

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 ethanol⁸ or lithium aluminum hydride-aluminum chloride.¹³ 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.⁹ 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° (N₂). Recrystallization of this solid from xylene-heptane produced a product of mp 277–278° (lit.¹⁴ mp 278–280°); a mixture melting point determination with an authentic sample¹⁴ 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.¹⁴

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.¹⁵ 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.^{4,11}

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.¹⁶ 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⁻¹ (ferrocenyl group), 2897 cm⁻¹ (aliphatic C-H), and other principal peaks at 3020, 1598, 1485, 1450, 926, 775 and 705 cm⁻¹ which may be assignable to the phenyl groups. The nmr spectrum of **6** indicated a multiplet centered at τ 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.¹¹

Thermal Decomposition of *p*-Tosylhydrazones

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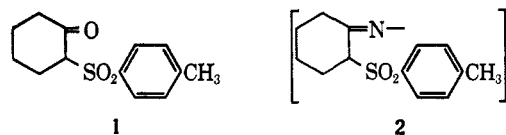
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Received May 16, 1967

Since Bamford and Stevens¹ 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 Just² 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*-toluenethiosulfonate, *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**.

(13) K. Schlögl, A. Mohar, and M. Peterlik, *Monatsh.*, **92**, 921 (1961).

(14) P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 3880 (1962).

(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 ^a	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 ^b	Infrared, synthesis, nmr ^c
		3 ^d	1	Synthesis
		<i>n</i> -Propylbenzene ^e	2	Glpc, nmr, infrared
		<i>cis</i> - ω -Methylstyrene ^e	Trace	Glpc, nmr, infrared
		<i>trans</i> - ω -Methylstyrene ^e	7	Glpc, nmr, infrared
		Phenylmethylacetylene ^e	3	Glpc, nmr, infrared
Benzalacetophenone ^f	Acetic acid, 90°, 2 hr, plus 8 days, 25°	Acetophenone ^e	Trace	Glpc, nmr, infrared
		Benzaldehyde ^e	Trace	Glpc, nmr, infrared
Dibenzalacetone ^f	Acetic acid, 11 days, 25°	5	29	Synthesis, infrared, nmr ^c
<i>n</i> -Butyraldehyde	Refluxing ethanol	6	11	Nmr
2-Butanone	135–145° (1 mm), 3 hr	2-Ethylhexen-1-ol ^d		
		3,4-Dimethylhexanone-2 ^e	~1	Glpc, mass spectrum
Phenylacetaldehyde	Acetic acid, 90°, 10 min	Methylethylketazine ^e	2.6	Glpc, mass spectrum
		7	11	Nmr ^h
1-Phenyl-2-propanone	Acetic acid, 25°, 26 days	8 and 9		Nmr ⁱ (9, synthesis)
1-Phenyl-2-propanone	140–150° (1 mm), 6.5 hr	Phenylmethylacetylene ^e	18	Glpc, nmr, infrared
Benzaldehyde	170–200°, 15 min	10		Infrared
Benzophenone	180–185°, 30 min	11	33	Infrared, nmr ^j

^a 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. ^b The yield in the 80° experiment was only 1.7%. ^c In trifluoroacetic acid: τ 2.39 (quartet, 4 protons), 5.6 (broad, 1 proton), 6.6–8.6 (multiplet, 8 protons), 7.50 (singlet, 3 protons). ^d Isolated as its 2,4-dinitrophenylhydrazone. ^e In distillate collected in Dry Ice-acetone cooled trap. ^f Tosylhydrazone prepared and decomposed *in situ*. ^g In CDCl₃: τ 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). ^h In DMSO-*d*₆: τ 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). ⁱ For 8 in CDCl₃: τ 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). ^j In CDCl₃: τ 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 ^a	C ₁₅ H ₁₈ O ₂ 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 ₂₂ H ₂₆ N ₄ O ₆ S	Ethanol	197–198			11.96	6.84			11.56	6.80
2	2- <i>p</i> -Tosylcyclohexanoneazine	C ₂₈ H ₃₂ N ₂ O ₄ S ₂	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 ^b	C ₁₉ H ₂₆ N ₄ O ₆ 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 ^c	C ₂₈ H ₃₄ N ₂ O ₄ S ₂	Ethanol	167–168	57.12	5.75	6.66	15.25	57.03	5.52	6.79	15.01
	3- <i>p</i> -Tosylcyclohexanone ^d	C ₁₅ H ₁₈ O ₂ S	Cyclohexane-benzene (3:2)	26–27 ^e	61.88	6.39		12.71	62.05	6.59		12.67
	3- <i>p</i> -Tosylcyclohexanone DNP	C ₁₉ H ₂₆ N ₄ O ₆ S	Ethanol	171–172			12.96	7.41			13.02	7.38
	3- <i>p</i> -Tosylcyclohexanone TH	C ₂₈ H ₃₄ N ₂ O ₄ S ₂	Ethanol	166.5–167.5 ^f	57.12	5.75	6.66	15.25	57.18	6.14	6.62	14.55
3	α -(<i>p</i> -Tosyl)propiophenone ^g	C ₁₆ H ₁₈ O ₂ S	Cyclohexane	99–100	66.64	5.59		11.12	66.17	5.39		11.22
	α -(<i>p</i> -Tosyl)propiophenone DNP	C ₂₂ H ₂₆ N ₄ O ₆ S	Ethanol	243–244 ^h	56.40	4.30		6.84	56.11	4.34		6.67
	α -(<i>p</i> -Tosyl)propiophenone DNP	C ₂₂ H ₂₆ N ₄ O ₆ S	Ethanol	211–212 ⁱ	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 ^j	C ₁₆ H ₁₈ O ₂ 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 ₂₇ H ₃₀ O ₂ 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 ₂₄ H ₂₈ O ₂ 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 ₂₈ H ₃₂ N ₂ O ₂ S	Benzene	182–184	70.74	5.68	7.18	8.21	70.88	5.68	7.17	8.18
	4-Phenyl-5-benzylpyrazole ^k	C ₁₆ H ₁₄ N ₂	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 ₂₈ H ₃₂ N ₂ O ₂ 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 ₂₁ H ₂₄ N ₄ O ₄ S ₂ ^l	Ethanol or benzene	162–163			11.56	13.23			11.63	13.28
	1-Phenyl-1,2-propanedione bis-DNP	C ₂₁ H ₁₈ N ₆ O ₆	Ethanol	256–259	49.84	3.53	21.77		49.61	3.17	22.04	
	1-Phenyl-2-propanone TH	C ₁₈ H ₁₈ N ₂ O ₂ S	Benzene	133–134	63.55	6.00	9.27		63.97	6.11	9.26	
10	Benzyl <i>p</i> -tolyl sulfone	C ₁₄ H ₁₄ O ₂ S	Ethanol	144.5–145.5 ^m	68.26	5.73		13.01	68.48	5.48		13.24
11	Diphenylmethyl <i>p</i> -tolyl sulfone	C ₂₀ H ₁₈ O ₂ S	Ethanol	192–193	74.50	5.63		9.94	74.34	5.64		9.89

^a Also prepared in 94% yield by refluxing equimolar amounts of 2-chlorocyclohexanone and sodium *p*-toluenesulfonate dihydrate in acetonitrile for 7 days. ^b DNP = 2,4-dinitrophenylhydrazone. ^c TH = *p*-tosylhydrazone. ^d A quantitative yield was obtained by mixing equivalent amounts of 2-cyclohexenone and *p*-toluenesulfonic acid in acetonitrile. ^e After several weeks converted to a form melting at 69–70.5°; admixture with the 2 isomer lowered the melting point to 55–58°. ^f Admixed with the corresponding 2 isomer, mp 145–150°. ^g Prepared from α -bromopropiophenone and sodium *p*-toluenesulfonate dihydrate in acetonitrile. ^h Felted yellow needles. ⁱ Orange plates. ^j Prepared from 1-bromo-1-phenyl-2-propanone and sodium *p*-toluenesulfonate in refluxing acetonitrile. ^k From the hydrolysis of 7 in ethanolic potassium hydroxide. In CDCl₃ (TMS reference): τ 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). ^l 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. ^m R. Otto [*Ber.*, 13, 1272 (1880)] reported 144–145°.

