The ultraviolet absorption spectrum of this product, determined in ethanol solution, showed 239 mμ max. (ε 25,300). The infrared spectrum showed characteristic[8] NO_2 absorption at 1332 and 1553 cm.$^{-1}$ These values compare with 235 mμ max. (ε 14,700), 285 mμ max. (ε 8030), and NO_2 absorption at 1320 and 1515 cm.$^{-1}$, for the monomer I.

The molecular weight of the dimer was determined by the freezing point depression method using benzene and nitrobenzene as the solvent. The product was relatively insoluble in benzene.

Calcd. M.W. 422. Found (average of three determinations each): in benzene, 448; in nitrobenzene, 406.

Oxidation of dimer with potassium permanganate. The oxidation of the dimer (129 mg.), with subsequent conversion of the resulting potassium benzene disulfonate to benzene-*o*-disulfonyl chloride, was carried out by a procedure previously described using 2-nitrobenzo-1,4-dithiadiene.[8] The yield of pure benzene-*o*-disulfonyl chloride (m.p. and mixture m.p. 145–146°) was 52 mg. (31%).

Chlomercuration of Benzo-1,4-dithiadiene. Mercuric chloride (1.80 g., 0.0076 mole) was added to a solution of benzo-1,4-dithiadiene[8] (1.10 g., 0.0066 mole) in 95% ethanol, and the resulting solution was heated at the reflux temperature for 1 hr. Water (35 ml.) was added to the cool reaction mixture, and the resulting pale yellow solid (m.p. 125–130° with previous softening at 100°) was recrystallized from ethanol-water. The light yellow needles that resulted (2.10 g., 79% yield) melted at 127–130°.

Anal. Calcd. for $C_6H_5S_2ClHg$: C, 23.94; H, 1.26. Found: 24.23; H, 1.74.

Hydrolysis of 2-chloromercuribenzo-1,4-dithiadiene. A mixture containing IV (0.919 g., 0.00229 mole), concentrated hydrochloric acid (5 ml.), and water (20 ml.) was distilled with steam. The yellow oil in the distillate was recovered by ether extraction, and was shown to be benzo-1,4-dithiadiene (0.341 g., 90% yield, n_D^{25} 1.6706) by comparison of its ultraviolet spectrum with authentic III,[8] and by its conversion into 2-nitrobenzo-1,4-dithiadiene (m.p. and mixture m.p. 105–107°).

Reaction of benzo-1,4-dithiadiene with mercuric acetate. (*A*) A solution of benzo-1,4-dithiadiene (1.00 g., 0.006 mole), mercuric acetate (4.80 g., 0.0151 mole), glacial acetic acid (5 drops), ethanol (30 ml.), and water (10 ml.) was heated at the reflux temperature for 5 hr. It was noted that considerable free mercury formed in the reaction. The mixture of yellow amorphous solid and free mercury (3.35 g.) was collected by filtration; the high melting (>300°) yellow solid was insoluble in all common solvents employed, and no method was found to remove all of the free mercury.

(*B*) A mixture identical to that described in A was heated for 30 min. No free mercury was noted, and there was obtained 1.78 g. of yellow solid. This material was insoluble in all solvents tested, and it did not melt at 300°; however, the material changed from orange to pink to brown during the attempted melting.

Anal. Found: C, 13.61; H, 1.15.

(*C*) A solution of III (1.00 g., 0.0060 mole), mercuric acetate (2.10 g., 0.0066 mole), glacial acetic acid (5 drops), ethanol (50 ml.), and water (15 ml.) was allowed to stand for 4 days at room temperature. The fine pale yellow solid (1.01 g.) was isolated by centrifugation. This material underwent a series of color changes, orange to pink to brown, when heated, and melted at 212–214°.

Anal. Found: C, 16.72; H, 1.57.

Attempts to purify this material by recrystallization from ethanol were unsuccessful because of its partial decomposition into free mercury.

(*D*) A mixture containing III (2.00 g., 0.0120 mole), mercuric acetate (4.03 g., 0.0126 mole), and 50% aqueous acetic acid (30 ml.) was stirred for 5 hr. at 45–50°. The resulting gummy solid which precipitated was soluble in acetic acid; however, when it was reprecipitated by the addition of water, the resulting product was insoluble in all solvents tried. A sample of this material was triturated with chloroform, benzene, and finally twice with hot glacial acetic acid. The light brown solid showed no change when heated to 300°.

Anal. Calcd. for $C_{12}H_{10}O_4S_2Hg_2$: C, 21.08; H, 1.47. Found: C, 21.90; H, 0.90.

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Synthesis of Cycloheptatriene

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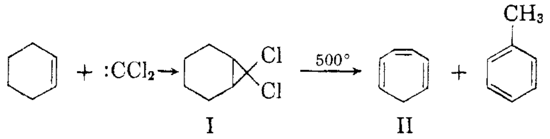
Several methods involving ring expansions are available for the synthesis of 1,3,5-cycloheptatriene (II). In the classical route,[1] the intermediate cycloheptanone is obtained by ring expansion of cyclohexanone. A more convenient preparation of cycloheptatriene is the irradiation by ultraviolet light of a solution of diazomethane in benzene.[2] In a third synthesis,[3] the solvolysis of the methanesulfonate of bicyclo[3.2.0]hept-2-en-6-ol was found to give a 50% yield of cycloheptatriene. More recently, II has been obtained by the thermal isomerization of bicyclo[2.2.1]heptadiene.[4]

A new two-step route to cycloheptatriene has now been discovered. It involves the preparation of 7,7-dichlorobicyclo[4.1.0]heptane (I), which can be obtained in 59% yield from dichlorocarbene and cyclohexene,[5] and its pyrolysis to a mixture of cycloheptatriene and toluene. At 500°, a 57% yield of a mixture of toluene (65%) and cycloheptatriene (35%) is obtained. The resulting solutions may be utilized to prepare derivatives of II, including tropylium bromide and Diels-Alder adducts.



The effect of varying the temperature and residence time in the pyrolysis of I has not been ex-

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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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