

DIARYLNITROXIDES: THEIR FORMATION FROM DIARYLAMINES  
BY OXIDATION WITH PEROXYBENZOIC ACID  
AND DECOMPOSITION ON ALUMINA

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(Received 11 November 1964)

The action of peroxybenzoic acid on diarylamines was found to give the corresponding diarylnitroxides  $Ar_2NO\cdot$  in ether or in dichloromethane at  $0^\circ C$ , a new route to the diarylnitroxides which have usually been prepared from the corresponding hydroxylamines (1). Thus, a solution of 4,4'-dimethoxydiphenylamine in ether (0.60 g. in 30 cc.), on treatment with an ethereal solution of peroxybenzoic acid (0.66 g. in 8 cc.), instantaneously deposited 4,4'-dimethoxydiphenylnitroxide (0.45 g.) in 70% yield, m.p.  $150-1^\circ C$  with decomposition (recrystallized from warm ethyl acetate) (Found: C, 68.75; H, 6.08; N, 6.18. Calcd. for  $C_{14}H_{14}NO_3$ : C, 68.84; H, 5.78; N, 5.73%), identified by comparison of its ESR and visible and ultraviolet spectra with those of an authentic sample prepared by Meyer's method (2). Diphenylamine, similarly treated with peroxybenzoic acid, gave a solution showing an ESR spectrum indicating the formation of diphenylnitroxide

in a nearly quantitative yield; isolation by condensation and crystallization afforded this radical in crystalline form, m.p. 61-2°C (recrystallized from petroleum ether, in a yield of 10%) (Found: N, 7.47. Calcd. for  $C_{12}H_{10}NO$ : N, 7.60%), together with N-phenyl-p-benzoquinoneimine-N-oxide, m.p. 140°C (in a yield of 25%), in addition to benzoic acid and tarry matter. When Gambarajan oxidized diphenylamine with peroxybenzoic acid, he reported an unidentified crystalline substance, m.p. 138-42°C (Found: N, 7.38%) as the only isolable compound besides benzoic acid (3); this compound must be N-phenyl-p-benzoquinoneimine-N-oxide. Similarly, 4,4'- and 3,3'-dichlorodiphenylamine gave the corresponding nitroxides in dichloromethane in yields of 60% as revealed by ESR measurements; thus, an ethereal solution of 4,4'-dichlorodiphenylamine oxidized with peroxybenzoic acid, on concentration under reduced pressure in a stream of nitrogen, deposited red needles, which showed a strong ESR signal, but, on contact with air, it soon darkened and decomposed, and the only isolable product other than benzoic acid was N-(p-chlorophenyl)-p-benzoquinoneimine-N-oxide, m.p. 134-5°C (from ethanol) (Found: C, 61.45; H, 3.50; N, 5.84. Calcd. for  $C_{12}H_8ClNO_2$ : C, 61.66; H, 3.45; N, 5.99%). 4,4'-dinitro-, 4-nitro- and 4,4'-di-(methoxycarbonyl)-diphenylamine were shown by ESR measurements to give the corresponding nitroxides only in very low yields even after prolonged reaction time; isolation of these radicals was therefore not attempted.

N,N-Diphenylhydroxylamine, a probable intermediate in

the formation of diphenylnitroxide from diphenylamine and peroxybenzoic acid, also reacted rapidly in ether with peroxybenzoic acid at 0°C to give diphenylnitroxide.

When the mixture of products from a reaction between diphenylamine and peroxybenzoic acid was chromatographed on alumina in a mixture of benzene and petroleum ether and eluted with an increasing amount of ether, acetone and finally with methanol in attempt to isolate the diphenylnitroxide formed, only a small amount of this was recovered besides N-phenyl-p-benzoquinoneimine, its N-oxide, and trace of N-(p-hydroxyphenyl)-p-benzoquinoneimine. Separate experiments showed that an authentic specimen of diphenylnitroxide, similarly chromatographed, was converted into diphenylamine(30%), N-phenyl-p-benzoquinoneimine(20%) and N-phenyl-p-benzoquinoneimine-N-oxide(30%) and that the recovery of the radical was very low. On being chromatographed on silica-gel or powdered cellulose, however, diphenylnitroxide suffered no change at all. When this radical was left alone for two weeks in a benzene solution or in the solid state at room temperature in air and subsequently submitted to chromatography on silica-gel in a mixture of benzene and petroleum ether, diphenylamine(20-40%), N-phenyl-p-benzoquinoneimine(trace), its N-oxide(40-60%) and tarry matter were obtained, and N-(p-hydroxyphenyl)-p-benzoquinoneimine(trace) and the starting nitroxide(trace) were detected in the elute by visible and ESR spectroscopy, respectively. It is therefore evident that diphenylnitroxide, on being kept at room temperature, spontaneously undergoes a

gradual and complicated change including disproportionation and rearrangement, and that the alumina accelerates this transformation. It is to be noted that alumina is especially effective in causing the formation of N-phenyl-p-benzoquinoneimine. 4,4'-Dimethoxydiphenylnitroxide, however, is stable enough not to be affected by alumina.

The authors' thanks are due to Dr. Minoru Kinoshita for his kind help with ESR measurements.

#### References

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