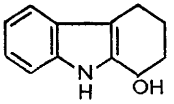
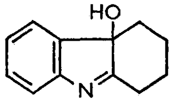
# **906.** *The Synthesis of 1 : 9-9′ : 1′-Dicarbazolylene, and Related Experiments.*

By A. E. Jean Herbert and Muriel Tomlinson.

1 : 9-9′ : 1′-Dicarbazolylene has been synthesised by heating 1 : 6-diphenylphenazine *N*-oxide with palladium–charcoal. In a similar way 1-phenylphenazine 5-oxide afforded 5 : 10-dihydro-1 : 5-*o*-phenylenephenazine. Evidence is described which throws doubt on Wieland and Lecher's claim to have obtained 5 : 10-di-*p*-nitrophenylphenazine by heating 4-nitro-*N*-nitrosodiphenylamine.

The substance obtained by dehydration of 1 : 2 : 3 : 4-tetrahydro-1-hydroxycarbazole (I) and 1 : 2 : 3 : 4-tetrahydro-11-hydroxycarbazolenine (II), and first described as " 2 : 3-dihydrocarbazole," was later shown to have formula $C_{24}H_{22}N_2$ and not $C_{12}H_{11}N$. It seemed probable that it is really 1 : 2 : 3 : 4 : 1′ : 2′ : 3′ : 4′-octahydro-(1 : 9-9′ : 1′)-dicarbazolylene (III), and that the yellow substance obtained by its dehydrogenation is therefore 1 : 9-9′ : 1′-dicarbazolylene[1] (IV).


(I)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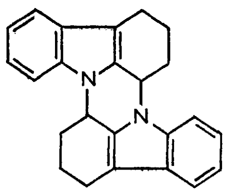
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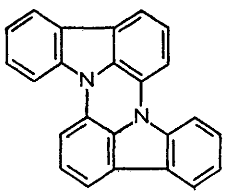
(IV)

Several attempts to synthesise the compound (IV) have been described.[2] One was based on Wieland and Lecher's statement[3] that 4-nitro-*N*-nitrosodiphenylamine when boiled in xylene gives some 5 : 10-dihydro-5 : 10-di-*p*-nitrophenylphenazine. It was found[2] that 2-nitro-*N*-nitrosodiphenylamine did not afford 5 : 10-dihydro-5 : 10-di-*o*-nitrophenylphenazine, from which it had been hoped that 1 : 9 : 9′ : 1′-dicarbazolylene might be obtained by reduction, diazotisation, and internal coupling: the principal products of the decomposition are 2-nitrodiphenylamine and 2 : 4′-dinitrodiphenylamine, so it seemed possible that decomposition of *N*-nitrosodiphenylamines in which the *para*-positions are blocked, *e.g.*, by methyl groups or chlorine atoms, might better afford dihydrodi-*o*-nitrophenylphenazines of the type required. A number of such compounds were therefore prepared and investigated but the only products isolated (apart from the original 2-nitrodiphenylamine) were dinitrodiphenylamines. It was therefore, desirable to repeat Wieland and Lecher's work, and although we obtained a substance which roughly corresponded in properties and analysis to their " dihydrodi-*p*-nitrophenylphenazine " this was clearly not homogeneous. Chromatography of the product obtained as by them led to isolation of 4-nitrodiphenylamine, 4 : 4′-dinitrodiphenylamine, and 4 : 2′-dinitrodiphenylamine, and many small bands were seen on the alumina. When this work was nearing completion, Gilman and Dietrich[4] reported the synthesis of 5 : 10-dihydro-5 : 10-diphenylphenazine which was quite different from the substance which Wieland[5] had obtained by heating tetraphenylhydrazine in toluene. (Wieland attributed the formation of phenazine derivatives in both of the above reactions to the dimerisation of $Ar_2N$ radicals formed by dissociation of nitrosamines and hydrazines.)

We employed many of the ways that have been described for preparing nitrodiphenylamines, but yields were generally poor and the method given seems the most satisfactory.

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[1] Plant and Tomlinson, *J.*, 1931, 3324; 1933, 298; 1950, 2127.

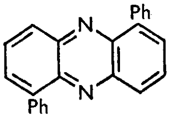
[2] Geale, Linnell, and Tomlinson, *J.*, 1956, 1124.

[3] Wieland and Lecher, *Annalen*, 1912, **392**, 165.

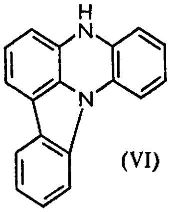
[4] Gilman and Dietrich, *J. Amer. Chem. Soc.*, 1957, **79**, 6178.

[5] Wieland, *Annalen*, 1911, **381**, 200.

We then hoped to prepare 1 : 9-9′ : 1′-dicarbazolylene by dehydrogenation of 1 : 6-diphenylphenazine (V) which we tried to prepare by Wohl and Aue's phenazine synthesis.[6] From 2-nitrodiphenyl and aniline we obtained 1-phenylphenazine, whereas from 2-aminodiphenyl and nitrobenzene the product was a phenazine oxide, presumably 1-phenylphenazine 5-oxide. This was reduced to 1-phenylphenazine. Our experiments showed that the use of benzene as solvent [7] greatly improves the Wohl and Aue phenazine synthesis, and in this way we obtained, from 2-nitrodiphenyl and 2-aminodiphenyl, 1 : 6-diphenylphenazine *N*-oxide, which was reduced to 1 : 6-diphenylphenazine with iron.



(V)



(VI)

When 1 : 6-diphenylphenazine *N*-oxide was heated with palladium–charcoal it was converted, in good yield, into 1 : 9-9′ : 1′-dicarbazolylene, identical in all respects with a specimen obtained from tetrahydrocarbazole in the original investigation. In a similar way 6 : 10-dihydro-1 : 6-*o*-phenylenephenazine (8*H*-indolo[3,2,1-*de*]phenazine) (VI was prepared from 1-phenylphenazine and from its *N*-oxide. Waterman and Vivian [8] claim to have prepared a substance with the structure (VI) (which they called 1 : 9-dihydrophenazininocarbazole) by heating 9-*o*-nitrophenylcarbazole with ferrous oxalate. They give neither m. p. nor analysis, and our attempts to repeat this reaction have been unsuccessful.

## EXPERIMENTAL

4 : 4′-*Dimethyl-2-nitrodiphenylamine.*—A mixture of 4-chloro-3-nitrotoluene (24 g.), *p*-toluidine (42 g.), and anhydrous sodium acetate (24 g.) was heated at 190—200° (36 hr.), The product was washed with hydrochloric acid and steam-distilled from an acid solution. The remaining solid was collected, dried, and chromatographed on alumina (type H) in benzene. 4 : 4′-Dimethyl-2-nitrodiphenylamine was obtained as red plates, m. p. 85° (13 g.). Other diphenylamines were made similarly; *e.g.*, 4 : 4′-dichloro-2-nitrodiphenylamine (yield 48%), 4-chloro-4′-methyl-2-nitrodiphenylamine (97%), etc.

4-*Methyl-2′-nitro-*N-*nitrosodiphenylamine.* Potassium nitrite (2 g.), in a little water, was added to 4-methyl-2′-nitrodiphenylamine (4·6 g.) in glacial acetic acid (100 c.c.). After 1 hr. water was added. The precipitated 4-*methyl-2′-nitro-*N-*nitrosodiphenylamine* recrystallised from alcohol as yellow plates, m. p. 102° (decomp.) (4·5 c.c.) (Found: C, 60·9; H, 4·4. $C_{13}H_{13}O_3N$ requires C, 60·7; H, 4·3%). In a similar way were obtained 4-*chloro-2′-nitro-*, yellow prisms, m. p. 101° (from alcohol) (Found: Cl, 12·5. $C_{12}H_8O_3N_3Cl$ requires Cl, 12·8%), 4-*chloro-4′-methyl-2-nitro-*, yellow plates, m. p. 96° (from alcohol) (Found: C, 53·3; H, 3·8. $C_{13}H_{10}O_3N_3Cl$ requires C, 53·6; H, 3·4%), and 4 : 4′-*dimethyl-2-nitro-*N-*nitrosodiphenylamines*, yellow needles, m. p. 93° (from alcohol) (Found: C, 62·5; H, 4·9. $C_{14}H_{13}O_3N_3$ requires C, 62·0; H, 4·8%).

*Decomposition of* 4-*Methyl-2′-nitro-*N-*nitrosodiphenylamine.*—This nitrosamine (5 g.) was heated in boiling xylene (5 c.c.) until evolution of nitric oxide ceased (1½ hr.). The xylene was distilled and the residue, in benzene, was chromatographed on alumina. Three fractions afforded, severally, 4-methyl-2′-nitrodiphenylamine, m. p. 68°, 4-methyl-2′ : 4′-dinitrodiphenylamine, m. p. 135° (Found: C, 57·0; H, 4·4. Calc. for $C_{13}H_{11}O_4N_3$: C, 57·1; H, 4·0%), and an unidentified 4-methyldinitrodiphenylamine, orange needles, m. p. 177° (Found: C, 57·3; H, 4·1%).

In a similar way 4 : 4′-dimethyl-2-nitro-*N*-nitrosodiphenylamine gave 4 : 4′-dimethyl-2-nitrodiphenylamine, m. p. 85°, and 4 : 4′-dimethyl-2 : 2′-dinitrodiphenylamine, orange plates, m. p. 199° (Found: C, 58·7; H, 4·7; N, 14·2. Calc. for $C_{14}H_{13}O_4N_3$: C, 58·5; H, 4·5; N, 14·6%),

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[6] Wohl and Aue, *Ber.*, 1901, **34**, 2446.

[7] Pachter and Kloetzel, *J. Amer. Chem. Soc.*, 1951, **73**, 4958.

[8] Waterman and Vivian, U.S.P. 2,292,808.

and 4-chloro-2′-nitro-*N*-nitrosodiphenylamine gave 4-chloro-2′-nitrodiphenylamine, m. p. 143·5°, and 4-chloro-2′ : 4′-dinitrodiphenylamine, m. p. 165°.

*Decomposition of* 4-*Nitro*-N-*nitrosodiphenylamine.*—(*a*) Wieland and Lecher's experiment [3] was repeated, nitrosamine (5 g.) in xylene (25 c.c.) being used. The solvent was evaporated *in vacuo*, and the residue repeatedly extracted with alcohol. The insoluble fraction was dissolved in chloroform and precipitated with alcohol (3 times); the solid, m. p. 200—208° (sintering at 180°) (Found: C, 68·8; H, 4·9%), thus obtained did not appear to be crystalline. This, Wieland and Lecher claimed, was 5 : 10-dihydro-5 : 10-di-*p*-nitrophenylphenazine [they give m. p. 183°, not sharp, sintering at 154° (Found: C, 67·45; H, 4·1. $C_{24}H_{16}O_4N_4$ requires C, 67·9; H, 3·8%)]. (*b*) The nitrosamine (12 g.) was boiled in xylene (60 c.c.) until no more nitric oxide was evolved and the solvent was removed *in vacuo*. The product was extracted first with benzene and then with chloroform, and the two fractions were separately chromatographed on alumina. The products identified (mixed m. p.) were 4-nitro-, 4 : 2′-dinitro-, and 4 : 4′-dinitro-diphenylamine.

1-*Phenylphenazine.*—A mixture of 2-nitrodiphenyl [9] (5 g.), aniline (2·4 g.), and dry powdered potassium hydroxide (4 g.) was heated in boiling benzene (40 c.c.) for 24 hr., with stirring. The product was washed with water, and the dried benzene layer chromatographed on alumina. The first fraction contained 2-nitrodiphenyl, and the second gave a solid which crystallised from alcohol to give 1-*phenylphenazine* (0·54 g.) as yellow needles, m. p. 157° (Found: C, 84·3; H, 4·7. $C_{18}H_{12}N_2$ requires C, 84·4; H, 4·7%).

1-*Phenylphenazine 5-Oxide.*—This *oxide* was prepared in a similar way from 2-aminodiphenyl [10] (4·2 g.), nitrobenzene (3·13 g.), and potassium hydroxide (4 g.) in benzene (40 c.c.). It crystallised from alcohol as yellow needles, m. p. 198° (Found: C, 79·6; H, 4·6. $C_{18}H_{12}ON_2$ requires C, 79·4; H, 4·4%). When this oxide, in acetic acid, was shaken with zinc dust, and the green solution so obtained was (after filtration) exposed to air for 30 min. it became yellow. Addition of water to it then precipitated 1-phenylphenazine, m. p. 157°, identical with the above.

1 : 6-*Diphenylphenazine* N-*Oxide.*—This was prepared, as above, from 2-nitrodiphenyl (5 g.), 2-aminodiphenyl (4·2 g.), and potassium hydroxide (4 g.) in benzene (40 c.c.) (24 hr.). A solid separated and was collected. (The benzene layer contained only starting materials.) The solid was recrystallised from chloroform and afforded 1 : 6-*diphenylphenazine* N-*oxide* as yellow needles, m. p. 270° (1·1 g.) (Found: C, 83·0; H, 4·6; N, 7·9. $C_{24}H_{16}ON_2$ requires C, 82·7; H, 4·6; N, 8·0%).

1 : 6-*Diphenylphenazine.*—The last *N*-oxide (0·3 g.) was heated with iron powder in dry carbon dioxide at 300°. Crystals sublimed and recrystallisation from xylene gave 1 : 6-*diphenylphenazine* (0·2 g.) as yellow needles, m. p. 262—265° (Found: C, 86·7; H, 5·1. $C_{24}H_{16}N_2$ requires C, 86·7; H, 4·8%).

1 : 9-9′ : 1′-*Dicarbazolylene.*—When 1 : 6-diphenylphenazine *N*-oxide (0·35 g.) was mixed with 10% palladium–charcoal (0·5 g.) it became green: when heated in a stream of hydrogen (or carbon dioxide) fusion occurred at 270°, and at 400° the colour became yellow again; at 450° 1 : 9-9′ : 1′-dicarbazolylene began to sublime. Recrystallisation from xylene (the solution shows a vivid violet fluorescence) afforded the dicarbazolylene as yellow needles, m. p. 337° (0·3 g.), not depressed on admixture with a sample, m. p. 337°, prepared from tetrahydrocarbazole. The infrared spectra of the two samples were identical and the light absorption in dioxan, $\lambda_{max.}$ 2530, 2890, 3920, and 4140 Å (log ε 4·68, 4·35, 4·08, and 4·3), were also identical.

5 : 10-*Dihydro*-1 : 5-o-*phenylenephenazine* (8H-*indolo*[3,2,1-de]*phenazine* (VI).—1-Phenylphenazine 5-oxide (0·25 g.) was heated with palladium–charcoal (0·5 g.) as above. Fusion occurred at 200° and the green liquid became yellow at 330°. At 380° the product sublimed. Recrystallisation from benzene–light petroleum (b. p. 60—80°) afforded the pentacyclic *phenazine*, m. p. 190° (0·1 g.) (Found: C, 84·4; H, 4·7. $C_{18}H_{12}N_2$ requires C, 84·4; H, 4·7%). Solutions in benzene show intense blue-violet fluorescence; the infrared spectrum contains a sharp band at 3380 cm.$^{-1}$ (NH). $\lambda_{max.}$ in ethanol were at 2540, 2860, 3430, 3900 Å (log ε 4·75, 3·69, 3·51, and 3·67).

In a similar way 1-phenylphenazine (0·5 g.) also afforded this compound (0·2 g.).

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[9] Elks, Haworth, and Hey, *J.*, 1940, 1285.

[10] Scarborough and Waters, *J.*, 1927, 91.