316. *A Rearrangement of* o-*Aminodiphenyl Ethers. Part III. 2-Acylamidodiphenyl Ethers.*

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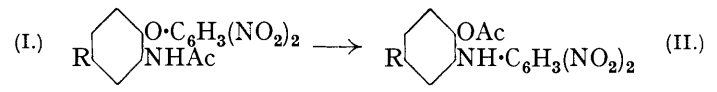
THE novel intramolecular change (J., 1934, 727) whereby some 2-acylamidodiphenyl ethers (I, R = Me) yield 2-acyloxydiphenylamines (II, R = Me) has been further investigated for a range of substituents (R = H, Me, I, Br, Cl; Ac = acetyl, benzoyl, *m*-nitrobenzoyl,



o-nitrobenzoyl, picryl). In general the results (cf. Table) bear out the conclusions already drawn (*loc. cit.*, p. 727), (*a*) that the acyl derivatives undergo rearrangement more slowly than do the parent ethers, and (*b*) that the rate of change falls off with increasing strength of the acid corresponding to acyl.

Rates of Rearrangement (mins.) of 2-Acylamidodiphenyl Ethers.

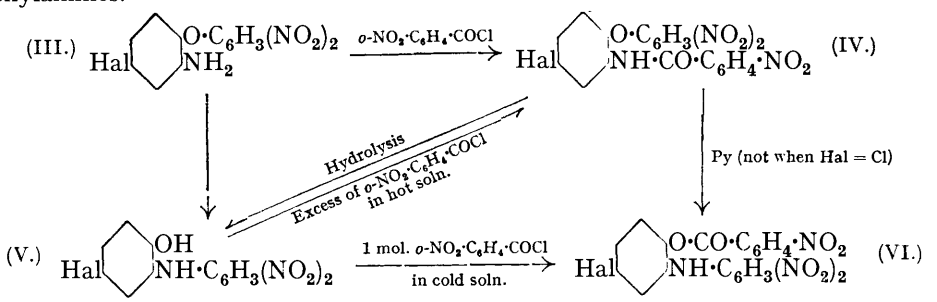
R=	Me.	H.	I.	Br.	Cl.
2-Substituent.					
Amino	7	5	15	30	60
Acetamido	In all cases rearrangement took many hours				
Benzamido	—	—	—	45	—
m-Nitrobenzamido	—	—	—	(120)	75
o-Nitrobenzamido	Rearrangement immeasurably slow				No rearr.
Picramido	—	No rearr.	—	—	—

The observations recorded in the Table were made with solutions under the same conditions as those (this vol., p. 198) used in measuring the rate of rearrangement of the parent ethers, relevant results for which are quoted. The figure in parenthesis is unreliable owing to separation of the very sparingly soluble product of rearrangement. In the limited number of cases observed, the benzoyl and *m*-nitrobenzoyl derivatives underwent rearrangement more rapidly than did the corresponding derivatives of the relatively weak acetic acid. An anomaly of this type has been reported by Jones (J., 1934, 210) in connection with the influence of acyl on the reactivity of amines. The derivatives of the relatively strong *o*-nitrobenzoic and picric acids, as anticipated, underwent rearrangement only very slowly or not at all (cf. Evans and Smiles, this vol., p. 184).

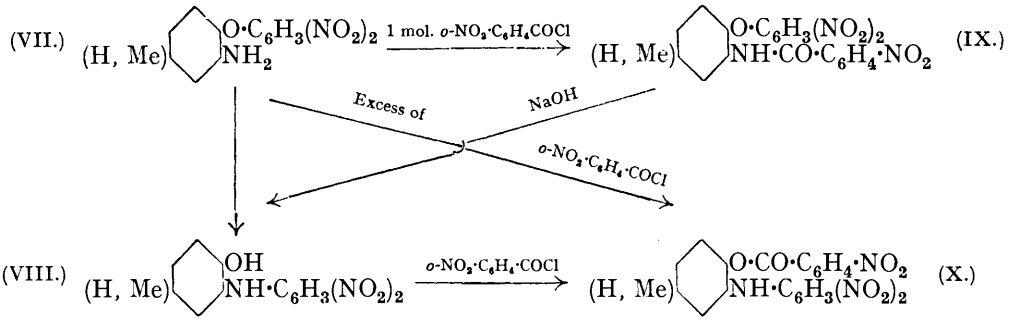
The results now recorded may be explained in terms of the mechanism of the change suggested in Part II (this vol., p. 197). The effect of acyl will be to reduce the availability of the unshared electrons of nitrogen and so to diminish the possibility of formation of the $N \longrightarrow C_\alpha$ link which is postulated as a stage in the change. In the extreme cases of the *o*-nitrobenzoyl derivative of the chloro-ether and of the picryl derivative of the unsubstituted ether (I, R = H), the effects of the substituents are sufficient to inhibit completely the formation of the link, even under much more searching conditions than those used in compiling the above Table. It is suggested that the unusual migration of acyl rather than of proton (cf. Evans and Smiles, this vol., p. 182) is in some way due to the action of the negative centre (oxygen, nitrogen) present in the catalysing solvents, typical of which are pyridine, aniline, water, alcohols, and in some cases acetic acid.

The above cases of complete inhibition of the rearrangement suggested that a direct reversal of the change, *viz.*, a rearrangement of a diphenylamine to a diphenyl ether, might

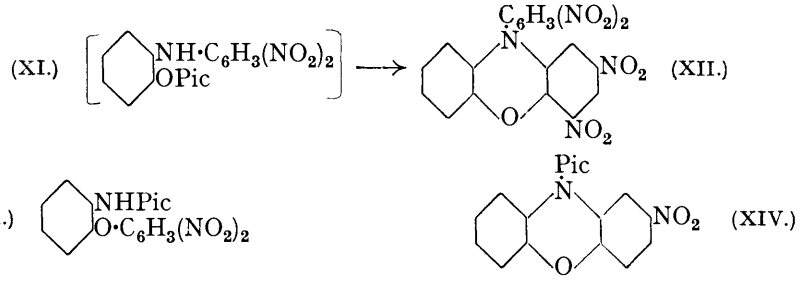
be met with in presence of suitable substituents. Though this has not been observed, all the 2-acyloxydiphenylamines prepared being stable under a great variety of conditions, the *o*-nitrobenzoylation of the 5-halogeno-2-hydroxydiphenylamines (V) presents a feature of considerable interest. When this reaction is carried out in cold acetone with one mol. of the acid chloride, the expected *O*-acyl derivatives (VI) are obtained, but in warm acetone with an excess of the reagent the product is in all three cases the acylamido-derivative (IV) of the isomeric diphenyl ether. Hydrolysis of the acylamidodiphenyl ethers is accompanied, as in other cases, by rearrangement of the product to the isomeric hydroxydiphenylamines.



Attempts to obtain *o*-nitrobenzoyl derivatives of the 5-carboxydiphenyl ether and the isomeric diphenylamine (I and II, R = CO_2H) were unsuccessful. Also, no *p*-toluenesulphonate of the 4-chloro-ether could be obtained. The behaviour of the 5-methyl and unsubstituted diphenylamines (VIII) with *o*-nitrobenzoyl chloride was normal. When this acylation of the isomeric ethers (VII) was carried out in acetone, the products were either the 2-acylamido-derivatives (IX) of the ethers or the 2-acyloxy-derivatives (X) of the corresponding diphenylamines according to the conditions used.



Picrylation of 2′ : 4′-dinitro-2-hydroxydiphenylamine yielded the unstable derivative (XI), which was converted in aqueous pyridine into the scarlet phenoxazine (XII). 2 : 4-Dinitrophenylation of 2-hydroxyphenylpicrylamine yielded either the derivative (XIII) or the magenta oxazine (XIV) isomeric with (XII) according to the conditions used. Phenoxazine formation from (XIII) in aqueous pyridine is preceded by hydrolysis, yielding 1 : 3-dinitrophenoxazine, described by Turpin (J., 1891, **59**, 723).



Experimental.

2′ : 4′-Dinitro-2-hydroxydiphenylamine yielded an o-*nitrobenzoate* by usual methods. It formed golden-yellow plates from glacial acetic acid, m. p. 151° (Found : N, 13·0. $C_{19}H_{12}O_8N_4$ requires N, 13·2%). The picrate (XI) resulted when the diphenylamine in alcohol was treated at room temperature with picryl chloride in presence of either sodium acetate or sodium ethoxide. It was purified from benzene as an unstable, deep yellow substance (decomp. 140—145°), which gave indeterminate results on analysis, but in contact with warm aqueous pyridine yielded a scarlet *phenoxazine* (XII), decomp. 305—310° (Found : C, 49·4; H, 2·1; N, 15·6. $C_{18}H_9O_9N_5$ requires C, 49·2; H, 2·0; N, 15·9%).

2′ : 4′-Dinitro-2-aminodiphenyl ether (3 g.) in 50% aqueous acetic acid (10 c.c.), shaken in the cold with a slight excess of acetic anhydride, yielded an *acetyl* derivative, colourless needles from benzene, m. p. 146° (Found : N, 13·3. $C_{14}H_{11}O_6N_3$ requires N, 13·2%). The substance underwent rearrangement to the *O*-acetate of the corresponding diphenylamine in hot alcohol, pyridine, or water. The o-*nitrobenzoyl* derivative, obtained by use of *o*-nitrobenzoyl chloride (1 mol.) in acetone in presence of anhydrous sodium carbonate, formed white plates from benzene, m. p. 232° (Found : N, 13·2. $C_{19}H_{12}O_8N_4$ requires N, 13·2%). It was rearranged slowly in pyridine. Use of an excess of the acid chloride in this acylation resulted in the formation of the *o*-nitrobenzoate of the isomeric diphenylamine. Picrylation appeared to be preceded by rearrangement of the ether in the solvent alcohol, since it yielded only the isomeric derivative (XI). The *picryl* derivative (XIII) was obtained by treatment of 2-hydroxyphenylpicrylamine with chlorodinitrobenzene in alcohol in presence of anhydrous sodium acetate at room temperature : yellow prisms from benzene which darkened at 225° and decomposed at 245—250° (Found : C, 44·8; H, 2·0. $C_{18}H_{10}O_{11}N_6$ requires C, 44·4; H, 2·0%). The above reactants in alcohol in presence of sodium ethoxide (1 mol.) at room temperature yielded 2-*nitro*-N-*picrylphenoxazine* (XIV), deep magenta prisms from benzene, m. p. 225—230° (Found : N, 15·9. $C_{18}H_9O_9N_5$ requires N, 15·9%). Treatment of (XIII) with aqueous pyridine on the water-bath yielded 1 : 3-dinitrophenoxazine by hydrolysis and ring closure (Found : C, 52·6; H, 2·6. Calc. for $C_{12}H_7O_5N_3$: C, 52·7; H, 2·5%).

5-Iodo-2′ : 4′-dinitro-2-hydroxydiphenylamine yielded with acetic anhydride and a few drops of pyridine an *acetate*, which crystallised from alcohol or acetic acid in yellow needles, m. p. 200° (Found : N, 9·8. $C_{14}H_{10}O_6N_3I$ requires N, 9·5%). The o-*nitrobenzoate*, prepared in the usual manner in acetone in presence of anhydrous sodium carbonate, crystallised from glacial acetic acid in golden-yellow prisms, m. p. 174° (Found : N, 10·2. $C_{19}H_{11}O_8N_4I$ requires N, 10·1%). Treatment of the iododiphenylamine in warm acetone with an excess of *o*-nitrobenzoyl chloride yielded the *o*-nitrobenzoate of the isomeric iodoaminodiphenyl ether (cf. below). The *o*-nitrobenzoate of the diphenylamine was itself, however, stable.

4-Iodo-2′ : 4′-dinitro-2-aminodiphenyl ether (2 g.) in 50% aqueous acetic acid (10 c.c.), shaken in the cold with aqueous acetic anhydride (2 c.c.), yielded an *acetyl* derivative, white needles from benzene, m. p. 163° (Found : N, 9·8. $C_{14}H_{10}O_6N_3I$ requires N, 9·5%). The substance was readily rearranged in pyridine, ethyl alcohol, or water to the isomeric *O*-acetyldiphenylamine. Hydrolysis of the substance with aqueous alkali was accompanied by rearrangement to the diphenylamine. The o-*nitrobenzoate*, obtained by usual methods, formed white plates, m. p. 194°, from benzene or acetic acid. It was insoluble in alcohol and was rearranged only slowly in hot pyridine (Found : N, 10·0. $C_{19}H_{11}O_8N_4I$ requires N, 10·1%). It was also obtained (cf. above) by acylation of the corresponding iodohydroxydiphenylamine under suitable conditions.

5-*Bromo*-2′ : 4′-*dinitro*-2-*hydroxydiphenylamine*.—The *acetate*, formed in acetic anhydride in presence of a few drops of pyridine, formed small, bright yellow needles from alcohol or glacial acetic acid, m. p. 205° (Found : N, 10·9. $C_{14}H_{10}O_6N_3Br$ requires N, 10·6%). The *benzoate* (yellow matted needles from alcohol) melted at 172° (Found : N, 9·2. $C_{19}H_{12}O_6N_3Br$ requires N, 9·1%). The m-*nitrobenzoate* (yellow flocculent needles from alcohol) melted at 183° (Found : N, 11·2. $C_{19}H_{11}O_8N_4Br$ requires N, 11·1%). The o-*nitrobenzoate* was obtained when the bromodiphenylamine (3·5 g.) in acetone (20 c.c.) was shaken at room temperature with *o*-nitrobenzoyl chloride (1 mol.) in presence of anhydrous sodium carbonate. It formed small yellow matted needles from alcohol, m. p. 202° (Found : N, 11·1. $C_{19}H_{11}O_8N_4Br$ requires N, 11·1%). On treating the diphenylamine in warm acetone with an excess of *o*-nitrobenzoyl chloride, the white *o*-nitrobenzoyl derivative of the isomeric diphenyl ether (cf. below) was obtained. The *o*-nitrobenzoate of the diphenylamine, however, did not undergo isomeric change under any of the conditions tried. The p-*toluenesulphonate*, formed by shaking the diphenylamine (2 g.) with

aqueous alkali (10 c.c.), alcohol (10 c.c.), and *p*-toluenesulphonyl chloride (1·25 mols.), crystallised from alcohol in yellow hair-like needles, m. p. 211° (Found : N, 8·4. $C_{19}H_{14}O_7N_3BrS$ requires N, 8·2%).

4-*Bromo*-2′ : 4′-*dinitro*-2-*aminodiphenyl Ether*.—The *acetyl* derivative formed colourless needles from benzene, m. p. 171° (Found : N, 10·4. $C_{14}H_{10}O_6N_3Br$ requires N, 10·6%). The substance was readily rearranged in the usual solvents. The *benzoyl* derivative was obtained as white needles from benzene, m. p. 176° (Found : N, 8·8. $C_{19}H_{12}O_6N_3Br$ requires N, 9·1%). Rearrangement took place in pyridine and in alcohol, but not in acetic acid or in water. Hydrolysis of both the above derivatives with aqueous alkali was accompanied by rearrangement to the isomeric hydroxydiphenylamine. The m-*nitrobenzoyl* derivative formed pale yellow needles from benzene, m. p. 189° (Found : N, 11·3. $C_{19}H_{11}O_8N_4Br$ requires N, 11·1%). Rearrangement was of the normal type. The bromodiphenyl ether (2 g.) in acetone (20 c.c.), treated in the cold with *o*-nitrobenzoyl chloride (1 g.) and anhydrous sodium carbonate (1 g.), yielded the o-*nitrobenzoyl* derivative, which formed small white plates, m. p. 178°, from benzene (Found : N, 11·0. $C_{19}H_{11}O_8N_4Br$ requires N, 11·1%). The substance was also obtained as described above by acylation of the isomeric bromodiphenylamine under suitable conditions. It was very sparingly soluble in alcohol, but underwent rearrangement slowly in hot pyridine. Attempts to prepare a *p*-toluenesulphonate of the bromodiphenyl ether were unsuccessful.

5-*Chloro*-2′ : 4′-*dinitro*-2-*hydroxydiphenylamine*.—The *acetate* (from acetic anhydride in presence of pyridine) was obtained in long yellow matted needles, m. p. 207° (Found : N, 11·9. $C_{14}H_{10}O_6N_3Cl$ requires N, 11·9%). The m-*nitrobenzoate* (formed with *m*-nitrobenzoyl chloride in warm acetone in presence of anhydrous sodium carbonate) crystallised from alcohol or glacial acetic acid in small yellow needles, m. p. 184° (Found : N, 12·4. $C_{19}H_{11}O_8N_4Cl$ requires N, 12·2%). The diphenylamine (2 g.) in acetone (10 c.c.), shaken with *o*-nitrobenzoyl chloride (1 mol.) and anhydrous sodium carbonate at room temperature, yielded the o-*nitrobenzoate*. The yellow substance purified from glacial acetic acid or benzene melted at 196° (Found : N, 12·2. $C_{19}H_{11}O_8N_4Cl$ requires N, 12·2%). On treatment of the hydroxydiphenylamine in boiling acetone with excess of *o*-nitrobenzoyl chloride (2 mols.), the *o*-nitrobenzoyl derivative of the isomeric chlorodiphenyl ether (cf. below) was obtained. The *o*-nitrobenzoate of the diphenylamine was, however, not observed to undergo rearrangement.

4-*Chloro*-2′ : 4′-*dinitro*-2-*aminodiphenyl Ether*.—The *acetyl* derivative [from the parent ether (2 g.) with 50% aqueous acetic acid (20 c.c.) and acetic anhydride (2 c.c.) at room temperature] formed white needles from benzene, m. p. 160° (Found : N, 12·1. $C_{14}H_{10}O_6N_3Cl$ requires N, 11·9%). The normal rearrangement took place in hot pyridine and in hot aqueous alcohol, but not in acetic acid. The m-*nitrobenzoyl* derivative, formed in acetone solution in presence of anhydrous sodium carbonate, was recrystallised from benzene and obtained in pale yellow needles, m. p. 197° (Found : N, 12·0. $C_{19}H_{11}O_8N_4Cl$ requires N, 12·2%). Rearrangement took place readily in hot pyridine or in hot alcohol, and slowly in aqueous acetic acid. The o-*nitrobenzoyl* derivative, prepared from the amino-ether (2 g.) in acetone (20 c.c.) on treatment at the boiling point with *o*-nitrobenzoyl chloride (1·25 mols.) and anhydrous sodium carbonate (3 g.), formed small white prisms, m. p. 200°, from benzene (Found : N, 12·0. $C_{19}H_{11}O_8N_4Cl$ requires N, 12·2%). The substance was also obtained as described above by acylation of the isomeric chlorodiphenylamine under suitable conditions. Treatment of the substance with aqueous pyridine in a sealed tube at 150° for 1 hour effected hydrolysis and rearrangement to the corresponding chlorohydroxydiphenylamine. Hot aqueous alkali had the same effect.

Attempts to prepare *o*-nitrobenzoyl derivatives of 2′ : 4′-dinitro-2-hydroxy-5-carboxydiphenylamine and the isomeric 2-amino-4-carboxydiphenyl ether or of their dinitrophenyl esters were unsuccessful.

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