Acknowledgment.—Members of the Analytical and Microanalytical groups performed the analyses here.

Experimental

β-Dimethylaminopropionamide.—A mixture of dimethylamine (49.5 g., 1.10 moles) and acrylamide (71.0 g., 1.00 mole) in methanol (300 ml.) stood for three days at room temperature. It was then distilled to give 73.0 g. (63%) of product, b.p. 107–110° (3.5 mm.). It was distilled again, b.p. 96° (0.5 mm.), m.p. 39.8–40.3°.

Anal. Calcd. for $C_5H_{12}N_2O$: C, 51.69; H, 10.42; N, 24.12. Found: C, 51.51, 51.66; H, 10.50, 10.60; N, 23.27.

β-Dipropylaminopropionamide.—A mixture of dipropylamine (110.0 g., 1.09 moles) and acrylamide (71.0 g., 1.00 mole) in 95% alcohol (85 ml.) stood at room temperature for two weeks. It was then distilled, giving 138.4 g. (80%) of product, b.p. 154–157° (3.5 mm.).

Anal. Calcd. for $C_9H_{20}N_2O$: N, 16.27. Found: N, 16.09.

β-Dibutylaminopropionamide.—A mixture of dibutylamine (142.0 g., 1.10 moles) and acrylamide (71.0 g., 1.00 mole) in 95% alcohol (85 ml.) stood for eight days at room temperature. It was then distilled to give 148.8 g. (74%) of product, b.p. 162–167° (3 mm.).

Anal. Calcd. for $C_{11}H_{24}N_2O$: C, 65.95; H, 12.08; N, 13.99. Found: C, 65.97, 65.94; H, 11.70, 11.77; N, 14.07, 14.38.

β-4-Morpholinylpropionamide.—Morpholine (98.0 g., 1.12 moles) was added to a solution of acrylamide (71.0 g., 1.00 mole) in 95% alcohol (85 ml.). The reaction was more vigorous than were the preceding three, and cooling with a water-bath was necessary to hold the temperature at 35–40°. After several hours, the solution was evaporated to a volume of 200 ml., then chilled. The crystallized product was filtered off and dried; wt. 78.2 g. (49%), m.p. 97.5–100°. After two recrystallizations from benzene, the m.p. was 98–100°.

Anal. Calcd. for $C_7H_{14}N_2O_2$: C, 53.14; H, 8.92; N, 17.71. Found: C, 53.29, 53.20; H, 8.81, 9.02; N, 17.49, 17.67.

N,N-Dimethyl-β-dimethylaminopropionamide.—A mixture of ethyl acrylate (50.0 g., 0.50 mole) and dimethylamine (67.5 g., 1.50 moles) was heated for 18 hours at 200°. Distillation gave 58.2 g. (81%) of product, b.p. 111–114° (15 mm.). It was distilled again, b.p. 112° (15 mm.), $n^{25}D$ 1.4590.

Anal. Calcd. for $C_7H_{16}N_2O$: C, 58.30; H, 11.18; N, 19.43. Found: C, 58.16, 58.21; H, 11.40, 11.27; N, 18.83.

Decomposition Experiment.—A mixture of N,N-dimethyl-β-dimethylaminopropionamide (50.0 g., 0.35 mole) and hydroquinone (1.0 g.) was heated at 200° for 20 minutes. No change was noticed at this temperature so the mixture was heated to 210–215°, when it boiled vigorously. After having been refluxed for four hours at this temperature, the mixture had lost 10.2 g. of weight. Distillation of the mixture gave 13.0 g. (38%) of N,N-dimethylacrylamide, b.p. 96–104° (35 mm.). The mixture became very viscous during distillation; apparently extensive polymerization of the acrylamide occurred.

Anal. Calcd. for C_5H_9NO: N, 14.13; I_2 no. (cg. of I_2 per g. of sample), 256. Found: N, 14.44; I_2 no., 226.

The iodine numbers of substituted acrylamides are difficult to determine precisely because of the uncertainty in judging the end-point.

N,N-Dimethyl-β-dimethylaminoisobutyramide.—A mixture of methyl methacrylate (50.0 g., 0.50 mole) and dimethylamine (67.5 g., 1.50 moles) was heated 16 hours at 200°. Distillation of the product gave 28.5 g. (36%) of product, b.p. 108–117° (15 mm.). The material appeared to decompose to some extent during distillation and a sharper boiling point could therefore not be taken. The distilled material had a pronounced odor of dimethylamine.

Anal. Calcd. for $C_8H_{18}N_2O$: N, 17.71. Found: N, 16.94.

Decomposition Experiment with N,N-Diethyl-β-diethylaminopropionamide.—A mixture of the amide (100.0 g., 0.50 mole) and hydroquinone (1.0 g.) was heated in a flask to which was attached a six-inch column packed with glass beads. Heating was continued for 15 minutes at 180–200° while diethylamine (18.1 g.) was condensed and drawn off at the top of the column. The residue weighed 78.7 g. It was fractionated to yield 46.6 g. of N,N-diethylacrylamide, b.p. 95–99° (18 mm.).

Anal. Calcd. for $C_7H_{13}NO$: N, 11.02; I_2 no., 200. Found: N, 10.58; I_2 no., 179.

N,N-Dibutyl-β-dibutylaminopropionamide.—A mixture of methyl acrylate (251 g., 2.92 moles) and dibutylamine (920 g., 7.13 moles) was refluxed under a short column attached to a take-off head. The temperature of the refluxing mixture was kept high by removal of the methanol formed through the head. After 40 hours of heating, the formation of methanol had ceased. The mixture was distilled under reduced pressure to give unreacted dibutylamine, 334.4 g. of N,N-dibutylacrylamide, b.p. 95–102° (1 mm.), and 138.5 g. of N,N-dibutyl-β-dibutylaminopropionamide, b.p. 120–138° (1 mm.). That this product decomposes during distillation is indicated by the fact that the 138.5 g., redistilled, gave only 40.0 g. of material, b.p. 120–125° (1 mm.). There was a substantial forerun from this redistillation. Complete purification for analysis appeared impossible because of the ease with which decomposition took place.

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The Reaction of Trityl Methyl Ether with Phenyllithium and with *n*-Butyllithium

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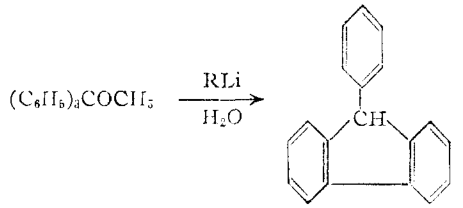
RECEIVED JULY 1, 1952

A number of reactions of trityl ethers and halides with organometallic compounds have been studied. Trityl methyl, ethyl and phenyl ethers react with phenylmagnesium bromide under forcing conditions to yield varying amounts of tetraphenylmethane.[1] The same hydrocarbon is obtained, together with triphenylmethane and a large amount of diphenyl-*p*-xenylmethane, from the reaction of trityl chloride with phenylmagnesium bromide.[2] Small amounts of higher molecular weight hydrocarbons, such as phenyldi-*p*-xenylmethane, are also formed.[3] Trityl chloride reacts with *n*-butyllithium in petroleum ether to produce 1-tritylbutane,[4] while the reaction with phenyllithium in diethyl ether leads to *p*-benzohydryltetraphenylmethane.[5]

We have found that trityl methyl ether reacts with phenyllithium under forcing conditions, and with *n*-butyllithium under mild conditions, to produce a scarlet mixture which yields 9-phenylfluorene on hydrolysis.



When a mixture of trityl methyl ether and phenyllithium is carbonated, 9-phenylfluorene-9-car-

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(1) M. Gomberg and O. Kamm, THIS JOURNAL, **39**, 2009 (1917).

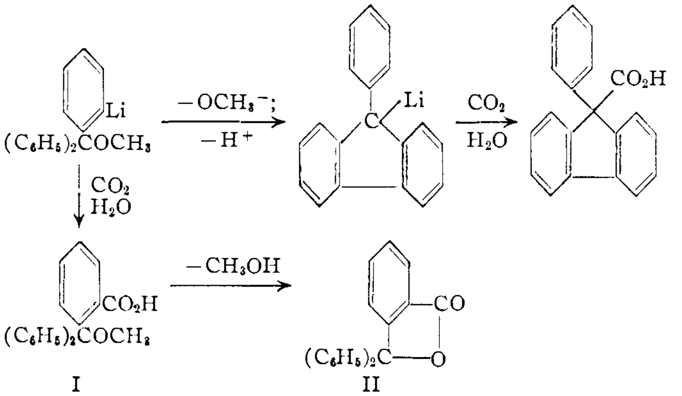
(2) H. Gilman and H. L. Jones, *ibid.*, **51**, 2840 (1929).

(3) C. S. Schoepfle and S. G. Trepp, *ibid.*, **58**, 791 (1936).

(4) C. S. Marvel, F. D. Hager and D. D. Coffman, *ibid.*, **49**, 2323 (1927).

(5) J. Wynstra, Doctoral Dissertation, University of Michigan, 1943 [*Microfilm Abstr.*, **5**, 15 (1943); *C. A.*, **38**, 3637 (1944)].

boxylic acid is isolated. It seems reasonable to suppose that the reaction proceeds through preliminary metalation of the ether in an ortho position, followed by ring closure with loss of a methoxide ion and a proton to yield 9-phenyl-9-fluorenyllithium. That the metalation product does not decompose quantitatively into 9-phenyl-9-fluorenyllithium is indicated by the isolation of 3,3-diphenylphthalide (II) from the carbonation of a mixture of trityl methyl ether and *n*-butyllithium. This product presumably arises from the loss of methanol from the initially formed acid I,[6] produced by the carbonation of the metalated ether. The postulated metalation is similar to the ortho-metalation of triphenylcarbinol by *n*-butyllithium.[7] In the latter reaction no ring closure occurs, presumably because of the difficulty of elimination of the lithoxide ion-pair.



Further work relating to the scope and mechanism of this reaction is in progress.

Experimental

Trityl Methyl Ether.—The ether was prepared from triphenylcarbinol by the method of Smith and Smith.[8] Yields of 77–88% were obtained in preparations starting with 20 g. (0.077 mole) of the carbinol. It is possible to modify the procedure by using concentrated sulfuric acid instead of 100% sulfuric acid. In one such modified preparation, a yield of 91% of the pure ether was obtained from 50 g. of triphenylcarbinol. In all cases, the lower-melting form of the ether, m.p. 83–84°,[9] was obtained.

Reactions of Trityl Methyl Ether with Phenyllithium. Run I.—Trityl methyl ether (27.4 g., 0.10 mole) was dissolved in 100 ml. of anhydrous diethyl ether, and 0.11 mole of an ethereal solution of phenyllithium was added. The reaction mixture was refluxed overnight. (When the reaction was interrupted at this point by hydrolysis, trityl methyl ether was recovered.) The solvent was then distilled from the reaction mixture until the residue was almost sirupy. At this point, foaming occurred and a scarlet color developed. The mixture was hydrolyzed with water and extracted with a large volume of diethyl ether. From the organic layer was obtained 8.2 g. (34%) of crude 9-phenylfluorene, m.p. 120–130°. Recrystallization from benzene yielded 5.0 g. (21%) of pure 9-phenylfluorene, m.p. 144.5–145.5°, identified by a mixed melting point with an authentic specimen.

Run II.—To 10 g. (0.036 mole) of trityl methyl ether was added 0.073 mole of an ethereal solution of phenyllithium. The solvent was removed by distillation, and 60 ml. of toluene was added to the sirupy residue. The resulting brown suspension was refluxed for 24 hours. A crimson color and precipitate appeared shortly after refluxing began. The mixture was hydrolyzed with iced, dilute sulfuric acid, and the organic layer was separated and freed of solvent by distillation. The residue was refluxed with 95% ethanol, and the mixture cooled and filtered to yield 6.28 g. (71% crude yield) of brown powder, m.p. 120–130°. Recrystallization from ethanol and then from benzene yielded 2.30 g. of 9-phenylfluorene, m.p. 146–147°. An additional 0.72 g. was recovered from the mother liquor bringing the total yield of pure material to 3.02 g. (34%).

Run III.—The amounts and procedure were the same as those of Run II, except that the crimson mixture was carbonated by pouring over a slurry of Dry Ice and diethyl ether. After the Dry Ice had evaporated, the mixture was hydrolyzed with ice-water, and the water layer was separated and acidified with hydrochloric acid. The resulting precipitate was filtered off, washed with water, and dried to yield 6.0 g. (57% crude yield) of acidic material, m.p. 170–192°. The crude product was extracted with boiling diethyl ether, and the residue was dissolved in the minimum amount of benzene at room temperature. The solution was filtered to remove a trace of suspended material, and the filtrate was diluted with a twofold volume of petroleum ether (b.p. 60–70°). The solution deposited crystals after standing for several hours at room temperature. These were filtered off, washed with petroleum ether (b.p. 60–70°), and dried to yield 1.36 g. (13%) of 9-phenylfluorene-9-carboxylic acid, m.p. 192–193° dec. A mixed melting point with an authentic specimen (for preparation, see the following section) was undepressed.

9-Phenylfluorene-9-carboxylic Acid.[10]—A solution of 1.0 g. (0.0041 mole) of 9-phenylfluorene in 20 ml. of diethyl ether was treated with 0.01 mole of an ethereal solution of *n*-butyllithium. Heat was evolved, and an orange color developed immediately. The solution was refluxed for five hours and then poured over a slurry of Dry Ice and diethyl ether. After the Dry Ice had evaporated, the mixture was hydrolyzed with ice-water. The aqueous layer was separated and acidified with hydrochloric acid. The mixture was allowed to stand for several hours until the precipitated acid had coagulated sufficiently to permit filtration. The fine, white needles of 9-phenylfluorene-9-carboxylic acid were filtered off, washed with water, and dried. The yield was 0.94 g. (80%) of material melting at 189–190.5° with decomposition.

Reactions of Trityl Methyl Ether with *n*-Butyllithium. Run I.—Thirteen grams (0.0475 mole) of trityl methyl ether was refluxed with 0.14 mole of *n*-butyllithium in 150 ml. of diethyl ether for 24 hours. The scarlet mixture was hydrolyzed with ice. The organic layer was separated and evaporated to yield a yellow tar. This was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on alumina, using benzene as an eluent. Most of the fractions so obtained yielded yellow sirups when the solvent was evaporated, but one large fraction of semi-crystalline material was isolated. This was digested with 95% ethanol to yield 1.96 g. (20%) of 9-phenylfluorene, m.p. 145–147°, identified by mixed melting point with an authentic specimen.

Run II.—Ten grams (0.036 mole) of trityl methyl ether was refluxed with 0.036 mole of *n*-butyllithium in 60 ml. of diethyl ether for 24 hours, and the resulting mixture was poured over a slurry of Dry Ice and diethyl ether. An intense purple color developed immediately (no such color was observed in the carbonation of the reaction mixture of trityl methyl ether and phenyllithium described above). After the Dry Ice had evaporated, water was added, and the aqueous layer was separated and acidified with iced, dilute hydrochloric acid. The color changed from purple to orange during acidification, and an orange tar separated. This was extracted with diethyl ether. The extract was freed of solvent to yield a dark tar which, on standing at room temperature for several days, dried to a purple semisolid. The latter was dissolved in benzene and the resulting solution was treated with petroleum ether (b.p. 60–70°). The mixture was filtered to remove a little dark solid, and the

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[6] The spontaneous loss of methanol from the analogous acid, *o*-carboxybenzyl methyl ether, has been noted: S. N. McGeoch and T. S. Stevens, *J. Chem. Soc.*, 1465 (1934).

[7] H. Gilman, G. E. Brown, F. J. Webb and S. M. Spatz, This Journal, **62**, 977 (1940).

[8] H. A. Smith and R. J. Smith, *ibid.*, **70**, 2400 (1948).

[9] H. H. Hatt, *J. Chem. Soc.*, 483 (1938).

[10] For an analogous preparation of this compound by the carbonation of 9-phenyl-9-fluorenylsodium, see W. Schlenk and E. Bergmann, *Ann.*, **463**, 98 (1928).

filtrate was evaporated to a sirup which, on being triturated with 95% ethanol, deposited white crystals. These were filtered off, washed with cold 95% ethanol, and dried to yield 1.77 g. (18.2%) of 3,3-diphenylphthalide, m.p. 117.5–118.5°. Identification was made by a mixed melting point with an authentic specimen, and by comparison of the infrared absorption spectrum with that of an authentic specimen.

Run III.—A solution of 12.3 g. (0.045 mole) of trityl methyl ether and 0.091 mole of *n*-butyllithium in 100 ml. of diethyl ether was distilled under nitrogen until most of the solvent had been removed. A red color developed during this time. Ninety ml. of toluene was added to the residue, and the resulting mixture was refluxed for 24 hours and then hydrolyzed with iced, dilute sulfuric acid. The organic layer was separated and evaporated to yield a dark brown sirup. This material, and all fractions later obtained from it, were exceptionally difficult to purify. Some tarry crystals were obtained by refluxing the sirup with benzene and cooling; an additional crop of crystals was obtained by evaporating the benzene filtrate and triturating the residue with a mixture of acetone and carbon tetrachloride. The combined crystals (3.1 g., m.p. 123–131°) were dissolved in benzene and chromatographed on alumina, using benzene as an eluent. Most of the fractions so obtained were sirups or tars. Several semi-crystalline fractions were combined and recrystallized from a mixture of benzene and 95% ethanol to yield 1.91 g. (17.5% crude yield) of yellow solid, m.p. 128–139°. The product was dissolved in methanol, treated with Norit A, and filtered. The filtrate was evaporated to yield a yellow solid, which was dissolved in benzene and chromatographed on alumina, using petroleum ether (b.p. 60–70°) as an eluent. The crystalline fractions so obtained were extracted with a small volume of boiling methanol. The undissolved material weighed 0.40 g. (3.8%) and melted at 145–147°. A mixed melting point with an authentic specimen of 9-phenylfluorene was undepressed.

Acknowledgment.—The authors are grateful to Dr. V. A. Fassel and Mr. Marvin Margoshes for the measurement of infrared absorption spectra, which will be reported elsewhere.

CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY
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Low Pressure Catalytic Hydrogenation of Nitroparaffins

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RECEIVED AUGUST 18, 1952

Although low pressure catalytic hydrogenation of aromatic nitro-compounds is routine, few applications to nitroparaffins have been reported. The use of Raney nickel and hydrogen as low as six atmospheres pressure is reported to reduce nitroparaffins to amines[1]; however, the use of platinum and hydrogen is referred to as "mainly for aromatic nitro compounds."[2] Hydrogenation at two to three atmospheres pressure with palladium in the presence of oxalic acid is stated to yield hydroxylamine derivatives from nitroparaffins.[3] Recently a study of the use of nitro compounds (including nitroethane) as hydrogen acceptors in the presence of platinum catalyst has been described[4]; however, neither the isolation of the hydrogenation products nor yields were reported.

In view of this, the impression is frequently obtained that catalyzed low pressure hydrogenation of nitroparaffins to amines is unsatisfactory. We have found that platinum-catalyzed low pressure (two to three atmospheres) hydrogenation of simple nitroparaffins in 95% ethanol produces aliphatic amines in good yield and is a convenient laboratory operation. The per cent. conversion to amine and melting point for phenylthiourea derivatives of the amines isolated are summarized in Table I.

TABLE I

CONVERSION OF RNO_2 TO RNH_2 BY LOW PRESSURE CATALYTIC HYDROGENATION

R	Conversion to RNH_2,[a] %	Amine isolated, %	M.p. C_6H_5NCS derivatives, °C.
CH_3-	48	..	111–112[b]
C_2H_5–	79	..	102–103[b]
n-C_3H_7–	83	69	64–65[b]
i-C_3H_7–	88	64	100–101[c]
n-C_4H_9–	91	76	62–63

[a] These values are based on the titration of an aliquot with standard acid; see Experimental. [b] M. L. Willard and M. Z. Jones, THIS JOURNAL, **62**, 2876 (1940), report the following values: methyl, 112–113°; ethyl, 101–102°; *n*-propyl, 64°; *n*-butyl, 63°. [c] O. C. Dermer and J. W. Hutcheson, *Proc. Oklahoma Acad. Sci.*, **23**, 60 (1943), report 102°.

The addition of a trace of hydrochloric acid in the hydrogenation solvent did not affect the conversion to amine or the time required for the reduction. The introduction of as little as 1% by volume of acetic acid in the solvent increased the time required for the reduction by as much as 140–150% but did not change the conversion. With higher concentrations of acetic acid the effect of increasing the time of hydrogenation was more pronounced. This effect of acetic acid in the hydrogenation of nitroparaffins is consistent with the observations of Line, Wyatt and Smith[4a] in their hydrogenation of nitroethane.

Experimental

The following procedure was used for reducing all nitroparaffins indicated in Table I. Two-tenths mole of freshly distilled 2-nitropropane was dissolved in 100 ml. of 95% ethyl alcohol containing 0.1 g. of platinum oxide catalyst and shaken for nine hours at room temperature with hydrogen at two to three atmospheres pressure in a Parr low pressure hydrogenation apparatus. By this time the theoretical amount of hydrogen had been absorbed to reduce the nitro group to an amine. The hydrogenation was slightly exothermic. The reduction mixture was filtered, diluted with 100 ml. of water, acidified with about 0.25 equivalent of 85% phosphoric acid and distilled until the distillate was free of alcohol. The aqueous solution remaining was made alkaline with 25% aqueous sodium hydroxide and distilled through a 15-cm. Vigreux column until about 100 ml. of distillate was collected in a receiver containing 100 ml. of water. The receiver was cooled in an ice–water-bath. The distillate was diluted to exactly 250 ml.; titration of the amine in a 5.00-ml. aliquot required 35.10 ml. of 0.100 *N* hydrochloric acid using methyl red indicator. The yield of amine was 88%.[5]

A 200-ml. aliquot of the aqueous amine solution was saturated with potassium carbonate keeping the temperature at 0 to 5° and the amine which separated was carefully decanted and dried with sodium hydroxide pellets. Six grams of isopropylamine was obtained which distilled at 32–36°. The isolated amine yielded a substituted phenyl-

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(1) K. Johnson and E. F. Degering, THIS JOURNAL, **61**, 3194 (1939).

(2) H. B. Hass and E. F. Riley, *Chem. Revs.*, **32**, 389 (1943).

(3) E. Schmidt, A. Ascherl and L. Mayer, *Ber.*, **58**, 2430 (1925).

(4) (a) L. E. Line, B. Wyatt and H. A. Smith, THIS JOURNAL, **74**, 1808 (1952); (b) H. W. Smith and W. C. Bedoit, *J. Phys. Colloid Chem.*, **55**, 1085 (1951).

(5) The validity of the titration was demonstrated by a blank measurement on a solution of 100 ml. of alcohol containing 0.0750 mole of pure isopropylamine. By the above procedure the 5.00-ml. aliquot required 14.75 ml. of 0.100 *N* hydrochloric acid indicating a recovery of 0.0737 mole or 98% of the original amine.