in acetone. Table I lists the compounds prepared together with their melting points, yields, and elemental analyses.

ACKNOWLEDGMENT

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Acylbisdiazomethanes

CHARLES D. HURD and KENNETH C. PETERSEN
Northwestern University, Evanston, Ill. 60201

Adipoylbisdiazomethane and terephthaloylbisdiazomethane were used in testing the following new or modified reactions: silver acetate and water to initiate the Wolff rearrangement, 12% hydriodic acid to change the diazomethyl group to iodomethyl, iodine to convert diazomethyl to diiodomethyl, and nitric acid (without sodium nitrate) in ether solution to synthesize nitric esters.

MANY different systems have been used to initiate the rearrangement of acyldiazomethanes: $RCOCHN_2 + H_2O$ (catal.) $\rightarrow RCH_2COOH$. Originally, Wolff (*9*) used ammoniacal silver nitrate, but this and many other systems have proved to be quite erratic. Newman and Beal (*6*) reported an effective system, namely, silver benzoate and triethylamine, and they stressed the need for the triethylamine or a comparable base. This study shows that water works effectively in place of triethylamine and that silver acetate may replace silver benzoate. If used with ammonia, the new procedure (silver acetate and water) gives rise to amides, and if used with methanol, it yields methyl esters.

This rearrangement and other reactions were tested with acylbisdiazomethanes, $N_2CH—CO—R'—CO—CHN_2$, rather than the simpler acyldiazomethanes, $RCOCHN_2$. From adipoylbisdiazomethane (*8*), $(—CH_2CH_2COCHN_2)_2$, were obtained good yields of suberic acid, its amide, or its methyl ester.

Halomethyl ketones have been made from acyldiazomethanes by reaction with hydrochloric and hydrobromic acids but not with hydriodic acid: $RCOCHN_2 + HX \rightarrow RCOCH_2X + N_2$. In one reported application (*11*) of 48% hydroiodic acid there was reduction rather than iodination—e.g., benzoyldiazomethane into acetophenone. Iodomethyl ketones have been made previously by reaction of chloromethyl ketones with sodium iodide. If the concentration of hydriodic acid is about 12%, it is now established that iodination proceeds smoothly. In this manner, terephthaloylbisdiazomethane (*3, 7*) $N_2CHCO—C_6H_4—COCHN_2$, was converted into *p*-bis(iodoacetyl)benzene, $C_6H_4(COCH_2I)_2$.

Wolff (*10*) established in 1902 that iodine reacts with acyldiazomethanes: $RCOCHN_2 + I_2 \rightarrow RCOCHI_2 + N_2$, but the reaction has not been tested with acylbisdiazomethanes. In dioxane solution, iodine reacts smoothly with both adipoyl- and terephthaloylbisdiazomethane to yield, respectively, 1,1,8,8-tetraiodo-2,7-octanedione and *p*-bis(diiodoacetyl)benzene.

Fahr (*4*) synthesized 2,7-dioxo-1,8-octanediol dinitrate, $(—CH_2CH_2COCH_2ONO_2)_2$, in 41% yield from adipoylbisdiazomethane in methanol, using an aqueous mixture of nitric acid and sodium nitrate. To prepare the same compound in 62% yield, sodium nitrate was omitted, and ether was used as solvent for the mixture of adipoylbisdiazomethane and 70% nitric acid. Fahr's difficulty in combustion analysis was confirmed and both his value and ours for hydrogen were good, but both results for carbon and nitrogen were outside desired limits. Terephthaloylbis(methyl nitrate), $C_6H_4(COCH_2ONO_2)_2$, a new compound, was similarly synthesized from terephthaloylbisdiazomethane and 70% nitric acid in dioxane. Again, its analysis for nitrogen was unsatisfactory in spite of the apparent purity of the crystalline product.

EXPERIMENTAL

Reagents. Adipoylbisdiazomethane (*8*), prepared from adipoyl chloride and diazomethane, was obtained as yellow crystals, m.p. 70–72.5° C. Terephthaloylbisdiazomethane was reported by Ross (*7*) to decompose at 200° and by Dashevskaya (*3*) at 169° C. Both of their syntheses were by way of terephthaloyl chloride and diazomethane in dry ether. The decomposition point of the product made by their method was influenced by the purity of the acyl chloride since the diazo product did not lend itself to purification by crystallization. If the chloride was crystallized from hexane just before use, the decomposition point of the yellow crystals was 194°; otherwise, it was 180–4° C. Crystallization of the product from benzene lowered the decomposition point from 194° to 187° C. Its infrared spectrum showed a strong absorption at 4.73 microns which checks with the position of diazo absorption (*2,4*) for other diazo ketones.

p-Bis(iodoacetyl)benzene. Hydriodic acid (47%, 5 ml.) was diluted with 15 cc. of water, and then was added to 0.5 gram of terephthaloylbisdiazomethane. The mixture was warmed to 45° C. until a black-brown deposit appeared on the side of the flask. It was then cooled to 35° C., and 30 ml. of water was added. Nitrogen came off noticeably. The solution became red-brown and a precipitate formed. The mixture was left for a week before filtration; the yield was 0.6 gram (62%) of yellow needles which were recrystallized from methanol, m.p. 135–6° C. [lit. (*7*) 135°].

2,7-Dioxo-1,8-octanediol Dinitrate. To 10 ml. of ether, which contained 3 ml. of 70% nitric acid, was added 0.50 gram of adipoylbisdiazomethane in 40 ml. of dry ether. A vigorous effervescence continued for 20 minutes. After 2 hours the solution had evaporated to 25 ml. At 0° C., 0.42 gram of white solid separated, m.p. 107.5–8.5° C. [lit. (*4*) 108–8.6°].

Terephthaloylbis(methyl nitrate). Addition of 0.2 gram of terephthaloylbisdiazomethane to a solution of 2 ml. of concentrated nitric acid in 5 ml. of dioxane caused vigorous effervescence. Afterwards, the mixture was heated at 100° C. for 15 minutes, then water was added until a cloudy emulsion was observed. The precipitate that appeared on cooling to 0° C. was recrystallized twice: once from dioxane-water, m.p. 134–5° C.; then from methanol-water, m.p. 134–5° C.: yield, 0.15 gram. *It exploded when heated on a spatula.*

1,1,8,8-Tetraiodo-2,7-octanedione. A 10% solution of iodine was added to 0.3 gram of adipoylbisdiazomethane, both dissolved in dioxane, until the iodine color persisted. Nitrogen was evolved. After 15 minutes the mixture was filtered and 35 ml. of hexane was added. The 0.7 gram (70%) of precipitate was collected, rinsed with hexane, and recrystallized from methanol. The yellow plates melted at 125–6° C. to a red liquid. The crystals decomposed during 2 weeks of standing to a black tar.

Anal. Calcd. for $C_8H_{10}I_4O_2$: C, 14.9; H, 1.55. Found: C, 14.9; H, 1.48.

p-Bis(diiodoacetyl)benzene. The following details are typical of five separate syntheses of this diketone. To a slurry of 0.52 gram of terephthaloylbisdiazomethane in 15 ml. of dioxane was added a solution of 1.1 grams of iodine in 11 ml. of dioxane in 1-ml. portions. The color of iodine persisted at the end. After 15 minutes, 75 ml. of hexane was added causing precipitation (at 0° C.) of 0.96 gram (59%) of yellow solid. On heating, it liberated violet fumes at about 200° C. and melted with decomposition at 216° C. After crystallization from hot methanol, the decomposition point still was 216° C.

Anal. Calcd. for $C_{10}H_6I_4O_2$: C, 18.0; H, 0.91. Found: C, 18.8; H, 1.12.

The above diketone (0.15 gram) was treated with sodium hydroxide and iodine in aqueous dioxane. Iodoform separated within a few minutes and terephthalic acid was obtained on acidifying the filtrate.

Suberic Acid. Adipoylbisdiazomethane (25 mg.) was added to 10 ml. of water containing 10 mg. of silver acetate. The solution become warm and turned brown immediately with evolution of nitrogen. When reaction was completed the mixture was evaporated at 100° C. The brown residue was triturated with hot methanol (6 ml.). Filtration left a metallic black solid (12 mg.). The clear filtrate was then evaporated and 3 ml. of water was added to the white residue. The slurry was cooled and 19.2 mg. (86%) of white crystals of suberic acid was obtained, m.p. 138–40° C.

In contrast, only a 16% yield of suberic acid was realized from 200 mg. of adipoylbisdiazomethane (in 40 ml. of dioxane and 5 ml. of water) by ultraviolet irradiation.

Suberamide. A mixture of 100 ml. of 28% ammonium hydroxide, 0.10 gram of silver acetate, and 0.5 gram of adipoylbisdiazomethane was kept at 40° to 55° C. for 20 minutes. Nitrogen came off vigorously. The mixture was cooled and filtered. The brown precipitate (0.5 gram) was treated with 40 ml. of hot methanol. Filtration (hot) removed 0.1 gram of brown solid. The filtrate was concentrated to 10 ml., whereupon 0.35 gram (80%) of white, crystalline suberamide appeared; m.p. after recrystallization from methanol, 215–16.5° C. [lit. (*1*) 216°].

Methyl Suberate. A mixture of 0.1 gram of adipoylbisdiazomethane, absolute methanol (10 ml.) and silver acetate (15 mg.) did not react noticeably until 3 ml. of water was added. Then nitrogen bubbled out and the solution became dark brown and warm. After the solution had stood, it was processed for suberic ester by filtration to remove a black solid, evaporation to 2 ml., extraction with 20 ml. of ether, evaporation, and then addition of 1 ml. of water and re-extraction with ether. The ether layer was concentrated to 2 ml. and transferred to a microboiling point tube. Residual ether was evaporated, leaving one drop of colorless oil; b.p. 262° C. [lit. (*5*) 268°]. Saponification of this oil yielded suberic acid, m.p. 139–40° C.

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