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.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MAINE
ORONO, MAINE

RECEIVED DECEMBER 10, 1949

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.

(1) Department of Surgery, University of Chicago, Chicago, Illinois.

(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).

JONES CHEMICAL LABORATORY
UNIVERSITY OF CHICAGO
CHICAGO, ILL.

RECEIVED FEBRUARY 8, 1950

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-

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

action of aniline and methylnitrosonitroguanidine in aqueous solution is N-methylaniline. Because the methylaniline is not formed at the expense of phenylnitroguanidine, the two reactions are not consuming methylnitrosonitroguanidine competitively. Small quantities of phenylmethylnitrosamine are also formed by a nitrosation of the methylaniline; the nitrous acid results from a slow hydrolysis[1b,2] of methylnitrosonitroguanidine.

Although McKay[2] has demonstrated that diazomethane is evolved when methylnitrosonitroguanidine is treated with aqueous potassium hydroxide, diazomethane does not methylate aniline under the conditions of this reaction.[3] An alternative mechanism would involve the formation of the 1(or 3)-methyl-3(or 1)-phenyltriazene from aniline and methylnitrosamine (or its rearrangement product, methyldiazohydroxide), followed by a loss of nitrogen. Although Dimroth[4] previously reported that this triazene decomposed on heating with water into methyl alcohol, aniline and nitrogen, a substantial amount of N-methylaniline is produced when it decomposes in the presence of aniline.

Aniline and 1-methyl-1-nitrosourea also react in a similar manner to yield phenylurea and N-methylaniline.

The list of dialkylamines that were found by McKay and Wright[1] to react with methylnitrosonitroguanidine to yield N-dialkyl-N′-nitroguanidines has been extended to include morpholine and piperidine. Benzalaminoguanidine forms a 1:1 addition compound with methylnitrosonitroguanidine.

Experimental[5]

By-products Formed in the Reaction of Aniline with Methylnitrosonitroguanidine.—The reaction of methylnitrosonitroguanidine with aniline was performed according to the procedure of McKay and Wright.[1] The oily material contaminating the product was extracted with diethyl ether. For each 1.4 g. of aniline employed, there was recovered approximately 0.4 to 0.5 g. of oil. A Hinsberg separation was made on 1.8 g. of this oil using 32 ml. of water, 4.3 g. of potassium hydroxide and 5.3 g. of benzenesulfonyl chloride. There was recovered 0.7 g. of material which did not form a sulfonamide. This fraction was characterized as follows: After carefully drying the material, it was dissolved in 3 ml. of absolute diethyl ether and the solution added to 4 g. of absolute ethanol saturated with dry hydrochloric acid. Orange-yellow needles separated after two days at 0°. This material did not melt although it decomposed about 165° when plunged into a hot bath. The free base that was recovered from this hydrochloride crystallized from benzene as greenish plates with a blue sheen; m. p. 114–115°. A mixed melting point with an authentic sample of *p*-nitrosomethylaniline was 115°. The picrate crystallized from ethanol as dark, olive-green needles with a blue sheen; m. p. 145–146° (dec.); a mixed melting point with a known specimen of *p*-nitrosomethylaniline picrate was the same.

The yield of alkali insoluble sulfonamide amounted to 1.5 g.; m. p. 75–77°. One recrystallization from aqueous ethanol raised the melting point to 79°. A mixed melting point with an authentic sample of N-methyl-N-phenylbenzenesulfonamide was 79°.

In another experiment in which methylnitrosonitroguanidine and aniline (1 to 4 molar ratio) reacted at 15 to 20° in a 50% aqueous ethanol solution, the yields of phenylnitroguanidine, phenylmethylnitrosamine and N-methylaniline (as the sulfonamide) were 92.6, 6.1 and 44.5%, respectively.

When a mixture of 3.0 g. of methylaniline, 2.0 g. of methylnitrosonitroguanidine and 10 ml. of water was allowed to stand at room temperature for three weeks, there were recovered 1.4 g. of methylnitroguanidine, m. p. 161–162°, and 1.0 g. of phenylmethylnitrosamine, characterized by conversion to *p*-nitrosomethylaniline.

Reaction of Aniline with 1-Methyl-1-nitrosourea.—Methylnitrosourea (4.12 g., 0.04 mole) was added all at once to a solution of 14.9 g. of aniline (0.16 mole) in 40 ml. of 50% aqueous ethanol at 10°. The mixture became homogeneous after standing about sixty hours at room temperature; gas was slowly evolved. The solution was extracted with five 50-ml. portions of petroleum ether (Skellysolve B) to remove the excess aniline and other oily products. By chilling the extracted aqueous solution there was recovered 2.44 g. of a compound melting at 148°. A mixed melting point with an authentic specimen of phenylurea was 148–149°. When the ether extracts were combined and evaporated, there was left 12.2 g. of a mixture of both solid and oily material. By trituration with a small volume of a 2:1 mixture of petroleum ether and diethyl ether, 1.27 g. more of phenylurea was recovered; the total yield of phenylurea amounted to 86.7%. A Hinsberg separation on the remaining oily products gave 2.6 g. of N-phenyl-N-methylbenzenesulfonamide, m. p. 78–79°; this recovery corresponded to a 26.3% conversion of aniline to methylaniline.

Decomposition of 1(or 3)-Methyl-3(or 1)-phenyltriazene in the Presence of Aniline.—The two-phase system formed by adding 12 g. of methylphenyltriazene[6] to a solution of 10 ml. of aniline, 35 ml. of 95% ethanol and 25 ml. of water was allowed to stand for two weeks at room temperature. A very slow evolution of gas occurred. When five drops of concentrated hydrochloric acid was added to adjust the *p*H to 6–6.5, there was a very vigorous and persistent evolution of gas; much of the oily layer disappeared. When gas evolution ceased, the solution was made strongly acid, and repeatedly extracted with diethyl ether. The aqueous layer was made alkaline and the amines extracted with petroleum ether. A Hinsberg separation on the recovered amines gave 5.0 g. of alkali insoluble sulfonamide, m. p. 77–78°. A mixed melting point with a sample of N′-phenyl-N-methylbenzenesulfonamide was 78–79°. The conversion to methylaniline amounted to 22.8%.

N-Nitroguanylmorpholine.—A solution of 0.9 g. (0.01 mole) of morpholine in 5 ml. of water was added during five minutes to a slurry of 1.47 g. (0.01 mole) of methylnitrosonitroguanidine in 5 ml. of water cooled in an ice-water-bath. The mixture was allowed to stand at 0° until gassing ceased. The white solid was removed by filtration and washed with two 5-ml. portions of cold water. The yield of product, melting at 187–188°, was 1.35 g. (77.6%). One recrystallization from 30 ml. of 95% ethanol, gave large, flat prisms; m. p. 188–189°.

Anal. Calcd. for $C_5H_{10}O_3N_4$: C, 34.48; H, 5.79; N, 32.17. Found: C, 34.37; H, 5.65; N, 31.51.

N-Nitroguanylpiperidine.—From 0.9 g. of piperidine there was obtained 0.62 g. of product (36.0%); m. p.

(2) McKay, THIS JOURNAL, **70**, 1974 (1948).

(3) This was pointed out to the author by Dr. George F Wright and has been confirmed experimentally. However, Werner, *J. Chem. Soc.*, **115**, 1096 (1919), in a study of the analogous reaction of ammonia with 1-methyl-1-nitrosourea also explained the formation of the by-products by assuming that diazomethane reacted with ammonia. Only a very limited number of examples are reported in which diazomethane has methylated an amine: with *p*-toluidine to give N-methyl-*p*-toluidine, v. Pechmann, *Ber.*, **28**, 858 (1895); with glycine to give betaine, Biltz and Paetzold, *ibid.*, **55**, 1067 (1922); and with hydrazine to give methylhydrazine, Staudinger and Kupfer, *ibid.*, **45**, 501 (1912).

(4) Dimroth, *ibid.*, **36**, 911 (1903).

(5) All melting points are corrected.

(6) Dimroth, *Ber.*, **38**, 2329 (1905).

154–156°. After one recrystallization from 15 ml. of ethanol, the melting point was 155–156°.

Anal. Calcd. for $C_6H_{12}O_2N_4$: N, 32.54. Found: N, 32.36.

Benzalaminoguanidonium Salt of Methylnitrosonitroguanidine.—A solution of 1.62 g. (0.01 mole) of benzalaminoguanidine in 10 ml. of water and 5 ml. of ethanol was mixed with 1.47 g. (0.01 mole) of methylnitrosonitroguanidine. The mixture was allowed to stand for twenty-four hours at room temperature. There was some gas evolution. After chilling the solution at 0° for one hour, the white solid was removed by filtration and washed with a small volume of cold water; yield 2.6 g. (84.1%); m. p. 123–124°. A rapid recrystallization from 110 ml. of absolute ethanol gave small, flat, white needles; m. p. 124–125° with decomposition. A mixed melting point with methylnitrosonitroguanidine was 110°.

Anal. Calcd. for $C_8H_{10}N_4 \cdot C_2H_5O_3N_5$: C, 38.83; H, 4.89; N, 40.76. Found: C, 39.01; H, 4.94; N, 41.14.

An absolute ethanol solution of this compound gave a picrate decomposing at 255°; a mixed melting point with an authentic sample of benzalaminoguanidine was 254–255°.

A slurry of 1.0 g. of the addition compound, 0.8 g. of aniline and 5 ml. of water evolved gas for two days at room temperature. The resulting paste was chilled to 0°, and the *p*H adjusted to about 4.5 with concentrated hydrochloric acid. The solid material was removed by filtration and washed with two 5-ml. portions of cold ethanol. The yield of dried product was 0.2 g.; m. p. 151–152°. A mixed melting point with a sample of phenylnitroguanidine was 153°.

This salt decomposed with gas evolution when boiled for a few minutes with 95% ethanol. Both benzalaminoguanidine picrate (m. p. 254–255°) and an unknown picrate, melting at 208–209° (dec.) after recrystallization, were recovered by treating the resulting solution with picric acid.

INORGANIC CHEMISTRY BRANCH
CHEMISTRY DIVISION, RESEARCH DEPARTMENT
U. S. NAVAL ORDNANCE TEST STATION
CHINA LAKE, CALIFORNIA RECEIVED SEPTEMBER 13, 1949

3-Chloro-1,1,1-trifluoro-2-propanone

BY HUBERT M. HILL, E. B. TOWNE AND J. B. DICKEY

The only reference in the literature to 3-chloro-1,1,1-trifluoro-2-propanone is that included in a patent.[1] The method of preparation, which was not given, consisted in the acid hydrolysis of ethyl α-chloro-γ,γ,γ-trifluoroacetoacetate. This compound was prepared by the chlorination of ethyl γ,γ,γ-trifluoroacetoacetate.

Both of these compounds are powerful nasal irritants and should be handled only under a hood.

Ethyl α-Chloro-γ,γ,γ-trifluoroacetoacetate.—Chlorine was passed through 120 g. of ethyl γ,γ,γ-trifluoroacetoacetate at 20° until a gain in weight of 26 g. was obtained. The dissolved hydrogen chloride was removed by blowing air through the solution. Rectification yielded 25 g. of prerun to 67° (23 mm.) and 112 g. of product, b.p. 67–69° (23 mm.), $n^{19.5}D$ 1.3890.

Anal. Calcd. for $C_6H_6ClF_3O_3$: Cl, 16.2. Found: Cl, 16.1.

3-Chloro-1,1,1-trifluoro-2-propanone.—A mixture of 86.5 g. of ethyl α-chloro-γ,γ,γ-trifluoroacetoacetate and 200 ml. of 30% sulfuric acid was refluxed, with stirring, for eight hours. The resultant solution was extracted with six 50-ml. portions of ether, and the extract was dried by treatment with phosphorus pentoxide and rectified from fresh phosphorus pentoxide. There was obtained 23.7 g. of product, b.p. 71–72°, $n^{20}D$ 1.3440.

Anal. Calcd. for $C_3H_2ClF_3O$: Cl, 24.2. Found: Cl, 23.6.

(1) Dickey and McNally, U. S. Patent 2,442,345, June 1, 1948.

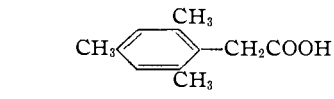
RESEARCH LABORATORY
KODAK PARK WORKS
EASTMAN KODAK COMPANY
ROCHESTER 4, NEW YORK RECEIVED FEBRUARY 21, 1950

Coupling of Certain Benzyl Halides in the Formation of Grignard Reagents

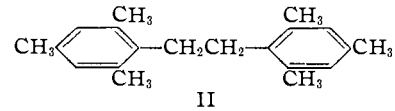
BY WILBERT J. HUMPHLETT AND CHARLES R. HAUSER

The tendency of certain substituted benzyl halides to undergo coupling in the preparation of their Grignard reagents is well known. Some new observations of this sort are reported below.

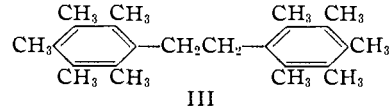
α²-Chloroisodurene (2,4,6-trimethylbenzyl chloride), on treatment with magnesium under the usual conditions, followed by carbonation, gave only a 13% yield of the corresponding acid (I) and a 59% yield of the coupled product (II). Pentamethylbenzyl chloride,[1] on similar treatment, gave only a trace of the corresponding acid and a 70% yield of the coupled product (III). Under similar conditions benzyl chloride produced an 82% yield of phenylacetic acid. Under conditions which produce a good yield of allylmagnesium chloride, α²-chloroisodurene gave, on carbonation of the Grignard reagent, a 29% yield of the acid (I) and a 40% yield of the coupled product (II). 2,4,6-Tribromobenzyl bromide failed to react with magnesium in refluxing ether even in the presence of added iodine. However, when treated with methylmagnesium iodide this halide underwent coupling to form (IV) in 62% yield.



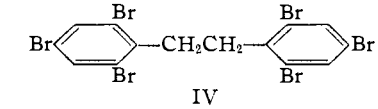
I



II



III



IV

(1) In connection with another study, an attempt was made to treat this chloride with sodium cyanide in ethanol and with cuprous cyanide by the von Braun method, but no appreciable amounts of the corresponding nitrile were obtained. This seems rather surprising in view of the good yield of nitrile produced in the corresponding reaction between α²-chloroisodurene and sodium cyanide; see Fuson and Rabjohn, "Organic Syntheses," Vol. 25, John Wiley and Sons, Inc., New York, N. Y., 1945, p. 65.