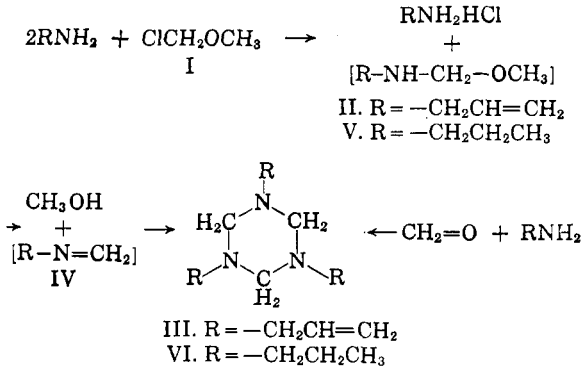
The structure of the product is deduced from its infrared spectrum which showed the absence of C—O—C absorption, and its identity with a sample of III prepared from formaldehyde and allylamine according to Dominikiewicz.[3]



Our attempt to prepare *n*-propylmethoxymethylamine V from *n*-propylamine and chloromethyl ether failed and again we obtained instead 1,3,5-tri-*n*-propylhexahydro-*s*-triazine VI identical with a sample prepared from formaldehyde and *n*-propylamine.[4]

EXPERIMENTAL

Allylamine and chloromethyl ether. To 38 g. allylamine in 100 ml. of dry benzene, 27 g. of chloromethyl ether in 100 ml. of dry benzene was added with stirring and ice cooling over a period of 45 min. The allylamine hydrochloride precipitated as a heavy oil on the bottom. The reaction mixture was extracted with 200 ml. of water and the benzene layer afforded on distillation 21.1 g. (46%) of 1,3,5-triallylhexahydro-*s*-triazine (III) b.p. 107–109° (7 mm.) (reported[1] b.p. 113°/7.5 mm.); n_D^{27} 1.4859.

Allylamine and formaldehyde. To 11.4 g. of allylamine in 75 ml. of diethyl ether 16.2 g. 37% formaldehyde was added dropwise with ice cooling. After stirring for 2 hr. the diethyl ether was separated from the aqueous layer and distilled *in vacuo*. Thus 12.2 g. (88.5%) of III, b.p. 117–119° (7.5 mm.); n_D^{23} 1.4872 was obtained. The infrared spectrum was identical with the infrared spectrum from the reaction product of allylamine and chloromethyl ether.

n-Propylamine and chloromethyl ether. To 89 g. (1.5 moles) of *n*-propylamine dissolved in 150 ml. of dry diethyl ether cooled in a Dry Ice-acetone bath to −76°, 55 g. (0.7 mole) of chloromethyl ether in 150 ml. of dry diethyl ether was added dropwise with stirring over a period of 2 hr. It was filtered while cold and the quantitative amount of *n*-propylamine hydrochloride, m.p. 156–157° was collected. The diethyl ether was removed under reduced pressure and distillation afforded 44 g. (89%) of 1,3,5-tri-*n*-propylhexahydro-*s*-triazine (VI), b.p. 87° (2 mm.); n_D^{25} 1.4570 (reported[4] n_D^{18} 1.4597).

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(3) M. Dominikiewicz, *Arch. Chem. Farm.* **2**, 160 (1935); *Chem. Abstr.* **30**, 1030[6]. He reported a b.p. of 138–141°C. for III while in our hands a b.p. of 107–109°/7 mm. was observed. This discrepancy most probably could be attributed to a typographical error.

(4) L. Henry, *Bull. Acad. Belg.*, (3) **26**, 200 (1893); (3) **29**, 23 (1895); R. Cambier and A. Brochet, *Bull. Soc. Chim.* (3), **13**, 404 (1895); L. Kahovec, *Z. Physik. Chem.*, **B43**, 364 (1939).

Condensation of Methyl Aryl Ketones with Their Oximes[1]

ALEX ROSENTHAL

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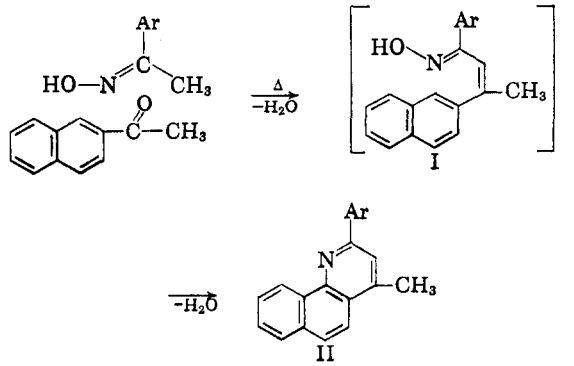
This paper deals mainly with the condensation of 2-acetonaphthone with its oxime to yield 2-(β-naphthyl)-4-methylbenzo[h]quinoline. This investigation arose as a consequence of our previous study[2] on the high pressure carbonylation of 2-acetonaphthoxime. In the aformentioned publication we reported the isolation and proof of structure of an abnormal product, namely 2-(β-naphthyl)-4-methylbenzo[h]quinoline. As the latter compound must have been formed by some type of condensation reaction, it appeared of interest to determine its mechanism of formation.

The fact that a compound identical to 2-(β-naphthyl)-4-methylbenzo[h]quinoline was produced by simply heating 2-acetonaphthoxime dissolved in benzene in an autoclave at 235° was evidence that the condensation reaction was independent of the presence of carbon monoxide, hydrogen, and dicobalt octacarbonyl. The yield of the benzoquinoline was doubled by heating equimolar quantities of 2-acetonaphthone with its oxime in the presence of benzene for prolonged periods of time. Water was removed continuously by azeotropic distillation in an apparatus fitted with a Dean-Stark distilling receiver. A further significant increase in the yield (about 40%) of the benzoquinoline was obtained by carrying out the condensation of the ketone with its oxime under identical conditions except that *p*-toluenesulfonic acid was used as a catalyst. In the latter case 1.2 moles of water per mole of oxime were produced. All these reactions strongly suggest that 2-acetonaphthone undergoes an aldol type of condensation with 2-acetonaphthoxime to yield compound (I) followed by its dehydration to yield 2-(β-naphthyl)-4-methylbenzo[h]quinoline (II) as pictured below:



Confirmatory evidence for the ring closure of oximes by dehydration has been recently reported by Blomquist.[3] Attempts to isolate compound I were unsuccessful.

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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(1) Financial assistance by the National Research Council, Canada, and by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. Presented in part, at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September 1959.

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

HENRY FEUER, EMIL H. WHITE, AND STANLEY M. PIER[1a,b]

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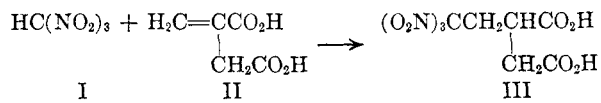
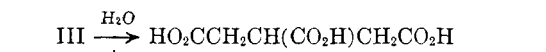
The reaction of equimolar quantities of trinitromethane (I) and itaconic acid (II) in methyl ethyl ketone has been found to yield (2,2,2-trinitroethyl)succinic acid (III) in 75% yield. The feasibility of utilizing I in Michael-type reactions has also been shown by Schimmelschmidt,[2] who prepared 5,5,5-trinitro-2-pentanone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



I II III

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



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

(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.