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3,6-ENDOXOCYCLOHEXANES AND -CYCLOHEXENES. XXV*. SOME REACTIONS OF DIMETHYL 4,5-(1-BENZYL-1,2,3-TRIAZOLINE)-3,6-ENDOXOHEXAHYDROPHTHALATE

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The anhydride and dimethyl ester of 4,5-(1-benzyl-1,2,3-triazoline)-3,6-endohexahydrophthalic acid, having a triazoline ring with an exo-cis configuration, are synthesized by reaction of benzyl azide with the furan-maleic anhydride adduct. Opening of the triazoline ring under the action of hydrochloric and acetic acids takes place with the separation of nitrogen and formation of the chloro and acetoxy derivatives, respectively, unaccompanied by a Wagner-Meerwein type of rearrangement.

In the previous paper [1] it was shown that opening the N-phenylethylenimine ring ring in dimethyl exo-cis-4,5-N-phenylimino-3,6-endoxohexahydrophthalate takes place without a Wagner-Meerwein (W-M) transformation. Since one of the factors which determines the ability of a compound to react and suffer a W-M rearrangement is the stability of the intermediate onium ion [2, 3], it was of interest to investigate the effect of other substituents of the nitrogen atom on the ability of the resultant compounds to react with simultaneous rearrangement.

In this paper a study is made of the addition of benzyl azide to dimethyl 3,6-endoxo-Δ^4-tetrahydrophthalate (I). Like phenyl azide, benzyl azide adds to the double bond in this ester, to give the corresponding N-benzyltriazoline derivative [4, 5], dimethyl exo-cis-4,5-(1-benzyl-1,2,3-triazoline)-3,6-endoxohexahydrophthalate (II). The triazoline II was also prepared by the action of benzyl azide on the furan-maleic anhydride adduct (III) followed by methylation of IV with an ether-methanol solution of diazomethane. However, all attempts to obtain the benzylimino derivative from the triazoline II were unsuccessful. When subjected to thermal decomposition, the dimethyl ester of triazoline II either gave back the starting material, or else yielded unidentified decomposition products. This further confirms the resistance of N-benzyltriazoline derivatives to thermal decomposition, previously recorded in the literature for the corresponding norbornane derivatives [6]. Decomposition of dimethyl ester II in acetic acid gives the acetate V, while the action of hydrochloric acid on II gives the hydrochloride VI.

It is known that addition of phenyl azide to a derivative of 3,6-endoxocyclohexane takes place exo [7]. Here it was found that when II and VI are boiled with sodium methylate and water added, the ester groups are isomerized to give the lactone acid VII, methylated with diazomethane to the ester of a lactone acid (VIII). This confirms the exo configuration of the triazoline ring in II, and the exo addition of benzyl azide to the anhydride and dimethyl ester of 3,6-endoxo-Δ^4-tetrahydrophthalic acid.

EXPERIMENTAL

Dimethyl 4,5-(1-benzyl-1,2,3-triazoline)-3,6-endoxohexahydrophthalate (II). 5 g dimethyl ester of acid I in 30 ml acetone is left for a week with 3.4 g benzyl azide [8]. After distilling off the acetone in a vacuum, 7.8 g (96%) II is obtained m.p. 137° (from benzene-petroleum ether). Found: C 58.73, 58.79; H 5.61, 5.68; N 12.43, 12.56%. Calculated for $C_{17}H_{19}N_3O_5$: C 59.12; H 5.54; N 12.6%.

4,5-(1-Benzyl-1,2,3-triazoline)-3,6-endoxohexahydrophthalic anhydride (IV). 1.6 g of the furan adduct III is dissolved in 20 ml dry acetone, 1.35 g benzyl azide is added, and the whole is left for a week. After distilling off the solvent 2.6 g (90%) IV is obtained, m.p. 205-206° (from dioxan). Found: C 59.96, 60.04; H 4.50, 4.63%. Calculated for $C_{15}H_{13}N_3O_4$: C 60.16; H 4.3%.

Treatment of IV with an ether-methanol solution of diazomethane gave II, m.p. 136-137° (from benzene-petroleum ether), melting point undepressed on mixing with the material mentioned above.

Dimethyl 4-chloro-5-N-benzylamino-3,6-endoxohexahydrophthalate hydrochloride (VI). 3.4 g II are added, with vigorous stirring, to 30 ml 20% hydrochloric acid at 0°, solution takes place with evolution of nitrogen. After some time a solid begins to separate, and this is filtered off and dried in air. Yield 1.2 g (32%) VI, m.p. 238-240° (from methanol-ether). Found: C 51.95; 52.12; H 5.51; 5.46%. Calculated for $C_{17}H_{21}O_5NCl_2$: C 52.31; H 5.42%.

Treatment of VI with aqueous ammonia gives dimethyl 4-chloro-5-N-benzylamino-3,6-endoxohexahydrophthalate (IX), m.p. 78-79° (from methanol). Found: C 57.32; 57.39; H 5.63; 5.64%. Calculated for $C_{17}H_{20}O_5NCl$: C 57.71; H 5.69%.

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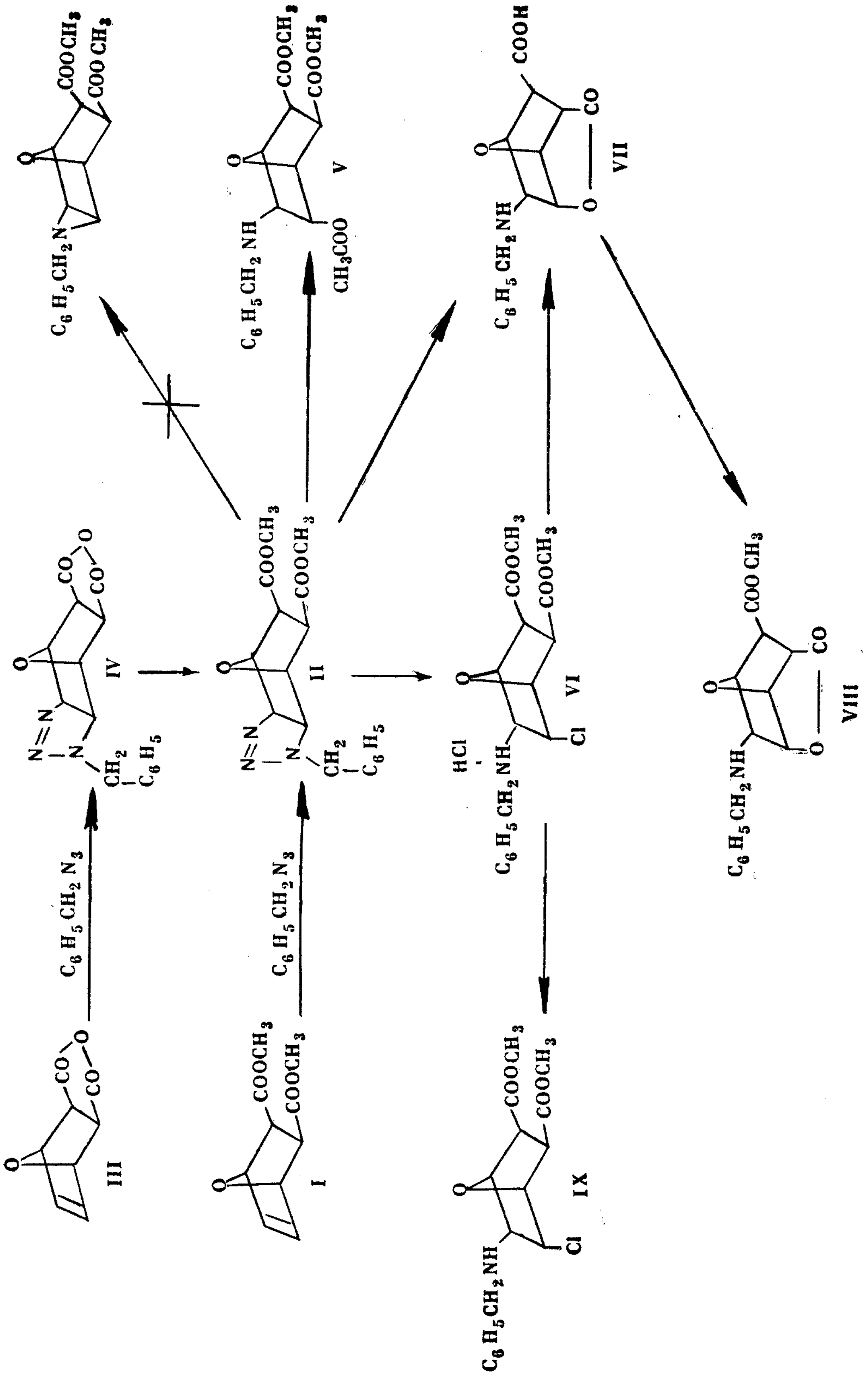
*Part XXIV, see [1].


III
I
IX
$C_6H_5CH_2N_3$
$C_6H_5CH_2N_3$
IV
II
VI
VIII
V
VII
HCl

Dimethyl 4-acetoxy-5-benzylamino-3, 6-endoxohexahydrophthalate (V). 1 g II is dissolved in 2 ml acetic acid, and after vigorous evolution of nitrogen the mixture is neutralized with sodium bicarbonate solution and extracted with chloroform. The extract is dried over sodium sulfate, and the solvent taken off in a vacuum. Yield 1 g (91%), m. p. 132-133.5° (from ethyl acetate-petroleum ether). Found: C 60.02, 60.15; H 6.37, 6.36%. Calculated for $C_{19}H_{23}NO_7$: C 60.46; H 6.14%.

Lactone of 4-hydroxy-5-N-benzylamino-3, 6-endoxohexahydrophthalic acid (VII).

a) 0.5 g II are dissolved in 10 ml dry methanol, a solution of 0.2 g sodium in 5 ml dry methanol is added, and the whole refluxed for 10 hrs. 2 ml water are then added, boiling is continued for a further 2 hrs, the methanol distilled off, and the residue dissolved in 3 ml water and acidified with 2N hydrochloric acid. The dark brown oily material which separates is repeatedly boiled with carbon in methanol and gives 0.16 g (40%) VII m. p. 234-236° (from methanol). Found: C 62.60; 62.73; H 4.90; 4.94%. Calculated for $C_{15}H_{15}NO_5$: C 62.32; H 5.22%.

The IR spectrum of VII contains bands characteristic of a γ-lactone (1766 cm^{-1}) and of the carboxyl group (1720 cm^{-1}).

b) In a similar way 0.20 g hydrochloride of VI gives 0.08 g of the same lactonic acid VII, m. p. 234-236° (from methanol). A mixed melting point determination with two specimens of the lactonic acid IX showed no depression.

The methyl ester VIII is obtained by methylating VII with a solution of diazomethane in ether-methanol, m. p. 168-170° (from methanol). Found: C 63.30; 63.38; H 5.40; 5.43%. Calculated for $C_{16}H_{17}O_5$: C 63.39; H 5.65%.

REFERENCES

1. N. S. Zefirov, G. P. Krutetskaya, L. P. Prikazchikova, Yu. K. Yur'ev, ZhOKh, 35, 1965.
2. Yu. K. Yur'ev, N. S. Zefirov, ZhOKh, 32, 773, 1962.
3. Yu. K. Yur'ev, N. S. Zefirov, ZhOKh, 33, 804, 1963.
4. K. Alder, G. Stein, Ann., 485, 211, 1931.
5. K. Henkel, F. Weygand, Ber., 76, 812, 1943.
6. U. Post, Über einige Reaktionen von Aziden mit der Aktiven Doppelbindung des Bicyclo [1.2.2] Hepten Systems, Inaugural-Dissertation, Köln, 1960.
7. Yu. K. Yur'ev, N. S. Zefirov, ZhOKh, 31, 1125, 1961.
8. T. Curtius, G. Ehrhart, Ber., 55, 1559, 1922.

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