amined. Since it has been shown[4c] that cycloheptatriene can be almost quantitatively converted to toluene at 478°, a study of these variables might lead to improved yield of cycloheptatriene from I.

Related ring expansions resulting from reactions of dichlorocarbene have been reported and references to these are given by Skell and Sandler.[6]

It has been found that dichlorocarbene can be conveniently generated in anhydrous systems by reaction of chloroform with commercially available sodium methoxide in place of potassium *t*-butoxide. The reaction is carried out at 60–70° by adding solid sodium methoxide portionwise to a mixture of chloroform and carbene acceptor, or chloroform may be added dropwise to a slurry of sodium methoxide and the acceptor. With less available olefins, nonreactive diluents such as benzene may be used to provide fluid reaction mixtures. Although the stoichiometry of the reaction has not been examined in detail, titration of several reaction mixtures gave values consistent with the reaction of two moles of base with one mole of chloroform.

EXPERIMENTAL

7,7-Dichlorobicyclo[4.1.0]heptane from cyclohexene, chloroform, and sodium methoxide. In a dry flask connected to an auxiliary flask by large-bore rubber tubing and equipped with a stirrer, thermometer, and reflux condenser fitted with a calcium chloride drying tube, there was placed 400 ml. of purified cyclohexene and 40 ml. (0.5 mole) of reagent grade chloroform. The solution was heated to 65–70° and commercial sodium methoxide[7] was added portionwise from the auxiliary flask. The reaction was exothermic and the temperature was maintained between the above limits by intermittent cooling. A total of 54 g. (1 mole) of base was added over 2 hr. The mixture was then stirred at 65–70° for an additional 30 min. and finally was poured on ice water. The organic phase was separated, washed three times with water, and dried over anhydrous magnesium sulfate. Titration of all of the aqueous layers indicated only 0.012 mole of base remaining at the end of the reaction. Distillation of the organic phase gave 31 g. (38%) of 7,7-dichlorobicyclo-[*4.1.0*]heptane, b.p. 84–88° (18 mm.). The infrared spectrum was in agreement with that reported.[5]

Cycloheptatriene.[8] A pyrolysis tube $1^3/_4$ in. in diameter, containing a 5-in. section packed with glass tubing, was heated to an internal temperature of 490°. Over a period of 2.5 hr., 75 g. (0.455 mole) of 7,7-dichlorobicyclo[4.1.0]heptane was dropped into the tube. During this time the internal temperature was maintained between 490–520°, and a slow stream of nitrogen was also passed through the tube. Distillation of the pyrolysis product through a small ring-packed still at atmospheric pressure gave 24 g. of liquid, boiling over the range 107–110°, n_D^{25} 1.4970–1.5030. This corresponds to 57% of theory for C_7H_8. The mixture contained no halogen and reacted with 2% potassium permanganate and with bromine in carbon tetrachloride. A comparison of the infrared spectrum of the mixture with those of toluene and cycloheptatriene showed the mixture to consist of approximately 65% toluene and 35% cycloheptatriene. Quantitative hydrogenation[9] in 95% ethanol with PtO_2 catalyst gave values of 0.0217 and 0.0212 gram of hydrogen per gram of mixture. On the basis of the unsaturation being due to cycloheptatriene, the average hydrogenation value indicates the mixture to contain 33% cycloheptatriene.

A Diels-Alder adduct was prepared by mixing 1 g. of maleic anhydride and 2.9 g. of the cycloheptatriene-toluene mixture in 10 ml. of xylene. After refluxing for 12 hr. the toluene and xylene were removed under vacuum. The white residue melted at 94–98°, and after crystallization from chloroform melted at 99–101°, wt. 0.92 g. (48%). A further crystallization from hexane raised the melting point to 102–104°, reported m.p. 102–104°.[1b]

The mixture was further characterized by conversion to tropylium bromide.[10] Eleven grams of the C_7H_8 mixture (assumed to contain 30% cycloheptatriene) diluted with 30 ml. of carbon tetrachloride was cooled in an ice bath and a solution of 6.45 g. of bromine in 30 ml. of carbon tetrachloride was then added slowly. The solvents were removed under vacuum and the solid residue heated at 70° (1–4 mm.) for 9 hr. The residue was washed with ether and acetone to give 0.8 g. (13%) of tropylium bromide, m.p. 198–200° (dec.), reported m.p. 198–200° (dec.).[10]

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A Synthesis for *p*-Dimethylaminobenzoylformamides and Some of Their Reactions

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Staudinger and Stockmann[2] have shown that oxalyl chloride reacts readily with dimethylaniline to yield *p*-dimethylaminobenzoylformyl chloride (I). These authors showed also that treatment of this acid chloride, without isolation, with aniline gave the corresponding anilide.

We have found that treatment of the acid chloride (I) with aliphatic or cycloaliphatic secondary amines leads to the corresponding *p*-dimethylaminobenzoylformamides (II) in good over-all yield.

The secondary amines used were dimethylamine, diethylamine and *N*-methylpiperazine. The over-all yield for the two steps varied from 45% to 70%. The reactions may be carried out conveniently by adding one mole of oxalyl chloride to two moles of dimethylaniline in ether at ice bath temperatures followed by an excess of the amine. The amides are separated by filtration and purified by recrystallization.

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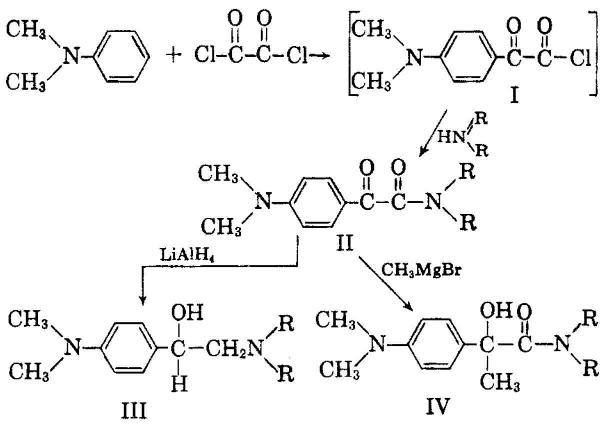
(2) H. Staudinger and H. Stockmann, *Chem. Ber.*, **42,** 3485 (1909).



Treatment of the amides II with lithium aluminum hydride gave the corresponding amino alcohols III in very good yield. These were isolated either in the form of the free base if a solid, or as the *dihydrochlorides*. Treatment of one of the amides, namely *N*,*N*-dimethyl-*p*-dimethylaminobenzoylformamide (II, R = CH_3), with an excess of methylmagnesium bromide in a benzene-ether solution gave *p*-dimethylamino-*N*,*N*-dimethylatrolactamide (IV) in 79% yield.

EXPERIMENTAL[3,4]

N,N-Dimethyl-p-dimethylaminobenzoylformamide. To a stirred solution of 38.1 g. (0.3 mole) of oxalyl chloride in 250 ml. of anhydrous ether cooled in an ice bath was added dropwise over the course of about 30 min., a solution of 72.7 g. (0.6 mole) of *N*,*N*-dimethylaniline in 250 ml. of anhydrous ether. The dark brown solution containing much solid was allowed to stand overnight in a refrigerator at 0–5°. To the reaction mixture (again cooled in an ice bath) was added 100 ml. of dimethylamine over the course of about 15 min. Stirring was continued at ice bath temperature for 0.5 hr. and at room temperature for 1.5 hr.

To the mixture was added *cautiously* a slurry of 50.4 g. of sodium bicarbonate in 100 ml. of water. The mixture was stirred well and filtered. The green solid was dissolved in chloroform and the chloroform solution washed with water. Evaporation of the chloroform gave a solid which after recrystallization from benzene–petroleum ether (b.p. 85–100°) with charcoal decolorization consisted of light yellow platelets melting at 136–137°; weight 44.6 g. (68%).

Anal. Calcd. for $C_{12}H_{16}N_2O_2$: C, 65.43; H, 7.32; N, 12.72. Found: C, 65.26; H, 7.08: N, 13.01.

N,N-Diethyl-p-dimethylaminobenzoylformamide. The substitution of 70 ml. of diethylamine in the above procedure gave 33.4 g. (45%) of yellow slender prisms melting at 102–103° after recrystallization from a benzene-cyclohexane mixture (2:5).

Anal. Calcd. for $C_{14}H_{20}N_2O_2$: C, 67.71; H, 8.12; N, 11.28. Found: C, 68.07; H, 8.16; N, 10.95.

1-Methyl-4-p-dimethylaminobenzoylformylpiperazine. The procedure described above for *N*,*N*-dimethyl-*p*-dimethylaminobenzoylformamide was employed using 125 ml. of *N*-methylpiperazine. There was obtained 57.5 g. (70%) of material melting at 117–117.5° and consisting of light yellow needles after recrystallization from a petroleum ether–benzene mixture (5:1).

Anal. Calcd. for $C_{15}H_{21}N_3O_2$: C, 65.43; H, 7.69; N, 15.26. Found: C, 65.18; H, 7.36; N, 14.99.

N,N-Dimethyl-β-hydroxy-p-dimethylaminophenethylamine dihydrochloride. To a mixture of 1.9 g. (0.05 mole) of lithium aluminum hydride in 75 ml. of anhydrous ether was added dropwise a solution of 5.5 g. (0.025 mole) of *N*,*N*-dimethyl-*p*-dimethylaminobenzoylformamide in 110 ml. of dry tetrahydrofuran. The reaction mixture was heated under reflux for 9 hr. and decomposed by the successive addition of 2 ml. of water, 2 ml. of a 10% sodium hydroxide solution, and 2.5 ml. of water. The reaction mixture was filtered and the solid washed well with ether. The ethereal filtrate was dried over anhydrous magnesium sulfate and the ether and tetrahydrofuran removed by distillation. The oily residue was redissolved in anhydrous ether and the *dihydrochloride* precipitated with gaseous hydrogen chloride. There was obtained 6.29 g. (90%) of colorless material melting at 124.5–125°. Recrystallization from ethanol gave material possessing the same melting point.

Anal. Calcd. for $C_{12}H_{20}N_2O.2HCl$: C, 51.25; H, 7.89; Cl, 25.21; N, 9.96. Found: C, 51.60; H, 8.19; Cl, 24.94; N, 10.07.

N,N-Diethyl-β-hydroxy-p-dimethylaminophenethylamine dihydrochloride was prepared in a similar manner from 6.2 g. (0.025 mole) of *N*,*N*-diethyl-*p*-dimethylaminobenzoylformide. There was obtained 6.5 g. (85%) of colorless prisms melting at 117.5–118° after recrystallization from anhydrous ethanol.

Anal. Calcd. for $C_{14}H_{24}N_2O.2HCl$: C, 54.36; H, 8.47; N, 9.06; Cl, 22.93. Found: C, 54.14; H, 8.17; N, 8.80; Cl, 22.83.

1-Methyl-4-(β-hydroxy-p-dimethylaminophenethyl)piperazine. The procedure described above for *N*,*N*-dimethyl-β-hydroxy-*p*-dimethylaminophenethylamine dihydrochloride was employed using 6.88 g. (0.025 mole) of 1-methyl-4-*p*-dimethylaminobenzoylformylpiperazine dissolved in 35 ml. of tetrahydrofuran. After hydrolysis of the reaction mixture and removal of the inorganic salts by filtration, a white solid began to precipitate in the organic mother liquors. This was removed by filtration. Additional material was obtained by stirring the inorganic salts with several portions of benzene and removing the benzene by distillation. The total yield of material was 4.05 g. (62%) melting at 126–126.5°. Recrystallization from petroleum ether (b.p. 85–100°) raised the melting point to 127–127.5°. No additional material could be obtained from the ether tetrahydrofuran mother liquors.

Anal. Calcd. for $C_{15}H_{25}N_3O$: C, 68.40; H, 9.57; N, 15.96. Found: C, 68.61; H, 9.81; N, 16.23.

p-Dimethylamino-N,N-dimethylatrolactamide. Sixty ml. of an ethereal methyl magnesium bromide solution (Arapahoe Chemical Co.) containing 0.15 mole of CH_3MgBr was added slowly to a stirred solution of 15 g. (0.0682 mole) of *N*,*N*-dimethyl-*p*-dimethylaminobenzoylformamide in 600 ml. of anhydrous benzene. After addition was started, the mixture was cooled in an ice bath. When addition was complete the ice bath was removed and the mixture stirred at room temperature for 1.5 hr. The mixture was decomposed by the addition of a 20% ammonium chloride solution. Solid separated in the mixture upon standing. This was removed by filtration and the filtrate transferred to a separatory funnel and the ether-benzene layer separated. Concentration and cooling of this solution gave additional solid material. The product after recrystallization from isopropyl alcohol melted at 144–146°; weight 12.68 g. (79%).

Anal. Calcd. for $C_{13}H_{20}N_2O_2$: C, 66.07; H, 8.53; N, 11.86. Found: C, 66.21; H, 8.28; N, 12.14.

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(3) All melting points and boiling points are uncorrected for stem exposure.

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