tion and the acetone distilled from the filtrate. The residue was crystallized by solution in 5 drops of ethyl acetate which was cooled in ice and diluted with a few drops of benzin. The supernatant fluid was decanted from the precipitate that formed and the process of recrystallization repeated. The product was obtained as white flaky crystals, 15 mg., m.p. 93-95°.

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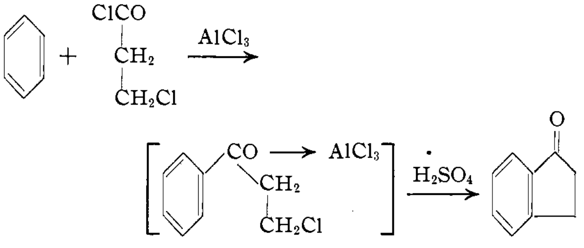
Acylation–Alkylation Studies. I[1]

BY ROBERT T. HART AND R. F. TEBBE[2]

The purpose of this investigation has been to effect the condensation of a bifunctional molecule with an aromatic nucleus to produce a number of indanones in a one-step reaction involving acylation and alkylation of the nucleus.

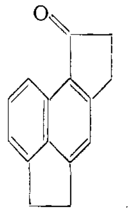
In general, two methods were employed: (a) a modification of the classical procedure involving a simplification of manipulation, *i.e.*, the regular Friedel–Crafts acylation is carried out and, after removal of solvent, the oily complex is heated with concentrated sulfuric acid at 80–100° for thirty to forty-five minutes before being poured onto crushed ice. In this procedure the acid not only decomposes the aluminum chloride–ketone complex but simultaneously causes intramolecular ring closure by cycli-alkylation



Although the yields by this method were generally somewhat lower than by the conventional two-step procedure in which the intermediary product of acylation was isolated, the present method affords an improvement in that the ketones are thus produced more easily and quickly. (b) The hydrogen fluoride method of Fieser and Hershberg[3] was extended to cover three additional cases.

For the bifunctional condensation of unsaturated acids and unsaturated acid chlorides with the aromatic nucleus, method (a) was found to be inferior to other methods previously reported.[4,5] Also, although method (b) gave excellent results in effecting the bifunctional condensation of unsaturated acids with the aromatic nucleus, it was found to be unsuccessful for the bifunctional condensation of β-chloropropionyl chloride, β-chloropropionic acid, β-propiolactone, acrylyl chloride, acrylic acid and hydracrylic acid with the aromatic nucleus, large amounts of intractable tars being formed.

An interesting exception was found when β-chloropropionyl chloride was condensed with a particularly reactive aromatic nucleus, acenaphthene. When this reaction was carried out at room temperature for eighteen hours followed by three hours of reaction at 90°, 29.7% of a chlorine-free ketone, m. p. 160–161°, which gave a correct analysis for $C_{15}H_{12}O$, was isolated indicating that bifunctional condensation had occurred. It is clear that this condensation did not occur across the peri positions of acenaphthene since the compound which would have resulted in such a case, 3,4-aceperinaphthane-7-one, m. p. 102.6–103.4°, has been reported previously.[6] It is therefore probable that the compound was formed by initial acylation in the α-position followed by cyclization into the β-position to give α-acenaphthindane-1-one (I). A compound having this probable structure was reported by Greune[7] to melt at 162–163°. Also, it should be noted that this structure is analogous to that obtained by Fieser and Hershberg[3] who found that acenaphthene reacts smoothly with crotonic acid in the presence of anhydrous hydrogen fluoride to give 1′-methyl-3′-keto-2,3-cyclopentenoacenaphthene.



I

Experimental

β-Chloropropionyl Chloride.—A mixture of 174 g. (2.42 moles) of β-propiolactone and 346 g. (2.9 moles) of thionyl chloride was allowed to react according to the method of Gresham and Shaver.[8] The chloride was obtained by distillation at the water-pump, 218 g. (71%), b. p. 80–83° (100 mm.).

Method (a): 4,7-Dimethyl-indanone-1.—A solution of 26.6 g. (0.21 mole) of β-chloropropionyl chloride and 21.2 g. (0.20 mole) of *p*-xylene in 25 cc. of carbon disulfide was added over forty-five minutes to 32 g. (0.24 mole) of anhydrous aluminum chloride covered with 125 cc. of carbon disulfide in a 1-liter three-necked round-bottomed flask fitted with condenser, stirrer, and addition tube. After

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[3] Fieser and Hershberg, THIS JOURNAL, **61**, 1272 (1939).

[4] Plattner and Furst, *Helv. Chim. Acta*, **28**, 1636 (1945).

[5] Koelsch, THIS JOURNAL, **65**, 59 (1943).

[6] Fieser and Jones, *ibid.*, **64**, 1666 (1942).

[7] Greune, *Chem. Zentr.*, **103**, II, 2238 (1932).

[8] Gresham and Shaver, U. S. Patent 2,411,875 (Dec. 3, 1946).

TABLE I

Aromatic nucleus	Bifunctional reactant	Catalyst	Yield, %	Indanone-1	M. p., °C.
Benzene	$ClCH_2CH_2COCl$	$AlCl_3$–H_2SO_4	54.5	Indanone-1	40–41
p-Xylene	$ClCH_2CH_2COCl$	$AlCl_3$–H_2SO_4	72.5	4,7-Dimethyl-[a,g]	76–77
α-Methylnaphthalene	$ClCH_2CH_2COCl$	$AlCl_3$–H_2SO_4	52.3	5-Methyl-(6,7-benzo)-[a]	130.5–131.5
o-Chlorotoluene	$ClCH_2CH_2COCl$	$AlCl_3$–H_2SO_4	45.0	5-Chloro-4(6)-methyl-[a]	77.5–78
p-Xylene	$CH_3CH{=}CHCOCl$	$AlCl_3$–H_2SO_4	35.4	3,4,7-Trimethyl-[b]	31–32
Benzene	$CH_3CH{=}CHCOCl$	$AlCl_3$–H_2SO_4	52.5	3-Methyl-[c,d]	Oil
p-Xylene	$CH_3CH{=}CHCOOH$	HF	81.0	3,4,7-Trimethyl-[b]	31–32
p-Xylene	$C_6H_5CH{=}CHCOOH$	HF	84.4	3-Phenyl-4,7-dimethyl-[e]	93.5–94.5
p-Xylene	$CH_2{=}C(CH_3)COOH$	HF	62.1	2,4,7-Trimethyl-[f]	Oil

[a] Mayer and Muller, *Ber.*, **60**, 2278 (1927). [b] Ref. 4. [c] Ref. 5. [d] B. p. 108–110° (4 mm.); semicarbazone, m. p. 206–207°. [e] V. Auwers and Risse, *Ann.*, **502**, 282 (1933). [f] New compound; see Experimental. [g] Plattner and Wyss, *Helv. Chim. Acta*, **24**, 483 (1941).

three hours of stirring at room temperature, the carbon disulfide was removed at the water-pump. To the residual oily complex was added 250 cc. of concentrated sulfuric acid and the mixture heated at 90° for forty-five minutes. After cooling the mixture to room temperature, it was poured onto 1 kg. of crushed ice. The flocculent yellow precipitate was extracted thoroughly with ether and benzene and the combined extracts washed successively with water, sodium carbonate solution, and water, and dried over anhydrous sodium sulfate. Replacement of the solvents by methanol yielded 23.2 g. (72.5%) of 4,7-dimethyl-indanone-1, m. p. 75.5–76.5°. Recrystallization from methanol raised the m. p. to 76–77°. This procedure is typical of that used for preparing all six indanones by method (a) as reported in Table I.

Method (b): 2,4,7-Trimethyl-indanone-1.—A mixture of 10 g. (0.094 mole) of *p*-xylene and 20.2 g. of 40% aqueous methacrylic acid (0.094 mole) was added to 115 g. of cold anhydrous liquid hydrogen fluoride in a pressure reactor and the mixture shaken to aid in solution of the reactants. The reactor was capped tightly and heated at 90° for six hours. After cooling, the mixture was poured into sodium carbonate solution and worked up in the usual manner. Vacuum distillation of the resultant oil yielded 10.2 g. (62.1%) of colorless oil, 2,4,7-trimethyl-indanone-1, b. p. 118–120° (3.5 mm.): n^{22}_D, 1.5550. *Anal.* Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.42; H, 8.67.

2,4-Dinitrophenylhydrazone, scarlet needles, m. p. 185.2–186° (cor.). *Anal.* Calcd. for $C_{18}H_{18}O_4N_4$: C, 61.01; H, 5.12; N, 15.83. Found: C, 61.52; H, 5.56; N, 15.55.

This procedure is typical of that used for preparing the three indanones by method (b) as reported in Table I.

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Preparation of Xanthene from Phenol

BY JANE HANAFIN[1]

The reaction of aluminum chloride with phenol, or with *o*-cresol–phenol mixtures, has been noted by investigators[2] as yielding diphenyl ether and xanthene. The small quantity of xanthene obtained could be attributed to cresol or other impurities present in the phenol, but no determination of the purity of the phenol used appears in the literature. The experiments reported below indicate that the impurities in the phenol here used were insufficient to account for the xanthene produced, and that the phenol itself must provide the methylene linkage between the aromatic rings in xanthene. The author is grateful to Dr. G. W. Wheland for suggesting and encouraging this work.

Experimental

Xanthene was prepared by the method of Merz and Weith,[2a] using only phenol and aluminum chloride in somewhat smaller amounts, *i. e.*, 103 g. and 60 g., respectively. Steam distillation was used to isolate the products. Xanthene was identified by its m. p., mixed m. p. with authentic samples, green fluorescence in sulfuric acid, and oxidation to xanthone; yield, 18 g. (20%) of the ether, 1.2 g. (1.3%) of the xanthene.

The amount of impurities in the phenol used was established by comparison of the cooling curves of an *o*-cresol–phenol mixture (0.49 mole % *o*-cresol) and of the phenol alone. This sensitive method is described by Schwab and Wichers.[3] The maximum impurity was found to be 0.16 mole %, insufficient to account for the 0.56 mole % xanthene recovered, even if the contaminant had been wholly *o*-cresol.

Previous experiments with *o*-cresol–phenol mixtures and aluminum chloride gave 4% xanthene. Mixed m. p.'s with other samples indicated that no methylxanthenes, reported to be a product with *o*-cresol,[4] were present.

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[2] (a) Merz and Weith, *Ber.*, **14**, 191 (1881); (b) Graebe, *ibid.*, **16**, 862 (1888).

[3] Schwab and Wichers, "Temperature, Its Measurement and Control," Am. Institute of Physics, 1941, p. 256.

[4] Postowsky and Lougowkin, *J. prakt. Chem.*, [2] **122**, 141 (1929).

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The Reaction of Amines with N-Methyl-N-nitroso-N'-nitroguanidine

BY RONALD A. HENRY

McKay and Wright[1] have shown that primary alkyl or arylamines and N-methyl-N-nitroso-N'-nitroguanidine react with the elimination of the methylnitrosamino group and formation of the corresponding alkyl or aryl substituted nitroguanidine. No mention is made, however, of the fate of the methylnitrosamino group. It has now been found that this latter group serves, either directly or indirectly, as a methylating agent since the principal by-product in the re-

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[1] McKay and Wright, THIS JOURNAL, **69**, 3028 (1947); (b) McKay, *ibid.*, **71**, 1968 (1949).