for $C_{25}H_{25}ClN_2O_3$: C, 68.76; H, 5.77; N, 6.42. Found: C, 66.49; H, 5.56; N, 5.79. This was same material as the authentic specimen.

5b: IR (KBr) 1715, 1705 cm^{-1}; NMR (Me_2SO-d_6) τ 2.1–3.5 (m, 13 H of aromatic and methine), 7.00 and 7.02 (s, 12 H of NMe); UV ($CHCl_3$) 323 nm (ϵ 54 000). Anal. Calcd for $C_{25}H_{25}N_2O_3Cl$: C, 68.76; H, 5.77; N, 6.42. Found: C, 67.83; H, 5.22; N, 6.64.

Reaction of 4-Nitrobenzil (2c) with NaCN. 4-Nitrobenzil (**2c**, 0.64 g) was added to a solution of NaCN (0.03 g) in Me_2SO (15 mL). Reaction was allowed to occur at room temperature for 1 h and then the mixture was poured into acidic ice–water to produce a light green precipitate. This precipitate was washed with ethanol and recrystallized from benzene–ethanol to give 4-nitrostilbenediol 4′-nitrodibenzoate (**9c**) in the form of light yellow crystals (0.16 g, 25%), mp 212–216 °C, which were identified by IR and NMR spectra and elemental analysis. Only a small amount of yellow solid (0.01 g), mp 175–180 °C, was recovered from the combined ethanol washings and mother liquor.

9c: IR (KBr) 1740, 1520, 1340 cm^{-1}; NMR ($CDCl_3$) τ 1.69 (s, 4 H of 4-nitrobenzoyloxy), 1.7–2.3 (m, 2 H meta to NO_2 and 4 H ortho to C=O; 1.82 d and 2.22 d, J = 9 Hz), 2.3–2.7 (m, 5 H of Ph and 3 H meta and para to C=O); MS *m/e* 510, 255, 240, 239, 150, 135, 122, 105. Anal. Calcd for $C_{28}H_{18}N_2O_8$: C, 65.88; H, 3.55; N, 5.49. Found: C, 65.75; H, 3.82; N, 5.69. Treatment of the sample with methanolic MeONa gave an equimolar mixture of methyl benzoate and methyl 4-nitrobenzoate (1:0.84) as determined by GLC analysis.

Reaction of Benzoin Benzoate with Benzoyl Cyanide in the Presence of NaH. Benzoin benzoate (1.58 g, 5 mmol) was converted into the enolate ion by treatment with NaH dispersed in mineral oil (0.50 g, 5 mmol) in Me_2SO (30 mL) under N_2 to give a deep green colored solution. Addition of benzoyl cyanide (0.68, g, 5 mmol) at room temperature caused the solution to become very dark. After 20 min the mixture was poured into ice-cold aqueous H_2SO_4, giving a precipitate (1.84 g). This precipitate was recrystallized from benzene–petroleum to give stilbenediol dibenzoate (SDD) (0.53 g, 25%), in the form of crystals, mp 191–193 °C. An additional SDD (0.13 g, total 31%) was isolated as a second crop (mp 179–193 °C). Evaporation of the filtrate to dryness and crystallization of the residue from EtOH gave benzoin benzoate (0.59 g, 37%) in the form of crystals, mp 124–126 °C.

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Registry No.—**2a**, 22711-20-2; **2b**, 60955-65-9; **2c**, 22711-24-6; **3a**, 62139-42-8; **3b**, 62139-43-9; **5b**, 62139-44-0; **6a**, 62139-45-1; **7a**, 65-85-0; **7b**, 74-11-3; **8a**, 619-84-1; **9c**, 62139-46-2; NaCN, 143-33-9; benzaldehyde, 100-52-7; methyl 4-dimethylaminobenzoate, 1202-25-1; benzoin benzoate, 1459-20-7; benzoyl cyanide, 613-90-1; stilbenediol dibenzoate, 1924-29-4; dimethyl sulfoxide, 67-68-5.

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Disproportionation and Pyrolysis of *p*-Toluenesulfonylhydrazine

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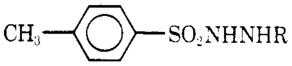
p-Toluenesulfonylhydrazine (**1**) is a standard reagent, widely used in the synthesis of organic compounds.[1] Its chemistry, particularly deviations from the normal behavior of hydrazine derivatives, is thus of interest. In 1965, Chang[2] found that an anomalous reaction between **1** and 12-oxocholane produced 12-oxocholane azine in addition to the expected tosylhydrazone. The azine presumably arose via a disproportionation of **1** into hydrazine and di(*p*-toluenesulfonyl)hydrazine (**2**), but the disubstituted hydrazine was not isolated. We found that a similar disproportionation occurred when 1,3-dioxolen-2-one was heated with **1** in the presence of sulfuric acid; and **2**, shown below to be the 1,2 isomer, was formed in low yield.



1, R = H
2, R = *p*-$CH_3C_6H_4SO_2$

A better synthesis of **2** involved deprotonation of **1** with bases such as *n*-butyllithium or triethylamine followed by reaction with *p*-toluenesulfonyl chloride. Recrystallization from acetonitrile yielded 1,2-di(*p*-toluenesulfonyl)hydrazine as white needles, mp 194–195 °C dec. The compound underwent extensive fragmentation on electron impact and no parent ion was observed in the mass spectrum. Instead, a cluster of peaks due to $C_7H_7SO_2^+$, $C_7H_7SO_2H^+$, and $C_7H_7SO_2H_2^+$, respectively, was observed. The methane chemical ionization mass spectrum showed the *m/e* 157 ($C_7H_7SO_2H_2^+$) ion as the base peak. In contrast, the mass spectrum of **1** showed a readily identifiable M^+ peak at *m/e* 186.

The infrared spectrum of **2** in acetonitrile exhibited strong bands at 1165 and 1345 cm^{-1} due to the sulfonyl groups. An additional band at 3180 cm^{-1}, which shifted to 2350 cm^{-1} on crystallization of **2** from tetrahydrofuran–D_2O, was assigned to ν_{NH}. The presence of only one N–H stretching band implies that only secondary amine groups are present, for otherwise, two bands, symmetric and asymmetric stretch, would be observed.[3] Further evidence that **2** is the 1,2 isomer was obtained from the ^1H NMR spectrum in which the NH protons appeared as a broad singlet at 3.4_2 ppm (Me_2SO-d_6). The shifts of the NH protons are 3.4_2 (2 H) and 4.1_1 ppm (1 H) for **1** and 3.4 ppm for *p*-toluenesulfonamide. This indicates that NH protons adjacent to a *p*-toluenesulfonyl group resonate at ~3.4 ppm, as observed in **2**.

It is probable that **2** is formed by nucleophilic attack by the conjugate base on **1** on toluenesulfonyl chloride. In this case, it is interesting to note that proton abstraction from N-2 takes place rather than from N-1, adjacent to the electron-withdrawing tosyl group.

The melt pyrolysis of *p*-toluenesulfonylhydrazine was studied to determine whether thermal disproportionation would occur. Upon heating at 140 °C under vacuum, the hydrazine derivative decomposed to give nitrogen, ammonium *p*-toluenesulfonate (**3**), *p*-toluenesulfonamide, and *p*-ditolyl disulfide dioxide (**4**). Identification of **3** followed from its elemental analysis and behavior as a 1:1 electrolyte in nitromethane. The electron impact and methane chemical ionization showed only peaks due to ions derived from p-toluenesulfonic acid.

$$1 \xrightarrow{\Delta} \underset{3}{NH_4^+p\text{-}CH_3C_6H_4SO_3^-} + N_2 + \underset{4}{p\text{-}CH_3C_6H_4SO_2SC_6H_4CH_3\text{-}p} + p\text{-}CH_3C_6H_4SO_2NH_2$$

The unsymmetrical structure of **4** deduced from the ^1H NMR spectrum[4] is confirmed by the observation of two nonequivalent methyl resonances at 21.5 and 21.3 ppm in the ^{13}C NMR spectrum and by the infrared spectrum, which reveals symmetrical and asymmetrical S–O stretching modes.[5,6]

Melt pyrolysis of **1** presumably generates N_2H_2 and p-toluenesulfinic acid (**5**) by 1,2-elimination as suggested by Dewey and Van Tamelen.[7] Reduction of added olefins is good evidence for the generation of N_2H_2 as an intermediate. Subsequent disproportionation of the sulfinic acid to p-toluenethiol and p-toluenesulfonic acid (**6**), followed by loss of water, would form **4**. Condensation of ammonia, derived from N_2H_2, and **6** would produce both **3** and p-toluenesulfonic acid. Di-p-tolyl disulfide, observed as a pyrolysis product by Meier and Menzel,[8] was not isolated. Our reactions were carried out under vacuum and it is possible that the disulfide is produced by air oxidation of p-toluenethiol. These workers did not analyze the benzene-insoluble reaction products and did not report the formation of **3**. p-Toluenesulfinic acid was not observed among the pyrolysis products[7] and it is probably unstable under the conditions required for its formation from **1**. This is in agreement with Otto and Von Gruber[9] with the work of Yoshida et al.,[10] who reported facile disproportionations of benzenesulfinic acid.

We conclude that solid **1** decomposes by 1,2-elimination to form toluenesulfinic acid and diimide as the primary products and does not generate the symmetrical ditosylhydrazine **2**. Formation of this derivative in solution requires the presence of acid and may arise by attack at sulfur in the conjugate acid of **1** by additional **1**. An analogous mechanism has been previously proposed to account for the acid-catalyzed conversion of tosylhydrazones to azines.[11]

Experimental Section[12]

Commercial p-toluenesulfonylhydrazine was crystallized from tetrahydrofuran–hexane. Infrared spectra were recorded on a grating spectrometer. ^1H and ^{13}C NMR spectra were obtained at 60 and 22.6 MHz, respectively, and chemical shifts are reported with respect to internal $(CH_3)_4Si$; positive shifts arbitrarily refer to lower field. Elemental analyses were performed by Schwarzkopf Laboratories. Melting points are uncorrected. Mass spectra were obtained by using a direct insertion probe and a quadrupole spectrometer. Electron impact spectra were obtained at 70 eV. Methane was used as the reagent gas in chemical ionization experiments.

1,2-Di(p-toluenesulfonyl)hydrazine (2). A solution of 0.65 g (3.5 mmol) of **1** in 10 mL of tetrahydrofuran was cooled to −78 °C and 2.2 mL of 1.6 M n-butyllithium in hexane added dropwise with rapid stirring. p-Toluenesulfonyl chloride (0.67 g, 3.5 mmol) in 10 mL of tetrahydrofuran was then added. The cold bath was removed, and the reaction mixture stirred overnight, then filtered. The filtrate was evaporated to 10 mL and treated with 80 mL of petroleum ether to give, after chilling, a gummy product. This was dissolved in methanol and slowly added to cold water. The white precipitate was recrystallized from acetonitrile to give 0.2 g (17%) of product as white needles, mp 194–195 °C dec. Anal. Calcd for $C_{14}H_{16}N_2O_4S_2$: C, 49.41; H, 4.70; N, 8.24; S, 18.82. Found: C, 49.29; H, 4.88; N, 8.50; S, 19.36. IR (CH_3CN) 3180 (br), 1600 (w), 1345 (m), 1190 (w), 1185 (s), 1165 (s), 1090 (m), 815 (m), 710 (m, br), 750 cm^{-1} (m). Electronic spectrum [ethanol, λ_{max} (log ϵ)] 228 (4.24). ^1H NMR (Me_2SO-d_6) 7.6 (m, 4 H), 3.4 (br, s 1 H), 2.42 (s, 3 H). Mass spectrum [m/e (assignment, rel abundance)] 185 ($C_7H_7SO_2N_2H_2$, 0.8), 157 ($C_7H_7SO_2H_2^+$, 15), 156 ($C_7H_7SO_2H^+$, 44), 155 ($C_7H_7SO^+$, 20), 91 ($C_7H_7^+$, 100).

Reaction of Vinylene Carbonate and p-Toluenesulfonylhydrazine. A solution of 1.86 g (10 mmol) of p-toluenesulfonylhydrazine, 0.86 g (10 mmol) of vinylene carbonate, and 2 drops of concentrated sulfuric acid in 30 mL of 1:1 ethanol–chloroform was refluxed for 10 h. The reaction mixture was filtered and evaporated to give an oily residue which was extracted with petroleum ether. Evaporation of the petroleum ether yielded a solid which was recrystallized from acetonitrile to give 0.08 g of **2** (4%), identified by its infrared and mass spectra and melting point. This product was not isolated when the acid was omitted.

Melt Pyrolysis of p-Toluenesulfonylhydrazine. A 1.05-g sample of **1** was placed in a small flask which was evacuated and heated with an oil bath whose temperature was gradually raised to 140 °C. Heating was continued for 15 min after gas evolution ceased.

The material remaining in the flask was extracted with 5 mL of dichloromethane. Insoluble ammonium p-toluenesulfonate (**3**) was collected on a filter and recrystallized by slow evaporation of methanol–acetonitrile solution to give 0.06 g of thin, colorless plates, mp 330–333 °C (lit. 340,[13] 325–330 °C[14]). Anal. Calcd for $C_7H_{11}NO_3S$: C, 44.44; H, 5.82; N, 7.40; S, 16.93. Found: C, 45.07; N, 5.87; N, 7.74; S, 17.20. IR (Nujol) 3125 (br, s), 1160 (br, s), 1030 (m), 1010 (m), 810 (s), 680 (s). The mass spectrum matched that of p-toluenesulfonic acid. Λ_M (CH_3NO_2, 8.8×10^{-4} M) 70.8 $mol^{-1}\ ohm^{-1}\ cm^2$.

The dichloromethane solution was chromatographed on a 12 × 1 in. silica gel column. Elution with dichloromethane afforded 0.41 g of di-p-tolyl disulfide dioxide (**4**) which was recrystallized from methylcyclohexane to give colorless needles: mp 72–73.5 °C (lit.[15] 76 °C); IR ($CHCl_3$) 3030 (w), 2980 (w), 1595 (m), 1490 (m), 1330 (s), 1305 (m), 1290 (w), 1140 (s), 1080 (m), 1015 (w), 810 (s), 650 (s), 580 (s), 525 (m), 510 cm^{-1} (m); electronic spectrum (C_2H_5OH) λ_{max} 234 (3.96), 212 (sh); (^1H) ^{13}C NMR (acetone-d_6) 145.5, 142.7, 141.3, 136.9, 130.8, 130.2, 128.1, 125.4, 21.5, 21.3 ppm; mass spectrum m/e 280 ($C_{14}H_{14}O_2{}^{32}S{}^{34}S^+$, 10), 279 ($^{13}C^{12}C_{13}H_{14}O_2S_2^+$, 17), 278 ($M^+$, 100), 155 ($C_7H_7SO_2^+$, 15), 139 ($C_7H_7SO^+$, 58), 123 ($C_7H_7S^+$, 18), 91 ($C_7H_7^+$, 26).

Continued elution of the column with acetone yielded 0.12 g of p-toluenesulfonamide which was identified by comparison of its infrared and mass spectra with those of an authentic sample.

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Registry No.—**1**, 1576-35-8; **2**, 14062-05-6; **3**, 4124-42-9; **4**, 2943-42-2; p-toluenesulfonyl chloride, 98-59-9; vinylene carbonate, 872-36-6.

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