

collected for characterization by preparative glpc. Its nmr spectrum (CCl_4) showed characteristic $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ absorption, *i.e.*, complex multiplets centered at 2.66, 1.32, and 0.91 ppm downfield from TMS. Its infrared spectrum (pure liquid) showed bands at 2965 (s), 2940 (s), 2870 (m), 1680 (m), 1610 (w), 1460 (m), 1377 (m), 1193 (s), 1104 (s), 948 (m), 913 (m), 874 (w), 831 (w), 806 (w), and 762 (s), cm^{-1} . The band at 1610 cm^{-1} can be identified as $\nu_{\text{C}=\text{C}}$,¹² and the band at 948 cm^{-1} as $\nu_{\text{C}-\text{N}}$.¹² The mass spectrum of the product showed molecular ion peaks at m/e 257, 259, 261, and 263 in a ratio of 27:25:9:1 (calcd: 257, 259, 261, 263 in a ratio of 27:27:9:1). The other major peaks occurred at m/e 222, 224, 226 (9:6:1 ratio), corresponding to $\text{M} - \text{Cl}$; 214, 216, 218, 220 (ratio 27:26:9:1), corresponding to $\text{M} - \text{C}_2\text{H}_5$; 180, 182, 184 (9:6:1 ratio), corresponding to $\text{M} - \text{C}_2\text{H}_5$ and Cl ; 172, 174, 176, 178 (27:27:9:1), corresponding to $\text{M} - \text{C}_2\text{H}_5$ and C_2H_5 . Although a satisfactory combustion analysis could not be obtained, the data above are consistent with the identification of the product as $(\text{C}_6\text{H}_5)_2\text{NCCl}=\text{CCl}_2$. This compound was formed in this reaction in 20% yield; phenylmercuric chloride was produced in 80% yield.

Reaction of Phenyl(bromochloromethyl)mercury with Triethylamine at Room Temperature.—A 25-ml flask was charged with 1.34 g (3.3 mmoles) of $\text{C}_6\text{H}_5\text{HgCHBrCl}$ ¹⁵ (mp 65–66°), 1.35 g (13.2 mmoles) of triethylamine, and 4 ml of dry benzene. After the mixture had been stirred for 10 min, a pale yellow oil separated to the bottom of the flask. After 1 hr, the oil apparently had solidified. The reaction mixture was evaporated under reduced pressure, leaving 1.60 g of pale yellow solid, mp 142–160° dec. Recrystallization from 1:1 ether–THF afforded 1.30 g (48%) of a white, powdery material, which melted at 162° with decomposition. This compound was characterized as $[\text{C}_6\text{H}_5\text{HgCHCl}(\text{C}_2\text{H}_5)_3]\text{Br}$ by its elemental analysis and its spectroscopic properties, and by synthesis of its tetraphenylborate derivative.

Anal. Calcd for $\text{C}_{13}\text{H}_{21}\text{BrClNHg}$: C, 30.78; H, 4.17; halogen, 30.75 mg of sample should give 20.07 mg of AgX ; Hg, 39.54; N, 2.76. Found: C, 30.61; H, 3.92; halogen, 30.75 mg of sample gave 20.75 mg of AgX ; Hg, 38.42; N, 2.65.

The infrared spectrum (KBr pellet) of the compound showed absorptions at 3060–3000 (w), 2980 (m), 2950 (w), 1578 (w), 1480–1450 (s), 1395 (m), 1300 (w), 1278 (w), 1189 (w), 1158 (s), 1105 (w), 1078 (w), 1054 (w), 1030 (m), 1004 (m), 902 (w), 795 (m), 738 (s), 708 (s), and 620 (m), cm^{-1} . Its nmr spectrum (CDCl_3) showed phenyl absorption from 7.82 to 6.85, a one-proton singlet at 5.50, a six-proton quartet at 3.52, and a nine-proton triplet at 1.38 ppm downfield from TMS.

The tetraphenylborate was prepared by treating 0.507 g (1 mmole) of this product with 0.350 g (1 mmole) of sodium tetraphenylborate in 5 ml of chloroform. After 15 min the reaction flask was filled with solid. Filtration afforded 0.83 g of white, flakey material, mp 170° dec. Recrystallization from methylene chloride and from 1:1 ether–THF gave 0.71 g of white flakes, mp 164° dec.

Anal. Calcd for $\text{C}_{37}\text{H}_{41}\text{ClNBHg}$: C, 59.52; H, 5.54; Cl, 4.75; N, 1.88. Found: C, 58.91; H, 5.59; Cl, 4.72; N, 2.12.

The infrared spectrum (KBr) of this derivative showed absorptions at 3070–2960 (w), 1580 (w), 1475 (s), 1430 (m), 1390 (w), 1270 (w), 1190 (m), 1158 (m), 1069 (w), 1032 (w), 1000 (w), 925–890 (w), 855 (w), 778 (w), 743 (s), 711 (s), and 605 (m) cm^{-1} .

Reaction of Phenyl(trichloromethyl)mercury with Triethylamine in Acetone Solution.—A dry, 50-ml, three-necked flask fitted with a reflux condenser and a magnetic stirring assembly was charged with 10 mmoles of $\text{C}_6\text{H}_5\text{HgCCl}_3$. Ten milliliters of anhydrous acetone and 12 mmoles of triethylamine were added and the reaction mixture was heated at reflux with stirring. Within 5 min a white precipitate formed, but this redissolved within 1 hr. The reaction mixture was heated for 22 hr; at that time the solution was yellow-orange in color and thin layer chromatography¹⁴ showed that the starting mercurial had been consumed completely. The reaction mixture was distilled at 0.02 mm (pot temperature up to 80°) into a receiver at –78°. The clear distillate was analyzed by glpc (chlorobenzene internal standard); triethylamine, acetone, and chloroform (80%) were found to be present. At best only a trace (<1%) of dimethyl-

(trichloromethyl)carbinol was present. The distillation residue, a brown oil, contained some white crystals which were identified as diphenylmercury by thin layer chromatography.

The $\text{C}_6\text{H}_5\text{HgCCl}_3 + (\text{C}_2\text{H}_5)_3\text{N} + \text{acetone}$ reaction is more complicated than is apparent at first sight. Firstly, dimethyl-(trichloromethyl)carbinol is formed in only trace yield, whereas in the displacement of CCl_3^- from $\text{C}_6\text{H}_5\text{HgCCl}_3$ by sodium iodide in acetone, this alcohol is formed in substantial yield.⁹ Furthermore, in another experiment which was interrupted at a stage just before precipitation of the white solid mentioned above by distillation of all volatiles under vacuum at room temperature, it was established that triethylamine consumption had been less than 20%, but that the chloroform yield already was 50%.

Acknowledgments.—The authors are grateful to the U. S. Army Research Office (Durham) for generous support of this work. This investigation was supported in part by Public Health Service Fellowships 5-F1-GM-20,106-03 to M. E. G. and 1-F1-GM-24,781-02 to R. D.

A Novel Ketone Reduction by Diimide

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Received August 3, 1966

We wish to report an example of the reduction of ketones to alcohols by diimide ($\text{NH}=\text{NH}$). Even more surprising, one ketone (1) retained a carbon-carbon double bond which is generally reduced by diimide.^{1,2} Carbonyl-group reduction by this reagent has been reported to occur with benzaldehyde,³ but ketones were found to be unreactive.

While the reactions of benzophenone were being compared with those of 5H-dibenzo[*a,d*]cyclohepten-5-one (1) and 10,11-dihydro-5H-dibenzo[*a,d*]cyclohepten-5-one (2), it was noted that tosylhydrazone formation did not occur with these ketones under conditions which caused benzophenone to react. The preparation of these tosylhydrazones has recently been reported without experimental details.⁴ When the reaction was forced (refluxing ethanol for 15 hr), a nitrogen-free product was obtained in each case; no tosylhydrazone was isolated. The infrared spectrum of the product from ketone 1 showed sulfone bands (1310 and 1140 cm^{-1}) and the nmr spectrum (Experimental Section) suggested structure 3 for the sulfone. An independent synthesis of compound 3 from 5-chloro-5H-dibenzo[*a,d*]cycloheptene and sodium *p*-toluenesulfinate confirmed this assignment. Similarly, the product from ketone 2 was found to be the corresponding sulfone, 10,11-dihydro-5H-dibenzo[*a,d*]cyclohepten-5-yl *p*-tolyl sulfone (4).

The most reasonable mechanism for the formation of sulfone 3 is reduction of ketone 1 to alcohol 5, which then reacts with *p*-toluenesulfonic acid to form the product. The reducing agent, diimide, is provided by

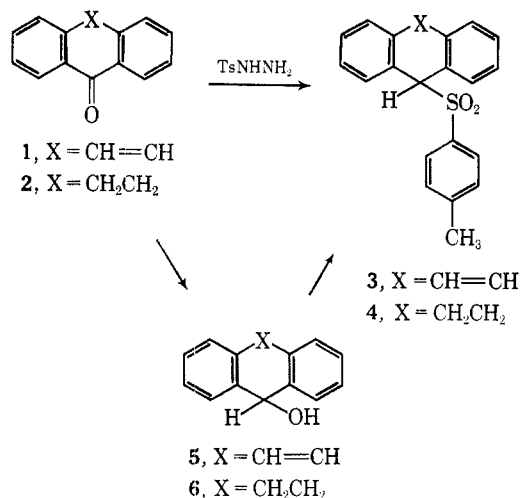
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thermal decomposition of tosylhydrazine.⁵ This reaction has also been shown to produce *p*-toluenesulfonic acid, the other required reactant. Reaction of alcohol **5**, obtained by reduction of ketone **1**, with *p*-toluenesulfonic acid was shown to produce sulfone **3** under the original reaction conditions. Alcohol **6**, obtained by reduction of ketone **2**, behaved similarly and gave sulfone **4**. In support of this mechanism, it was found that ketone **1** is reduced to alcohol **5** when heated in alcohol with anthracene-9,10-biimine,⁶ a source of diimide. The reduction of ketones in this manner may occur when the carbonyl group is sufficiently inert to nucleophilic attack by tosylhydrazine to permit diimide formation by the thermal process.

An alternative mechanism considered was formation of the tosylhydrazone, decomposition to the diazo compound, conversion to the carbonium ion in the protic medium, and sulfone formation with *p*-toluenesulfonic acid. This is ruled out because the tosylhydrazone, prepared from 5,5-dichloro-5H-dibenzo[*a,d*]cycloheptene, is recovered unchanged when subjected to these reaction conditions.

Experimental Section⁷

Reaction of 5H-Dibenzo[*a,d*]cyclohepten-5-one with Tosylhydrazine.—A mixture of 5.0 g (0.024 mole) of ketone **1**, 7.0 g (0.038 mole) of tosylhydrazine, 100 ml of ethanol, and 1 ml of acetic acid was heated at reflux for 15 hr. The solid that separated was collected and recrystallized from ethanol-chloroform to give 3.4 g (39%) of sulfone **3**, mp 210–211°.

Anal. Calcd for C₂₂H₁₈O₂S: C, 76.4; H, 5.2; S, 9.3. Found: C, 76.5; H, 5.3; S, 9.3.

The nmr spectrum (DMSO) had peaks at τ 2.6–2.8 m (aromatic), 3.37 s (olefinic), 4.12 s (benzylic), and 7.93 s (methyl) in an area ratio of 12:2:1:3. The infrared spectrum (KBr) showed strong sulfone bands at 1310 and 1140 cm⁻¹. A mixture melting point with an authentic sample, prepared as described below, was not depressed.

When 5 g (0.024 mole) of 10,11-dihydro-5H-dibenzo[*a,d*]cyclohepten-5-one (**2**) was used in place of the unsaturated ketone **1**, 1.1 g (13%) of the corresponding sulfone (**4**) was obtained, mp 187–188°. A mixture melting point with an authentic sample, prepared as described below, was not depressed.

Anal. Calcd for C₂₂H₂₀O₂S: C, 75.9; H, 5.8; S, 9.2. Found: C, 75.9; H, 5.9; S, 9.0.

***p*-Tolyl 5H-Dibenzo[*a,d*]cyclohepten-5-yl Sulfone (**3**).**—A 1.0-g (0.0048 mole) portion of 5-hydroxy-5H-dibenzo[*a,d*]cyclo-

heptene (**5**) was converted into the chloride by heating the mixture for 5 min with thionyl chloride and removing volatile material under reduced pressure. A suspension of 4 g (0.02 mole) of sodium *p*-toluenesulfonate dihydrate in 50 ml of ethanol was added to the chloride and the mixture was heated for 30 min at reflux before being poured into ice-water. The solid was collected, washed with water, and dried, giving 1.5 g (90%) of sulfone **3**, mp 210–211°.

By using the same procedure, *p*-tolyl 10,11-dihydro-5H-dibenzo[*a,d*]cyclohepten-5-yl sulfone (**4**) was prepared from 5-hydroxy-10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene (**6**); the yield was 0.4 g (23%), mp 187–188°.

Reaction of 5-Hydroxy-5H-dibenzo[*a,d*]cycloheptene with *p*-Toluenesulfonic Acid.—To a solution of 1.0 g of sodium *p*-toluenesulfonate dihydrate in 25 ml of ethanol and 2 ml of acetic acid was added 0.5 g (0.0024 mole) of 5-hydroxy-5H-dibenzo[*a,d*]cycloheptene (**5**). After the solution had been heated at reflux for 30 min, the solid was collected; the yield was 0.70 g (85%), mp 210–211°. A mixture melting point with sulfone **3** was not depressed.

In a similar manner, 5-hydroxy-10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene (**6**) gave a 15% yield of *p*-tolyl 10,11-dihydro-5H-dibenzo[*a,d*]cyclohepten-5-yl sulfone (**4**), mp 187–188°. A mixture melting point with the authentic sample was not depressed.

Reduction of 5H-dibenzo[*a,d*]cyclohepten-5-one with Anthracene-9,10-biimine.—A mixture of 1.0 g (0.050 mole) of ketone **1**, 3.0 g (0.15 mole) of anthracene-9,10-biimine,⁸ and 50 ml of ethanol was heated at reflux for 1 hr. After cooling to room temperature, the anthracene was removed by filtration and the filtrate was concentrated and chromatographed on alumina (20 g). Anthracene and starting ketone were removed with benzene, and alcohol **5** was eluted with ethanol; the yield was 0.25 g (25%), mp 118–120°. A mixture melting point was not depressed, and the infrared spectrum was identical with that of an authentic sample.

5H-Dibenzo[*a,d*]cyclohepten-5-one *p*-Toluenesulfonylhydrazone.—A 3.7-g (0.02 mole) portion of tosylhydrazine was added to a solution of 5,5-dichloro-5H-dibenzo[*a,d*]cycloheptene,⁸ obtained from 4.0 g (0.020 mole) of ketone **1**, in 60 ml of acetonitrile. The mixture was stirred overnight and the solid was collected. Additional material was obtained by concentration of the filtrate, and the solid was recrystallized from ethanol-acetonitrile to give 5.2 g (70%) of the tosylhydrazone, mp 213–215° dec (lit.⁴ mp 204°). The nmr spectrum is in agreement with the proposed structure.

Anal. Calcd for C₂₂H₁₈N₂O₂S: C, 70.6; H, 4.8; N, 7.5; S, 8.6. Found: C, 70.9; H, 4.6; N, 7.7; S, 8.6.

The tosylhydrazone (1.0 g) was recovered quantitatively after treatment for 16 hr at reflux in 20 ml of ethanol containing 0.5 ml of acetic acid.

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Bicyclic Enamines. III. Reduction of Enamines with Secondary Amines^{1,2}

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Received August 24, 1966

The reduction of enamines derived from both bicyclic and monocyclic ketones by secondary amines has recently been reported.¹ The only secondary amine used in these reductions, however, was hexamethyl- enimine. The reduction of enamine intermediates by methanolic solutions of either dimethylamine or piper-

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(7) The nmr spectrum was measured on a Varian Associates Model A-60 spectrometer and the infrared spectrum was measured on a Perkin-Elmer Model 137B spectrometer. Melting points are uncorrected.

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(2) Support of this work by a grant from the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged.