

compounds with potassium fluoride in dimethyl sulfoxide solution.

EXPERIMENTAL

2,4-Dinitroiodobenzene, optimum conditions. To 200 cc. of redistilled dimethylformamide, 150 g. (1.0 mole) of sodium iodide and 40.5 g. (0.2 mole) of 2,4-dinitrochlorobenzene (Eastman Kodak white label) were added. The mixture was heated at reflux by means of a free flame for 15 min.; during the period of heating to reflux temperature, the flame was played against the side of the flask so as to dissolve the sodium iodide from the top downward. The hot reaction mixture was poured into ice and water and the precipitated tan solid was collected on a suction filter. The damp product was recrystallized from a mixture of 375 cc. of petroleum ether (b.p. 90–100°) and 125 cc. of benzene with use of charcoal and with final chilling to –20° in a freezing cabinet. The resulting orange-yellow crystalline product, m.p. 87–89°, weighed 41.4 g. (70%). Recrystallization of this product from petroleum ether (b.p. 90–100°) furnished lemon-yellow crystals, m.p. 88.5–90°. Körner⁴ reported m.p. 88.5°.

A run at five times the above scale gave comparable results.

Formation of 2,4-dinitrophenyl methyl sulfide in dimethyl sulfoxide solvent. The reaction was conducted as described above except that 200 cc. of commercial dimethyl sulfoxide (Stepan Chemical Co.) was used as solvent and the period of reflux was 1 hr. The reaction mixture was poured into water and allowed to stand 5 days. By suction filtration, a brick-red solid was collected. This solid was extracted with hot petroleum ether (b.p. 90–100°); orange crystals were obtained by cooling the extract. Recrystallization from ethanol with use of charcoal furnished 2.7 g. (5%) of yellow-orange flakes, m.p. 126–127°. A mixed melting point with an authentic sample of 2,4-dinitrophenyl methyl sulfide of m.p. 127–128.5° was not depressed.

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(4) W. Körner, *Gazz. chim. ital.*, **4**, 323 (1874).

2-Diphenylmethylene-3-dimethylamino-oxazolidine-4,5-dione

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A series of 2-dialkylmethylene-3-alkyloxazolidine-4,5-diones¹ has been prepared by the action of oxalyl chloride on *N*-alkyldialkylacetamides. We have extended this reaction by using *N*-diphenylacetyl-*N,N'*-dimethylhydrazine (I) in place of the amide. The resulting compound possesses typical oxazolidinedione properties and is formulated as 2-diphenylmethylene-3-dimethylamino-oxazolidine-4,5-dione (II).

The infrared spectrum for this compound shows bands which can be attributed to a lactone and two

carbonyl functions. The spectrum agrees with those of previously reported oxazolidinediones. Likewise, the behavior toward bromine in carbon tetrachloride and potassium permanganate in acetone is the same.

The behavior of the previously studied oxazolidine-4,5-diones in ethanol depends on the type and degree of substitution. 3-Alkyl-2-monoalkylmethyleneoxazolidine-4,5-diones rearrange to the corresponding hydroxymaleimides. Similar treatment of the 2-monoalkyl- or 2-dialkylmethyleneoxazolidine-4,5-diones results in cleavage to the corresponding amides. 3-Alkyl-2-dialkylmethyleneoxazolidine-4,5-diones rearrange to trialkylpyrrolidine-2,3,5-triones. It is, therefore, of interest to report from this study that II undergoes neither of the above reactions with alcohol. In this case, the ring opens at position 2 to give ethyl diphenylacetate.

In the course of this work previously unreported *N*-dialkylacetyl-*N,N'*-dimethylhydrazines were prepared.

EXPERIMENTAL

Preparation of I. To a stirred solution of 19.5 g. (0.325 mole) of *N,N*-dimethylhydrazine in 100 ml. of ether was added dropwise an ether solution of 75.0 g. (0.325 mole) of diphenylacetyl chloride. Simultaneously at a somewhat slower rate, a solution of 13.0 g. (0.325 mole) of sodium hydroxide in 65 ml. of water was added. The white precipitate was filtered and crystallized from 95 percent ethanol, yield 72 g. (87%), m.p. 168°.

Anal. Calcd. for C₁₆H₁₈ON₂: C, 75.56; H, 7.13; N, 11.02. Found: C, 75.39; H, 7.16; N, 11.01.

N-Diethylacetyl-N,N'-dimethylhydrazine. Similarly, from 30.0 g. (0.50 mole) of *N,N*-dimethylhydrazine in 150 ml. of ether, 67.3 g. (0.50 mole) of diethylacetyl chloride, and 20.0 g. (0.50 mole) of sodium hydroxide in 100 ml. of water, there was obtained from the ether layer 75.5 g. of a yellow oil which did not crystallize after standing 48 hr. in an ice bath. Distillation yielded 10.5 g. of a yellow oil, b.p. 85–108° (1.6 mm.) which did not solidify and 56 g., b.p. 109–114° (1.6 mm.) which was obtained as a sticky white solid, m.p. 93–97°. Redistillation gave 52 g. (66%), b.p. 109–112° (1.6 mm.), m.p. 95–96°.

Anal. Calcd. for C₈H₁₈ON₂: C, 60.72; H, 11.46; N, 17.71. Found: C, 61.04; H, 11.43; N, 17.89.

Preparation of II. To a stirred solution of 60 g. (0.26 mole) of I in 500 ml. of dry benzene at 55° was added during one hour 23 ml. (0.27 mole) of oxalyl chloride. One half of the theoretical amount of hydrogen chloride had been evolved at the end of this time. The mixture was then stirred for two hours at 55°. After cooling, the yellow precipitate was filtered with suction. Upon washing with benzene and then with petroleum ether a white residue of starting material remained. Distillation of the yellow filtrate to dryness under diminished pressure left 45 g. of a yellow solid, m.p. 169–175°. Recrystallization from 1:1 toluene-ligroin gave 42.5 g. (53%) of a yellow crystalline substance, m.p. 175–176°.

Anal. Calcd. for C₁₈H₁₆O₃N₂: C, 70.11; H, 5.23; N, 9.09. Found: C, 69.88; H, 5.27; N, 9.26.

Reaction of II with ethanol. A solution of 1.0 g. of II in 30 ml. of 95% ethanol was refluxed for 24 hr. No crystalline product separated on cooling. After the solution was concentrated under diminished pressure to one-third of its volume 0.2 g. of a white compound, m.p. 59–60°, was obtained. Addition of water to the filtrate caused the precipitation of 0.4 g. more of the same substance. Saponification gave diphenylacetic acid, m.p. 148°. The substance when mixed

(1) Glenn S. Skinner and Richard E. Ludwig, *J. Am. Chem. Soc.*, **78**, 4656 (1956).

with an authentic sample of ethyl diphenylacetate gave no depression in the melting point. Identical results were obtained using both 90% and absolute ethanol and varying the time of reflux from 8 to 30 hr.

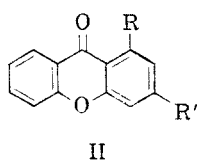
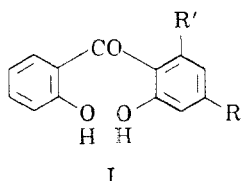
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2,2',4- and 2,2',6-Trihydroxybenzophenone

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We have applied Grover, Shah, and Shah's¹ new synthesis of polyhydroxyxanthenones to the preparation of 1-hydroxy-9-xanthenone² which is obtained in low yields by the usual methods.^{3,4} Condensation of salicylic acid and resorcinol in the presence of anhydrous zinc chloride and phosphoryl chloride yielded a trihydroxybenzophenone. This substance has the same melting point as, and similar solubility properties to, 2,2',6-trihydroxybenzophenone obtained by Michael³ by fusing the same reactants in the absence of a condensing agent. Michael's compound was assigned the structure of 2,2',6-trihydroxybenzophenone (I; R = H; R' = OH) because it cyclized with zinc chloride to give 1-hydroxy-9-xanthenone (II; R = OH; R' = H).^{3,5} Our product, however, could not be made to cyclize with zinc chloride, but gave a quantitative yield of 3-hydroxy-9-xanthenone (II; R = H; R' = OH), when heated with water in a sealed tube at 200–250°. This benzophenone is thus proved to be 2,2',4-trihydroxybenzophenone (I; R = OH; R' = H). Moreover the nonidentity of the two ketones was confirmed by a depression in their melting points and those of their triacetyl derivatives on admixture.



It is, therefore, possible by varying the reaction conditions to obtain either 2,2',4- or 2,2',6-trihydroxybenzophenone from the same reactants. The formation of 2,2',4-trihydroxybenzophenone in the presence of phosphoryl chloride and zinc

chloride is consistent with the findings of Grover, Shah, and Shah¹ who report that under these conditions hydroxybenzoic acids will substitute the resorcinol nucleus in the β -position only.

2,2',4-Trihydroxybenzophenone has been previously mentioned by Atkinson and Heilbron⁶ in connection with a by-product isolated from their preparation of 3-hydroxy-9-xanthenone (II; R = H; R' = OH). No structural evidence was, however, given, except that, by drawing attention to its similarity to Michael's compound, the identity of the two substances was implied.

EXPERIMENTAL⁷

2,2',4-Trihydroxybenzophenone. Salicylic acid (5 g.), resorcinol (6 g.), anhydrous zinc chloride (20 g.), and phosphoryl chloride (25 cc.) were heated on a water bath at 75–80° for 2 hr. The deep-red reaction mixture was poured onto crushed ice (400 cc.) containing concentrated hydrochloric acid (25 cc.). A red gum formed on standing and its mother liquor A was decanted off. On triturating the residue with aqueous sodium hydrogen carbonate an orange solid was obtained which yielded on recrystallization from water and from petroleum ether (b.p. 100–120°) 2,2',4-trihydroxybenzophenone, m.p. 133° (0.37 g.) as colorless plates. More ketone (1.85 g.) was obtained from mother liquor A which deposited it as yellow needles on standing for 2 days and by acidification of the sodium hydrogen carbonate extract.

Anal. Calcd. for $C_{13}H_{10}O_4$: C, 67.8; H, 4.4. Found: C, 68.1; H, 4.4.

The ketone gives a deep red ferric color in water and dissolves in alkali to form a yellow solution. The triacetate was obtained in the usual way and crystallized from a mixture of ethyl acetate and petroleum ether (b.p. 40–60°) as blunt needles, m.p. 69–70°.

Anal. Calcd. for $C_{15}H_{12}O_7$: C, 64.0; H, 4.5. Found: C, 64.0; H, 4.7.

3-Hydroxy-9-xanthenone. 2,2',4-Trihydroxybenzophenone (0.4 g.) and water (1.5 cc.) were heated in a sealed tube (50 cc.) for 2.5 hr. at 200–250°. Crude 3-hydroxy-9-xanthenone was obtained in theoretical yield as a yellow crystalline residue, m.p. 238–241°. Recrystallization from aqueous ethanol yielded the xanthenone as white needles, m.p. 242° (Atkinson and Heilbron⁶ give m.p. 246°).

Anal. Calcd. for $C_{13}H_8O_3$: C, 73.6; H, 3.8. Found: C, 73.8; H, 4.0.

The acetyl derivative had m.p. 156°. Kostanecki and Rutishauser⁸ give m.p. 157–158°.

Anal. Calcd. for $C_{15}H_{10}O_4$: C, 71.3; H, 4.0. Found: C, 71.1; H, 4.0.

Attempts to cyclize 2,2',4-trihydroxybenzophenone with fused zinc chloride gave only starting material.

2,2',6-Trihydroxybenzophenone was prepared as described by Michael.³ The product crystallizes from petroleum ether (b.p. 100–120°) as white plates, m.p. 134–135° (Michael³ gives m.p. 133–134°). Its mixed melting point with 2,2',4-trihydroxybenzophenone was depressed.

Anal. Calcd. for $C_{13}H_{10}O_4$: C, 67.8; H, 4.4. Found: C, 67.7; H, 4.4.

The triacetate prepared by the acetic anhydride-pyridine method crystallized as blunt needles, m.p. 80–81° from a mixture of ethyl acetate and petroleum ether (b.p. 40–60°).

(6) H. Atkinson and I. M. Heilbron, *J. Chem. Soc.*, 2688 (1926).

(7) All melting points are uncorrected. The analyses were done by Drs. Weiler and Strauss, Oxford.

(8) St. v. Kostanecki and R. Rutishauser, *Ber.*, 25, 1651 (1892).

* Deceased.

(1) P. K. Grover, G. D. Shah, and R. C. Shah, *Chemistry & Industry*, 62 (1955); *J. Chem. Soc.*, 3982 (1955).

(2) 1-Hydroxy-9-xanthenone was needed for other work: see J. S. H. Davies, F. Scheinmann, and H. Suschitzky, *J. Chem. Soc.*, 2140 (1956).

(3) A. Michael, *Am. Chem. J.*, 5, 81 (1883).

(4) K. S. Pankajamani and T. R. Seshadri, *J. Sci. Ind. Research (India)*, 13B, 396 (1954).

(5) E. Dreher and St. v. Kostanecki, *Ber.*, 26, 71 (1893).