C, 65.0; H, 5.18; S, 17.35; N, 3.79. Found: C, 65.0; H, 5.16; S, 17.34; N, 3.84.

2-Amino-5,5′-dimethoxy-2′-phenylthiodiphenyl sulfide was obtained from the parent nitro derivative by reduction as described above, mp 105–107 °C. Anal. Calcd for $C_{20}H_{19}NO_2S_2$: C, 65.0; H, 5.18; S, 17.35; N, 3.79. Found: C, 65.0; H, 5.31; S, 17.23; N, 3.90.

2,7-Dimethoxythianthrene (11a) was synthesized as described in the literature.[26] *n*-Pentyl nitrite (0.015 mol) was added to a solution of 2-amino-4,5′-dimethoxy-2′-phenylthiodiphenyl sulfide (0.01 mol) in ethyl acetate (50 ml). The mixture was kept at 50 °C for 5 h and then the solvent was evaporated. The residue was chromatographed on a silica gel column, and the thianthrene (**11a**) obtained in 45% yield: mp 134–135 °C (lit. 131,[27] 133 °C[28]); IR ν (CS_2) 1290 (s), 1260 (s), 1230 (s), 1220 (s), 1180 (m), 1105 (m), 1050 (s), 1040 (s), 1020 (m), 870 (m), 860 (m), 840 (s), 810 (s), 800 cm^{-1} (s).

2,8-Dimethoxythianthrene (11b) was obtained from 2-amino-5,5′-dimethoxy-2′-phenylthiodiphenyl sulfide in 45% yield as described above: mp 104–105 °C; IR ν (CS_2) 1295 (s), 1290 (s), 1280 (m), 1260 (s, doublet), 1230 (s, doublet), 1225 (s), 1220 (s), 1180 (m), 1105 (m), 1050 (s), 1045 (s), 1040 (s), 1030 (m), 870 (m), 860 (m), 840 (s), 810 (s), 800 cm^{-1} (s).

Thermal Decomposition of 1,2,3-Benzothiadiazole (1). A. In Ethyl Acetate. A solution of 1 (2.70 g, 0.02 mol) in ethyl acetate (50 ml) was kept in a "bomb" at 220 °C for 18 h. The crude was washed with 5% aqueous NaOH. From alkaline solution, after acidification and extraction with Et_2O, thiophenol was separated (0.1 g, 5%). The organic layer was chromatographed on a silica gel column; dibenzothiophene (**6**, 0.11 g, 6%), thianthrene **2**, 0.43 g, 20%), and dibenzo[*c,e*]-*o*-dithiin (**5**, 0.48 g, 22%) with small amounts of diphenyl disulfide (0.04 g, 2%) were separated. Independent experiments were carried out to prove the thermal stability of the products in reaction conditions. Thianthrene (**2**), dibenzothiophene (**6**), and thiophenol (**7**) were recovered unchanged, while dibenzodithiin (**5**) gave dibenzothiophene (3%).

B. In Toluene. A solution of 1 (3.3 g, 0.024 mol) in toluene (33 ml) was kept in a "bomb" at 220 °C for 18 h. By column chromatography on silica gel of the crude was separated, with **2, 5,** and **6**, a mixture of 1-, 2-, 3-, and 4-methyldibenzothiophene (~12%). The relative yields, determined by ratio of peak areas of methyl groups in the NMR spectrum, are 42, 14, 20, and 24%, respectively. The assignment of peaks was determined by comparison with NMR spectra of authentic specimens.

C. In Methyl Benzoate. A solution of 1 (2.6 g, 0.019 mol) in methyl benzoate (30 ml) was treated as described above. The relative yield of 1-, 2-, 3-, and 4-methoxycarbonyldibenzothiophene (~12%) separated by chromatography on a silica gel column, determined by GLC analysis, are 57, 6, 19, and 18%, respectively.

D. In Diphenylacetylene. A solution of 1 (1.36 g, 0.01 mol) and tolane (**13**, 1.78 g, 0.01 mol) in ethyl acetate (15 ml) was thermolyzed at 220 °C for 18 h. By column chromatography on a silica gel column dibenzothiophene (**6**, 3%), thianthrene (**2**, 11%), dibenzo[*c,e*]-*o*-dithiin (**5**, 12%), 2,3-diphenylbenzothiophene (**15**, 7%), and a cis–trans mixture of 1-phenylthiostilbene (7%) were separated. The indicated yields were detected by GLC analysis of the reaction mixture.

E. In Phenylacetylene. A solution of 1 (1.36 g, 0.01 mol) and phenylacetylene (1.00 g, 0.01 mol) in ethyl acetate (15 ml) was thermolyzed as above. By column chromatography **6** (5% yield), **2** (17%), **5** (18%), 2-phenylbenzothiophene (**13a**, 10%), and 3-phenylbenzothiophene (**13b**, 4%) were separated.

Thermal Decomposition of 6-Methoxy-1,2,3-benzothiadiazole (10). **10** was heated at 205 °C for 18 h in a "bomb". The crude was chromatographed on a silica gel column and the thianthrene was isolated: mp 134–135 °C; IR spectra of this fraction and **11a** were identical; mixture melting point with **11a** was undepressed.

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Registry No.—**1,** 273-77-8; **2,** 92-85-3; **5,** 230-26-2; **6,** 132-65-0; **10,** 1753-90-8; **11a,** 54815-69-9; **11b,** 60718-98-1; **13a,** 1207-95-0; **13b,** 14315-12-9; **15,** 22751-52-6; 2-nitro-4,5′-dimethoxy-2′-phenylthiodiphenyl sulfide, 60718-99-2; 2-mercapto-4-methoxydiphenyl sulfide, 60718-00-8; 2-nitro-4-methoxychlorobenzene, 10298-80-3; 2-nitro-5,5′-dimethoxy-2′-phenylthiodiphenyl sulfide, 60719-01-9; 2-nitro-5-methoxychlorobenzene, 28987-59-9; 2-amino-4,5′-dimethoxy-2′-phenylthiodiphenyl sulfide, 60719-02-0; 2-amino-5,5′-dimethoxy-2′-phenylthiodiphenyl sulfide, 60719-03-1; diphenyl disulfide, 882-33-7; *cis*-1-phenylthiostilbene, 41796-39-8; *trans*-phenylthiostilbene, 24466-59-9; phenylacetylene, 501-65-5.

References and Notes

(1) P. Jacobson and H. Janssen, *Justus Liebigs Ann. Chem.*, **277,** 209 (1893).

(2) K. P. Zeller, H. Meier, and E. Müller, *Tetrahedron Lett.*, 537 (1971).

(3) G. Seybold and C. Heibl, *Angew. Chem., Int. Ed. Engl.*, **14,** 248 (1975).

(4) W. Kirmse and L. Horner, *Justus Liebigs Ann. Chem.*, **614,** 4 (1958).

(5) R. Huisgen and V. Werberndorfer, *Experientia,* **14,** 566 (1961).

(6) L. Benati, P. C. Montevecchi, A. Tundo, and G. Zanardi, *J. Chem. Soc., Perkin Trans. 1,* 1276 (1974).

(7) L. Benati, P. C. Montevecchi, A. Tundo, and G. Zanardi, *J. Org. Chem.*, in press.

(8) J. I. G. Cadogan, J. T. Sharp, and M. J. Trattles, *J. Chem. Soc., Chem. Commun.*, 900 (1974).

(9) T. L. Gilchrist, P. G. Mento, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1,* 2165 (1972).

(10) N. Kharasch and C. Y. Meyers in "The Chemistry of Organic Sulfur Compounds", Vol. 2, Pergamon Press, Oxford, 1967, p 246.

(11) L. Benati, P. C. Montevecchi, A. Tundo, and G. Zanardi, *Gazz. Chim. Ital.*, **105,** 841 (1975).

(12) W. L. F. Amarego and E. E. Turner, *J. Chem. Soc.*, 1665 (1965).

(13) H. Lecker, *Ber.*, **58,** 409 (1925).

(14) H. Gilmann and G. R. Wilder, *J. Org. Chem.*, **22,** 523 (1957).

(15) H. Gilmann and A. L. Jacoby, *J. Org. Chem.*, **3,** 108 (1938).

(16) H. Gilmann, A. L. Jacoby, and H. A. Pacevitz, *J. Org. Chem.*, **3,** 120 (1938).

(17) P. Kirby, S. B. Soloway, J. H. Davies, and S. B. Webb, *J. Chem. Soc. C,* 2250 (1970).

(18) J. Russel, *J. Am. Chem. Soc.*, **74,** 4950 (1952).

(19) S. Middleton, *Aust. J. Chem.*, **12,** 218 (1959).

(20) H. Staudinger and J. Siegwart, *Helv. Chim. Acta,* **3,** 840 (1920).

(21) E. E. Campaigne and J. R. Leal, *J. Am. Chem. Soc.*, **76,** 1272 (1954).

(22) J. Schumtz, F. Kuenzle, F. Hunziker, and A. Buerki, *Helv. Chim. Acta,* **48,** 336 (1965).

(23) E. E. Campaigne and S. W. Osborn, *J. Org. Chem.*, **22,** 561 (1957).

(24) H. H. Hodgson and J. H. Crook, *J. Chem. Soc.*, 1812 (1932).

(25) H. H. Hodgson and F. W. Handley, *J. Chem. Soc.*, 543 (1926).

(26) L. Benati, P. C. Montevecchi, A. Tundo, and G. Zanardi, *J. Chem. Soc., Perkin Trans. 1,* 1272 (1974).

(27) K. Fries and E. Engelbertz, *Justus Liebigs Ann. Chem.*, **407,** 194 (1915).

(28) H. Baw, G. M. Bennett, and P. Dearns, *J. Chem. Soc.*, 680 (1934).

An Improved Synthesis of 1-Picryl-2,2-diphenylhydrazyl Radical. Purification and Storage of 1,1-Diphenylhydrazine as the Tosylate Salt[1]

Sally E. O'Connor and Robert I. Walter*

Chemistry Department, University of Illinois at Chicago Circle,
P.O. Box 4348, Chicago, Illinois 60680

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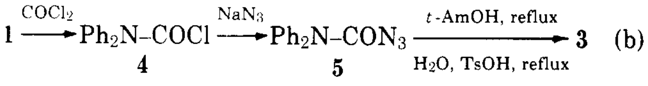
The conventional synthesis of 1-picryl-2,2-diphenylhydrazyl (DPPH) free radical requires as an intermediate 1,1-diphenylhydrazine (**3**), which is picrylated and then oxidized to the radical with lead dioxide.[2] The classical (and until recently the only) synthesis of **3** proceeds from diphenylamine by sequence a:[3]

$$\underset{\mathbf{1}}{Ph_2NH} \xrightarrow[\text{or NOCl}]{\text{HONO}} \underset{\mathbf{2}}{Ph_2N\text{-}NO} \xrightarrow[\text{or LiAlH}_4]{\text{Zn, AcOH}} \underset{\mathbf{3}}{Ph_2N\text{-}NH_2} \qquad (a)$$

Simultaneous reductive cleavage of the N–N bond during conversion of **2** to **3** has been well documented,[4] as have the labor and erratic results in the separation of the "pure" hydrazine. Heroic efforts devoted to purification of **3** give a crystalline solid variously reported[5] to melt through the range 31–44 °C, but the usual product is an oil identified only by its boiling point in a vacuum distillation. Furthermore, in our experience both the hydrazine and its hydrochloride deteriorate upon storage after purification, so it is impossible to maintain a stock of the compound which can be relied upon for further synthetic work.

Anselme and Koga[6] have published an alternate route to **3** from **1** by Curtius rearrangement of 1,1-diphenylcarbamyl azide (**5**) dissolved in a tertiary alcohol, followed by hydrolysis of the *tert*-alkyl 3,3-diphenylcarbazate formed:



$$\mathbf{1} \xrightarrow{COCl_2} \underset{\mathbf{4}}{Ph_2N\text{-}COCl} \xrightarrow{NaN_3} \underset{\mathbf{5}}{Ph_2N\text{-}CON_3} \xrightarrow[H_2O,\ TsOH,\ reflux]{t\text{-}AmOH,\ reflux} \mathbf{3} \quad (b)$$

When we repeated their sequence, we observed formation of a small amount of solid in the hydrolysis mixture. This was identified as the salt of **3** with *p*-toluenesulfonic acid (TsOH), **6**. It proved to be readily purified and quite stable. It can be precipitated directly by adding excess TsOH in *tert*-amyl alcohol to an ether solution of **3**, and the latter can be regenerated immediately before use by addition of a base to a solution of the salt, **6**.

Our comparison of these routes to **3** was motivated by a need to synthesize isotopically labelled derivatives of **3** and of DPPH. Clearly it is necessary for this purpose to use procedures which are reliable even on a small scale, and give maximum yields. By these criteria, we have had significantly better success with both sequences when **3** was isolated as its salt **6** with TsOH. Overall yields have averaged 70–80% from **1** by both routes, even on a 1-g scale.

The advantage of a source of pure **3** becomes clear during its subsequent picrylation in the sequence of reactions for the preparation of DPPH: yields of the hydrazine are close to 99% before recrystallization. In contrast, picrylation yields by our older procedure in normal cases not complicated by the substituents present were in the range 75–95%.[7]

Experimental Section

All melting points were taken on a Thomas calibrated hot stage. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

2,2-Diphenylhydrazinium Tosylate (6) from 2. 2 (0.1 mol) in 50 ml of ether was reduced with 50% excess powdered lithium aluminum hydride using the inverse addition procedure of Poirier and Benington.[8] After decomposition of the reduction intermediate,[7] the mixture was stirred for 1 h, and the ether layer separated, combined with an ether wash of the aqueous layer, and dried over sodium sulfate. A solution of 0.12 mol of TsOH in 20 ml of *tert*-amyl alcohol was added, and the colorless, crystalline precipitate filtered, washed well with ether, and dried. The average yield is 76%, mp 189.0–189.5 °C dec. NMR in $Me_2SO\text{-}d_6$ shows peaks at 10.1 ($-NH_3^+$, broad, variable position) and 2.28 ppm ($-CH_3$) with equal areas, and multiple lines from 7.1 to 7.6 ppm for the 14 aromatic protons. Anal. Calcd for $C_{19}H_{20}N_2O_3S$: C, 64.04; H, 5.62; N, 7.86; S, 8.99. Found: C, 64.26; H, 5.74; N, 7.99; S, 8.79.

2,2-Diphenylhydrazinium Tosylate (6) from 5. Anselme and Koga's procedure[6] for conversion of **5** to **3** was followed, except that the amount of TsOH added was increased to 20 g. After the 5-h reflux period, the precipitated product was filtered off and thoroughly washed with ether. Yield was 80%, with properties identical with those already described above.

***N*-Aminocarbazole Hydrogen Tosylate (7).** *N*-Aminocarbazole was converted by the first procedure above to **7**. Product was obtained as colorless crystals in 65% yield, with mp 199.0–199.5 °C. The NMR in $Me_2SO\text{-}d_6$ shows peaks at 10.8 ($-NH_3^+$, variable position) and 2.28 ppm ($-CH_3$) with equal areas, and multiple lines from 7.1 to 8.25 ppm for the aromatic protons. Anal. Calcd for $C_{19}H_{18}N_2O_3S$: C, 64.41; H, 5.08; N, 7.91; S, 9.04. Found: C, 64.40; H, 5.15; N, 8.01; S, 8.88.

Recovery of 3 as the Tosylate Salt. A known amount of pure **3** was generated from a solution of 1.0 g of **6** in 20 ml of methanol by adding a solution of 0.3 g of sodium carbonate in 10 ml of water. Most of the solvents were removed on a rotary evaporator, and the residue taken up in 1:1 ether-water. The ether layer was combined with two ether washes of the aqueous layer and dried. A solution of 0.6 g of TsOH in *tert*-amyl alcohol was added, and the colorless needles filtered and dried. Recovery was 95%.

1-Picryl-2,2-diphenylhydrazine. Salt **6** and picryl chloride (0.1 mol each) were dissolved in 50 ml of methanol, 0.5 g of sodium carbonate in 20 ml of H_2O added, and the mixture stirred for 2 h. The brick-red product was filtered, washed with fresh solvent mixture, and dried. The yield was 99%, with mp 174–175 °C before recrystallization; the product is pure enough to use directly for preparation of DPPH, by the conventional lead dioxide oxidation.[2,7]

Registry No.—**2,** 86-30-6; **3,** 530-50-7; **5,** 17223-83-5; **6,** 61064-13-9; **7,** 61064-14-0; TsOH, 104-15-4; *N*-aminocarbazole, 17223-85-7; 1-picryl-2,2-diphenylhydrazine, 1707-75-1; picryl chloride, 88-88-0; 1-picryl-2,2-diphenylhydrazyl radical, 1898-66-4.

References and Notes

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(2) S. Goldschmidt and K. Renn, *Chem. Ber.*, **55B,** 628–643 (1922).

(3) E. Fischer, *Justus Liebigs Ann. Chem.*, **190,** 174–176 (1878).

(4) N. Koga and J.-P. Anselme, *J. Org. Chem.*, **33,** 3963–3964 (1968).

(5) The highest melting point, 44 °C, is reported by F. M. Jaeger, *Z. Kristallogr. Mineral.*, **42,** 160 (1907). He acknowledges his sample as a gift, with no mention of the method of preparation.

(6) J.-P. Anselme and N. Koga, *Org. Prep. Proced.*, **2,** 125–128 (1970).

(7) M. M. Chen, A. F. D'Adamo, and R. I. Walter, *J. Org. Chem.*, **26,** 2721–2727 (1961).

(8) R. H. Poirier and F. Benington, *J. Am. Chem. Soc.*, **74,** 3192 (1952).