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The Use of Nickel Peroxide as Oxidizing Agent of Phenylhydrazine for the Generation of Phenyl Radicals

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It was reported that phenylhydrazine was oxidized with silver oxide,[1] mercuric oxide,[1] and lead tetraacetate[2] to give, probably *via* phenyldiimide, phenyl radicals, which can substitute on aromatic substrates to afford biaryls. These reactions as well as the decomposition of *N*-nitrosoacetanilide have often been employed to generate phenyl radicals at room temperature, though it is not convenient since silver oxide and *N*-nitrosoacetanilide have to be freshly prepared immediately before use and lead tetraacetate must be stored in acetic acid until use. With mercuric oxide, phenylhydrazine undergoes somewhat complicated reactions accompanied by the production of diphenylmercury.[1] In order to find a convenient procedure for the generation of phenyl radicals at room temperature, we investigated the treatment of phenylhydrazine with nickel peroxide, a new oxidizing agent of current interest,[3] on account of its ready availability and its stability during the course of storage. As a result, the reaction was found to be adequate for the present purpose.

Results and Discussion

Gradual addition of phenylhydrazine dissolved in a solvent to a suspension of excess nickel peroxide in the same solvent as above under stirring at room temperature under nitrogen atmosphere gave rise to a mild exothermic reaction with evolution of gas. The reaction carried out in cyclohexane gave benzene (68% yield based on the hydrazine used) together with a small amount of biphenyl (less than 1%). The reaction in carbon tetrachloride afforded chlorobenzene (53.5%), benzene (less than 2%), biphenyl (less than 2%), and hexachloroethane (10.1%). The reaction in benzene gave biphenyl (30%) along with very small amount of 1,4-dihydrobiphenyl (less than 0.2%) and phenol (trace). Treatment of *p*-nitrophenylhydrazine with nickel peroxide in benzene yielded *p*-nitrobiphenyl (34.8%) and nitrobenzene (5.6%).

These results indicate that phenylhydrazine, on treatment with nickel peroxide, gives phenyl radicals, which abstract hydrogen atoms from cyclohexane to afford benzene, or abstract chlorine atoms from carbon tetrachloride to give chlorobenzene[4] and trichloromethyl radicals followed by their dimerization to hexachloroethane.

Formation of biphenyl in benzene is mostly attributable to the substitution of phenyl radicals on benzene, although less than 2% of biphenyl might arise solely from phenylhydrazine moiety without participation of benzene in view of the formation of a small amount of biphenyl in cyclohexane or in carbon tetrachloride. Production of very low yield of 1,4-dihydrobiphenyl suggests that either dihydrobiphenyl does not result appreciably from the reaction or it is once formed but subsequently oxidized to biphenyl by nickel peroxide as demonstrated by a separate experiment. However, the absence of quaterphenyl in addition to the very low yield of dihydrobiphenyl among the products from benzene suggest that phenyl radicals add to benzene to give phenylcyclohexadienyl radicals, which may be oxidized with nickel peroxide to biphenyl rather than disproportionate or dimerize to give biphenyl and 1,4-

Table 1. Distribution of isomeric biaryls resulting from the phenylation of aromatic substrates

Substrate	Reaction condition[a]	Biaryls			
		Total yield[b]	Isomer distribution (%)		
			o	*m*	*p*
Toluene	PH–NiPO (1:1)	28	67	19	14
	PH–NiPO (1:3)	34	68	19	13
	NNA[8]		71	18	11
Chlorobenzene	PH–NiPO (1:1)	22	63	20	17
	PH–NiPO (1:3)	30	66	17	17
	PH–Ag_2O[1]		65	22	13
	PH–$Pb(OAc)_4$[2]	38	61	25	14
	NNA[8]		64	21	15
Nitrobenzene	PH–NiPO (1:1)	33	62	7	31
	PH–NiPO (1:3)	48	58	7	35
	PH–$Pb(OAc)_4$[2]	41	60	10	30
	NNA[8]		62	8	30

a) PH, NiPO, and NNA stand for phenylhydrazine, nickel peroxide, and *N*-nitrosoacetanilide, respectively. Figures in parentheses indicate the ratios of moles of phenylhydrazine to g-atoms of nickel peroxide employed.
b) Based on phenylhydrazine used.

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[1] R. L. Hardie and R. H. Thomson, *J. Chem. Soc.*, **1957**, 2512.

[2] J. B. Aylward, *J. Chem. Soc., C*, **1969**, 1663.

[3] a) K. Nakagawa, R. Konaka, and T. Nakata, *J. Org. Chem.*, **27**, 1597 (1962). b) R. Konaka, S. Terabe, and K. Kimura, *ibid.*, **34**, 1334 (1969). c) S. Terabe and R. Konaka, *J. Amer. Chem. Soc.*, **91**, 5655 (1969).

[4] Formation of chlorobenzene by way of benzenediazonium chloride, though not detected in the present reaction, cannot be completely excluded in view of reports for the detection of benzenediazonium salt in the reaction of phenylhydrazine with lead tetraacetate in dichloromethane[2] and in the decomposition of *N*-nitrosoacetanilide in carbon tetrachloride (W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, **1934**, 1797; C. Rüchardt, Chuan-Cheng Tan, and B. Freudenberg, *Tetrahedron Lett.*, **1968**, 4019.

dihydrobiphenyl or tetrahydroquaterphenyl.[5,6] Production of a trace of phenol shows that phenyl radicals are not readily oxidized with nickel peroxide to phenol, in contrast to triphenylmethyl radicals which were reported to suffer oxidation with nickel peroxide to afford triphenylmethanol.[3b)]

Oxidation of phenylhydrazine with nickel peroxide in chlorobenzene, nitrobenzene, and toluene gave *o*-, *m*-, and *p*-chloro-, nitro-, or methyl-biphenyl, respectively, the total yields of the respective isomeric biaryls being 30—50%, together with a small amount of biphenyl. The isomer ratios of the biaryls are summarized in Table 1. The increase in the ratio of nickel peroxide to phenylhydrazine from 1: 1 to 3: 1 equivalents caused only 1.4 fold increase in the yield of the isomeric biaryls without affecting the distribution among the isomers. The observed ratios of the isomeric biaryls accord well with those obtained from the decomposition of benzoyl peroxide[7] or *N*-nitrosoacetanilide,[8] or the treatment of phenylhydrazine with silver oxide[1] or with lead tetraacetate[2] in aromatic substrates, showing the generation of phenyl radicals from the present reactions.

Experimental

Reagents. Nickel peroxide was determined by iodometric titration,[3a)] to contain 0.00323 g-atom of active oxygen per 1 g. Phenylhydrazine was distilled through a spinning band distillation column under reduced pressure and stored in a desiccator under nitrogen.

Solvents. Cyclohexane, benzene, carbon tetrachloride, toluene, and chlorobenzene were purified by conventional methods, and finally distilled through a 1 m high Vigreux column. Nitrobenzene was purified by partial freezing, dried with phosphorus pentoxide and finally distilled.

Authentic Samples. Biphenyl derivatives were prepared and purified by the well-known methods.[9] 1,4-Dihydrobiphenyl was prepared according to the reported procedure.[10]

Reaction of Phenylhydrazine with Nickel Peroxide. In a 100 m*l* three necked round bottomed flask fitted with a nitrogen inlet tube and a reflux condenser was placed 3 g of nickel peroxide and 10 m*l* of a solvent, and the mixture was stirred with a magnetic stirrer in nitrogen stream. After 20 min, 3 mmol of phenylhydrazine dissolved in 10 m*l* of the same solvent as above was gradually added, stirring was continued further 1 hr. The reaction mixture was filtered through a quantitative filter paper on a funnel and the precipitate was successively washed and the combined filtrate and washings were concentrated. No tetrahydroquaterphenyl was precipitated or detected by spectroscopy. The concentrated solution was subsequently examined by gas chromatography.

Reaction of 1,4-Dihydrobiphenyl with Nickel Peroxide. A benzene solution of 1,4-dihydrobiphenyl, 0.315 g, was treated with nickel peroxide, 2.1306 g (6.78 mg atom of active oxygen), under nitrogen and kept to stand overnight and worked up as above. In a control run, the dihydrobiphenyl in benzene was kept to stand without nickel peroxide to confirm that the dihydrobiphenyl was not consumed.

Gas Chromatographic Analysis. A Hitachi K-52 TCD gas chromatograph was used with a 2 m column of 10% silicone grease on chromosorb H for the determination of chlorobenzene, nitrobenzene, and hexachloroethane, with a 2 m column of 10% diisodesyl phthalate on chromosorb P for benzene and a 6 m column of 10% silicone grease on chromosorb H for biaryls.

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[5] Decomposition of benzoyl peroxide in benzene at 80°C carried out in the presence of nickel peroxide was shown to give 1,4-dihydrobiphenyl in a negligible amount and biphenyl in moderately higher yield than without nickel peroxide (O. Simamura and Hiromichi Ohta, private communication).

[6] As a general reference for homolytic aromatic substitution, see, for example, D. H. Hey, in G. H. Williams ed., "Advances in Free-radical Chemistry," Vol. II, Logos Press, London (1967), p. 47; O. Simamura, T. Migita, N. Inamoto, and K. Tokumaru, "Yuriki Hanno," Tokyo Kagaku Dozin, Tokyo (1969), Chapter 11.

[7] D. H. Hey, S. Orman, and G. H. Williams, *J. Chem. Soc.*, **1961**, 565.

[8] R. Ito, T. Migita, N. Morikawa, and O. Simamura, *Tetrahedron*, **21**, 955 (1965).

[9] W. E. Bachmann and R. A. Hoffman, "Organic Reactions," Vol. 2, p. 248 (1944).

[10] W. Hückel and R. Schwen, *Chem. Ber.*, **89**, 150 (1956).