Further studies on the applicability and mechanism of the reaction were discouraging. Thus, when acetophenone and its oxime were treated under similar conditions no substituted quinoline was produced, although about one mole of water per mole of oxime was evolved during heating for about five days. Similarly, the reaction of toluene with benzophenone oxime was even more sluggish as evidenced by the fact that only about 0.2 mole of water per mole of oxime was produced during heating under reflux for three days.

EXPERIMENTAL

Condensation of 2-acetonaphthone with 2-acetonaphthoxime (cis-methyl) to yield 2-(β-naphthyl)-4-methylbenzo[h]quinoline. Procedure A. A solution of 8.5 g. of 2-acetonaphthone (0.05 mole), 9.3 g. of 2-acetonaphthoxime (0.05 mole), and 0.04 g. of *p*-toluenesulfonic acid monohydrate in 50 ml. of anhydrous benzene was heated under reflux for 3 days. Water (1.20 ml.) was removed from the system by azeotropic distillation with benzene using a Dean-Stark apparatus. A trace of crystalline material, m.p. 185–198°, precipitated out of the distillate in the Dean-Stark tube. The benzene was removed from the reaction flask by evaporation under reduced pressure.

A portion of the above residue (0.17 g.) was dissolved in a minimum of benzene and added to the top of a glass column containing a 120 × 10 mm. (diam.) adsorbent column of alumina. The column was developed with benzene–petroleum ether (b.p. 30–60°) (1:3 v.:v.) until the fluorescent zone was eluted. Evaporation of the eluate gave a fluorescent crystalline compound (0.063 g.; about 40%) which was recrystallized several times from ethanol, m.p. 123–124° (corr.); mixed m.p. with an authentic sample[2] of 2-(β-naphthyl)-4-methylbenzo[h]quinoline, 122–124°. The infrared spectra of both compounds were identical. All attempts to isolate compound I in pure form were unsuccessful.

Procedure B. When the condensation was performed as in Procedure *A* except that *p*-toluenesulfonic acid was absent as catalyst, 0.9 ml. (0.05 mole) of water was formed and removed by azeotropic distillation. The benzoquinoline (18% yield) was isolated as described in Procedure *A*.

Procedure C. A solution of 1.70 g. of 2-acetonaphthone, 1.85 g. of 2-acetonaphthoxime, and 10 ml. of anhydrous benzene was heated in a rocking autoclave at 235° for 90 min. 2-(β-Naphthyl)-4-methylbenzo[h]quinoline (0.29 g., 9% yield) was isolated from the reaction mixture by the same method as described in Procedure *A*.

Condensation of acetophenone and acetophenone oxime. Acetophenone (0.1 mole) and acetophenone oxime (0.1 mole) were treated as described in procedure *A*. Water (1.8 ml.) was removed by azeotropic distillation during 4.5 days of continuous reflux. No substituted quinoline was present in the reaction product.

Condensation of benzophenone oxime and toluene. Benzophenone oxime (0.05 mole) and toluene (40 ml.) were refluxed for 4 days. Water (about 0.2 ml.) was azeotroped from the reaction mixture. The reaction mixture was not worked up because very little water was produced.

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The preliminary experimental work was done by Mr. A. R. Hubscher and Mr. Wing Wai.

(2) A. Rosenthal and A. Hubscher, *J. Org. Chem.*, in press.

(3) A. T. Blomquist, 16th National Organic Chemistry Symposium of the American Chemical Society, Seattle, Wash., June 15–17, 1959.

The Chemistry of Trinitromethane. III. Preparation of (2,2,2-Trinitroethyl)succinic Acid and Derivatives

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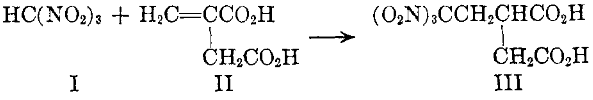
The reaction of equimolar quantities of trinitromethane (I) and itaconic acid (II) in methyl ethyl ketone has been found to yield (2,2,2-trinitroethyl)succinic acid (III) in 75% yield. The feasibility of utilizing I in Michael-type reactions has also been shown by Schimmelschmidt,[2] who prepared 5,5,5-trinitro-2-pentanone and alkyl 4,4,4-trinitrobutanoates by the addition of I to methyl vinyl ketone and to various acrylic esters.



$$\underset{\text{I}}{HC(NO_2)_3} + \underset{\text{II}}{H_2C{=}\underset{|\atop CH_2CO_2H}{C}CO_2H} \longrightarrow \underset{\text{III}}{(O_2N)_3CCH_2\underset{|\atop CH_2CO_2H}{C}HCO_2H}$$

III co-crystallized with II to give a product which had an analysis agreeing approximately with one mole III and two moles of II. Recrystallization of this mixture from water gave pure compound III.

III was stable in solutions of strong acids; however, in hot water it decomposed rapidly with the evolution of oxides of nitrogen to give 1,2,3-propanetricarboxylic acid. This hydrolysis of a

$$\text{III} \xrightarrow[\Delta]{H_2O} HO_2CCH_2CH(CO_2H)CH_2CO_2H$$

trinitromethyl group to a carboxyl group seems to be general except in those cases where 2,2,2-trinitroethanol can be formed. For instance, 4,4,4-trinitrobutanoic acid was converted into succinic acid; on the other hand, trinitroethyl esters[3] or *N*-trinitroethylamides[4] eliminated 2,2,2-trinitroethanol, which in turn was cleaved to I and formaldehyde.

In contrast to the trinitromethyl group, we found that a *gem*-dinitro group is not hydrolized under

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(1) (a) Abstracted from the Ph.D. thesis of E. H. White, Purdue University, 1950. (b) This research was supported by the Office of Naval Research.

(2) K. Schimmelschmidt, Ger. Patent **852,684,** Oct. 16, 1952.

(3) Unpublished studies of R. D. Lowrey, Ph.D. thesis, Purdue University, 1950.

(4) Unpublished studies of U. E. Lynch, Ph.D. thesis, Purdue University, 1952.

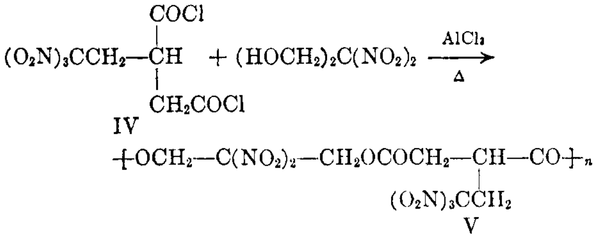
neutral, acidic, or basic conditions; for instance, 4,4-dinitropimelic acid was recovered unchanged from these reactions.

The addition of I to dimethyl itaconate gave dimethyl (2,2,2-trinitroethyl)succinate. This ester could not be obtained analytically pure, but its structure was established by conversion to acid III.

Treatment of III with thionyl chloride did not give the acid chloride; instead cyclization took place with the formation of (2,2,2-trinitroethyl)succinic anhydride. Its structure was established by elemental analysis and hydrolysis to III.

Attempts to prepare (2,2,2-trinitroethyl)succinoyl chloride (IV) by transchlorination with phthaloyl chloride[5] led only to decomposition. Compound IV was, however, obtained in 50% yield on treating III with phosphorus pentachloride. Compound IV was also formed by the addition of I to itaconyl chloride, as evidenced by the fact that addition of water to the crude reaction mixture gave III. However, attempts to isolate the acid chloride IV by distilling in high vacuum resulted in extensive decomposition.

In an attempt to utilize IV in the preparation of polyesters, it was refluxed in benzene with 2,2-dinitropropanediol in an atmosphere of nitrogen. This led only to the recovery of the starting materials. However, when the reaction was carried out in methylene chloride and in the presence of aluminum chloride as a catalyst, a high melting highly hygroscopic polymer was obtained the elemental analysis of which was in fair agreement with structure V.



$$\mathrm{(O_2N)_3CCH_2{-}\underset{\underset{\textstyle CH_2COCl}{|}}{\overset{\overset{\textstyle COCl}{|}}{C}}H + (HOCH_2)_2C(NO_2)_2 \xrightarrow[\Delta]{AlCl_3}}$$

IV

$$\mathrm{{-}\!\!\left[OCH_2{-}C(NO_2)_2{-}CH_2OCOCH_2{-}\underset{\underset{\textstyle (O_2N)_3CCH_2}{|}}{C}H{-}CO\right]_n}$$

V

EXPERIMENTAL

(2,2,2-Trinitroethyl)succinic acid (III). A solution of 15.1 g. (0.1 mole) of trinitromethane and 13 g. (0.1 mole) of itaconic acid in 90 ml. of methyl ethyl ketone was refluxed for 11 hr. The red solution was then evaporated *in vacuo* at room temperature. (*Caution must be exercised* in removing the solvent because the crude material explodes easily. Slow evaporation below 30° is recommended under vacuum provided by a water aspirator.) The residue, m.p. 147°, had an analysis agreeing approximately with a 1:2 molar ratio of compound III and itaconic acid.

Anal. Calcd. for $C_{16}H_{19}O_{18}N_3$: C, 35.48; H, 3.51; N, 7.76. Found: C, 35.50; H, 3.94; N, 8.71.

Recrystallization of the above residue with acidified (hydrochloric acid) water gave pure *(2,2,2-trinitroethyl)succinic acid*, m.p. 175°, 75% yield.

Anal. Calcd. for $C_6H_7O_{10}N_3$: C, 25.63; H, 2.51; N, 14.95; neut. equiv. 140. Found: C, 25.90; H, 2.34; N, 14.72; neut. equiv. 146.

Hydrolysis of III. One gram of acid III was heated in 40 ml. of water for 1 hr. Evaporation to dryness gave *1,2,3-propanetricarboxylic acid*, m.p. 160°; lit.[6] m.p. 166°.

Tris(p-bromophenacyl) ester, m.p. 137–138°, lit.[6] m.p. 138°.

Anal. Calcd. for $C_{30}H_{23}O_9Br_3$: C, 46.93; H, 3.00. Found: C, 46.52; H, 3.25.

Dimethyl (2,2,2-trinitroethyl)succinate. To a solution of 7.9 g. (0.05 mole) of dimethyl itaconate in 50 ml. of methyl ethyl ketone was added slowly 7.4 g. (0.05 mole) of trinitromethane, and the mixture refluxed for 6 hr. Removal of the solvent *in vacuo* and distillation of the residue gave 2.5 g. of unchanged ester, m.p. 76° and 5 g. (47%) of crude reaction product, b.p. 146–150° (4 mm.). Washing with water and redistilling gave dimethyl trinitroethylsuccinate, b.p. 137–140° (3 mm.); n_D^{20} 1.4643. Attempts to crystallize the oil from various solvents were fruitless. Hydrolyzing the oil with 10% hydrochloric acid gave acid III, m.p. 175°.

(2,2,2-Trinitroethyl)succinic anhydride. A mixture of 2 g. (7.1 mmoles) of (2,2,2-trinitroethyl)succinic acid and 20 ml. of thionyl chloride was refluxed for 3 hr. Removal of the excess thionyl chloride at reduced pressure left a solid. Recrystallization from methylene chloride gave (2,2,2-trinitroethyl)succinic anhydride, m.p. 86–87° (90% yield).

Anal. Calcd. for $C_6H_6O_9N_3$: C, 27.37; H, 1.90; N, 15.96. Found: C, 27.20; H, 2.12; N, 15.90.

(2,2,2-Trinitroethyl)succinoyl chloride. A mixture of 2.81 g. (0.01 mole) acid III and 4.25 g. (0.02 mole) of phosphorus pentachloride was placed in a flask fitted with a reflux condenser and drying tube. In a few minutes, a reaction set in causing liquefication of the mixture and evolution of hydrogen chloride. Gentle heating for about 4 hr. brought about complete solution, and the mixture was allowed to stand at 25° for 15 hr. The clear yellow solution was transferred to a "bulb still." (The still consisted of two bulbs of 3–4 cm. in diameter joined by 6–7 cm. of 10 mm.-tubing bent to an angle of about 5°). For several hours, a vacuum of about 1 mm. was maintained to permit any phosphorus oxychloride to distil into the cold trap. Using an oil bath the system was *slowly* warmed until a pale yellow liquid distilled at about 110° and 5 mm. The product, n_D^{20} 1.5052, solidified to a glass after being cooled to −75°. However, when the material warmed to room temperature a crystalline solid resulted. Recrystallization from ether gave (2,2,2-trinitroethyl)succinoyl chloride, m.p. 41–42° (50% yield).

Anal. Calcd. for $C_6H_5O_8N_3Cl_2$: C, 22.66; H, 1.59; N, 13.21. Found: C, 22.57; H, 1.80; N, 13.50.

Reaction of (2,2,2-trinitroethyl)succinoyl chloride with 2,2-dinitropropanediol. A mixture of 1.73 g. (5.45 mmoles) of (2,2,2-trinitroethyl)succinoyl chloride, 0.91 g. (5.45 mmoles) of 2,2-dinitropropanediol and 0.15 g. of resublimed aluminum chloride was heated gently for 6 hr. Filtering, dissolving in 5 ml. of dioxane and reprecipitating by the dropwise addition of acidified (hydrochloric acid) water gave 0.7 g. of polymer, m.p. 250°. The polymer was very hygroscopic and was dried *in vacuo* at 60°.

Anal. Calcd. for $C_9H_9O_{14}N_5$: C, 26.29; H, 2.21; N, 17.0. Found: C, 25.42; H, 2.60; N, 15.55.

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