hydrobromic acid in glacial acetic acid[4] to give methyl 2,3-di-*O*-acetyl-4-*O*-methyl-α-D-glucopyranoside (8.8 g.). This was dissolved in 60 ml. of methanol and 3 ml. of 0.5 $N$ barium methylate solution was added. After standing overnight at room temperature, the solution was neutralized by treatment with Amberlite resin IRC-50(H). The solution was then evaporated under vacuum to yield a faintly yellow colored sirup (5.8 g. or 31% over-all yield). On standing overnight, this sirup crystallized. Two recrystallizations from isopropyl alcohol gave needles with m.p. 144–145° and $[\alpha]^{25}\text{D}$ +154.7° ($c$ 1 in water).

Crystals with the same melting point were also obtained by recrystallizations from alcohol–benzene. For best results crude methyl 4-*O*-methyl-α-D-glucopyranoside was dissolved in hot absolute ethanol and benzene added until the solution became turbid. Crystallization occurred on cooling.

*Anal.* Calcd. for $C_8H_{16}O_6$: C, 46.2; H, 7.7; methoxyl, 29.8. Found: C, 46.2; H, 7.7; methoxyl, 29.6.

**Methyl 2,3,6-Tri-*O*-acetyl-4-*O*-methyl-α-D-glucopyranoside.**—One-half gram of crystalline methyl 4-*O*-methyl-α-D-glucopyranoside was acetylated with sodium acetate and acetic anhydride at 110° for 30 minutes. After the mixture was poured into ice-water with stirring, the triacetate was extracted with chloroform. The chloroform solution was dried over anhydrous sodium sulfate and was evaporated under vacuum to produce crystals of the triacetate. Two recrystallizations from 95% ethanol gave needles with m.p. 122–123° and $[\alpha]^{25}\text{D}$ +150.4° ($c$ 1 in chloroform).

*Anal.* Calcd. for $C_8H_{13}O_6(CH_3CO)_3$: C, 50.3; H, 6.6; acetyl, 38.6. Found: C, 50.3; H, 6.6; acetyl, 38.7.

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[4] B. Helferich and W. Klein, *Ann.*, **450**, 219 (1926).

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## A New Nortricyclene Derivative

BY ANTHONY WINSTON[1] AND PELHAM WILDER, JR.[2]

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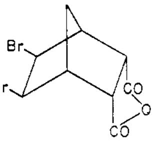
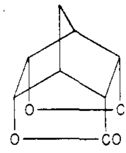
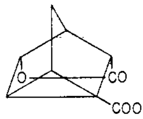
On account of recent investigations of the stereochemistry of bromination of some Diels–Alder adducts,[3,4] it is of interest at this time to report several reactions of *exo-cis*-4,5-dibromo-*endo*-3,6-endomethylenehexahydrophthalic anhydride[5] (I). Upon treatment with boiling aqueous sodium carbonate, the dibromide I yielded a neutral compound, the structure of which was proved to be the dilactone II previously prepared by Alder and Stein.[6] Treatment of this same dibromide with alcoholic potassium hydroxide, on the other hand, resulted in the formation of a monocarboxylic acid which upon analysis was found to be isomeric with the dilactone II above. The absorption at 5.58 $\mu$ in the infrared spectrum, Fig. 1, indicated the presence of a γ-lactone structure.[7,8] Several unsuccessful attempts to hydrogenate the acid over platinum oxide made the presence of unsaturation appear unlikely. On the basis of these observations it seems certain that the acid must be the nortricyclenic acid lactone[9] (III)



I



II



III

Recently Roberts and his co-workers[10] found that the nortricyclene system was easily prepared by the action of N-bromosuccinimide as well as by the action of bromine in the presence of pyridine upon norbornylene. The infrared absorption at 12.4–12.5 $\mu$ exhibited by nortricyclene systems[10,11] is found at 12.40 in the spectrum of the nortricyclenic acid lactone (III).

When dibromide I was treated for fifteen hours at room temperature with sodium methoxide in methanol solution, a small amount of the nortricyclene derivative III was isolated along with a mixture of bromides. When the dibromide was treated briefly with sodium methoxide in methanol solution at the reflux temperature, the only product isolated was a viscous, oily mass from which no single pure substance could be extracted.

NOTE ADDED IN PROOF.—Since this manuscript was submitted for publication, there has appeared a paper by Alder and Brochhagen [*Ber.*, **87**, 167 (1954)] which describes another synthesis of the nortricyclene derivative reported herein. The authors acknowledge the priority of Alder and Brochhagen.

### Experimental[12]

**Dibromide I.**—The dibromide of the cyclopentadiene–maleic anhydride adduct was prepared according to the method of Bartlett and Schneider[13]; micro m.p. 211–212°.

**Dilactone II.**—Ten grams of the dibromide I, suspended in 100 ml. of 5% sodium carbonate solution was heated under reflux for 3 hours. After acidification with hydrochloric acid the solution was subjected to continuous ether extraction for 24 hours. Upon evaporation of the ether there remained a neutral solid which upon crystallization from water yielded 3.5 g. of colorless crystals, m.p. 274–275° cor. (reported 264–266°[6]). Because of the discrepancy in the melting points, the compound was reanalyzed and the molecular weight was determined by the boiling point elevation of acetic acid.

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(1) Du Pont Predoctoral Fellow, 1953–1954.

(2) Author to whom communications should be directed.

(3) H. Kwart and L. A. Kaplan, THIS JOURNAL, **75**, 3356 (1953).

(4) J. A. Berson and R. Swidler, *ibid.*, **75**, 4366 (1953).

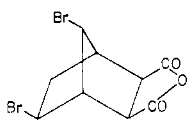
(5) H. Kwart and L. A. Kaplan, reported at the 124th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 6–11, 1953.

(6) K. Alder and G. Stein, *Ann.*, **514**, 1 (1934).

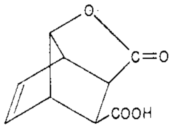
(7) S. Searles, M. Tamres and G. Barrow, THIS JOURNAL, **75**, 71 (1953).

(8) H. Conroy, *ibid.*, **74**, 491 (1952), footnote 26.

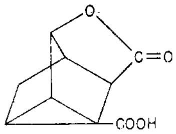
(9) As a result of dipole moment studies Kwart and Kaplan (*cf.* reference 3), assigned the structure A to the dibromide I. On the basis of this assignment, the product of alcoholic potassium hydroxide treatment would be acid B or acid C, or possibly both. It is interesting to note that acid C is, indeed, *identical* with acid III; consequently, the isolation of the nortricyclenic acid lactone above, then, may not be considered a proof of the structure of dibromide (I).



A



B



C

(10) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, THIS JOURNAL, **72**, 3116 (1950).

(11) E. R. Lippincott, *ibid.*, **73**, 2001 (1951).

(12) Microanalyses by Galbraith Laboratories, Knoxville, Tenn.

(13) P. D. Bartlett and A. Schneider, THIS JOURNAL, **68**, 6 (1946).

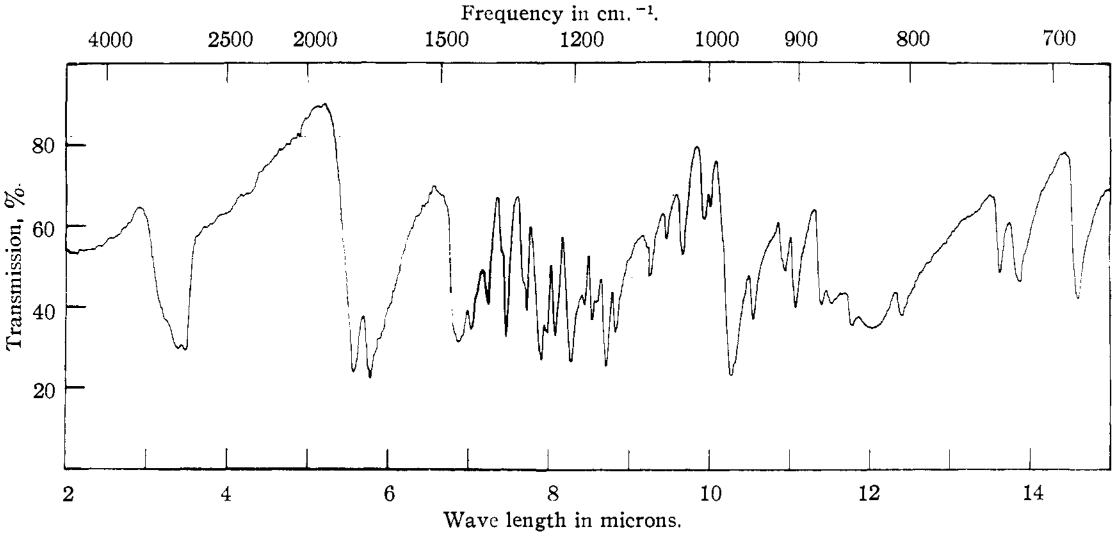


Fig. 1.—Infrared spectrum of nortricyclenic acid lactone (III) in a Nujol mull as recorded by the Perkin-Elmer model 21 double beam spectrophotometer, NaCl prism.

*Anal.* Calcd. for $C_9H_8O_4$; C, 60.00; H, 4.48; mol. wt., 180. Found: C, 59.94; H, 4.49; mol wt., 186, 189.

Two bands characteristic of $\gamma$-lactones were observed in the carbonyl region of the spectrum at 5.53 and 5.60 $\mu$.

**Nortricyclenic Acid Lactone (III).**—Three grams of dibromide I was suspended in 50 ml. of 90% ethanol in which had been dissolved 10 g. of potassium hydroxide. The mixture was heated under reflux for 3 hours. After removal of the precipitated potassium bromide the solution was acidified and was diluted with water to a volume of 125 ml. Most of the alcohol was evaporated; the aqueous solution was then subjected to continuous ether extraction for 24 hours. A solid separated from the ether extract and was crystallized from water. The yield was 0.5 g. of colorless crystals, micro m.p. 209–210°.

*Anal.* Calcd. for $C_9H_8O_4$; C, 60.00; H, 4.48; neut. equiv., 180. Found: C, 59.83; H, 4.63; neut. equiv., 181.

Twelve grams of the dibromide was heated for three hours under reflux in a solution made by the addition of 5 g. of sodium to 100 ml. of absolute methanol. After acidification with hydrochloric acid, the solution was evaporated to almost half of its former volume and the residue was thoroughly extracted with ether. Upon evaporation of the ether there remained a viscous oil which could not be induced to crystallize.

When the same reaction was carried out at room temperature over a period of fifteen hours, a solid product consisting principally of bromides was obtained. Through repeated crystallization from water, there was isolated about 200 mg. of nortricyclenic acid lactone.

**Attempted Hydrogenation of Nortricyclenic Acid Lactone (III).**—Hydrogenation of 1.0 g. of the nortricyclenic acid lactone was attempted in both ethyl acetate[14] and absolute ethanol solution over Adams catalyst. Upon evaporation of the solvent, a solid was obtained which after crystallization from water yielded 1.0 g. of colorless crystals, m.p. 207–209°. On admixture with an authentic sample of acid lactone III the melting point was unchanged. The infrared spectrum of the product was identical in every respect with that of nortricyclenic acid lactone.

**Acknowledgment.**—The authors are indebted to Professor Harold Kwart who has graciously supplied details of the proof of structure of the dibromide I prior to its publication and to the referee for his valuable comments concerning footnote 9

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[14] Purified by the method of Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 364.