Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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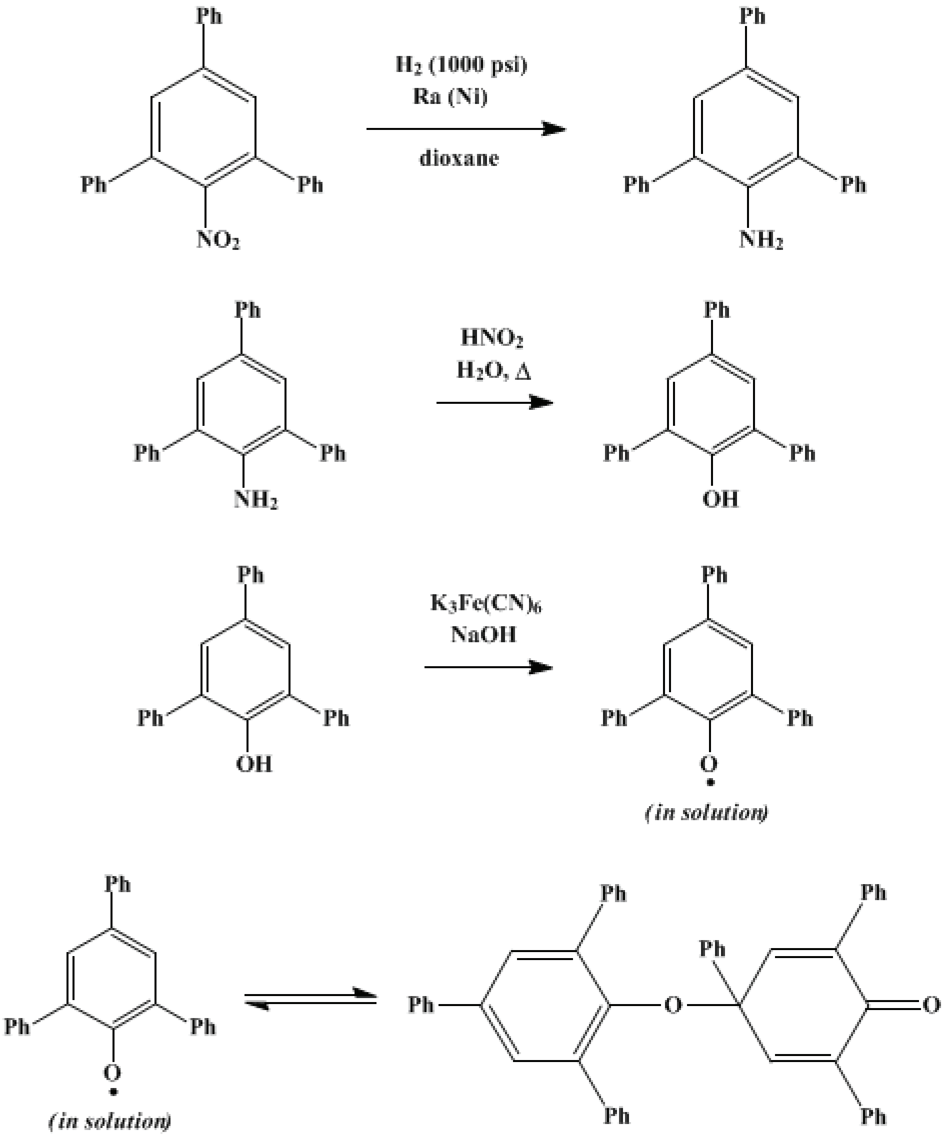
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.049.0116

Organic Syntheses, Coll. Vol. 5, p.1130 (1973); Vol. 49, p.116 (1969).

2,4,6-TRIPHENYLPHENOXYL

[Phenoxy, 2,4,6-triphenyl]



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Checked by E. K. W. Wat and R. E. Benson.

1. Procedure

A. *2,4,6-Triphenylaniline*. To a filtered solution of 70 g. (0.20 mole) of 2,4,6-triphenylnitrobenzene (Note 1) in 500 ml. of dioxane (total volume *ca.* 540 ml.) in a 1-l. pressure vessel equipped with a magnetic stirrer is added 10 g. of Raney nickel catalyst (Note 2) that has been previously rinsed with absolute ethanol. The head and fittings are attached, and the vessel is connected to a hydrogen cylinder. The system is alternately evacuated to 40–50 mm. and pressured with hydrogen to 30–40 p.s.i. three times (Note 3). After a final evacuation, hydrogen is introduced into the vessel until the pressure reaches 1000 p.s.i. (*ca.* 70 atm.). The reaction is allowed to proceed overnight (*ca.* 25 hours) (Note 4), during which time 0.6 mole (13.5 l.) of hydrogen is absorbed. The vessel is vented and the catalyst is removed by filtration from the reaction mixture and is washed with 30 ml. of dioxane. The filtrates are combined, and the solvent is removed by distillation under reduced pressure using a rotary evaporator at 40–50° (50 mm.) to leave an oil which solidifies on trituration with a small portion of methanol. The product is collected on a Buchner funnel and washed twice with 40-ml. portions of ice-cold methanol. The remaining light yellow 2,4,6-triphenylaniline (m.p. 135–136°) weighs 60–63 g. (94–98%) (Note 5).

B. *2,4,6-Triphenylphenol*. To a 2-l. three-necked flask equipped with a mechanical stirrer, a dropping funnel, and a thermometer are added 32 g. (0.10 mole) of 2,4,6-triphenylaniline and 300 ml. of glacial acetic acid. Stirring is begun and the contents of the flask are brought into solution by heating to 70°. Concentrated sulfuric acid (90 ml., *d* 1.84) is added dropwise while the temperature is lowered concurrently from 70° to 20° by cooling. After the addition is completed, the mixture is cooled to 0° with an ice-salt bath, and a solution of 9 g. (0.13 mole) of sodium nitrite in 50 ml. of water is added over a period of 20–30 minutes with stirring, the reaction temperature being kept at 0–5°. The stirring is continued for 20 minutes after the sodium nitrite solution has been added, then 300 ml. of ice-cold water and 3 g. of urea or amidosulphonic acid are added in small portions. The yellow diazonium salt solution is filtered with suction into an ice-cold flask and is kept cold (at 0°) while the next step is carried out.

To a 2-l. three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a dropping funnel is added a mixture of 600 ml. of water and 150 ml. of concentrated sulfuric acid (*d* 1.84). The acid solution is vigorously stirred and heated to boiling, and the cold diazonium salt solution is added at such a rate that the boiling is not interrupted (Note 6). The time required for this addition should not exceed 30 minutes. After the addition is completed, boiling is continued for 10 minutes and then the mixture is allowed to cool to room temperature with stirring. The product is collected on a Buchner funnel, washed, with water, and dried in a vacuum desiccator containing phosphorus pentoxide to give 28–32 g. of crude 2,4,6-triphenylphenol. After drying, the product is dissolved in *ca.* 200 ml. of benzene and filtered through a layer of 300 g. of alumina packed in a 30-mm. × 75-cm. chromatohgraphy column (Note 7). The product is eluted with benzene until about 500 ml. of eluate has been collected. The collected eluate is concentrated under reduced pressure using a rotary evaporator at 50 mm. pressure and 50° to yield light yellow crystals, which are recrystallized from glacial acetic acid (10 g. of 2,4,6-triphenylphenol requires *ca.* 30–35 ml. of acetic acid). The pure, nearly colorless product (13–15 g., 39–47%) melts at 149–150°.

C. *2,4,6-Triphenylphenoxyl*. In a 1-l. separatory funnel is placed a filtered solution of 10 g. (31 moles) of 2,4,6-triphenylphenol in 300 ml. of ether. To this solution is added 60 ml. of a filtered, saturated solution of potassium hexacyanoferrate(III) in 2N sodium hydroxide solution (Note 8), and the resulting mixture is vigorously shaken for about 10 minutes. After a few minutes the dimer of 2,4,6-triphenylphenoxyl begins to separate in the form of pink crystals. The crystals are isolated by filtration, washed with several portions of water (Note 9) and twice with ether. After drying in a vacuum desiccator over phosphorus pentoxide while protecting from light, the product weighs 8–9 g. (81–91%) and melts at 145–150° to a red liquid (Note 10). The purity of the 2,4,6-triphenylphenoxyl dimer (which in solution attains a rapid equilibrium with its red monomer) is established by titration with a solution of hydroquinone in acetone (Note 11). The radical titer of a freshly prepared solution of the dimer in benzene or acetone should be 98–99%.

2. Notes

1. The preparation of 2,4,6-triphenylnitrobenzene is described in *Organic Syntheses*, this volume, p. 1128.
2. The submitters used Raney nickel catalyst from the Badische Anilin- & Sodafabrik AG, Ludwigshafen (Rhein). Germany.
3. The checkers used a stainless steel pressure vessel that was cooled to −60° and then evacuated to 1 mm. The cold system was purged with hydrogen three times, evacuated, and placed in the rocker assembly before pressuring it to 1000 p.s.i. with hydrogen.
4. The checkers used a rocking-motion autoclave and the reduction required 48 hours to complete.
5. The 2,4,6-triphenylaniline resulting from this procedure is sufficiently pure for use in the preparation of 2,4,6-triphenylphenol, but it may be recrystallized from 100 ml. of glacial acetic acid to give 50–55 g. (78–86%) of pure 2,4,6-triphenylaniline, m.p. 136–137°. On occasions a product with initial m.p. 121–122° is obtained which solidifies on further heating and then melts at 136–137°

6. Contact of the diazonium salt solution with the hot wall of the flask before decomposition in the solution should be avoided in order to prevent the formation of a brown resin.
7. The submitters used Aluminiumoxid WOELM neutral, Aktivitätsstufe I.
8. A saturated solution requires *ca.*/35 g. (110 mmoles) of potassium hexacyanoferrate(III) per 100 ml. of 2*N* sodium hydroxide solution at room temperature.
9. The final wash water must be free of potassium hexacyanoferrate(III). The checkers washed the product until the filtrates were colorless.
10. The product obtained is analytically pure: Calcd. for $C_{24}H_{17}O$: C, 89.69; H, 5.33; O, 4.98. Found: C, 89.94; H, 5.27; O, 5.00. The product is stable for several months when stored in the dark. The 2,4,6-triphenylphenoxyl dimer is piezochromic; rubbing in a mortar produces a red color. Solutions of the colorless dimer in organic solvents are red owing to dissociation to the monomer radical.
11. The radical solution is titrated with 0.01*M* solution of analytically pure hydroquinone in pure acetone. The end point of the titration is marked by disappearance of the red color of the phenoxyl radical: 1 ml. of 0.01*M* hydroquinone solution is equivalent to 6.428 mg. of 2,4,6-triphenylphenoxyl dimer.

3. Discussion

The procedure for preparing 2,4,6-triphenylphenoxyl is based on the method described by Dimroth and co-workers.[2] This method represents the commonly used preparation of aroxyl radicals by oxidation of the corresponding phenol.[3] The chemistry of stable phenoxyl radicals has been reviewed.[4]

In solution the colorless 2,4,6-triphenylphenoxyl dimer attains a rapid equilibrium with its red monomer radical (dissociation constant in benzene 4×10^{-5} at 20°). The radical is surprisingly stable toward oxygen and can be stored in solution for a long time when it is protected from light. The stability of the 2,4,6-triphenylphenoxyl radical is ascribed to steric and mesomeric effects.[2,5] The e.s.r. spectrum[5] and an ENDOR-spectrum[6] of the radical are described.

The dimer belongs to the rare group of compounds which are piezochromic. Rubbing in a mortar produces a red color due to mechanical bond-breaking and dissociation into the red-colored monomer. The *p*-quinol structure of the 2,4,6-triphenylphenoxyl dimer has been confirmed by infrared studies of ^{18}O-labeled material[7] and by X-ray analysis of 3-bromo derivative.[8]

Other aroxyl radicals, especially those with *t*-butyl groups at the phenyl ring, are described by Cook[9] and by Müller.[10]

References and Notes

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

alumina

amidosulphonic acid

2,4,6-triphenylphenoxyl dimer

ethanol (64-17-5)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

Benzene (71-43-2)

methanol (67-56-1)

ether (60-29-7)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

hydroquinone (123-31-9)

oxygen (7782-44-7)

sodium nitrite (7632-00-0)

Raney nickel (7440-02-0)

acetone (67-64-1)

urea (57-13-6)

potassium hexacyanoferrate(III) (13746-66-2)

dioxane (123-91-1)

2,4,6-Triphenylnitrobenzene (10368-47-5)

2,4,6-Triphenylphenoxyl,
Phenoxy, 2,4,6-triphenyl (10384-15-3)

2,4,6-Triphenylaniline (6864-20-6)

2,4,6-Triphenylphenol (3140-01-0)

phosphorus pentoxide (1314-56-3)