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THE USE OF SILVER OXIDE IN THE PREPARATION OF DIARYLDIAZOMETHANES

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The classical method for the preparation of diaryldiazomethanes involves the oxidation of the appropriate benzophenone hydrazones with yellow mercuric oxide (1). By this method diphenyldiazomethane was prepared in quantitative yield by shaking a mixture of benzophenone hydrazone in petroleum ether with yellow mercuric oxide for six hours at room temperature (2).

When the classical method was extended to the preparation of *p*-chlorodiphenyldiazomethane erratic results were obtained despite the application of known methods for increasing the efficiency of this reaction. Alkaline catalysis (3) or change in solvent was not sufficient to give reproducible results.

When silver oxide was substituted for mercuric oxide the reaction proceeded smoothly and rapidly irrespective of the solvent or the presence or absence of catalyst to give a quantitative yield of the diaryldiazomethane. Silver oxide oxidation of benzophenone hydrazone resulted in a quantitative yield of diphenyldiazomethane in one half hour in contrast to the six hours required with mercuric oxide.

Measurement of the nitrogen evolved in a eudiometer tube when a solution of the diaryldiazomethane was treated with stannic chloride, served as an excellent method for estimating the yield of a given oxidation. This same procedure was employed by Roberts (4) in determining the purity of diphenyldiazomethane.

The yield in one instance was also determined by reacting an ether solution of *p*-chlorodiphenyldiazomethane with *p*-nitrobenzoic acid and weighing the ester produced. Benzoic acid has been used for determining the yield of diphenyldiazomethane (2) but *p*-chlorobenzhydrylbenzoate was obtained as an oil which could not be induced to crystallize.

In a paper concerning the oxidation of sugars with silver oxide, Busch, *et al.* (5) described a precise method for the preparation of the oxidant. No such procedure was found necessary in the present study. Commercially available USP silver oxide powder gave uniform results.

Other oxidizing agents such as lead oxide and copper oxide were tried without success. Oxidation with manganese dioxide proceeded very smoothly at first, then stopped at a point dependent upon the nature and amount of manganese dioxide added. A ten to twelve *molar* excess of commercial C. P. material was required for a good yield of diazomethane. Freshly prepared manganese dioxide behaved somewhat better but a five to six *molar* excess was still required to insure complete oxidation.

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The addition of a drying agent to remove the water formed in the reaction as described for the preparation of phenylbenzoyldiazomethane (3) was decidedly advantageous. In the absence of such a drying agent, a heavy sludge of water, silver, and unreacted silver oxide formed, which was difficult to suspend and seriously impeded the smooth progress of the oxidation.

Since the oxidation is exothermic and the temperature must be kept below 35° to avoid decomposition of the product, the preparation was conducted in either of two ways—dependent upon the quantity of hydrazone to be oxidized. Both of these methods are outlined in the experimental section.

EXPERIMENTAL

p-Chlorodiphenyldiazomethane. p-Chlorobenzhydryl p-nitrobenzoate. 1. *p*-Chlorobenzophenone hydrazone (6 g., 0.026 mole) (prepared by heating a mixture of 4-chlorobenzophenone and anhydrous hydrazine in propanol-2 for five hours at 150–160° in a stainless steel bomb) was dissolved in 100 ml. of ether, and 6.3 g. (0.027 mole) of silver oxide, and 2.0 g. of anhydrous magnesium sulfate were added all at once and the mixture was shaken for 30 minutes with occasional cooling to maintain the temperature at 30–32°. The silver and magnesium sulfate were then filtered off and the deep purple solution of *p*-chlorodiphenyldiazomethane was added to a slurry of 15.0 g. (0.089 mole) of *p*-nitrobenzoic acid in 100 ml. of ether. This slurry was warmed on the steam-bath with occasional shaking until the purple color had been discharged. The ether was evaporated and the residue was triturated with dilute sodium hydroxide to dissolve the excess acid. The ester was collected, washed with water, and dried to yield 9.5 g. (99.5%); m.p. 108–110°. One recrystallization from aqueous propanol-2 gave 7.5 g., m.p. 114–115°. The analytical sample was in turn recrystallized from petroleum ether and was obtained as white elongated plates; m.p. 114–115°.

Anal. Calc'd for $C_{20}H_{14}ClNO_4$: C, 65.43; H, 3.82.

Found: C, 65.63; H, 3.99.

Another solution of *p*-chlorodiphenyldiazomethane (0.01 mole) prepared in the same manner, rapidly evolved the theoretical amount of nitrogen when treated with a solution of 300 mg. of stannic chloride pentahydrate in a few milliliters of ether.

2. *p*-Chlorobenzophenone hydrazone (75 g., 0.324 mole), 15 g. of anhydrous magnesium sulfate, and 350 ml. of benzene were charged into a 1-l., three-necked flask fitted with an efficient stirrer, thermometer, and addition funnel. Stirring was started and a 5.0-g. portion of silver oxide was added. After a short time the purple color of the diazomethane was evident and the temperature rose to 30°. The flask was then surrounded by a water-bath at 20° and 4–5 g. portions of silver oxide were added so as to maintain the reaction temperature at 29–31° until 78 g. (0.336 mole) had been added. The addition took 25 minutes. The mixture was then stirred at room temperature for three hours to insure complete oxidation. Filtration gave a deep purple benzene solution of *p*-chlorodiphenyldiazomethane suitable for further reaction.

3. A mixture of 2.3 g. (0.01 mole) of *p*-chlorobenzophenone hydrazone, 5.2 g. (0.06 mole) of freshly prepared dry manganese dioxide, 1.0 g. of anhydrous magnesium sulfate and fifty ml. of ether was shaken for thirty minutes. The deep purple solution was decanted from the dark sludge and evolved the theoretical amount of nitrogen when 300 mg. of stannic chloride pentahydrate dissolved in a small amount of ether was added.

SUMMARY

The use of an equivalent amount of silver oxide for the smooth conversion of benzophenone hydrazones to the corresponding diazomethanes is described. The

same oxidation can be efficiently carried out employing a five mole excess of manganese dioxide.

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