pounds 2 and 4 (Table III) has also been published recently.

The compounds in Table III were prepared by alkylation of the appropriate phenothiazine with a tertiary aminoalkyl halide in an inert solvent, using sodamide as a condensing agent.[5] In Table I are listed the parent trifluoromethylphenothiazines prepared in this work which have not been described elsewhere.

The substituted phenothiazines were prepared by the method of Bernthsen,[6] using the appropriately substituted diphenylamines. The diphenylamines which have not been described elsewhere are listed in Table II. An alternative route to the trifluoromethylphenothiazines is found in the Smiles rearrangement.[7]

The sulfoxides listed in Table III were prepared by the action of hydrogen peroxide on the oxalate salts of the parent compound.[8]

4-Trifluoromethylphenothiazine (m.p. 71–72°) was isolated in yields of less than 5% as a side-product in the thionation of 3-trifluoromethyldiphenylamine. Its configuration as the 4-isomer was indicated by the peak in infrared at 12.5 microns, found in 1,2,3-trisubstituted benzene[9] rings, and by the absence of a peak at 12–12.1 microns, found in 2-trifluoromethylphenothiazine[3] and other 1,2,4-trisubstituted benzene compounds.[9]

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Preparation of 2,2′-Diaminobiphenyl by Reduction of 2,2′-Dinitrobiphenyl

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Attempts to prepare 2,2′-diaminobiphenyl from 2,2′-dinitrobiphenyl by chemical reduction according to methods reported in the literature and by various modifications of these methods gave erratic results. Occasionally good yields of the diamine were obtained, but frequently the products were unreacted dinitrobiphenyl, tar, benzo[*c*]cinnoline-5-oxide, or benzo[*c*]cinnoline-5,6-dioxide or various mixtures.

Catalytic reductions in general were more satisfactory. The procedure of S. D. Ross, Kahan, and Leach[1] using ethanol-ethyl acetate (1 v.: 3 v.) and Adams catalyst gave uniformly good yields. The amount of catalyst and time of reduction can be reduced if the hydrogenation is carried out at an elevated temperature. Thus a solution of 12 g. of 2,2′-dinitrobiphenyl in 200 cc. of mixed solvent with 0.006 g. of platinum oxide, which was placed in the hydrogenator at 60°, was reduced in 20 min., whereas a run of the same size using 0.1 g. of catalyst which was started at room temperature required 30 min. The addition of six drops of 6*N* acetic acid had no effect on the rate at room temperature. The addition of six drops of 6*N* aqueous sodium hydroxide greatly reduced the rate of hydrogenation for about 25 min., but then the rate approached that of the neutral or acidic runs. Evidently alkali decreases the rate but is removed by reaction with the ethyl acetate. Reductions in ethanol[2] have the disadvantage that only about 1 g. of dinitrobiphenyl can be dissolved in 200 cc. and that the rate of reduction is somewhat slower than in the mixed solvent. Neither acid nor base has an appreciable effect on the rate in this solvent.

Everett and W. C. J. Ross[3] report that catalytic reduction of an ethanol solution of 2,2′-dinitrobiphenyl in ethanol in the presence of Raney nickel gave benzo[*c*]cinnoline. The present work shows, however, that under the proper conditions W-2 Raney nickel[4] gives excellent yields of 2,2′-diaminobiphenyl. An initial gauge pressure of around 50 p.s.i. is preferred. At pressures of 600 p.s.i. and at 2000 p.s.i. the results were erratic, tars and benzo[*c*]cinnoline-5-oxide being among the products obtained. The ethanol-ethyl acetate (1 v.:3 v.) mixture was preferable as a solvent to methanol, ethanol, or dioxane. The usual concentration in this solvent was 12 g. per 200 cc. The rate of reduction definitely was dependent on the age of the catalyst. In a series of standard runs using 4 cc. of catalyst mush, starting with the solution at 60° and using catalyst that was 0, 6, 12, 20, and 24 months old, the time for complete reduction of 12 g. was 20,

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20, 110, 370, and 540 min. The addition of either acid or alkali to an old catalyst increased the rate of reduction. Thus a catalyst that brought about reduction in 510 min. in neutral solution, required 141 min. when two drops of 6*N* acetic acid was added, and 71 min. when two drops of 6*N* sodium hydroxide was added. The same effects were noted when ethanol was used as a solvent.

Solutions after reduction in the mixed solvent, using either Adams catalyst or Raney nickel, always were pale yellow and recrystallization from ethanol gave brown plates melting at 76–78°. Attempts to decolorize the solutions with Norit only intensified the color. To obtain pure material the product was distilled at 150–151° at 3 mm. The distillate was crystallized from a concentrated solution in ethanol to give colorless plates, m.p. 79–80°. Melting points of 80–81° and of 81° have been recorded.[1,5]

Recently the hydrogenation of benzo[*c*]cinnoline to 2,2′-diaminobiphenyl using Raney nickel catalyst was reported.[6] During the course of the present work benzo[*c*]cinnoline-5,6-dioxide was hydrogenated to benzo[*c*]cinnoline using either Raney nickel or Adams catalyst, but further reduction to 2,2′-diaminobiphenyl did not take place.

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Conversion of 1,6-Di-*O*-methylsulfonyl-2,4:3,5-di-*O*-methylene-L-iditol to D-*threo*-4,8-Dimethylene-1,3,5,7-naphthodioxane

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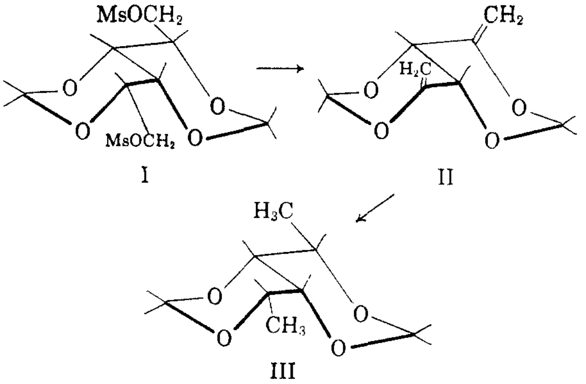
While formation of double bonds through loss of the elements of an alkyl or aryl sulfonic acid from adjacent carbon atoms under alkaline conditions has been reported repeatedly as an unwanted side reaction in the carbohydrate field,[2] the phenomenon has not received the study it deserves. We wish to report the very facile formation of the diene II from the dimesyl ester of the well-known 2,4:3,5-di-*O*-methylene-L-iditol (I).[3]

The structure of the diene was demonstrated through hydrogenation to 1,6-dideoxy-2,4:3,5-di-*O*-methylene-L-iditol (III), a substance which Hann and Hudson[3] have prepared through reduction of 1,6-dideoxy-1,6-diiodo-2,4:3,5-di-*O*-methylene-L-iditol. It is noteworthy that the diequatorial product III rather than the corresponding D-mannitol or D-glucitol analogs were isolated after the reduction of II. A crystalline tetrabromide prepared from II is also reported here. Conformational and mechanistic considerations indicate that both the bromomethyl groups in this substance are probably equatorial although evidence on this point is lacking.



EXPERIMENTAL[4]

*1,6-Di-O-methylsulfonyl-2,4:3,5-di-O-methylene-*L*-iditol* (*I*). 2,4:3,5-Di-*O*-methylene-L-iditol (16.5 g.), prepared by the method of Hann and Hudson,[3] was "mesylated" in pyridine solution with methanesulfonyl chloride in normal fashion to yield a crystalline product which, recrystallized from acetone-pentane, 2-butanone, and methyl Cellosolve amounted to 20.0 g. (69%). The pure product melted at 163–164°, $[\alpha]^{20}_{D}$ +26° in chloroform (*c* 0.8).

Anal. Calcd. for $C_{10}H_{18}O_{10}S_2$: C, 33.14; H, 5.01; S, 17.70. Found. C, 33.37; H, 5.37; S, 17.70.

D-*threo-4,8-Dimethylene-1,3,5,7-naphthodioxane* (*II*). 1,6-Di-*O*-methylsulfonyl-2,4:3,5-di-*O*-methylene-L-iditol (6.28 g.) was added to 30 ml. of dry methyl Cellosolve in which 0.95 g. of sodium had been dissolved and the resulting mixture refluxed for 20 min. One volume of benzene and one of ether were added to the cooled reaction mixture and the sodium mesylate (4.16 g., quantitative) removed after further cooling to 0°. The filtrate, diluted with more benzene, was washed twice with water, dried over sodium sulfate, and concentrated *in vacuo* at room temperature. The crystalline residue, recrystallized twice from dichloromethane-pentane at Dry-Ice temperature and dried briefly *in vacuo* (30 mm.) at 20°, weighed 1.7 g. (58%), m.p. at 80°, $[\alpha]^{20}_{D}$ +269.5° in acetone (*c* 0.56). The product has a significant vapor pressure and prolonged drying results in considerable loss.

Anal. Calcd. for $C_8H_{10}O_4$: C, 56.46; H, 5.92. Found: C, 56.36; H, 5.89.

The infrared absorption spectrum of the diene showed the absence of hydroxyl and carbonyl functions and had bands at 3.5 and 3.6 μ (C—H stretching) and 6.0 μ (C=C).

*1,6-Dideoxy-2,4:3,5-di-O-methylene-*L*-iditol* (*III*). D-*threo-4,8-Di-methylene-1,3,5,7-naphthodioxane* (230 mg.) was dissolved in 3 ml. of glacial acetic acid and hydrogenated at 25°, platinum from 30 mg. of PtO_2 being used as catalyst. When the calculated quantity of hydrogen had been absorbed (35 min.) warm ethyl acetate was added to dissolve the partially precipitated product. The catalyst was removed and the solution concentrated *in vacuo* to a dry, crystalline

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(1) Chemical Foundation Fellow 1956–1957.

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(4) Melting points are corrected.