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Thermal Dimerization of Sulfinyl Compounds

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The dimers (**2a—c**) of active methylene compounds were readily synthesized by heating the corresponding α-sulfinyl compounds (**1a—c**) in carbon tetrachloride or tetrahydrofuran in 14—90% yields.

Keywords——dimer of active methylene compound; sulfinylation; disproportionation; sulfinamide; sulfinyl radical

Various dimerization methods for active methylene compounds have recently been developed.[2] We report here the thermal dimerization of α-sulfinylated active methylene compounds not having a β-hydrogen atom. α-Sulfinyl compounds having a β-hydrogen atom have generally been utilized for the formation of C=C bonds.

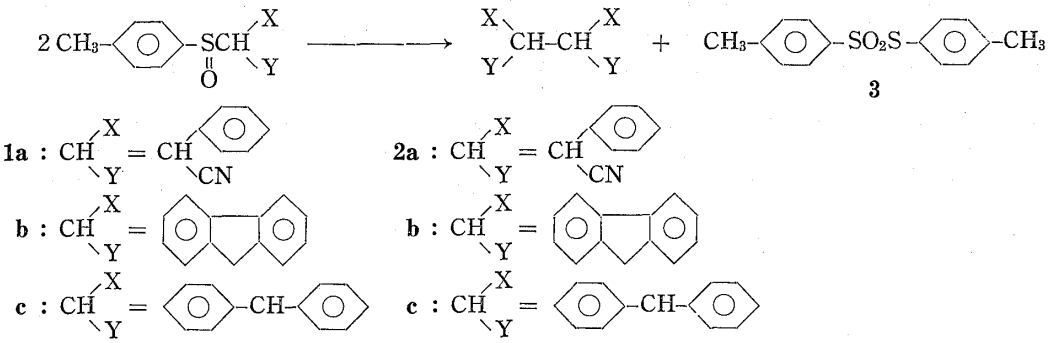

Chart 1

The sulfinyl compounds employed were synthesized by sulfinylation of active methylene compounds with methyl *p*-toluenesulfinate,[3] *p*-toluenesulfinyl chloride,[3] or *p*-toluenesulfinamide.[4] The compound **2a** obtained was confirmed to be meso form by direct comparison with an authentic sample prepared by an alternative method.[5] On heating the sulfinyl compounds in carbon tetrachloride or tetrahydrofuran, the corresponding dimers with elimination of the sulfinyl group were readily formed in 14—19% yields. The dimer **2c** was also directly obtained by sulfinylation of the diphenylmethylcarbanion, prepared using *n*-butyllithium, with *p*-toluenesulfinamides, **4a** and **4b**, in 44 and 22% yields, respectively, no trace of any expected sulfinyl compound being isolated. In the sulfinylation of fluorene with **4a** under similar conditions, however, the corresponding sulfinyl compound **2b** was isolated in low yield. This result sug-

1) Location: *5-1, Oe-hon-machi, Kumamoto-shi, 862, Japan.*
2) T.L. Ho and G.A. Olah, *Synthesis*, **1977**, 170; N. Obata and K. Niimura, *Chem. Commun.*, **1977**, 238; S. Inaba and I. Ojima, *Tetrahedron Lett.*, **1977**, 2009; E. Klemm, D. Klemm, and H.H. Horhold, *Synthesis*, **1977**, 342; H.G. Thomas, M. Streukens, and R. Peek, *Tetrahedron Lett.*, **1978**, 45; S. Nakanishi, T. Shundo, T. Nishibuchi, and Y. Otsuji, *Chem. Lett.*, **1979**, 955.
3) H. Phillips, *J. Chem. Soc.*, **1925**, 2552.
4) M. Furukawa and T. Okawara, *Synthesis*, **1976**, 339.
5) R.B. Davis and J.A. Ward. Jr., "Organic Synthesis," Coll. Vol. IV, John Willy and Sons, Inc., NewYork, 1963, p. 392.

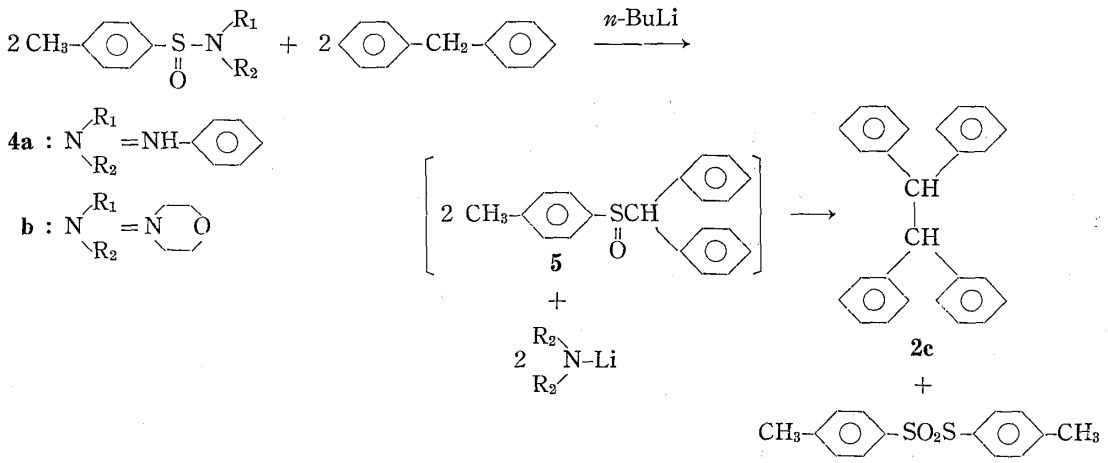

Chart 2

gests that the direct formation of **2c** from diphenylmethane proceeds through the α-sulfinyl intermediate. In order to determine whether this reaction proceeded *via* a radical, the thermal decomposition of the α-sulfinyl compound **1a** in carbon tetrachloride was examined by electron spin resonante (ESR) spectrometry. Fig. 1 shows the ESR spectrum of a solution of **1a** in carbon tetrachloride at 60—70°. The spectrum at room temperature(21°) showed no peak, but on heating (60—70°) a significant peak appeared. It is apparent that decomposition of the sulfinyl compounds **1** to the dimers **2** proceeds through radical formation.

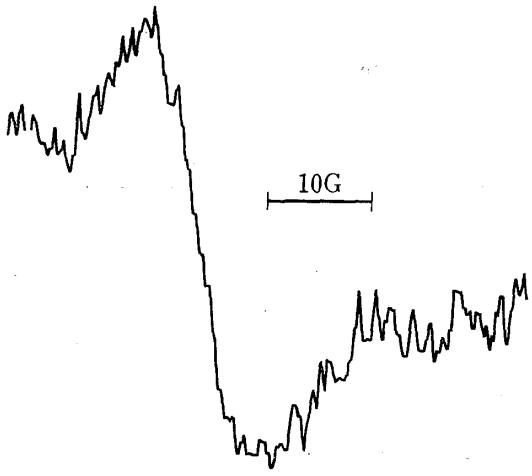

Fig. 1. ESR Spectrum of a Solution of **1a** in CCl_4 at 60—70°

The initially formed disubstituted methyl radical **6** undergoes prompt dimerization to the corresponding dimers **2**. The simultaneously formed sulfinyl radical **7** similarly affords the extremely unstable bi-*p*-toluenesulfoxide **8**, which undergoes rapid conversion to *p*-tolyl *p*-toluenethiolsulfonate **3**.[6] Further studies are under way.

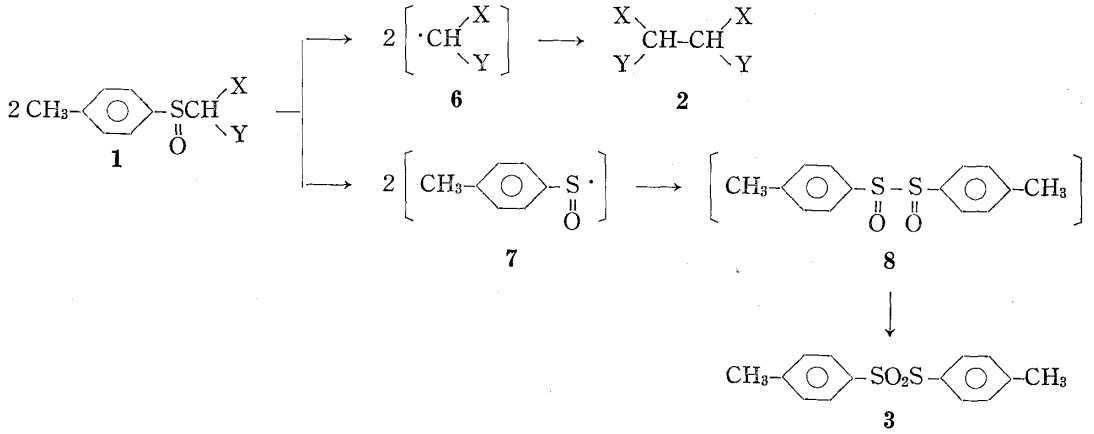

Chart 3

6) M. Furukawa, T. Okawara, Y. Noguchi, and M. Nishikawa, *Synthesis*, **1978**, 441.

Experimental

All the melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded with a JASCO IRA-1 grating infrared spectrometer. Nuclear magnetic resonance (^{1}NMR) spectra were determined with a JEOL C-60H high resolution NMR instrument. ESR spectra were recorded with a JES-FEIX ESR spectrometer. Mass spectra were measured with a JEOL-01SG mass spectrometer.

α-(*p*-Toluenesulfinyl)benzylcyanide (1a)——A solution of benzyl cyanide (0.59 g, 5 mmol) in anhydrous THF (10 ml) was added to a suspension of 50% sodium hydride (0.12 g, 5 mmol) in anhydrous THF (10 ml) under an atomosphere of nitrogen. The mixture was stirred for 0.5 hr under reflux, then a solution of methyl *p*-toluenesulfinate[3] (0.085 g, 5 mmol) in anhydrous THF (10 ml) was added and the stirred reaction mixture was refluxed for 4 hr. After removal of THF, small amounts of Et_2O and H_2O were added with stirring to the residue. The precipitates were collected by filtration, washed with H_2O, and recrystallized from EtOH. Yield 0.93 g (73%). mp 137—138°. IR ν_{max}^{KBr} cm^{-1}: 1043 (SO). NMR δ ($CDCl_3$): 2.35 (s, 3H, CH_3), 4.90 and 4.68 (threo and erythro), (s, 1H, CH), 7.05 (s, 5H, arom), 7.07 (q, 4H, arom). *Anal. Calcd* for $C_{15}H_{13}NOS$: C, 70.56; H, 5.13; N, 5.49. Found: C, 70.62; H, 5.11; N, 5.67.

9-(*p*-Tolylsulfinyl)fluorene (1b)——A solution of *n*-BuLi (1.01 g, 16.5 mmol) in *n*-hexane was added to a stierrd solution of N-(*p*-tolylsulfinyl) morpholine (**4b**)[4] (1.6 g, 7.5 mmol) and fluorene (1.18 g, 7.5 mmol) in anhydrous THF (20 ml) at −20° under an atmosphere of nitrogen. Stirring was continued for a further 2 hr, allowing the temperature to rise slowly to room temperature. After removal of THF, the residue was dissolved in Et_2O (50 ml), washed with H_2O (20 ml), three times with 1 N HCl (20 ml), and finally with H_2O(20 ml), then it was dried over anhydrous Na_2SO_4. After removal of Et_2O, the residue was recrystallized from EtOH. Yield 0.28 g (14%). mp 133—134°. IR ν_{max}^{KBr} cm^{-1}: 1050 (SO). NMR δ ($CDCl_3$): 2.17 (s, 3H, CH_3), 5.29 (s, 1H, CH), 6.5—7.8 (m, 12H, arom). *m/e*: 304 (M^+). *Anal.* Calcd for $C_{20}H_{16}OS$: C, 79.02; H, 5.30. Found: C, 79.69; H, 5.26.

2,3-Diphenylsuccinonitrile (2a) and *p*-Tolyl *p*-Toluenethiolsulfonate (3)[6]——A solution of **1a** (1.26 g, 5 mmol) in CCl_4 (5 ml) was refluxed for 3 hr. The solution was washed with 1% $NaHCO_3$ (5 ml) and H_2O (5 ml), and dried over anhydrous Na_2SO_4. After removal of CCl_4, the residue was recrystallized from EtOH. Yield 0.52 g (90%). mp 236—238°. IR ν_{max}^{KBr} cm^{-1}: 2230 (CN). NMR δ ($(CD_3)_2SO$): 5.08 (s, 2H, 2×CH), 7.30 (s, 10H, arom). MS *m/e*: 232 (M^+), 116 ($C_6H_5\overset{+}{C}HC_6H_5$), 77 ($C_6H_5^+$). *Anal.* Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.43; H, 5.58; N, 11.85.

One-fifth of the ethanolic filtrate of the recrystallization was applied to a silicagel column and eluted with benzene to give **3**. Yield 29 mg (23%). mp 75 —76°. IR ν_{max}^{KBr} cm^{-1}: 1590, 807 (*p*-tolyl), 1322, 1140 (SO_2S).

9,9′-Bifluorene (2b)——A solution of **1b** (0.28 g, 0.9 mmol) in anhydorus THF (5ml) was refluxed for 3 hr. After removal of THF, the residue was recrystallized from Et_2O. Yield 25 mg (17%). mp 240—242°. A small amount of **3** was also isolated. Compound **2b** was identified by comparison of its IR spectrum with that of an authentic sample. (The Aldrich Library of IR Spectra, 2 nd. ed.)

Tetraphenylethane (2c)——1) A solution of *n*-BuLi (1.99 g, 5 mmol) in *n*-hexane was added to a stirred solution of diphenylmethane (0.84 g, 5 mmol) in anhydrous THF (40 ml) at room temperature under an atmosphere of nitrogen. Stirring was continued for 1 hr. A solution of *p*-toluenesulfinyl chloride (5 mmol) in Et_2O (10 ml) was then added to the mixture at room temperature. The reaction mixture was stirred for 4 hr, then allowed to stand overnight. Water (40 ml) was added, and the mixture was extracted with H_2O (40 ml), washed with 1% $NaHCO_3$ (20 ml), then with H_2O (20 ml), and dried over anhydrous Na_2SO_4. After removal of Et_2O, the residue was applied to a silicagel column and eluted with $CHCl_3$ to give **2c**. Yield 0.11 g (14%) . mp207—209°. IR ν_{max}^{KBr} cm^{-1}: 1590, 740, 690 (C_6H_5). MS *m/e*: 334 (M^+), 167 ($C_6H_5\overset{+}{C}HC_6H_5$). A small amount of **3** was also isolated. 2) A solution of *n*-BuLi (1.34 g, 0.01 mol) in *n*-hexane was added to a solution of N-phenyl-*p*-toluenesulfinamide (**4a**) (2.31 g, 0.01 mol) and diphenylmethane (1.68 g, 0.01 mol) in anhydrous THF (20 ml) at −20° under an atomosphere of nitrogen. Stirring was continued for 4 hr, allowing the temperature to rise slowly to room temperature. After removal of THF, the residue was dissolved in Et_2O (50 ml), washed with H_2O (20 ml), then three times with 1 N HCl (40 ml), and finally with H_2O (20 ml), and dried over anhydrous Na_2SO_4. After removal of Et_2O, the residue was recrystallized from EtOH. Yield 0.77 g (44%). mp 208—210°. A small amount of **3** was also isolated.

In the case of N-(*p*-tolylsulfinyl)morpholine (**4b**), the yield of **2c** was 20%.