acetate for three hours. After evaporation *in vacuo* under nitrogen to dryness, the residue was extracted with hot benzene from which the diacetate was obtained as colorless short needles; m.p. 174° (recrystallized from benzene), absorption spectrum see Table I; no coloration with ferric chloride. Upon hydrolysis with 0.5 *N* aqueous hydrochloric acid, compound III was recovered in small yield.

Anal. Calcd. for $C_{13}H_{17}O_4N$: C, 62.13; H, 6.82; N, 5.57. Found: C, 62.17; H, 6.78; N, 5.79.

TABLE I

ABSORPTION SPECTRA

Compound	Solvent and *p*H	λ_{max}, mμ	ϵ_{max}
III	aq. 6.8	293	35,000
III	aq. 12.3	293	35,000
III	aq. 1.2	278	24,000
III	0.2 *N* HCl	276	25,500
III	95% EtOH	290	33,000
III	Ether	282	6,000
IV	aq. neutral	226 276	15,500 24,200
IV	MeOH	221 277	10,100 24,800
V	aq. neutral	290	24,500
V	0.1 *N* HCl	290	24,000
V	95% EtOH	290	22,000
V	Ether	289	20,900

Titration of III with Bromine.—A solution of 200 mg. of III in 40 ml. of abs. ethanol was carefully titrated with 0.34 *N* solution of bromine in ethanol until the yellow color persisted. Calcd.: 8.2 ml. for 2 atoms of bromine. Found: 7.6 ml. After acidification with hydrochloric acid and addition of 2 g. of potassium iodide, the solution was warmed. The released iodine was titrated with sodium thiosulfate; since the release of iodine was slow, the solution had to be kept warm during the titration. Calcd.: 25.8 ml. 0.1 *N* $Na_2S_2O_3$ for 7.6 ml. solution. Found: 24.0 ml.

Aromatization of III.—One-half gram of III was intimately mixed with 250 mg. of 5% palladium-on-charcoal and subjected to dry distillation. The temperature of the air-bath was raised during one hour to 250°. The presence of methylamine or ethylamine was indicated in the first fraction by smell. Later on, indole (or N-methylindole) was identified by its smell as well as by a positive indole test with vanillin, while ferric chloride gave no coloration. At about 200–250° a small quantity of an oil was collected which on repeated crystallization from petroleum ether (b.p. 85–100°) gave colorless needles of m.p. 135–136°. This compound gave both a green reaction with ferric chloride and a positive indole test. A mixture of this product with 5,6-dihydroxy-N-methylindole (II) showed a melting point depression; however, a mixture of this distillation product with an authentic sample of 5,6-dihydroxyindole[12] (m.p. 140°) melted at 135–136°. Because of lack of material no more definite identification was attempted.

Leuco-epinochrome (VI).—In some of the hydrogenation experiments with epinochrome ether extraction of the aqueous filtrate from the catalyst yielded small amounts of a compound which formed, on recrystallization from petroleum ether (b.p. 85–100°), colorless needles melting at 140–141°. It gave a green ferric chloride test and a positive indole reaction with vanillin (see above); ultraviolet absorption: λ_{max} 290 mμ; ϵ_{max} 25,000. This compound is believed to be 5,6-dihydroxy-N-methyl-2,3-dihydroindole, the true leuco form of epinochrome.

Anal. Calcd. for $C_9H_{11}O_2N$: C, 65.43; H, 6.71. Found: C, 65.79; H, 6.87.

Perhydrogenation Product (VII).—A solution of III in glacial acetic acid over platinum oxide absorbs two to three moles of hydrogen. The hydrochloride of the resulting perhydrogenated product melts at 231–233° (recrystallized from ethanol).

Anal. Calcd. for $C_9H_{18}O_2NCl$: C, 52.04; H, 8.73; N, 6.74; Cl, 17.07. Found: C, 52.29; H, 8.43; N, 6.59; Cl, 17.19.

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[12] R. J. S. Beer, K. Clarke, H. G. Khorana and A. Robertson, *J. Chem. Soc.*, 2223 (1948). We are indebted to Prof. Robertson for a sample of this compound.

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY OF LOUISIANA STATE UNIVERSITY]

Diazoketones as Reagents for the Identification of Organic Acids

BY J. L. E. ERICKSON, J. M. DECHARY AND M. R. KESLING

The cupric chloride-catalyzed decomposition of several α-diazoacetophenones in dioxane solution in the presence of an organic acid yielded phenacyl esters. The *p*-bromo- and *p*-phenylphenacyl esters of eleven representative organic acids have been prepared by the use of two new reagents, *p*-bromo- and *p*-phenyl-α-diazoacetophenone, and their melting points have been compared with values obtained from the literature. In the absence of protonic reagents the cupric chloride-catalyzed decomposition of diazoacetophenone yielded dibenzoylethylene.

Diazoketones lose nitrogen when catalytically decomposed, and if no opportunities are present for reaction with protonic reagents, the unstable radical which is formed may couple with itself to form ethylenic compounds.[1] If an inorganic acid such as hydrochloric acid is present during the

$$2RCOCHN_2 \longrightarrow 2N_2 + 2(RCOCH{=}) \longrightarrow RCOCH{=}CHCOR$$

decomposition of diazoketones, α-chloroketones[2] are formed, and recently Newman and Beale[3] have shown that β-phenethyl diazomethyl ketone yields di-(4-phenyl-2-ketobutyl) sulfate when treated with concentrated sulfuric acid. With the aid of boron trifluoride as a catalyst they were able to obtain α-alkoxyacetophenones[3] when diazoacetophenones were decomposed in the presence of alcohols. Bradley, *et al.*,[4] observed the formation of phenacyl acetate when diazoacetophenone was warmed in glacial acetic acid.

These results suggested that the decomposition of *p*-bromo- and *p*-phenyl-α-diazoacetophenones in the presence of an aliphatic or an aromatic acid might afford a convenient method for the preparation of *p*-bromo- and *p*-phenylphenacyl esters. These esters are ordinarily prepared from the corresponding *p*-bromo- and *p*-phenylphenacyl bromides, compounds which are disagreeable to use because of their lachrymatory properties. Even

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[1] C. Grundmann, *Ann.*, **536**, 29 (1938).

[2] D. A. Clibbens and M. Nierenstein, *J. Chem. Soc.*, **107**, 1491 (1915); F. Arndt, B. Eistert and W. Partale, *Ber.*, **60B**, 1364 (1927).

[3] M. S. Newman and P. F. Beale, THIS JOURNAL, **72**, 5161 (1950).

[4] W. Bradley and R. Robinson, *J. Chem. Soc.*, 1310 (1928); W. Bradley and G. Schwartzenbach, *ibid.*, 2904 (1928).

the crystalline esters prepared from phenacyl halides frequently adsorb enough halide to cause discomfort.

$$p\text{-Br—}C_6H_4\text{—COCHN}_2 + \text{RCOOH} \longrightarrow p\text{-Br—}C_6H_4\text{—COCH}_2\text{OCOR} + N_2$$

$$p\text{-}C_6H_5\text{—}C_6H_4\text{—COCHN}_2 + \text{RCOOH} \longrightarrow p\text{-}C_6H_5\text{—}C_6H_4\text{—COCH}_2\text{OCOR} + N_2$$

Preliminary experiments with diazoacetophenone and a few aromatic acids were carried out with the result that the phenacyl esters were obtained in good yield when the diazoketone was heated in dioxane with the acid and a very small quantity of cupric chloride which served to accelerate greatly the decomposition. These new reagents, *p*-bromo- and *p*-phenyl-α-diazoacetophenone, were prepared and found to be stable solid substances which easily decomposed catalytically, however, in the presence of an organic acid to yield phenacyl esters. A Wolff rearrangement of *p*-bromo-α-diazoacetophenone was carried out according to the procedure of Burger and Avakian[5] and the expected *p*-bromophenylacetamide was obtained.

It is of interest to note that when diazoacetophenone was catalytically decomposed with cupric chloride in benzene solution in the absence of acids, a 60% yield of dibenzoylethylene was obtained, the decomposition requiring only 9 mg. of catalyst per gram of diazoketone.

Table I

Phenacyl Esters Prepared from α-Diazoacetophenones

Acid	*p*-Bromophenacyl ester M.p.,[a] °C. Found	*p*-Bromophenacyl ester M.p. (lit.) Reported	*p*-Phenylphenacyl ester M.p.,[a] °C. Found	*p*-Phenylphenacyl ester M.p. (lit.) Reported
Formic	133.5–134.5	135.2[b,h]	75–75.5	74[e]
Acetic	85–86	86[b]	110.5–111	111[e]
Propionic	63.5–64	63.4[b]	103–103.5	102[e]
n-Butyric	63.5–64	63[b]	82–83	82[f]
Isovaleric	68	68[b]	75.5–77	76[e]
Benzoic	118.5–119	119[c]	167–167.5	167[e]
Salicylic	140	140[c]	148.5–149	148[g]
Cinnamic	145–146	145[c]	182–183.5	182.5[e]
p-Nitrobenzoic	136.5–137	136.5[d]	181.5–182.5	182[g]
p-Toluic	153	153[c]	165	165[e]
Succinic	209.5–210	211[c]	204–206	208[e,h]

[a] All melting points are uncorrected and were taken with the aid of a U. S. Bureau of Standards Certified thermometer. [b] C. G. Moses and E. E. Reid, This Journal, **54**, 2101 (1932). [c] W. L. Judefind and E. E. Reid, *ibid.*, **42**, 1043 (1920). [d] K. C. Chen and C. C. Shih, *Trans. Sci. Soc. China*, **7**, 81 (1931–1933). [e] N. L. Drake and J. Bronitsky, This Journal, **52**, 3715 (1930). [f] P. W. Clutterbuck, H. Raistrick and F. Reuter, *Biochem. J.*, **29**, 871 (1935). [g] N. L. Drake and J. P. Sweeny, This Journal, **54**, 2059 (1932). [h] *p*-Bromophenacyl formate and *p*-phenylphenacyl succinate were prepared from the requisite phenacyl bromides and were found to have exactly the same melting points as the same phenacyl esters prepared from *p*-bromo-α-diazoacetophenone and *p*-phenyl-α-diazoacetophenone. Repeated crystallization of these esters (prepared by both methods) from various solvents only served to increase the amount of decomposition as was deduced from the progressively lowered melting point and the yellow color of the crystal melt.

Experimental

***p*-Bromo-α-diazoacetophenone.**—A solution of 8.8 g. (0.04 mole) of *p*-bromobenzoyl chloride[6] in 40 ml. of dry ether was added with stirring over a period of 20–30 minutes to an ice-cold ethereal solution (400 ml.) containing at least 0.10 mole of diazomethane. The reaction mixture was kept at the temperature of the ice-bath for 8–9 hours, allowed to stand at room temperature 3 hours and the solvent evaporated in vacuum. The residue was crystallized from an ether-low-boiling petroleum ether mixture to yield 8.3 g. (92%) of fine yellow needles, m.p. 123.5–124° (gas evolution.).

Anal. Calcd. for $C_8H_5ON_2Br$: C, 42.7; H, 2.2. Found: C, 42.8; H, 2.2.

***p*-Phenyl-α-diazoacetophenone** was prepared in 95% yield from *p*-phenylbenzoyl chloride[7] and diazomethane in the same manner as was *p*-bromo-α-diazoacetophenone, except that the acid chloride was dissolved in 120 ml. of a solution composed of 30 ml. of dry ether and 90 ml. of dry benzene. The diazoketone crystallized from benzene in fine, pale, yellow needles, m.p. 117.5–118.5° (gas evolution).

Anal. Calcd. for $C_{14}H_{10}ON_2$: C, 75.7; H, 4.5. Found: C, 76.0; H, 4.7.

Preparation of Phenacyl Esters of Organic Acids.—Three millimoles of the acid was dissolved, by warming if necessary, in 10 ml. of dioxane placed in an 8-inch test-tube. The mixture was cooled to room temperature and 2 millimoles of the diazoketone added. After the diazoketone had dissolved, 2–4 mg. of solid cupric chloride was added and the mixture warmed until the evolution of nitrogen was steady. Heating was discontinued when the clear yellow solution became light brown in color (an intermediate change to light green was usually observed) and a vigorous evolution of gas set in. After a few minutes the evolution of gas ceased, and the solution was boiled for one minute and then poured into a well-stirred mixture containing 100 ml. of water, 5 ml. of 10% aqueous potassium carbonate and some ice. The crystals of the ester which formed were collected on a Witt filter plate, washed with a liberal quantity of water, sucked dry and crystallized from ethyl alcohol. A preliminary filtration was made to remove cupric chloride and decolorizing charcoal which was used when necessary. Phenacyl esters of the lower aliphatic acids were best crystallized from aqueous ethyl alcohol, while benzene or acetone was usually found to be more satisfactory for the phenacyl esters of aromatic acids. Dioxane was found to be suitable for crystallizing the phenacyl succinates. The yield of crude air-dried esters varied from 61 to 100%, depending upon the acid used. With the exception of *p*-bromophenacyl formate and *p*-bromo- and *p*-phenylphenacyl succinate our melting points of the esters prepared were identical with or slightly higher than those reported in the literature.

Dibenzoylethylene.—A solution of 4.4 g. (0.030 mole) of diazoacetophenone in 30 ml. of dry benzene was warmed with 40 mg. of cupric chloride by means of a water-bath maintained at 45° until a steady evolution of gas was produced. The water-bath was then removed and the reaction mixture cooled occasionally in an ice-bath. After 20–30 minutes the evolution of gas had ceased, and the reaction mixture was warmed at 50–60° for a short time. Removal of the solvent under reduced pressure yielded 2.1 g. (60%) crude dibenzoylethylene. After two crystallizations from ethyl alcohol, bright yellow needles were obtained, m.p. 109.5–110°. The following derivatives were prepared: 1,2-dibenzoylethane,[8] m.p. 142–143°; 3,6-diphenylpyridazine,[8] m.p. 222–223°. A similar experiment carried out at a lower temperature (6°) afforded a somewhat lower yield of the ethylenic compound, and irradiation of the mother liquors from which the compound crystallized yielded 10 mg. of silky white needles of the higher melting isomer,[8] m.p. 134°.

The Wolff Rearrangement of *p*-Bromo-α-diazoacetophenone.—A solution of 4.0 g. (0.018 mole) of the diazoketone in 20 ml. of dioxane was heated to 65° and then added to a mixture of 30 ml. of concentrated aqueous ammonium hydroxide and 6 ml. of a 10% aqueous silver nitrate solution in a 50-ml. round-bottomed flask fitted with a reflux condenser. The mixture was boiled under reflux two hours, cooled, filtered and the crude product dissolved in hot ethyl alcohol. The solution was filtered, concentrated and then cooled to yield 1.9 g. (50%) of *p*-bromophenylacetamide, m.p. 195–196°. Pschorr[9] reports m.p. 192–194°.

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