this laboratory for the preparation of 2,2′-dibromobiphenyl, which is an important intermediate in the preparation of some cyclic organosilicon compounds.[9]

### EXPERIMENTAL[10]

*2,2′-Dibromobiphenyl.* To a stirred solution of 47.26 g. (0.2 mole) of *o*-dibromobenzene in 450 ml. of anhydrous tetrahydrofuran[11] was added 76.4 ml. of an ethereal solution containing 0.1 mole of *n*-butyllithium[12] (molarity determined by the double titration method).[13] The *o*-dibromobenzene solution was cooled to the minimum temperature afforded by a dry ice–acetone bath, and the rate of addition was such that the temperature was not allowed to rise more than 5°. The reaction was instantaneous as was evidenced by a negative Color Test I[14] and Color Test II[15] immediately after completion of the addition.

The yellow-green reaction mixture was allowed to warm to 5° and then was hydrolyzed with 100 ml. of 5% hydrochloric acid. The resulting layers were separated and the aqueous layer was extracted with four 20-ml. portions of ether. The ether washings were combined with the original organic layer and dried over anhydrous sodium sulfate, filtered and concentrated by distillation until the distillation temperature reached 70°. The residue was treated with 50 ml. of absolute ethanol and cooled to give 11.74 g. of 2,2′-dibromobiphenyl, m.p. 80–81°. The filtrate was decolorized with activated charcoal, filtered and concentrated by evaporation to give an additional 11.26 g. of less pure product, m.p. 78–81°, or a total yield of 73.7%. One recrystallization from absolute ethanol gave pure 2,2′-dibromobiphenyl, m.p. 80–81°. A mixed melting point with an authentic sample showed no depression.

In a similar run, using 11.80 g. (0.05 mole) of *o*-dibromobenzene in 100 ml. of tetrahydrofuran and 19 ml. of 1.33 N *n*-butyllithium, there was obtained 5.18 g. (66.5%) of 2,2′-dibromobiphenyl, m.p. 79–80°.

*o-Dibromobenzene and n-butyllithium in diethyl ether.* To a stirred solution of 11.8 g. (0.05 mole) of *o*-dibromobenzene in 100 ml. of anhydrous diethyl ether, cooled to −78°, was added an ethereal solution containing 0.025 mole of *n*-butyllithium at such a rate that the temperature was not allowed to rise more than 5° during the addition. A white suspension developed in the pale yellow solution after only a few drops of *n*-butyllithium had been added. The reaction mixture exhibited a negative Color Test I immediately upon completion of the addition. The main product isolated after work-up in the usual manner was an unidentified ether insoluble white solid which melted over the range 304–340° with decomposition. A small amount of an unidentified yellow oil was obtained also.

*4,4′-Dibromobiphenyl.* To a stirred solution of 23.59 g. (0.1 mole) of *p*-dibromobenzene in 100 ml. of anhydrous tetrahydrofuran, cooled to −15°, was added 40 ml. of an ethereal solution containing 0.05 mole of *n*-butyllithium at such a rate that the temperature did not rise above −10°. The reaction mixture darkened upon the addition of only a few drops of the *n*-butyllithium solution and a brown precipitate was noticed toward the end of the addition. Both Color Tests I and II were found to be negative immediately after the addition was completed. The reaction mixture was then warmed to 20° and hydrolyzed with 5% hydrochloric acid. The resulting layers were separated and the aqueous layer was extracted with three small portions of ether. The ether extracts were combined with the now homogeneous brown organic layer and dried over anhydrous sodium sulfate, filtered and concentrated by evaporation. A little ethanol was added to the residue which resulted in the formation of a yellow precipitate. This solid was removed by filtration to give 2.6 g. of crude 4,4′-dibromobiphenyl, m.p. 158–164°. Further concentration of the mother liquor gave an additional 1.81 g. of impure 4,4′-dibromobiphenyl and a heavy brown oil. The combined solids were recrystallized from a mixture of ethanol and benzene to give 2.14 g. of pure 4,4′-dibromobiphenyl, m.p. 168–169°, and an additional 1.14 g. of less pure material, m.p. 165–167° or a combined yield of 21%. A mixed melting point with an authentic specimen showed no depression.

In a similar reaction using the same quantities of materials, the addition was carried out while maintaining a temperature between −35 and −40°. Color Test I was positive after completing the addition. Upon warming the reaction mixture to −20° during a 30-min. period, a negative Color Test I was obtained. The mixture was worked up in the same manner as described above to give 4.99 g. of crude 4,4′-dibromobiphenyl, m.p. 144–160°. One recrystallization from benzene, after decolorizing with activated charcoal, gave 2.5 g. (16.4%) of pure 4,4′-dibromobiphenyl and 1.02 g. (6.7%) of less pure material, m.p. 165–168°.

*4,4′-Dichlorobiphenyl.* To a stirred solution of 38.29 g. (0.2 mole) of *p*-chlorobromobenzene in 200 ml. of anhydrous tetrahydrofuran, cooled to −40° by a dry ice–acetone bath, was added dropwise 85 ml. of 1.19 molar *n*-butyllithium in ether. During the addition, the reaction mixture was allowed to warm to −20°. It then was stirred at this temperature for an additional 15 min. before giving a negative Color Test I. The product was worked up in a manner similar to that described for 4,4′-dibromobiphenyl to give 6.0 g. of an oily brown solid which was dissolved in benzene, decolorized with activated charcoal, concentrated and cooled to give 2.24 g. (10%) of pure 4,4′-dichlorobiphenyl, m.p. 149–150°, and an additional 1.75 g. (7.8%) of less pure material, m.p. 144–148°.

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[9] H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **77**, 6380 (1955).

[10] All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen and all melting points are uncorrected.

[11] The tetrahydrofuran was dried and purified by first shaking with sodium hydroxide pellets, refluxing over sodium metal for several hours and finally distilling, immediately before use, from lithium aluminum hydride.

[12] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

[13] H. Gilman and A. E. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

[14] H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

[15] H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, **62**, 1847 (1940).

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# Reactions of 1,3-Dienes with Activated Aldehydes, II

Wesley J. Dale and Anthony J. Sisti

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In an earlier publication,[1] it was reported that chloral was observed to react with various 1,3-dienes to produce substituted 5,6-dihydro-1,2-pyrans through a Diels-Alder type of reaction.

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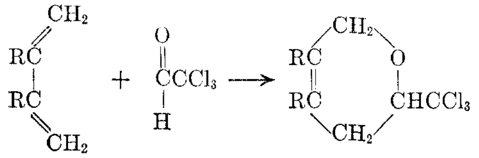
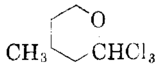
[1] W. J. Dale and A. J. Sisti, *J. Am. Chem. Soc.*, **76**, 81 (1954).

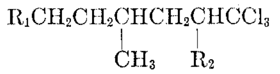


In the present study, an additional reaction of this type and a partial structural study of a previously reported cleavage product were undertaken. It has now been found that chloroacetaldehyde reacts with 2,3-dimethylbutadiene in a sealed tube, heated at 100° for 24 hr., to give 3,4-dimethyl-6-chloromethyl-5,6-dihydro-1,2-pyran (30% yield), from which the corresponding tetrahydropyran is obtained on hydrogenation. It was not possible under these conditions to effect a reaction between cyclopentadiene and chloral.

We have also observed that when the hydrogenated chloral-isoprene adduct (I), obtained in our first study[1] was treated with dry hydrogen bromide in acetic acid according to the method of Paul,[2] it suffered cleavage to give a bromoalcohol (IIa or IIb), rather than the dibromo derivative IIc, even though the work of Paul had shown that under these conditions, tetrahydropyrans undergo cleavage to give the dibromo derivatives. The explanation undoubtedly lies in the steric and electronegative influence of the neighboring trichloromethyl group during the cleavage process.



I



$$\underset{\displaystyle CH_3}{R_1CH_2CH_2CH}CH_2\underset{\displaystyle R_2}{CH}CCl_3$$

IIa, $R_1 = Br, R_2 = OH$
IIb, $R_1 = OH, R_2 = Br$
IIc, $R_1 = R_2 = Br$

When I was subjected to oxidative cleavage with chromic oxide in acetic acid, a white solid was obtained which, in addition to the acid function, contains an $\alpha$-ketotrichloromethyl group. Further work is being done on these compounds to confirm the assignments of structure of the original diene-chloral adducts, tentatively made on the basis of polarizations present in the combining molecules.

## EXPERIMENTAL

*Cleavage of the hydrogenated isoprene-chloral adduct.* Into a 125-ml. round bottomed flask were placed 12 g. (0.055 mole) of hydrogenated adduct (I)[1] and 50 ml. of glacial acetic acid. Dry hydrogen bromide gas was passed into the solution for a period of 2 hr., during which time the reaction solution was cooled intermittently with an ice bath. An insoluble oil began to separate after 1 hr. The oil was removed and triturated with 95% ethanol, after which a white solid separated. Recrystallization from ethanol yielded 8.1 g. (50%) of white crystalline material, m.p. 51.5–52°.

*Anal.* Calcd. for $C_7H_{12}OBrCl_3$: C, 28.15; H, 3.90. Found: C, 28.19; H, 3.55.

Ceric nitrate reagent and various acylating agents confirmed the presence of the hydroxy group.

*Oxidation of the hydrogenated isoprene-chloral adduct.* Into a 500-ml. three necked round bottomed flask, equipped with mechanical stirrer, were placed 10 g. (0.045 mole) of the saturated adduct (I), 20 ml. of concentrated hydrochloric acid, and sufficient acetic acid to produce a homogeneous solution. To this was added, very slowly and with stirring, a solution of 40 g. of chromic oxide dissolved in a minimum amount of acetic acid and water. The temperature of the reaction solution was not allowed to rise above 50°. After all the chromic acid had been added, the reaction mixture was allowed to stand 2 days at room temperature. The solution was then poured onto ice and water, which caused a flaky solid to separate. The solid was recrystallized from hot water, after which it melted at 79.5–80°. A total of 6 g. was obtained, which corresponded to 48% of the theoretical amount. Molecular wt., calcd., 247; neut. equiv., 243 and 245. Reaction with sodium hydroxide solution released chloroform, indicating the presence of the $\alpha$-ketotrichloromethyl group.

*Condensation of chloroacetaldehyde with 2,3-dimethylbutadiene. 3,4-Dimethyl-6-chloromethyl-5,6-dihydro-1,2-pyran.* Into a Carius tube were placed 18 ml. (0.15 mole) of 2,3-dimethylbutadiene, 20 ml. (containing 0.15 mole) of 80% chloroacetaldehyde, and a few milligrams of hydroquinone. (The chloroacetaldehyde used was a Dow product, containing 40% chloroacetaldehyde in water. Upon distillation, an 80% solution was obtained.) The sealed tube was heated in an oven at 100° for 21 hr. Upon fractionation of the reaction mixture, a clear, colorless liquid was obtained, b.p. 86–88° (20 mm.), $n_D^{25}$ 1.4960. Yield, 7.73 g. (30%). The product became yellow after a few days. Number of double bonds, 1.02, 1.04 (hydrogenation).

*Anal.* Calcd. for $C_8H_{13}OCl$: C, 60.00; H, 8.13. Found: C, 60.21; H, 8.90.

*Hydrogenation of 3,4-dimethyl-6-chloromethyl-5,6-dihydro-1,2-pyran. 3,4-Dimethyl-6-chloromethyltetrahydropyran.* Six g. (0.037 mole) of 3,4-dimethyl-6-chloromethyl-5,6-dihydro-1,2-pyran, dissolved in 50 ml. of 95% ethanol, was hydrogenated as previously described, using 50 lb. of pressure and 20 mg. of platinum oxide. Distillation of the product yielded 5.87 g. (98%) of a stable, clear, colorless liquid, b.p. 95–97° (20 mm.) $n_D^{25}$ 1.4560.

*Anal.* Calcd. for $C_8H_{15}OCl$: C, 58.88; H, 9.20; mol. wt. 162.5. Found: C, 58.50; H, 8.70; mol. wt. (Rast) 160.

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(2) R. Paul, *Bull. soc. chim. France* [4], **53**, 1489 (1933).

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# Direct Condensation of Dipalmitoxypantoic Acid with Ethyl $\beta$-Alanate[1]

Taketami Sakuragi and Fred A. Kummerow

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A previously unsuccessful attempt to condense dipalmitoxypantoic acid with ethyl $\beta$-alanate[2] proved feasible with the aid of dicyclohexyl carbodiimide. This condensation, representing a successful application of Sheehan's method of peptide

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(1) Supported by research grant No. A-257 from the National Institutes of Health, U. S. Public Health Service, Department of Health, Education, and Welfare.

(2) T. Sakuragi and F. A. Kummerow, *J. Am. Chem. Soc.*, **78**, 838 (1956).