mesitol,[3] m.p. 72.5–73°, with 10 ml. of 6*N* sodium hydroxide. The mesitoyl chloride was slowly added to the sodium mesitolate through about 30 min., in a 125-ml. Erlenmeyer flask, with shaking. Release of heat resulted. After heat evolution ceased, the mixture was refluxed on a water bath for 30 min. It was then chilled in an ice bath. The crystals which formed were collected by vacuum filtration, washed with water, and recrystallized from approximately 100 ml. of ethyl alcohol; yield 3.75 g. (40%), m.p. 70.5–71.5°.

Anal. Calcd. for ($C_{19}H_{22}O_2$): C, 80.85 H, 7.80. Found: C, 80.55 and 80.29; H, 7.63 and 7.75.[4]

Hydrolysis. Alkaline hydrolysis: Mesityl mesitoate is a hindered ester and as such should be highly resistant to formation and saponification.[5] The ester, 0.25 g., was refluxed 6 hr. with 5 ml. of 6*N* sodium hydroxide. There remained undissolved 0.23 g. of the mesityl mesitoate which was collected by vacuum filtration. The clear filtrate did produce a slight precipitate when acidified.

Acid hydrolysis: One g. of ester in 5 ml. of cold conc. sulfuric acid was drowned with 40 ml. of cold water. The resulting mixture was extracted with ether. The mesitoic acid was next removed from the ether by three sodium bicarbonate washings, (0.2 g. recovered, m.p. 152°). Mesitol, 0.15 g., was extracted from the ether solution by three washings with 2*N* sodium hydroxide, and precipitated with hydrochloric acid while in an ice bath. The crystals were collected by filtration and vacuum desiccated for 48 hr.; m.p. 70–71°. Mixed with mesitol from Organic Research Chemical Ltd., the m.p. was 70.5–71.5°.

All melting points are corrected.

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Monmouth College
Monmouth, Ill.

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(3) Supplied by Organic Research Chemical Ltd., Poyle Estate, Bucks, England.

(4) Clark Microanalytical Laboratory, P. O. Box 17, Urbana, Ill.

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Preparation of Crystalline Diphenyldiazomethane

J. B. Miller

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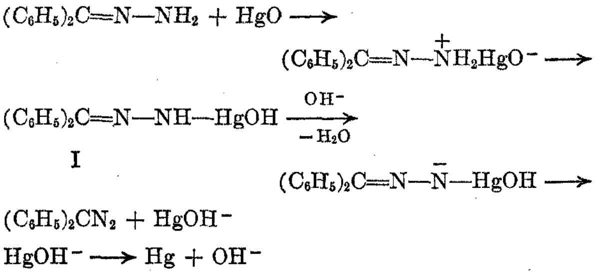
Diphenyldiazomethane has been used to analyze mixtures of carboxylic acids[1] and as a convenient "blocking agent" for acids since the resulting benzhydryl esters are easily hydrogenolyzed.[2] Benzhydryl esters should also prove useful as derivatives in view of their ease of preparation and the resulting increase in molecular weight.

Hydrazones have been converted to diazo compounds by treatment of the *N*-tosylates with base[3,4] and by oxidation of hydrazones with mercury acetamide,[5] potassium permanganate,[6] Tollens' reagent[6] mercuric oxide,[7] air,[8,9] silver oxide,[10] and manganese dioxide.[10]

The usual preparative method for diphenyldiazomethane by the mercuric oxide oxidation of benzophenone hydrazone requires six hours and yields an oil.[11] The procedure described here requires 75 minutes and gives a crystalline product in high yield. This procedure is an extrapolation of the method of Nenitzescu and Solomonica for the preparation of benzoylphenyldiazomethane[12] and diazofluorene.[12] Diethyl ether rather than petroleum ether[11] is used as the solvent in spite of the reported lower rate of oxidation in ether[13] because of the greater solubility of the hydrazone in ether. Most important is the use of a basic catalyst.

We suggest the role of the basic catalyst is that shown below.



$$(C_6H_5)_2C{=}N{-}NH_2 + HgO \longrightarrow (C_6H_5)_2C{=}N{-}\overset{+}{N}H_2HgO^- \longrightarrow$$

$$\underset{\text{I}}{(C_6H_5)_2C{=}N{-}NH{-}HgOH} \xrightarrow[-H_2O]{OH^-} (C_6H_5)_2C{=}N{-}\overset{-}{N}{-}HgOH \longrightarrow$$

$$(C_6H_5)_2CN_2 + HgOH^-$$

$$HgOH^- \longrightarrow Hg + OH^-$$

This reaction path is similar to that suggested for the mercuric acetate oxidation of tertiary amines[14] and an analogous mechanism serves to explain the mercuric oxide oxidation of 1,1-disubstituted hydrazines, R_2NNH_2, to tetrazines, $R_2NN{=}NNR_2$.[15] Mercuric acetate oxidation of hydrazones yields, in fact, organomercury compounds which are considered to be formed, however, by further reaction of the diazo compound initially formed.[16]

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The intermediate, I, has been previously postulated as the initial product of the reaction of mercuric oxide with a hydrazone.[17,18]

Yellow mercuric oxide is more effective than red mercuric oxide in this reaction and this is generally thought to be due to the smaller particle size[19] of the yellow form. However, since red mercuric oxide is usually prepared by igniting the nitrate whereas the yellow form is usually prepared by adding a base to a soluble mercuric salt, we feel that contamination of the yellow mercuric oxide by base may be more important than the particle size in explaining the long standing preference for the yellow form. This may also explain the preference for freshly precipitated material[20] and the observed variations with different samples of mercuric oxide.[8] In agreement with this we find that by using slightly more catalyst red mercuric oxide performs as well as the yellow form (see Table I).

TABLE I

PREPARATION OF DIPHENYLDIAZOMETHANE[a]

Mercuric Oxide, g.	Time, min.	Yield, %	M.P., °C.
35 (yellow)	75	12[b,c]	. . .
28.7 (yellow)	60	54.5	26.5–28.5
35 (yellow)	75	88, 95	30.1–31.1, 29–33
36.5 (yellow)	75	89	30–31
44 (yellow)	70	83	29–30.5
44 (yellow)	90	79	30–32
35 (red)	75	4, 9[b,c]	. . .
35 (red)	75	20.5, 30, 46, 55, 81, 88	26–28.5 to 29–31
35 (red)	75	81[d]	28–31.5
35 (red)	75	95[d]	29–33
35 (red)	75	86[d]	27–29

[a] From 13 g. of benzophenone hydrazone, 15 g. of anhydrous sodium sulfate, 200 ml. of ether, and 5 ml. of ethanol saturated with potassium hydroxide (except where noted). [b] Based on recovered hydrazone. [c] No basic catalyst. [d] Ten ml. of basic catalyst.

This method of oxidation is, however, not always applicable. Thus, although the mercuric oxide oxidation of the 2-hydrazone of 4,7-dimethyl-1,2-indanedione showed definite basic catalysis, the yield was very low[4] and the base catalyzed mercuric oxide oxidation of *p*-chlorobenzophenone hydrazone gave erratic results.[10] Similarly, we find that contrary to some reports[17,18,21] and in agreement with Vollmann[22] the base catalyzed mercuric oxide oxidation of camphor hydrazone yields diazocamphane but in only trace amounts.

EXPERIMENTAL

Diphenyldiazomethane. A mixture of 13 g. (0.066 mole) of benzophenone hydrazone, 15 g. of anhydrous sodium sulfate, 200 ml. of ether, 5 ml. (10 ml. if red mercuric oxide is used) of ethanol saturated with potassium hydroxide, and 35 g. (0.16 mole) of yellow (or red) mercuric oxide was shaken for 75 min. in a pressure bottle wrapped in a wet towel. The reaction mixture was filtered and the solvent removed from the filtrate under reduced pressure at room temperature. The dark red oil thus obtained was dissolved in petroleum ether (b.p. 30–60°) and again filtered. Removal of the solvent from the filtrate under reduced pressure at room temperature gave an oil. Freezing this oil in a stoppered flask with Dry Ice and then allowing the flask to warm spontaneously to room temperature gave dark red crystals which, after drying on a porous plate, had m.p. 29–32° (reported[13] 29–30°), average yield 89% (see Table I). Reaction of this product with benzoic acid[2] gave benzhydryl benzoate, m.p. 88–91° (reported[2] 87°).

Diazocamphane. A potassium-sodium *tert*-butoxide solution was prepared by dissolving 2.05 g. of potassium-sodium eutectic alloy[23] in 100 ml. of *tert*-butyl alcohol. A mixture of 5 ml. of the above solution, 35 g. of mercuric oxide (yellow), 15 g. of sodium sulfate, 150 ml. of ether, and 10.6 g. of camphor hydrazone[24] (m.p. 52–57°, b.p. 130–133° [22 mm.]) was stirred for 3 hr. and then filtered. This filtrate was bright red in agreement with Vollmann[22] and Heubaum[25] and effervesced on acidification. The presence of the diazo group was shown by infrared absorption at 4.82 microns[26] which disappeared on acidification or treatment with anhydrous copper sulfate. Ethanolic potassium hydroxide solution worked less well than the *tert*-butoxide solution but in neither case was sufficient diazo compound formed to allow its isolation as bornyl or isobornyl chloride.

EXPLOSIVES DEPARTMENT
EXPERIMENTAL STATION
E. I. DU PONT DE NEMOURS & CO., INC.
WILMINGTON, DEL.

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Acid Catalyzed Reactions between Carbonyl Compounds and Organic Azides. II. Aromatic Aldehydes[1]

J. H. BOYER AND L. R. MORGAN, JR.

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An acid-catalyzed reaction between aromatic aldehydes and alkyl azides leading to the formation of amides (II) was recently reported.[2] It was suggested that elimination of a proton at an intermediate stage such as I followed by or accom-

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