plete and the mixture was heated and stirred for an additional hour, then cooled and the contents dissolved in 2 l. of hot 2-propanol. The solution was filtered twice through Norit, then chilled, yielding 119.3 g. (66%) of colorless, shining platelets, m.p. 101–104°. This material was employed in the hydrolysis reaction below. Two additional recrystallizations from 2-propanol raised the melting point to a constant value of 105.5–107.5°. Since the melting point reported by Bourcet[7] for *p*-(dibromomethyl)benzophenone was 86.8°, the substance obtained was analyzed. A mixed melting point with the above *p*-benzoylbenzyl bromide (II), m.p. 112.5°, showed a marked depression, 84–98°.

Anal. Calcd. for $C_{14}H_{10}OBr_2$: C, 47.49; H, 2.85. Found: C, 47.52, 47.70; H, 2.88, 2.94.

p-Benzoylbenzaldehyde (XII). Hydrolysis of the above *p*-(dibromomethyl)benzophenone to *p*-benzoylbenzaldehyde was accomplished in two ways, the first employing sulfuric acid as the hydrolyzing agent and the second employing potassium oxalate in ethanol and water. The second method was found to give more reproducible results and is reported below. The aldehyde obtained by either procedure was contaminated with unchanged dibromide as well as *p*-benzoylbenzoic acid. Accordingly the product was isolated through its bisulfite addition compound, which was washed free of contaminants by means of ether, procedure preventing autooxidation of the aldehyde, which seemed to take place quite readily.

p-(Dibromomethyl)benzophenone (57.8 g.), potassium oxalate (31.0 g.), ethanol (400 ml.) and water (130 ml.) were heated under reflux for a period of 50 hr., after which the ethanol was distilled until the residue became heavily clouded with yellow oil, which solidified on cooling and stirring. The product was filtered, washed twice with water and then stirred into a saturated solution of sodium bisulfite. The resulting bisulfite addition compound was filtered, washed with ether until white and then dried. It weighed 42.1 g. (82%) and melted over a wide range from approximately 170 to 190°.

p-Benzoylmandelonitrile (XIII). The bisulfite addition compound prepared from 65 g. of *p*-(dibromomethyl)-benzophenone was placed in a beaker with water (200 ml.). The mixture was stirred while slowly adding a solution of sodium cyanide (9 g.) in water (50 ml.). Toward the end of the addition the last of the bisulfite addition compound had dissolved, and crystallization commenced. The white product was filtered, washed with water and dried. The crude product had m.p. 90–98°. A sample, recrystallized four times from toluene, had m.p. 105.5–107°.

Anal. Calcd. for $C_{15}H_{11}O_2N$: C, 75.93; H, 4.67. Found: C, 75.62, 75.44; H, 4.80, 4.81.

p-Benzoylmandelic acid (VI). The crude, moist *p*-benzoylmandelonitrile was immediately placed in a large evaporating dish containing concentrated hydrochloric acid (300 ml.). The covered mixture was allowed to stand overnight, during which time a heavy amber syrup settled. The mixture was heated on the steam bath for 30 min., whereupon the syrup dissolved and glistening, colorless crystals separated. The cooled *p*-benzoylmandelic acid was filtered, washed with water and dried, 38.7 g. (82%), m.p. 169–175°. One recrystallization from glacial acetic acid raised the m.p. to 176–179°, undepressed on admixture with the above sample of the same compound.

O-Acetyl-p-benzoylmandelic acid. p-Benzoylmandelic acid (4.446 g.) in acetyl chloride (20 ml.) was heated under reflux until a clear solution was obtained. The excess acetyl chloride was distilled *in vacuo*, and the residue crystallized on prolonged standing *in vacuo* at room temperature. The crude product weighed 4.68 g. (91%), m.p. 110–116°. Two recrystallizations from 1:1 benzene-ligroin raised the m.p. to a constant value of 135–136.5°.

Anal. Calcd. for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73. Found: C, 68.43, 68.56; H, 4.89, 4.81.

Methyl O-acetyl-p-benzoylmandelate. A solution of diazomethane in anhydrous ether was added dropwise with stirring to a solution of *O*-acetyl-*p*-benzoylmandelic acid (3.7 g.) in anhydrous ether until the yellow color of the diazomethane just persisted. Solvent evaporation yielded 3.9 g. of glistening white crystals. After one recrystallization from 2-propanol the product weighed 3.47 g. (89.7%) and had m.p. 80–82°.

Anal. Calcd. for $C_{18}H_{16}O_5$: C, 69.22; H, 5.16. Found: C, 69.46, 69.36; H, 5.29, 5.34.

Methyl p-benzoylmandelate. p-Benzoylmandelic acid (2.00 g.) was converted to its methyl ester using diazomethane in the manner described above. The crude product (1.91 g.; 89.9%), m.p. 107–109°, was purified by three recrystallizations from 2-propanol, m.p. 110–110.5°.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.99; H, 4.86.

Attempted Resolution of p-Benzoylmandelic Acid. Attempts to resolve *p*-benzoylmandelic acid using strychnine, brucine, cinchonine, nicotine and the α-phenylethylamines led to samples of amine salts which, on decomposition, gave acid samples, recrystallization of which yielded fractions of variable optical activity, indicating that resolution was incomplete. Our attempts to resolve this acid were thus only partially successful.

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Reaction of Chloromethyl Ether with Primary Amines

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The reaction of primary and secondary amines with chloromethyl ether (I) is reported[1] to give the alkylmethoxymethylamine derivatives. Several examples for the reaction of secondary amines are reported[1] whereas only one example of the reaction of a primary amine, namely allylamine, has been mentioned.[1]

In our attempt to prepare allylmethoxymethylamine (II) by the reaction of chloromethyl ether with allylamine, we have isolated instead of the expected product (II) 1,3,5-triallylhexahydro-*s*-triazine (III), which is probably formed by the trimerization of allylazomethine IV (R = $-CH_2-CH{=}CH_2$) an intermediate, produced from the initial product II by loss of methanol. This elimination is not surprising in view of the strong nucleophilic property of the amino group in the initial reaction product, allylmethoxymethylamine (II). The trimerization of IV is consistent with the fact that aliphatic aldimines, especially those from primary amines, trimerize rapidly, as evidenced by cryoscopic data.[2]

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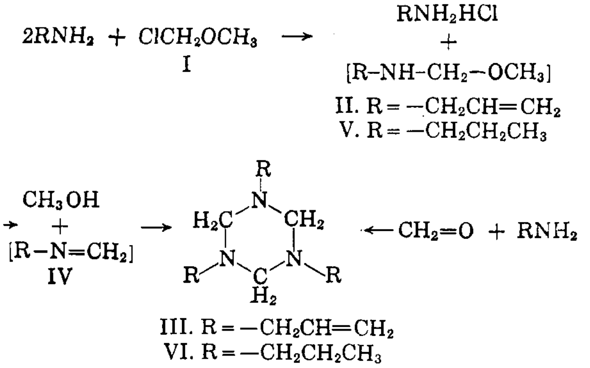
(1) F. E. Merck, German Patent **273,323** (1914); *Chem. Zentr.*, **1914 I**, 1718; *Frdl.*, **12**, 761.

(2) F. Klager, F. Kircher, and M. Block, *Ann.*, **547**, 23 (1941) in *The Chemistry of Heterocyclic Compounds, s-Triazine and Derivatives* by E. M. Smolin and L. Rapoport, Interscience, New York, 1959, p. 476.

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,** 1030⁶. 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]

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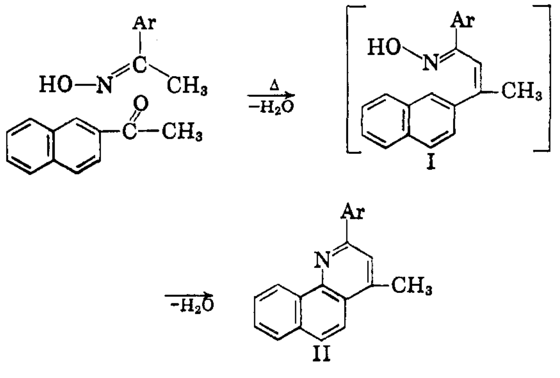
This paper deals mainly with the condensation of 2-acetonaphthone with its oxime to yield 2-(β-naphthyl)-4-methylbenzo[h]quinoline. This investigation arose as a consequence of our previous study[2] on the high pressure carbonylation of 2-acetonaphthoxime. In the aforementioned publication we reported 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.