(2·9)	(2·0)	(3·3)
B	5·5	29·6	5·4	12·5	8·4	1·7
		(5·5)	(1·0)	(2·3)	(1·6)	(0·3)
B[b]; 3,3 mol % $CoCl_2$	5·5	66·0	6·2	13·0	10·8	—
		(10·6)	(1·0)	(2·1)	(1·7)	—
B[b]; 10 mol % $CoCl_2$	5·5	57·1	3·4	12·0	6·2	3·2
		(16·8)	(1·0)	(3·5)	(1·8)	(0·9)
B[b]; 10 mol % CuCl	5·5	58·8	3·2	7·5	4·2	0·7
		(18·4)	(1·0)	(2·3)	(1·3)	(0·2)
B[b]; 100 mol % CuCl	5·5	59·1	27·9	3·2	0·0	1·3
		(2·1)	(1·0)	(0·1)	(0·0)	(0·1)
C	4·4	55·0	6·8	4·3	1·0	6·4
		(8·1)	(1·0)	(0·6)	(0·2)	(0·9)

A Reaction was carried out as described in the experimental part

B Reaction was carried out so that a solution of methyllithium in ether was added to the saturated solution I (7·75–10 mmoles) in tetrahydrofuran at room temperature, and the reaction mixture was then kept 2 hours at room temperature.

C Reaction was carried out using 9·68 mmoles I in the hexane medium with solid methyllithium etherate; it is described in more detail in the experimental part.

[a] The experiment was repeated in order to determine the reproducibility of the separation process.

[b] The metal salt was added to the solution I before the reaction, and the solution was stirred until the salt was dissolved (15 min.); mol % are referred to substance I.

[c] In the experiments carried out with a smaller amount of I it would be difficult to separate the substances VI and VII, or VIII and IX; therefore, only total yields of fractions containing these substances are listed in the Table.

A comparison of the results (Table 1), revealed that small amounts of cobalt (II) or copper (I) chloride promote the reduction. Only in the presence of a stoichiometric amounts of copper (I) chloride, is the ratio of 1,6- *vs* 1,4-addition substantially influenced, which suggests a reaction of methylcopper. In accordance with this assumption, the reaction of I with methylcopper prepared according to Gilman[14] afforded only compounds II and IIIa.

DISCUSSION

Undoubtedly, the corresponding semiquinone is an intermediate in the reduction of I to II, with organolithium reagents. In the case of mixing I with butyllithium an EPR signal was observed;[7a] we have made the same observation for the system I—methyllithium. Other electron acceptors react with bases in a similar way.[7a,b]

The mechanisms of 1,4- and 1,6-addition are less ambiguous. For addition of Grignard reagents to conjugated systems, two mechanisms are considered:[15a] (a) a mechanism supposing a cyclic transition state with a simultaneous shift of electron pairs; (b) a direct attack of the reagent molecule polarized by solvation onto an electron-deficient point of substrate. An argument against the general validity of mechanism (a) arose first from the observation that 1,4-addition takes place with the cyclic ketones possessing a transoid arrangement of the conjugated system (cyclo-hexen-1-one), where a cyclic transition state is impossible for steric reasons.[8] It was found that the yields of 1,4-addition in this case did not differ very much from those obtained with a ketone with the cisoid arrangement of the conjugated system ($\Delta^{8,9}$-octal-1-one).[9] Mechanism (b) is also assumed in cases of multiple additions, i.e. 1,6- and 1,8-ones, which were observed in reactions of aliphatic unsaturated acid esters with Grignard reagents.[15]

In our case, mechanism (a) is excluded for the 1,4- and 1,6-additions, hence, the 1,4-addition may proceed along mechanism (b) in analogy with cyclic ketones with the transoid arrangement of the conjugated system. The application of mechanism (b) to 1,6-additions in the series of unsaturated monocarboxylic acid esters does not justify an analogous explanation of reaction mechanism in our case. The former compounds should be polarized probably in such a manner that the positive defect would be located on the last C atom of the conjugated system, whereas the negative charge would pertain on the O atom of the carbonyl function, which distribution should enable even multiple additions, e.g. 1,6- or 1,8-, to proceed by the ionic mechanism (b). On the contrary, in the case of a quinone imine-type substrate, the most electron-deficient place of the molecule should be the central quinone ring. The charges localized on the respective atoms calculated by the simple method HMO*;[16]

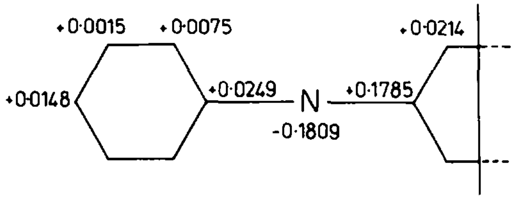

FIG. 2 Net charges in +e units.

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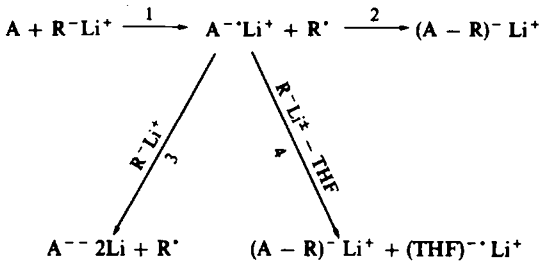
[*] For the calculation, the following standard values of parameters were taken: Coulombic integrals $h_C = 0$, $h'_N = 0{\cdot}5$; resonance integrals $k_{CN} = 1$; $k_{CC} = 1$ (in β units).

is illustrated in Fig. 2. Accordingly, an ionic mechanism, irrespective whether it is a or b, should give rise predominantly to the 1,2-addition, then to the 1,4-, and to the least extent to the 1,6-. Such an assumption is in agreement with the observation that 1,4-addition predominated over 1,6-addition and reduction, when a more basic reagent (in the reactions of methyllithium and phenyllithium) is used, or the reaction is run in a more polar medium.

The concomitant preference of reduction and 1,6-addition during reaction in a non-polar medium may be interpreted by assuming that the first step in both these reaction courses is represented by a mono-electron transition leading to an anion-radical (Chart 2).

CHART 2



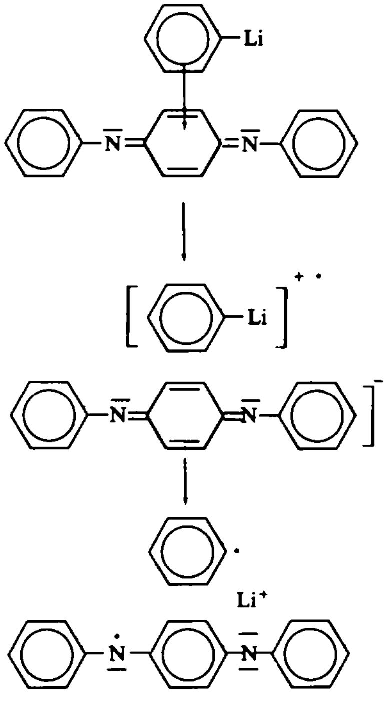
In order to determine if reaction 2 gives rise predominantly to a N-Me derivative, an estimate of unpaired-electron densities in semiquinone molecule[16] was made: The ratio of densities of the unpaired electron on the individual atoms was put equal to the ratio of squares of coefficients expressing the proportion of the respective atomic orbitals in the development of the molecular orbital containing the unpaired electron. The value of this ratio for nitrogen and one of the equivalent carbons of the central ring is 4:1, in agreement with the above assumption.

In analogy to other examples of competitive additions to conjugated systems,[13a,b; 15] again the presence of copper (I) chloride suppressed the "shorter-range" additions and reduction gained preference. For the course of a "conjugated addition" in the presence of copper (I) chloride, a mechanism was recently suggested,[17] which assumed an electron transfer between organocuprous compound and substrate and a subsequent reaction of the anion-radical thus formed with an organocupric compound. This explanation is also applicable to the present case.

However, as a theoretically possible alternative it must be considered that the N-substituted compounds originate from a direct attack of I with the free radicals generated by reduction or decomposition of methylcopper. In our view, such reactions would not occur to a significant extent in the cases discussed. By analogy with similar[18] reactions of oxygen-containing quinones, the hypothetical reaction of I with free radicals should afford also an N,N′-disubstituted derivative. However, the absence of any such compound in the mixture of products from reaction of I with methyllithium was proved by chromatography using an authentic sample for comparison. In the case of the reaction using phenyllithium the above hypothesis regarding mechanism of 1,6-addition is incompatible with the ratio of yields of 1,6-addition and reduction. Actually, the product of 1,6-addition was formed in a larger amount than would correspond to a hypothetical state, in which all phenyl radicals generated by reduction would react in the proposed direction.

The higher proportion of 1,6-addition *vs* reduction probably is related to the fact that the electron transition takes place via π–π complex (Chart 3). The phenyl radicals resulting by collapse of this complex could then be retained by π–π interaction in a close proximity of anion-radical enhancing the probability of recombination.

CHART 3



EXPERIMENTAL

Preparation of solns of organometallic reagents as well as the corresponding reactions were conducted in an atmosphere of argon. Samples for analysis were dried *in vacuo* (0·2 Torr) either at 80° for 4 hr or at ambient temp for 12 hr. M.ps were estimated on Kofler stage.

Materials. N,N'-Diphenyl-*p*-phenylenediimine was prepared as follows. To a soln of 10 g of N,N'-diphenyl-*p*-phenylenediamine in 1000 ml acetone, 13 g Ag_2O was added portionwise with stirring; the reaction mixture was stirred for an additional hr, filtered, and the precipitated silver extracted with hot acetone. After evaporation of acetone, the residue was crystallized from cyclohexane to yield 9 g (90·7%) of the wanted product, m.p. 185–186°.

THF was in each instance distilled from LAH before use. Silica gel for chromatography (size 60–120 μ) contained 12% water. Ether for chromatography was dried over $CaCl_2$, and distilled; pet. ether was a hydrocarbon fraction, b.p. 42–64°.

Reaction of N,N'*-diphenyl-*p*-quinone diimine* (I) *with phenyllithium*

To 100 ml of a soln of PhLi[19] (0·0648 mole), a suspension of 3·8 g (0·0147 mole) of I in 170 ml THF was added gradually with stirring. The reaction mixture was refluxed for 4 hr, allowed to stand at room temp for 12 hr, and decomposed with water. The organic layer was separated, and the aqueous one extracted with ether. The combined organic layers were dried with $MgSO_4$, and evaporated under reduced press. The residue was chromatographed over alumina (activity II–III; 80-fold excess; elution mixture: pet. ether–ether).

The first fraction was biphenyl. The residue from the second fraction (0·427 g; 7%) became crystalline on trituration with pentane, and was crystallized twice from EtOH; m.p. 142–143°. For this substance, structure IV was suggested. (Found: C, 87·14; H, 5·97; N, 6·83; H^+, 0·25. Calc. for $C_{30}H_{24}N_2$: C, 87·34; H, 5·86; N, 6·79; H^+, 0·25%).

The residue from the third fraction (2·63 g; 53%) became crystalline on trituration, and was crystallized twice from cyclohexane, m.p. 130–131° identical with IIIa,[20] m.p. 134°. This identity was confirmed by comparison (m.p.) of the acetyl derivatives (see the following paragraph). (Found: C, 85·83; H, 6·20; N, 8·07; H^+, 0·27. Calc. for $C_{24}H_{20}N_2$: C, 85·68, H, 5·99; N, 8·33; H^+, 0·30%).

The residue from the fourth fraction (0·65 g; 17%) was identified as N,N'-diphenyl-*p*-phenylenediamine by mixture m.p.

N,N,N'-*Triphenyl*-N'-*acetyl-p-phenylenediamine*

Compound IIIa (0·2 g) was heated with 4 ml Ac_2O at 100° for 3 hr, and cooled. By scratching with a glass rod, a product precipitated, which was in turn set aside for crystallization at 0°. Two crystallizations from EtOH, yielded a product, m.p. 184–184·5°. A sample for analysis was further purified by another crystallization leaving the m.p. unchanged. For N,N,N'-triphenyl-N'-acetyl-*p*-phenylenediamine, literature[20] records m.p. 184°. (Found: C, 82·09; H, 6·06; N, 7·46. Calc. for $C_{26}H_{22}N_2O$: C, 82·51; H, 5·86; N, 7·40%).

Reaction of N,N'-*diphenyl*-p-*quinone diimine* (I) *with methyllithium*

To 700 ml of an ethereal soln of MeLi (0·293 mole),[19] a suspension of 20 g (0·0774 mole) of I in 600 ml THF was added with vigorous shaking. The reaction mixture was refluxed for 3 hr, and then allowed to stand at room temp for 18 hr. The mixture was decomposed with water (150 ml), and worked up in the manner described for the reaction of I with PhLi. The residue (21 g) was adsorbed onto silica gel (40 g) and chromatographed (a column 218 × 8 cm, 5150 g of silica gel) using a mixture of pet. ether–ether (97:3). After 243 fractions, the proportion of ether was raised to 7%. Fractions 1 to 125 comprised 125 ml, and the remainder 250 ml. Purity of individual fractions was checked by TLC (detection with Br_2 vapour) of both original solns and samples of the solns after oxidation with Ag_2O.

The residue of combined fractions 18–20 (1·168 g; 7·64%) contained compound VIII. This was recrystallized twice from pentane at −75° to a constant m.p. 54·5–55°. (Found: C, 85·23; H, 7·75; N, 7·04; H^+, 0·49. Calc. for $C_{14}H_{15}N$: C, 85·23; H, 7·67; N, 7·10; H^+, 0·51%).

In analogous manner, the residue from combined fractions 36–44 (0·804 g; 5·36%) afforded IX, m.p. 53–54°. (Found: C, 85·50; H, 7·97; N, 7·01; H^+, 0·52. Calc. for $C_{14}H_{15}N$: C, 85·23; H, 7·67; N, 7·10; H^+, 0·51%).

The residue from combined fractions 151–187 (1·182 g; 5·44%) was crystallized twice from cyclohexane to yield IIIb, m.p. 104–105·5°. (Found: C, 83·23; H, 6·66; N, 10·10; H^+, 0·42. Calc. for $C_{19}H_{18}N_2$: C, 83·18; H, 6·61; N, 10·21; H^+, 0·37%).

The compound from combined fractions 230–241 (1·111 g), VII, is partly oxidized with air oxygen at heating with solvents. This compound was thus oxidized with Ag_2O to quinone imine derivative similarly to the preparation of I. The product was crystallized three times from EtOH m.p. 196–199°. Another portion of this substance was obtained by work-up of fractions 247–266 totalling the yield to 1·540 g (6·94%). (Found: C, 83·97; H, 6·52; N, 9·80. Calc. for $C_{20}H_{18}N_2$: C, 83·88; H, 6·33; N, 9·79%). By hydrogenation of a quinone imine carried out in soln in EtOH over Pd–C with heating, and by subsequent filtration and crystallization in an atmosphere of H_2, leucobase VII, m.p. 112–113°, was obtained.

The residue of the last fractions 247–266 (0·830 g) consisted of a mixture of VI and VII, was oxidized with Ag_2O into a mixture of quinone imine derivatives, and further separated by an additional chromatography over silica gel (200-fold excess; elution with a mixture pet. ether–ether 9:1) to give 0·275 g 2,5-dimethyl-*p*-quinone diimine and 0·384 g (1·72%) of a non-crystalline material. This in turn was hydrogenated in an ethereal soln, and crystallized from toluene to afford VI m.p. 121–122·5°. A sample for analysis was recrystallized from the same solvent. (Found: C, 83·33; H, 7·17; N, 9·69; H^+ 0·70. Calc. for $C_{20}H_{20}N_2$: C, 83·30; H, 6·99; N, 9·71; H^+, 0·70%).

The residue from combined fractions 271–307 (3·065 g); 14·43%) was crystallized three times from EtOH to a constant m.p. 102–102·5. This substance was shown to be V by degradation, described in detail later. (Found: C, 83·18; H, 6·75; N, 10·18; H^+, 0·77. Calc. for $C_{19}H_{18}N_2$: C, 83·66; H, 6·61; N, 10·21; H^+, 0·74%).

Further fractions contained N,N'-diphenyl-*p*-phenylenediamine, which was identical with an authentic sample (m.p.).

N-*Acetyl-2,5-dimethyldiphenylamine*

(a) *From compound* VIII. A mixture of 0·203 g (0·00103 mole) of VIII and 4 ml Ac_2O was heated to 110° for 5 hr. The Ac_2O was evaporated *in vacuo*, and the crystalline residue was crystallized twice from EtOH, m.p. 90–90·5° (0·190 g, 77·17%). (Found: C, 80·04; H, 7·30; N, 6·12. Calc. for $C_{16}H_{17}NO$: C, 80·30; H, 7·16; N, 5·85%).

(b) *An alternative synthesis.* A mixture of 5 g (0·0251 mole) 2,5-dimethylacetanilide, 4 g K_2CO_3, 4·1 g bromobenzene, and 25 ml nitrobenzene was refluxed with vigorous stirring for 15 hr. The mixture was freed of nitrobenzene by steam-distillation, and 40 ml 6N HCl was added to precipitate an oil, which was in turn taken up in ether. The residue from this extract (3·8 g) was purified by column chromatography over silica gel. The material from the main fraction (2·5 g; 41·64%) was crystallized twice from dil EtOH, m.p. 89·5–90·5° and identical with the sample prepared under (a).

N-*Acetyl*-3,4-*dimethyldiphenylamine*

(a) *From compound* IX. The preparation was analogous to the procedure (a) with N-acetyl-2,5-dimethyldiphenylamine; yield 76·11%, m.p. 95–96·5°. (Found: C, 80·20; H, 7·05; N, 5·98. Calc. for $C_{16}H_{17}NO$: C, 80·30; H, 7·16; N, 5·85%).

(b) An alternative synthesis was achieved according to procedure (b) using 3,4-dimethylacetanilide. Identity of the products from both experiments was established by mixture m.p. and comparison of IR-spectra.

N-*Methyl*-N,N'-*diphenyl*-p-*phenylenediamine* (IIIb)

To a soln of 1·288 g (0·005 mole) N,N'-diphenyl-*p*-phenylenediamine in THF, 8·7 ml of an ethereal soln of 0·0045 mole PhLi[19] was added dropwise. The mixture was refluxed for 75 min, cooled, and treated dropwise with a soln of 0·71 g (0·0045 mole) MeI in 20 ml THF with stirring and water-cooling. The mixture was refluxed for 3 hr, allowed to stand at room temp for 12 hr, decomposed with water, and worked up analogously as in the reaction of I with MeLi. The crude product (1·287 g) was separated by column chromatography over silica gel into 3 fractions: the first (0·249 g; 17·37%) afforded a material, m.p. 154·5–155·5°, which melted undepressed in mixture with authentic N,N'-dimethyl-N,N'-diphenyl-*p*-phenylenediamine.[21] The second fraction (0·378 g; 27·84%) after crystallization from cyclohexane, m.p. 105–105·5° was identical with IIIb by mixture m.p. and comparison of IR spectra. The third fraction contained unreacted N,N'-diphenyl-*p*-phenylenediamine.

2,5-*Dimethyl*-p-*quinone diimine*

A mixture of 0·36 g (0·00261 mole) 2,5-dimethylhydroquinone, 1·01 g anhyd $CaCl_2$, 0·18 g anhyd $ZnCl_2$, and 1·05 g aniline was heated to 210° in a sealed tube for 19 hr. The mixture was triturated successively with water and dil HCl, washed thoroughly with water, and dried. The crude product was separated by column chromatography over silica gel into two fractions. From the residue of the first fraction after crystallization from cyclohexane and heptane, a material, m.p. 105–105·5° was obtained which was probably 2,5-dimethyl-*p*-aminophenol. (Found: C, 78·96; H, 7·21; N, 6·40. Calc. for $C_{14}H_{15}NO$: C, 78·84; H, 7·09; 6·57%).

The residue of a further fraction was converted by oxidation with Ag_2O into a quinone diimine. By mixture m.p. and superimposability of IR-spectra, the identity with the quinone imine of leucobase VII was established.

N,N'-*Diphenyl*-2,6-*dimethyl*-p-*phenylenediamine* (VI)

A mixture of 2·0 g (0·0145 mole) 2,6-dimethylhydroquinone, 3·2 g anhyd $ZnCl_2$, and 5·6 ml aniline was heated to 215–220° in a sealed tube for 5 hr. The mixture was boiled successively with dil HCl (1:3) and a NaOHaq (with Zn dust added). The solid product was washed thoroughly with water, and chromatographed over silica gel and proved to be identical with VI by mixture m.p. and IR spectra.

Degradation of N,N'-*diphenyl-2-methyl*-p-*phenylenediamine*

In ethereal soln, 0·21 g N,N'-diphenyl-2-methyl-*p*-phenylenediamine (obtained from fraction 271–307 from the reaction of I with MeLi) was oxidized with Ag_2O to give the corresponding quinone diimine by the same method as in the preparation of I. To the product, 27% H_2SO_4 was added, and the mixture was refluxed for 30 min, cooled to room temp, neutralized with dil NH_4OH, and extracted 4 times with ether. The extract was dried with $MgSO_4$, evaporated, and the residue was distilled *in vacuo*. At about 100°, a liquid distillate passed over, which was in turn identified as aniline by IR spectroscopy; at 180°, a solidifying fraction distilled over, and was brought to crystallization on trituration with pentane. A mixture m.p. with an authentic sample of 2-methyl-hydroquinone showed no depression.

Reaction of N,N'*-diphenyl-*p*-quinone diimine with methyllithium in n-hexane*

To 120 ml of an ethereal soln of 0·068 mole MeLi,[19] 60 ml n-hexane was added, and the soln was evaporated to dryness under reduced press at 40°. The residue was dried for an additional 30 min at the same temp at 0·2 Torr. To this material, 80 ml n-hexane was added followed by a suspension of 2·6 g (0·0102 mole) of I in 250 ml n-hexane at room temp with stirring. The reaction mixture was homogenized by shaking, stirred for 40 hr at room temp, decomposed with water, and worked up in the same manner as in the preceding experiment using THF and ether. The residue (2·7 g) was separated by column chromatography over silica gel; the results of the separation are summarized in the Table 2.

Reaction of N,N'*-diphenyl-*p*-quinone diimine with methylcopper*

To a suspension of 2·16 g (0·0113 mole) copper (I) iodide in THF, 13 ml of a soln of 0·0101 mole MeLi was added with stirring at −30° within 6 min, and the mixture was stirred for an additional hr at the same temp. To this mixture, which gave a negative Gilman test, a pre-cooled soln of 0·52 g (0·00201 mole) of I in 75 ml THF was added by means of a cooled dropping funnel with continuing stirring and cooling to −30°. The reaction mixture was allowed to come slowly to room temp, then was heated at 30° for 10 min, and decomposed with water as usual. The mixture was shown by TLC using authentic reference samples to contain exclusively II and IIIb.

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