The Decomposition of 4,6-Dimethylbenzocyclobutenone *p*-Toluenesulfonylhydrazone

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Pyrolysis of 4,6-dimethylbenzocyclobutenone *p*-toluenesulfonylhydrazone sodium salt (**1b**) in acetamide gave 4,6-dimethylbenzocyclobutenyl *p*-tolyl sulfone (**2**) and 4,6-dimethylbenzocyclobutenylacetamide (**3**). Photolysis of this salt yielded sulfone **2** as well as a hydrocarbon, $C_{20}H_{20}$, tentatively identified as 1,1′-bi(4,6-dimethylbenzocyclobutylidene) (**6**). All of these products could arise through the intermediate formation of the benzocyclobutenyl carbene **5**.

As part of a study of the benzocyclobutene ring system,[2] it was felt that the benzocyclobutenyl carbene would be an interesting species to prepare. Ring contraction analogous to that observed for cyclobutylcarbenes[3,4] would yield methylenebenzocyclopropene, while hydrogen migration would lead to a benzocyclobutadiene structure.

The decomposition of *p*-toluenesulfonyl- (*p*-tosyl-) hydrazone salts was the method chosen to produce the desired carbene. The procedure is straightforward and has been used successfully by many experimenters;[3-7] moreover, carbenes can be generated by either a thermal[6] or a photolytic[7] process.

4,6-Dimethylbenzocyclobutenone *p*-tosylhydrazone (**1a**) was chosen as the starting material. 4,6-Dimethylbenzocyclobutenone[8] was readily prepared from mesitylene by the method of Hart and Fish[9b] and converted into **1a** with *p*-tosylhydrazine.

The thermal decomposition of this tosylhydrazone was carried out using the method of Powell and Whiting.[6] Sodium was dissolved in freshly distilled acetamide to give the sodium salt upon warming to 100°. Powdered 4,6-dimethylbenzocyclobutenone *p*-tosylhydrazone was then added. Heating the mixture at 155° for 5 min resulted in complete decomposition of the tosylhydrazone as measured by nitrogen evolution. Two major products, neither of them hydrocarbons, were isolated from the reaction mixture.

The first, a white, crystalline solid, mp 104–105° was obtained from a pentane extract of the reaction mixture. This compound was identified as 4,6-dimethylbenzocyclobutenyl *p*-tolyl sulfone (**2**). The formation of sulfones by decomposition of tosylhydrazones has been reported by Lemal and Fry, who obtained yields as high as 50% 3-nortricyclyl *p*-tolyl sulfone by photolysis of the corresponding sodium tosylhydrazone derivative.[10]

The second compound, isolated in 38% yield, was assigned the structure of 4′,6′-dimethylbenzocyclobutenylacetamide (**3**) on the basis of its elemental and spectral analyses and degradation products. Hydrolysis of **3** in 15% potassium hydroxide followed by acidification yielded a carboxylic acid, 4′,6′-dimethylbenzocyclobutenylacetic acid (**4**) (Scheme I). The structural assignment was based on elemental analysis and molecular weight.

One way to account for both of these products would be through the intermediate formation of carbene **5**. This species could react with the tolylsulfinate anion formed by initial heterolysis in a manner analogous to that suggested by Lemal and Fry[10] to give a relatively stable sulfone anion which, during work-up, would be protonated to sulfone **2**. Amide **3** could arise by carbene insertion into the solvent, acetamide.[11] Both **2** and **3** could have arisen without the intermediate formation of carbene **5**, although such reactions are more difficult to rationalize considering the conditions that were employed.

A portion of the pentane extract of the reaction mixture was analyzed by means of a gas chromatographic unit connected to a mass spectrometer. None of the products isolated and identified by this procedure proved to be hydrocarbons derived from the 4,6-dimethylbenzocyclobutenyl carbene.

Photolysis gave somewhat different results. The tosylhydrazone salt, formed with sodium hydride, was suspended in purified dioxane and irradiated for 30 min using a 550-W Hanovia mercury vapor insertion lamp. The reaction mixture was poured into water and extracted with pentane and benzene. Chromatography of the carefully washed organic extracts afforded three products. One, obtained in 14% yield, was identified as sulfone **2** on the basis of its melting point and infrared spectrum. The second was a hydrocarbon, mp 188–189°, obtained in 8.3% yield. The material gave a correct analysis for the structure $C_{10}H_{10}$, the empirical formula of carbene **5**. Mass spectral analysis showed it to be a dimer, $C_{20}H_{20}$ (mol wt 260). The infrared spectrum exhibited a weak peak at 1705, medium peaks at 1600, 1470, 1320, 1265, and 1040, and two strong peaks at 850 (very strong) and 725 cm^{-1}. The nuclear magnetic resonance spectrum showed three singlets at τ 3.23, 6.27, and 7.68, with a ratio of 0.98:

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[2] (a) A. T. Blomquist and C. G. Bottomley, *N. Y. Acad. Sci. Trans.*, **24**, 823 (1962); (b) A. T. Blomquist and V. J. Hruby, *J. Amer. Chem. Soc.*, **86**, 5041 (1964).

[3] L. Friedman and H. Schechter, *ibid.*, **82**, 1002 (1960).

[4] G. Maier and M. Strasser, *Tetrahedron Lett.*, 6453 (1966).

[5] E. Chinoporos, *Chem. Rev.*, **63**, 235 (1963).

[6] J. W. Powell and M. C. Whiting, *Tetrahedron*, **12**, 168 (1961).

[7] W. G. Dauben and F. G. Willey, *J. Amer. Chem. Soc.*, **84**, 1497 (1962).

[8] As was pointed out in a previous paper,[9a] this nomenclature is more convenient and easier to visualize than the more systematic name (3,5-dimethylbicyclo[4.2.0]octa-1,3,5-trien-7-one) and will be used throughout.

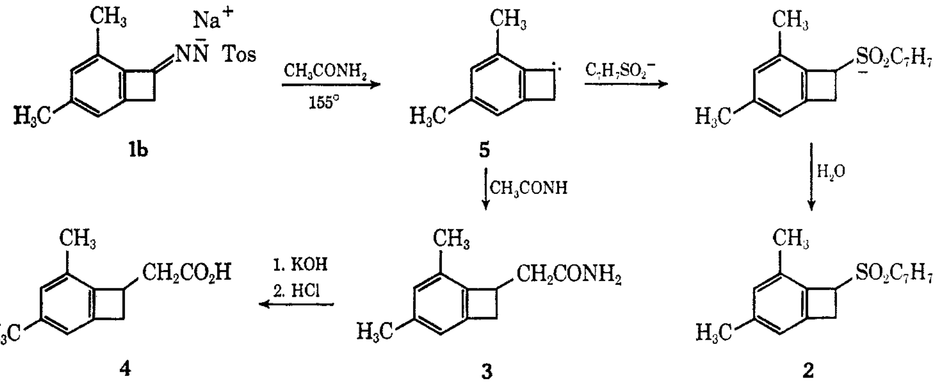
[9] (a) H. Hart, J. A. Hartlage, R. W. Fish, and R. R. Rafos, *J. Org. Chem.*, **31**, 2244 (1966); (b) H. Hart and R. W. Fish, *J. Amer. Chem. Soc.*, **82**, 749 (1960).

[10] D. M. Lemal and A. J. Fry, *J. Org. Chem.*, **29**, 1673 (1964).

[11] Although only one amide was recovered from the reaction mixture, it is possible that the N-substituted isomer was formed and not isolated. There is no clear precedent for either insertion reaction, since little has been reported on reactions of carbenes with amides.[12]

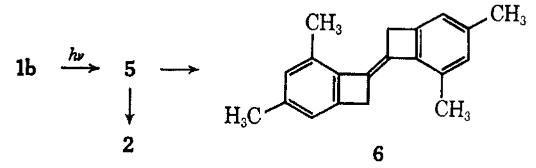
[12] J. Maas, G. B. R. DeGaaff, and H. J. Denttertog, *Rec. Trav. Chim.*, **74**, 175 (1955).

SCHEME I



1.00:3.09, respectively. A tentative structure for this hydrocarbon consistent with the spectral evidence is 1,1′-bi(4,6-dimethylbenzocyclobutylidene) (6) (see Scheme II). It could be formed by dimerization of carbene **5** or by reaction of the carbene with the tosylhydrazone salt **1b** or the corresponding diazo compound.

SCHEME II



Besides these two products, a yellow oil was obtained which could not be induced to crystallize.

Infrared analysis indicated the presence of both aromatic and ether groups, suggesting that carbene **5** may have reacted with the ether solvent.[13]

Experimental Section[14]

Preparation of 4,6-Dimethylbenzocyclobutenone.—The procedure was that of Hart and Fish.[9] Trichloromethylmesitylene (53 g, 74.4% yield) was prepared from 36 g (0.03 mol) of mesitylene, 80 g (0.6 mol) of anhydrous aluminum chloride, and 200 ml of carbon tetrachloride. When heated at 170° for 15 hr under a slow stream of nitrogen, trichloromethylmesitylene was converted almost quantitatively into 1,1-dichloro-4,6-dimethylbenzocyclobutene, mp 54–56° (reported mp 55–57°).[9] Hydrolysis was effected by refluxing an aqueous acetone solution (60%) of the *gem*-dichloride for 12 hr. Distillation through an 8-in. Vigreux column gave 26.1 g of 4,6-dimethylbenzocyclobutenone, bp 65° (0.45 mm), yield 79.5%, based on trichloromethylmesitylene. The ketone exhibits a split carbonyl absorption at 1750 and 1780 cm^{-1} and readily forms an azine derivative, mp 177–178°, with hydrazine hydrate.

Anal. (of azine). Calcd for $C_{20}H_{20}N_2$: C, 83.29; H, 6.99. Found: C, 83.01; H, 7.14.

Preparation of 4,6-Dimethylbenzocyclobutenone *p*-Tosylhydrazine.—A solution of 8.0 g (0.055 mol) of 4,6-dimethylbenzocyclobutenone and 10.2 g (0.055 mol) of *p*-tosylhydrazine in 50 ml of absolute ethanol containing 1 ml of acetic acid was heated under reflux for 5 min and stored overnight in the refrigerator. The white solid which precipitated was collected on a Büchner funnel and dried to yield 14.6 g (84.4%) of 4,6-dimethylbenzocyclobutenone *p*-tosylhydrazone, mp 166–167° dec. Two recrystallizations from ethanol gave an analytically pure sample, mp 169–170° dec.

Anal. Calcd for $C_{17}H_{18}SO_2N_2$: C, 64.95; H, 5.77; S, 10.18; N, 8.91. Found: C, 64.68; H, 5.83; S, 10.21; N, 9.09.

Pyrolysis of 4,6-Dimethylbenzocyclobutenone *p*-Tosylhydrazone Sodium Salt.—The procedure is patterned after that of Powell and Whiting.[6] Freshly cut pieces of sodium (0.69 g, 0.03 g-atom) were placed in a 100-ml flask containing 20 g of distilled acetamide. The flask was evacuated on an air pump and heated to 100°. The sodium rapidly reacted with the liquid acetamide, forming a pale yellow solution. The vacuum was broken and 3.14 g (0.01 mol) powdered 4,6-dimethylcyclobutenone *p*-tosylhydrazone was added. The reaction mixture was then heated in an oil bath maintained at 155°. Decomposition occurred rapidly at this temperature, and within 5 min nitrogen evolution had ceased. The mixture was poured into 300 ml of water and the aqueous solution was extracted with four 75-ml portions of pentane. The organic solution was washed with eight 75-ml portions of water and dried over sodium sulfate. Removal of solvent from the filtered solution left a tan oil which slowly solidified. Recrystallization from hexane–benzene gave 0.60 g of a white solid, mp 104–105°. Identification of the compound as 4,6-dimethylbenzocyclobutenyl *p*-tolyl sulfone (2) was made on the basis of its nmr spectrum. The aromatic protons of the tolyl group appear as a symmetrical quartet between τ 2.38 and 2.95, the benzocyclobutenyl aromatic protons as two singlets at 3.26 and 3.49, the butenyl proton next to the sulfone as a triplet centered at 5.37 (J = 5 cps), the other two butenyl protons as a doublet at 6.87 and 6.96 (J = 5 cps), and the nine methyl protons as three singlets at 7.64, 7.79, and 7.83.

Anal. Calcd for $C_{17}H_{18}SO_2$: C, 71.31; H, 6.34; S, 11.16; mol wt, 286. Found: C, 71.41; H, 6.38; S, 11.11; mol wt, 286 (mass spectroscopy).

A portion of the original pentane extract was analyzed on a gas chromatographic apparatus utilizing a 50 ft × 0.02 in. SCOT column (phenylmethylsilicone stationary phase) connected to a mass spectrometer by means of a Biemann molecular separator. Twelve components were separated and a mass spectrum of each was obtained. The following compounds were tentatively identified on the basis of their mass spectra: sulfone **2**, 4,6-dimethylbenzocyclobutenone, 4,6-dimethylbenzocyclobutenol, and 2,4-dimethylphenylacetic acid. The other materials were not identified other than establishing the fact that they were not hydrocarbons derived from the 2,4-dimethylbenzocyclobutenyl carbene (m/e 130 or a multiple thereof).

The tan precipitate which remained after pentane extraction was collected on a Bücher funnel, then recrystallized from ethanol–benzene to give 0.72 g of 4,6-dimethylbenzocyclobutenylacetamide, mp 193–194°.

Anal. Calcd for $C_{12}H_{15}NO$: C, 76.15; H, 7.99; N, 7.40; mol wt, 189. Found: C, 75.76; H, 8.14; N, 7.33; mol wt, 189 (mass spectroscopy).

A small portion of amide was hydrolyzed by heating it on a steam cone for 5 hr with a 15% solution of potassium hydroxide containing a small amount of ethanol. Acidification with 6 *N* hydrochloric acid formed a white solid. Recrystallization from 95% ethanol gave white needles of 4′,6′-dimethylbenzocyclobutenylacetic acid, mp 155–156°.

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[13] See, for example, W. R. Moore, H. R. Ward, and R. F. Merritt' *J. Amer. Chem. Soc.*, **83**, 2019 (1961).

[14] Melting points were determined on a Fisher-Johns melting point apparatus and are corrected. Infrared spectra were recorded on a Varian Infracord. Nmr spectra were measured at 60 Mcps on a Varian A-60 spectrometer. Mass spectra were determined using an AEI Model MS-12 mass spectrometer. Samples were introduced either by direct probe or by employing a Beckman GC-4 gas chromatograph coupled to the spectrometer *via* a Biemann molecular separator.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42; mol wt, 190. Found: C, 75.56; H, 7.49; mol wt, 190 (mass spectroscopy), 189 (titration).

Photolysis of 4,6-Dimethylbenzocyclobutenone *p*-Tosylhydrazone Sodium Salt.—The salt prepared from 3.14 g (0.01 mol) of 4,6-dimethylbenzocyclobutenone *p*-tosylhydrazone and 0.5 g (0.011 mol) of 54% sodium hydride dispersion in mineral oil was suspended in 250 ml of dry dioxane and irradiated for 30 min at 25° using a Hanovia 550-W mercury vapor insertion lamp. The reaction mixture was poured into 400 ml of water and extracted with three 75-ml portions of pentane and then three 75-ml portions of benzene. The combined organic extracts were dried over calcium chloride. Removal of solvent left 1.6 g of a brown gummy oil which was chromatographed on 80 g of acid-washed alumina. Elution with 8% ether–pentane gave a total of 108 mg of a white solid which melted at 188–189° after two recrystallizations from heptane. The infrared spectrum of this compound exhibited a weak peak at 1705, medium peaks at 1600, 1470, 1320, 1265, and 1040, and two strong peaks at 850 (very strong) and 725 cm^{-1}. The nmr spectrum showed three singlets at τ 3.23, 6.27, and 7.68, with a ratio of 0.98:1.00:3.09, respectively. Mass spectral analysis gave a molecular weight of 260. The material was assigned the structure of 1,1′-bi(4,6-dimethylbenzocyclobutylidene) on the basis of its elemental analysis and spectra.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74; mol wt, 260. Found: C, 91.96; H, 8.08; mol wt, 260 (mass spectroscopy).

Elution with 25% ether gave 0.2 g of a yellow oil which could not be induced to crystallize. The infrared spectrum showed peaks at 3020, 2900, 1610, 1500, 1130, and 890 cm^{-1}, indicating that both aromatic and ether groups were present. This material was not characterized further. With 50–75% ether, a total of 0.4 g (14%) of 4,6-dimethylbenzocyclobutenyl *p*-tolyl sulfone, mp 102–104°, was isolated. The infrared spectrum of this material was identical with that of the product obtained by pyrolysis; a mixture melting point of the two samples was not depressed.

Registry No.—4,6-Dimethylbenzocyclobutenone, 6670-28-6; 4,6-dimethylbenzocyclobutenone (azine derivative), 20643-22-5; **1a**, 20643-23-6; **2**, 20678-94-8; **3**, 20643-24-7; **4**, 20643-25-8; **6**, 20643-26-9.

The Sulfation of Hydroxamic Acids

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The reaction of hydroxamic acids with sulfur trioxide–tertiary amine complexes proceeds by O sulfation to give crystalline water-soluble *t*-ammonium N-acylhydroxylamine-O-sulfonates. The reaction of a solution of any of these salts with a base generates an isocyanate function *in situ*. If the base employed is a primary or secondary amine, urea derivatives are obtained in good yield. Carbamates are formed by the decomposition of the salts with phenoxide ion. Aliphatic isocyanates are prepared in good yield by treatment of the salts with tertiary amine in the presence of an inert solvent.

The Lossen rearrangement is a useful method for the preparation of organic isocyanates.[1] This conversion is accomplished by treating a hydroxamic acid with a dehydrating agent such as acetic anhydride, phosphorus pentoxide, or a carbodiimide,[2] forming an isocyanate. The reaction proceeds through an O-ester intermediate which is converted either thermally or by base treatment to an isocyanate and the acid corresponding to the O ester or its conjugate base. The ease of the rearrangement has been shown to be directly related to the acidity of the departing acid.[3]

The preparation of sulfate esters of hydroxamic acids has been examined. These products have been found to undergo a facile Lossen rearrangement to form isocyanates.

Discussion

Sulfation Reactions.—Treatment of benzohydroxamic acid with trimethylamine–sulfur trioxide gave a crystalline, water-soluble product in moderate yield.

$$C_6H_5CONHOH + R_3N{:}SO_3 \longrightarrow C_6H_5CONHOSO_3HNR_3$$

$$\text{I, } R_3 = (CH_3)_3$$

$$\text{II, } R_3 = C_5H_5$$

Elemental analysis and the nmr spectrum of this material indicated a 1:1 adduct. The latter in deuterium oxide contained a nine-proton singlet at 2.68 ppm $[DN(CH_3)_3{}^+]$ and a five-proton multiplet (C_6H_5) centered at 7.45 ppm. The infrared spectrum contained bands at 3225 cm^{-1} (NH), 1663 cm^{-1} (C=O), and 1200 and 1256 cm^{-1} (O=S=O).[4] Dissolution of the adduct in 5% ammonium hydroxide solution at room temperature gave an 82% yield of phenylurea, while treatment with hot 1.5 *N* potassium hydroxide solution gave a 68% yield of *sym*-diphenylurea. These data are consistent with the O-sulfation product (I).

A similar reaction was performed with the more reactive sulfating agent pyridine–sulfur trioxide.[5] The adduct (II) was obtained in 80% yield, employing conditions which were far milder than those required with the trimethylamine reagent. Owing to the high reactivity of this complex, further studies of the scope of the sulfation reaction were conducted with this material.

A number of other mono- and dihydroxamic acids have been treated with pyridine–sulfur trioxide to form the pyridinium N-acylhydroxylamine-O-sulfonates in yields of 70 to 89%. The data are summarized in Table I. With the exception of the stearic acid derivative, all of the salts are water soluble and quite stable in aqueous solution.[6] Another characteristic of these salts is the presence in their infrared spectra of two strong bands between 1200 and 1300 cm^{-1}. Generally, they occur at 1250 and 1300 ± 10 cm^{-1}. These are attributed to the symmetric and asymmetric stretching vibrations of the sulfonic acid function.[4]

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(1) R. G. Arnold, J. A. Nelson, and J. J. Verbane, *Chem. Rev.*, **57**, 47 (1957); H. L. Yale, *ibid.*, **33**, 209 (1943).

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(3) R. D. Bright and C. R. Hauser, *ibid.*, **61**, 618 (1939).

(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1959.

(5) E. E. Gilbert, "Sulfonation, Related Reactions," Interscience Publishers, Inc., New York, N. Y., 1965, p 12.

(6) A 10% aqueous solution of II underwent less than 5% decomposition during 10 days at room temperature.