

pinacolone **3** and may also conceivably serve as a precursor for **5** and **6**.

It is obvious from the present results and the findings of others that the Clemmensen reduction of benzoylferrocene produces a variety of products, depending on the nature of the reducing agent, the solvent used, the reaction time, etc. The reduction appears to have little synthetic value as a reliable route to benzylferrocene, since there are available much better methods employing sodium and ethanol<sup>8</sup> or lithium aluminum hydride-aluminum chloride.<sup>13</sup> The nature and mechanism of formation of the bimolecular products obtained from the Clemmensen reduction of aryl ferrocenyl ketones are of interest, however, and are under further investigation in our laboratory.

### Experimental Section

**General.**—Benzoylferrocene was prepared according to a published procedure.<sup>9</sup> Elemental analyses were carried out by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Nmr spectra were obtained in deuteriochloroform solution on a Varian A-60 spectrometer, and infrared spectra were obtained as potassium bromide pellets on a Beckman IR-10 spectrophotometer. Chromatography was generally performed on columns wrapped with aluminum foil to protect the compounds from light.

**Clemmensen Reduction of Benzoylferrocene.**—The yields of the various products produced in this reaction have been found to vary appreciably, and the following is given as a typical reaction procedure and work-up.

Into a 1-l. flask equipped with a mechanical stirrer and reflux condenser were placed 60 g (0.92 g atom) of zinc dust, 4.5 g (0.017 mole) of mercuric chloride, 75 ml of water, and 3.0 ml of concentrated hydrochloric acid. The mixture was heated with stirring to near reflux for 10 min, the water was then decanted, and to the resulting zinc amalgam was added 30 ml of water, 60 ml of concentrated hydrochloric acid, and 100 ml of toluene. To this mixture at reflux was added 17.4 (0.06 mole) of benzoylferrocene (**1**). The reaction mixture was then allowed to stir at reflux for 85 hr, with periodic addition of 150 ml of concentrated hydrochloric acid (25-ml portions every 12–15 hr).

The reaction mixture was allowed to cool to room temperature, filtered, and the filtered material was washed with water and hexane and was dried. There remained 4.57 g (28% yield) of 1,2-diphenyl-1,2-diferrocenylethene (**5**) in the form of an orange-red solid, mp 274–276° (N<sub>2</sub>). Recrystallization of this solid from xylene-heptane produced a product of mp 277–278° (lit.<sup>14</sup> mp 278–280°); a mixture melting point determination with an authentic sample<sup>14</sup> showed no depression. Both infrared and nmr spectra of **5** were consistent with the proposed formulation and were identical with analogous spectra obtained from an authentic sample.<sup>14</sup>

The solvent was evaporated from the organic portion after washing twice with 5% sodium bicarbonate solution. The resulting solid was triturated 5–6 times with hexane and was filtered. The filtrate was evaporated to give an oily product which was chromatographed on an alumina column. The first (main) band was eluted with hexane-benzene, and the product was recrystallized from hexane to produce 1.21 g (7%) of orange-yellow crystals of benzylferrocene (**2**), mp 73–74° (lit.<sup>15</sup> mp 76°). The second and third bands were eluted with benzene and produced very small amounts of **6** and **3**, respectively. These products were identified by tlc and by comparison of their nmr spectra with the spectra of authentic samples.<sup>4,11</sup>

The insoluble material after trituration with hexane was extracted with boiling acetone. A very small amount of red solid, identified as **5**, precipitated and was filtered. Concentration of the filtrate and subsequent cooling produced 0.68 g (4% yield) of 1,2-diferrocenyl-1,2-diphenylethane (**6**), mp 218–220° (lit.<sup>16</sup> mp 218–220°); a mixture melting point determination with

an authentic sample showed no depression. The infrared spectrum of **6** exhibited absorption peaks at 3070, 1102, 998 and 910 cm<sup>-1</sup> (ferrocenyl group), 2897 cm<sup>-1</sup> (aliphatic C-H), and other principal peaks at 3020, 1598, 1485, 1450, 926, 775 and 705 cm<sup>-1</sup> which may be assignable to the phenyl groups. The nmr spectrum of **6** indicated a multiplet centered at  $\tau$  2.77 (10 H, phenyl protons) and a multiplet between 5.9 and 6.4 (20 H, ferrocenyl and methine protons). Both infrared and nmr spectra were identical with analogous spectra obtained from an authentic sample.<sup>11</sup>

### Thermal Decomposition of *p*-Tosylhydrazones

RONALD A. HENRY AND DONALD W. MOORE

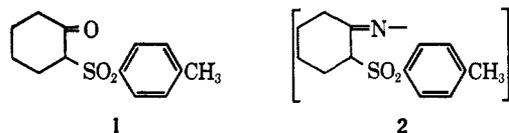
Chemistry Division, Research Department, Code 505,  
Naval Weapons Center, China Lake, California 93555

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Since Bamford and Stevens<sup>1</sup> first described the thermal decomposition of the anions of tosylhydrazones, there has been a widespread interest in this reaction. However, pyrolysis of the parent tosylhydrazones has been considered in only one Note during this period. Lin and Just<sup>2</sup> reported that acetone *p*-tosylhydrazone decomposed rapidly when heated to 160° and furnished a low yield of 1-*p*-tosyl-3,5,5-trimethyl-2-pyrazoline. These investigators also examined several other tosylhydrazones, but the pyrolysis products were not characterized.

Some additional examples of the thermal decomposition of tosylhydrazones have now been noted. The results (Table I and following discussion) suggest at least three types of reaction: tosyl ketone formation; aldol condensation and/or pyrazoline formation, and sulfone formation.

**Tosyl Ketone Formation.**—Cyclohexanone *p*-tosylhydrazone decomposed vigorously and exothermically when heated to 145–150°; even after 12 days at 80° the crystalline hydrazone was completely converted to a dark, resinous mass. The reaction could also be effected by refluxing cyclohexanone and *p*-toluenesulfonylhydrazine in glacial acetic acid. Work-up of these reaction mixtures revealed essentially the same products, which included ammonium *p*-toluenesulfonate, *p*-toluenesulfonamide, di-*p*-tolyl disulfide, *p*-tolyl-*p*-toluenethio-sulfonate, *p*-toluenesulfonylhydrazinium *p*-toluenesulfonate, together with small amounts of two compounds which still contained the cyclohexyl moiety. From the nmr and infrared spectra and the elemental analyses it was deduced that one of these compounds was a *p*-tosylcyclohexanone. That it was the 2-*p*-tosyl isomer, **1**, was proved by comparison with an authentic



sample; 2,4-dinitrophenylhydrazones from both samples of tosylcyclohexanone were also identical. (The isomeric 3-*p*-tosylcyclohexanone which was also made for the purpose of comparison was different.) The other compound was the azine of the 2-*p*-tosylcyclohexanone, **2**.

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(15) B. F. Hallam and P. L. Pauson, *ibid.*, 3030 (1956).

(16) A. Berger, W. E. McEwen, and J. Kleinberg, *J. Am. Chem. Soc.*, **83**, 2274 (1961).

(1) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

(2) Y.-C. Lin and G. Just, *Can. J. Chem.*, **43**, 3116 (1965).

TABLE I  
 DECOMPOSITION OF TOSYLHYDRAZONES

Hydrazone of	Decomposition conditions	Products <sup>a</sup>	Yield, mole %	Product identified by
Cyclohexanone	Refluxing acetic acid, 2 hr, or 80°, 12 days	1	19	Infrared, synthesis
Propiophenone	140–150° (1 mm), 24 hr	2	12 <sup>b</sup>	Infrared, synthesis, nmr <sup>c</sup>
		3 <sup>d</sup>	1	Synthesis
		<i>n</i> -Propylbenzene <sup>e</sup>	2	Glpc, nmr, infrared
		<i>cis</i> - $\omega$ -Methylstyrene <sup>e</sup>	Trace	Glpc, nmr, infrared
		<i>trans</i> - $\omega$ -Methylstyrene <sup>e</sup>	7	Glpc, nmr, infrared
		Phenylmethylacetylene <sup>e</sup>	3	Glpc, nmr, infrared
Benzalacetophenone <sup>f</sup>	Acetic acid, 90°, 2 hr, plus 8 days, 25°	Acetophenone <sup>e</sup>	Trace	Glpc, nmr, infrared
		Benzaldehyde <sup>e</sup>	Trace	Glpc, nmr, infrared
Dibenzalacetone <sup>f</sup>	Acetic acid, 11 days, 25°	5	29	Synthesis, infrared, nmr <sup>c</sup>
<i>n</i> -Butyraldehyde	Refluxing ethanol	6	11	Nmr
2-Butanone	135–145° (1 mm), 3 hr	2-Ethylhexen-1-ol <sup>d</sup>		
		3,4-Dimethylhexanone-2 <sup>e</sup>	~1	Glpc, mass spectrum
Phenylacetaldehyde	Acetic acid, 90°, 10 min	Methylethylketazine <sup>e</sup>	2.6	Glpc, mass spectrum
		7	11	Nmr <sup>h</sup>
1-Phenyl-2-propanone	Acetic acid, 25°, 26 days	8 and 9		Nmr <sup>i</sup> (9, synthesis)
1-Phenyl-2-propanone	140–150° (1 mm), 6.5 hr	Phenylmethylacetylene <sup>e</sup>	18	Glpc, nmr, infrared
Benzaldehyde	170–200°, 15 min	10		Infrared
Benzophenone	180–185°, 30 min	11	33	Infrared, nmr <sup>j</sup>

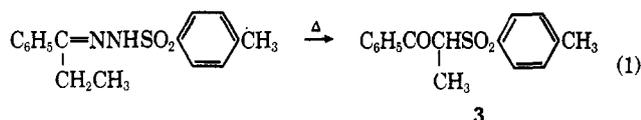
<sup>a</sup> Other than the hydrolysis products of the hydrazone or the usual thermal decomposition products of tosylhydrazine. In the experiments involving acetic acid, 1-acetyl-2-*p*-tosylhydrazine, mp 163–163.5°, was also generally formed. See Table II for names of numbered compounds. <sup>b</sup> The yield in the 80° experiment was only 1.7%. <sup>c</sup> In trifluoroacetic acid:  $\tau$  2.39 (quartet, 4 protons), 5.6 (broad, 1 proton), 6.6–8.6 (multiplet, 8 protons), 7.50 (singlet, 3 protons). <sup>d</sup> Isolated as its 2,4-dinitrophenylhydrazone. <sup>e</sup> In distillate collected in Dry Ice-acetone cooled trap. <sup>f</sup> Tosylhydrazone prepared and decomposed *in situ*. <sup>g</sup> In CDCl<sub>3</sub>:  $\tau$  2.25 (quartet, 4 protons), 2.54 (multiplet, 5 protons), 2.76 (singlet, 5 protons), 5.07 (quartet, 1 proton), 5.94 multiplet, 2 protons), 7.10 (singlet, 3 protons). <sup>h</sup> In DMSO-*d*<sub>6</sub>:  $\tau$  2.07 (quartet, 4 protons), 2.41 (singlet, 5 protons), 2.71 (multiplet, 3 aromatic protons and one pyrazoline ring CH), 3.85 (quartet, aromatic protons), 5.6 (multiplet, 2 protons), 6.50 (multiplet, 2 pyrazoline ring CH's), 7.24 (singlet, 3 protons). <sup>i</sup> For 8 in CDCl<sub>3</sub>:  $\tau$  1.9–3.2 (multiplet, 14 protons), 6.49 (singlet, 2 protons in benzyl methylene at C-2), 6.88 (singlet, 2 protons in benzyl methylene at C-5), 7.58 (singlet, 3 protons), 8.63 (singlet, 3 protons in methyl at C-5), 7.57,  $J_{ab}$  = 17 cps (quartet, 2 ring protons at C-3). <sup>j</sup> In CDCl<sub>3</sub>:  $\tau$  2.65 (multiplet, 14 protons); 4.7 (singlet, 1 proton); 7.65 (singlet, 3 protons).

 TABLE II  
 ANALYSES AND PHYSICAL PROPERTIES

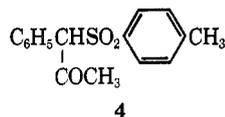
No.	Compound	Formula	Crystn solvent	Mp, °C	Calcd, %				Found, %			
					C	H	N	S	C	H	N	S
1	2- <i>p</i> -Tosylcyclohexanone <sup>a</sup>	C <sub>15</sub> H <sub>18</sub> O <sub>2</sub> S	Cyclohexane	81–82	61.88	6.39		12.71	62.13	6.34		12.66
	1-Phenyl-1-( <i>p</i> -tosyl)-2-propanone DNP	C <sub>22</sub> H <sub>26</sub> N <sub>4</sub> O <sub>6</sub> S	Ethanol	197–198			11.96	6.84			11.56	6.80
2	2- <i>p</i> -Tosylcyclohexanoneazine	C <sub>28</sub> H <sub>32</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	Acetonitrile	224.5–225.5	62.38	6.44	5.60	12.79	62.39	6.80	5.54	12.83
	2- <i>p</i> -Tosylcyclohexanone DNP <sup>b</sup>	C <sub>19</sub> H <sub>26</sub> N <sub>4</sub> O <sub>6</sub> S	Ethanol	204–205	52.77	4.66	12.96	7.41	52.74	4.73	13.07	7.17
	2- <i>p</i> -Tosylcyclohexanone TH <sup>c</sup>	C <sub>28</sub> H <sub>34</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	Ethanol	167–168	57.12	5.75	6.66	15.25	57.03	5.52	6.79	15.01
	3- <i>p</i> -Tosylcyclohexanone <sup>d</sup>	C <sub>15</sub> H <sub>18</sub> O <sub>2</sub> S	Cyclohexane-benzene (3:2)	26–27 <sup>e</sup>	61.88	6.39		12.71	62.05	6.59		12.67
	3- <i>p</i> -Tosylcyclohexanone DNP	C <sub>19</sub> H <sub>26</sub> N <sub>4</sub> O <sub>6</sub> S	Ethanol	171–172			12.96	7.41			13.02	7.38
	3- <i>p</i> -Tosylcyclohexanone TH	C <sub>28</sub> H <sub>34</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	Ethanol	166.5–167.5 <sup>f</sup>	57.12	5.75	6.66	15.25	57.18	6.14	6.62	14.55
3	$\alpha$ -( <i>p</i> -Tosyl)propiophenone <sup>g</sup>	C <sub>16</sub> H <sub>18</sub> O <sub>2</sub> S	Cyclohexane	99–100	66.64	5.59		11.12	66.17	5.39		11.22
	$\alpha$ -( <i>p</i> -Tosyl)propiophenone DNP	C <sub>22</sub> H <sub>26</sub> N <sub>4</sub> O <sub>6</sub> S	Ethanol	243–244 <sup>h</sup>	56.40	4.30		6.84	56.11	4.34		6.67
	$\alpha$ -( <i>p</i> -Tosyl)propiophenone DNP	C <sub>22</sub> H <sub>26</sub> N <sub>4</sub> O <sub>6</sub> S	Ethanol	211–212 <sup>i</sup>	56.40	4.30	11.96	6.84	56.41	4.36	11.97	6.82
4	1-Phenyl-1-( <i>p</i> -tosyl)-2-propanone <sup>j</sup>	C <sub>16</sub> H <sub>18</sub> O <sub>2</sub> S	Methanol	161–162	66.64	5.59		11.12	66.39	5.60		11.22
5	1,3-Diphenyl-3- <i>p</i> -tosyl-1-propanone	C <sub>27</sub> H <sub>30</sub> O <sub>2</sub> S	Ethanol-benzene (3:5)	170–171	72.50	5.53		8.80	72.37	5.50		8.73
6	1,5-Diphenyl-5- <i>p</i> -tosyl-1-penten-3-one	C <sub>24</sub> H <sub>28</sub> O <sub>2</sub> S	Ethanol-benzene (4:1)	177–178	73.18	5.61		8.49	73.47	5.62		8.39
7	1-( <i>p</i> -Tosyl)-4-phenyl-5-benzyl-2-pyrazoline	C <sub>28</sub> H <sub>32</sub> N <sub>2</sub> O <sub>2</sub> S	Benzene	182–184	70.74	5.68	7.18	8.21	70.88	5.68	7.17	8.18
	4-Phenyl-5-benzylpyrazole <sup>k</sup>	C <sub>16</sub> H <sub>14</sub> N <sub>2</sub>	Cyclohexane	125–126	82.02	6.02	11.96		82.15	6.18	11.59	
8	1-( <i>p</i> -Tosyl)-3,5-dibenzyl-5-methyl-2-pyrazoline	C <sub>28</sub> H <sub>32</sub> N <sub>2</sub> O <sub>2</sub> S	<i>n</i> -Hexane-benzene (2:1)	123.5–124.5	71.74	6.26	6.69	7.66	72.47	6.47	6.76	7.80
9	1-Phenyl-1,2-propanedione bis-TH	C <sub>21</sub> H <sub>24</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub> <sup>l</sup>	Ethanol or benzene	162–163			11.56	13.23			11.63	13.28
	1-Phenyl-1,2-propanedione bis-DNP	C <sub>21</sub> H <sub>18</sub> N <sub>6</sub> O <sub>6</sub>	Ethanol	256–259	49.84	3.53	21.77		49.61	3.17	22.04	
	1-Phenyl-2-propanone TH	C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> S	Benzene	133–134	63.55	6.00	9.27		63.97	6.11	9.26	
10	Benzyl <i>p</i> -tolyl sulfone	C <sub>14</sub> H <sub>14</sub> O <sub>2</sub> S	Ethanol	144.5–145.5 <sup>m</sup>	68.26	5.73		13.01	68.48	5.48		13.24
11	Diphenylmethyl <i>p</i> -tolyl sulfone	C <sub>20</sub> H <sub>18</sub> O <sub>2</sub> S	Ethanol	192–193	74.50	5.63		9.94	74.34	5.64		9.89

<sup>a</sup> Also prepared in 94% yield by refluxing equimolar amounts of 2-chlorocyclohexanone and sodium *p*-toluenesulfonate dihydrate in acetonitrile for 7 days. <sup>b</sup> DNP = 2,4-dinitrophenylhydrazone. <sup>c</sup> TH = *p*-tosylhydrazone. <sup>d</sup> A quantitative yield was obtained by mixing equivalent amounts of 2-cyclohexanone and *p*-toluenesulfonic acid in acetonitrile. <sup>e</sup> After several weeks converted to a form melting at 69–70.5°; admixture with the 2 isomer lowered the melting point to 55–58°. <sup>f</sup> Admixed with the corresponding 2 isomer, mp 145–150°. <sup>g</sup> Prepared from  $\alpha$ -bromopropiophenone and sodium *p*-toluenesulfonate dihydrate in acetonitrile. <sup>h</sup> Felted yellow needles. <sup>i</sup> Orange plates. <sup>j</sup> Prepared from 1-bromo-1-phenyl-2-propanone and sodium *p*-toluenesulfonate in refluxing acetonitrile. <sup>k</sup> From the hydrolysis of 7 in ethanolic potassium hydroxide. In CDCl<sub>3</sub> (TMS reference):  $\tau$  2.5 (singlet, proton at C-3), 2.68 (singlet, 5 protons), 2.79 (singlet, 5 protons), 5.85 (singlet, 2 protons), –1.75 (broad, 1 proton). <sup>l</sup> Recrystallization from ethanol gave a product which contained one molecule of the solvent (Calcd: 8.68. Found: 8.80), easily removed by drying at 75–80° (25 mm). With benzene, a hemisolvate was formed. <sup>m</sup> R. Otto [*Ber.*, 13, 1272 (1880)] reported 144–145°.

The pyrolysis of propiophenone *p*-tosylhydrazone gave  $\alpha$ -tosylpropiophenone (3) (eq 1), isolated in low



yield as its 2,4-dinitrophenylhydrazone, rather than the isomeric 1-phenyl-1-*p*-tosyl-2-propanone (4). This re-

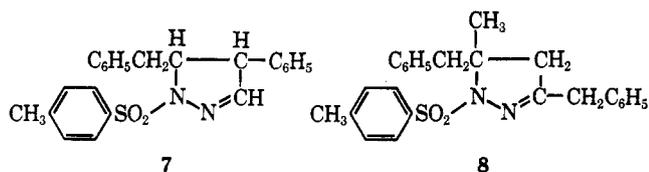


sult suggests that with some ketones which contain an  $\alpha$ -methylene group, the decomposition involves ultimately a migration of the tosyl moiety. This fact is not evident from the experiments with cyclohexanone *p*-tosylhydrazone. Whether these  $\alpha$ -tosyl ketones result from an intramolecular rearrangement involving a five-membered transition state or from a secondary reaction involving primary decomposition products was not ascertained.

A possibly related mode of decomposition was observed during attempts to prepare 1-tosylpyrazolines from benzalacetophenone and dibenzalacetone in acetic acid. In both cases the products (5 and 6 in Table II) were found to be  $\beta$ -tosyl ketones, identical with those obtained through the 1,4 addition of *p*-toluenesulfonic acid to the  $\alpha,\beta$ -unsaturated ketone. Since *p*-toluenesulfonic acid is a product in the thermal decomposition of tosylhydrazine,<sup>3</sup> this addition reaction might well be the route by which these products are formed rather than through a tosylhydrazone intermediate.

Although acetophenone *p*-tosylhydrazone readily pyrolyzed at 145–150°, no tosyl ketone was found. However, there was isolated a small quantity of a solid, whose partial characterization suggested that it was an addition product of *p*-toluenethiol to either  $\alpha$ - or  $\omega$ -(*p*-tosyl)styrene. In contrast to the behavior of cyclohexanone *p*-tosylhydrazone, the camphor derivative was fairly resistant to decomposition; even after 9 hr at 180–185° 70% of the starting hydrazone was recovered.

**Aldol Condensation and/or Pyrazoline Formation.**—Tosyl ketones were not detected in the residues left from the decomposition of the tosylhydrazones of *n*-butyraldehyde, 2-butanone, phenylacetaldehyde, or 1-phenyl-2-propanone. However, products which indicated self-condensation of the carbonyl compound were recovered in low yields. With the last two hydrazones, the results were analogous to that reported by Lin and Just<sup>2</sup> in that the condensation products were converted to and isolated as the substituted 1-(*p*-tosyl)pyrazolines, 7 and 8. Oxidation of the benzyl methy-

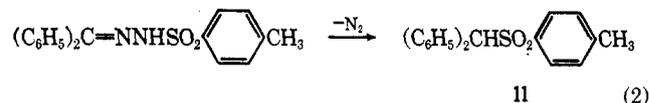


lene group during the decomposition of 1-phenyl-2-propanone *p*-tosylhydrazone in acetic acid at room

(3) R. S. Dewey and E. E. van Tamelen, *J. Am. Chem. Soc.*, **83**, 3729 (1961).

temperature also occurred since 1-phenyl-1,2-propanedione bis-*p*-tosylhydrazone, 9, was isolated.

**Sulfone Formation.**—The pyrolysis of benzaldehyde or benzophenone tosylhydrazones which possess no  $\alpha$ -methylene group furnished the sulfones 10 and 11, which result from the loss of nitrogen (eq 2). Sulfones



have been previously reported as by-products in the thermal decomposition of the anions of tosylhydrazones under both protic and aprotic conditions.<sup>4</sup>

### Experimental Section

The following examples are representative of the procedures used for decomposing the hydrazones and recovering the products. Analytical data for many of the compounds prepared are summarized in Table II.

**Thermolysis of Acetophenone *p*-Tosylhydrazone.**—The hydrazone (8.8 g) was heated for 4 hr at 155–160°. Much gassing occurred, water was evolved, and a strong odor of acetophenone developed. The dark brown, liquid product was cooled to ambient temperature, diluted with 15 ml of absolute ethanol, and chilled at 5° for several days. The solid was removed by filtration and washed twice with small volumes of cold ethanol. Water extraction of the solid left 0.25 g of insoluble material which melted at 183–185° after two recrystallizations from ethanol. The elemental analyses, the infrared spectrum ( $-\text{SO}_2-$  at 7.7 and 8.8  $\mu$ ), and the nmr spectrum in  $\text{CDCl}_3$  (multiplet at  $\tau$  2.33–3.11, 13 aromatic protons; multiplet at 5.35–5.57, 1 methine proton; multiplet at 6.16–6.40, 2 methylene protons; and a doublet at 7.64 and 7.69, 6 methyl protons) are consistent with either of the isomeric compounds 1- or 2-phenyl-2-(*p*-tosyl)ethyl *p*-tolyl sulfide.

*Anal.* Calcd for  $\text{C}_{22}\text{H}_{22}\text{S}_2\text{O}_2$ : C, 69.08; H, 5.79; S, 16.76; mol wt, 382.5. Found: C, 68.48, 68.33; H, 5.60, 5.76; S, 16.98; mol wt, 379.

**Decomposition of Phenylacetaldehyde *p*-Tosylhydrazone in Acetic Acid.**—Phenylacetaldehyde (12.0 g, 0.1 mole) and 18.6 g (0.1 mole) of *p*-toluenesulfonylhydrazine were dissolved in 25 ml of glacial acetic acid; gas evolution began immediately and the rate increased markedly when the temperature was raised to about 90°. Although the solution was promptly cooled to 5°, no hydrazone separated. Addition of 25 ml of benzene and further cooling gave some crystalline material which was filtered and washed twice (25-ml portions) with benzene-pentane (1:1) and once with pentane to yield 2.0 g (11%), mp 181–182°. After one recrystallization from benzene, the melting point was 182–184°. The infrared spectrum showed no NH stretch. The analyses and nmr agreed with those required for 1-(*p*-tosyl)-4-phenyl-5-benzyl-2-pyrazoline, 7.

**Diphenylmethyl *p*-Tolyl Sulfone (11).**—Benzophenone *p*-tosylhydrazone (0.5 g) was heated at 180–185° for 30 min; the melt became very dark. The product was dissolved in 20 ml of hot 95% ethanol and the solution was cooled to room temperature. The title compound (0.15 g, 33%) separated as flat, white needles. Recrystallization did not change the melting point.

**Registry No.**—1, 14195-09-6; 1 DNP, 14195-10-9; 1 TH, 14195-11-0; 2, 14195-12-1; 3-*p*-tosylcyclohexanone, 14444-30-5; 3-*p*-tosylcyclohexanone DNP, 14195-13-2; 3-*p*-tosylcyclohexanone TH, 14195-14-3; 3, 14195-15-4; 3 DNP, 14195-16-5; 4, 14195-17-6; 4 DNP, 14195-18-7; 5, 7477-61-4; 6, 14195-20-1; 7, 14195-21-2; 4-phenyl-5-benzylpyrazole, 14195-22-3; 8, 14362-61-9; 9, 14444-31-6; 1-phenyl-1,2-propanedione bis-DNP, 14195-23-4; 1-phenyl-2-propanone TH, 14195-24-5; 10, 5395-20-0; 11, 5433-78-3.

(4) (a) See J. W. Wilt, C. A. Schneider, H. F. Dabek, Jr., J. F. Kraemer, and W. J. Wagner, *J. Org. Chem.*, **31**, 1543 (1966), for a summary of sulfone formation in the Bamford-Stevens reaction and a discussion of the possible mechanisms by which they might arise. (b) Also see J. J. Looker, *J. Org. Chem.*, **32**, 472 (1967), for discussion of another reasonable mechanism.