[Contribution from the Wm. H. Chandler Chemistry Laboratory, Lehigh University]

REACTION OF EPOXIDES WITH DIPHENYLACETONITRILE

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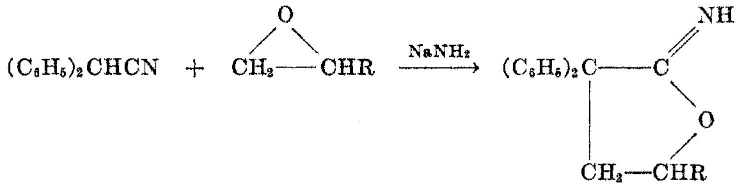
The reaction of propylene oxide with diphenylacetonitrile in the presence of either sodamide (1) or potassium *tert*-butoxide (2) has been reported. The reaction between ethylene oxide and diphenylacetonitrile is also recorded in the literature (3). This reaction is outlined in equation A. In some cases the imidolactone was not isolated but directly hydrolyzed to the corresponding lactone.

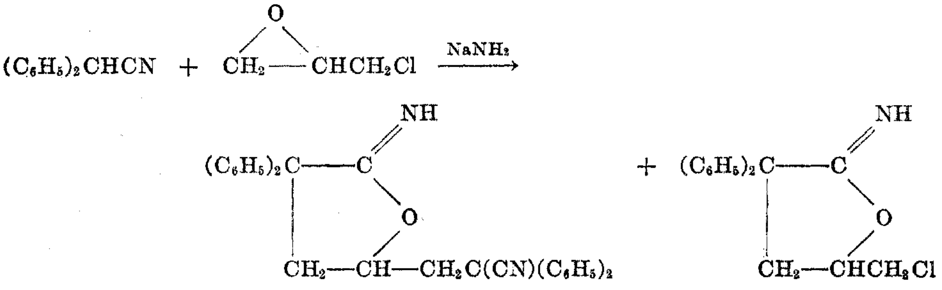
A.



A further study has been made using epichlorohydrin, N,N-diethylepihydrinamine, and allyl glycidyl ether. In these cases R = $-CH_2Cl$, $-CH_2N(C_2H_5)_2$, and $-CH_2OCH_2CH{=}CH_2$ respectively. When epichlorohydrin is added to the sodium salt of diphenylacetonitrile two compounds are produced. The predominant product, which contains two molecules of diphenylacetonitrile for each one of epichlorohydrin, has been assigned the structure (I). This structure is based on the analyses of the compound itself and of the lactone which is formed on hydrolysis. The second compound, which is obtained in small yield from the mother liquors, is the expected material (II). It is found that an 81% yield of I can be obtained when the ratio of two moles of diphenylacetonitrile per mole of epichlorohydrin is employed.

When the reverse method is used, that is when the sodium salt of diphenylacetonitrile is added to an excess of epichlorohydrin, II is the only basic product which is obtained.

These experiments serve to substantiate further the structure assigned to I.



I

II

The hydrochloride of I is very insoluble in an ether-benzene mixture and precipitates immediately whereas the hydrochloride of II crystallizes slowly. This allows a simple means of separating the two products.

The intermediate imidolactone from diphenylacetonitrile and N,N-diethylepihydrinamine was hydrolyzed to give 5-diethylamino-2,2-diphenyl-4-pentanolactone, which has been prepared (4) previously from 5-bromo-2,2-diphenyl-4-pentanolactone.

The 5-chloro-2,2-diphenylpentanolactone which was prepared by hydrolysis of II was condensed with morpholine, and the product was converted to the hydrochloride which was identical to that previously shown to be 5-morpholine-2,2-diphenyl-4-pentanolactone hydrochloride (4).

In general the hydrochlorides of the imidolactones were easily purified except for the hydrochloride of I which was not obtained in an analytically pure state.

The lactones were obtained in good yields by the hydrolysis of the corresponding imidolactones.

EXPERIMENTAL

Reaction of epichlorohydrin with diphenylacetonitrile. A. Normal addition. A mixture of 12 g. of sodamide, 60 g. of diphenylacetonitrile, and 100 ml. of benzene was refluxed with vigorous stirring until the precipitation of the sodium salt made stirring very difficult. The mixture was cooled to 20° and 28.5 g. of epichlorohydrin was added at such a rate that the temperature remained between 20° and 30°. After the addition had been completed, the resulting mixture was heated to reflux, cooled to room temperature, and poured into water. The benzene layer was separated and the water layer was extracted twice with ether. The benzene-ether mixture was dried over magnesium sulfate and concentrated to dryness at reduced pressure. The residue was dissolved in dry ether and an alcoholic solution of hydrogen chloride was added. A solid which melted at 178–180° was obtained in small yield; however, the use of two moles of diphenylacetonitrile to one of epichlorohydrin gave an 81% yield of this material. Since this compound was very difficult to purify, it was neutralized in the following manner. The hydrochloride was dissolved in ethanol and water was added until the solution was cloudy; the mixture was then made strongly basic with 20% sodium hydroxide. The oily layer was extracted with ether, and the ether solution was dried over magnesium sulfate and concentrated at reduced pressure. The 3,3-diphenyl-5-(diphenylcyanomethyl)tetrahydro-2-furanoneimine (I) after recrystallization from methanol and then from ethanol melted at 153–154.5°.

Anal. Calc'd for $C_{31}H_{26}N_2O$; C, 84.13; H, 5.92; N, 6.33.

Found: C, 84.00; H, 5.86; N, 6.31.

B. Reverse addition. To a solution of 18 g. (25% excess) of epichlorohydrin in 100 ml. of benzene there was added slowly, with stirring, a slurry of the sodium salt of diphenylacetonitrile prepared from 6 g. of sodamide, 30 g. of diphenylacetonitrile, and 100 ml. of benzene. The resulting mixture was heated to 60° at which temperature a gelatinous precipitate started to form. The mixture was cooled and poured into water, and the benzene layer was separated and dried over magnesium sulfate. To the dried benzene solution there was added an alcoholic solution of hydrogen chloride. Since no precipitate appeared as in part *A*, the mixture was placed in the refrigerator. The solid which separated weighed 10 g. and melted at 216–219°. A second crop of 6 g. was obtained by concentrating the mother liquor to dryness, taking the residue up in absolute ethanol, and adding isopropyl ether. After recrystallization from a mixture of ethanol and isopropyl ether, the 3,3-diphenyl-5-(chloromethyl)tetrahydro-2-furanoneimine hydrochloride melted at 223–225° with decomposition.

Anal. Calc'd for $C_{17}H_{17}Cl_2NO$: C, 63.36; H, 5.32; Cl, 22.01.
Found: C, 63.35; H, 5.63; Cl, 21.50.

A small yield of this compound was obtained from the mother liquors of Part *A*.

Reaction of N,N-diethylepihydrinamine with diphenylacetonitrile. The reaction was accomplished as in part *A* above using 12 g. of sodamide, 60 g. of diphenylacetonitrile, and 40 g. of N,N-diethylepihydrinamine (5). After drying the organic layer, a solution of hydrogen chloride in absolute ethanol was added. The precipitate which formed weighed 53.6 g. and melted at 165–167°. A second crop of 6 g. melting at 160–165° was also obtained. After recrystallization from a mixture of ethanol and isopropyl ether the 3,3-diphenyl-5-diethylaminomethyl-tetrahydro-2-furanoneimine monohydrochloride melted at 167–169°.

Anal. Calc'd for $C_{21}H_{27}ClN_2O$: Cl, 9.88; N, 7.81.
Found: Cl, 9.76; N, 7.60.

From the mother liquors there was obtained 29.3 g. of the hydrochloride of 5-diethylamino-2,2-diphenyl-4-pentanolactone melting at 197–200°.

Reaction of diphenylacetonitrile with allyl glycidyl ether. This reaction was run as in part *A* above using 6 g. of sodamide, 30 g. of diphenylacetonitrile, and 20 g. of allyl glycidyl ether. A yield of 18.7 g. of product melting at 168–171° and a second crop of 11 g. melting at 166–169° was obtained. After recrystallization from a mixture of absolute ethanol and isopropyl ether, the 3,3-diphenyl-5-allyloxymethyl-tetrahydro-2-furanoneimine hydrochloride melted at 169–171°.

Anal. Calc'd for $C_{20}H_{22}ClNO$: Cl, 10.81; N, 4.28.
Found: Cl, 10.93; N, 4.28.

Hydrolysis of the imidolactones. The hydrochlorides of the imidolactones were boiled with water. The solution first became clear and then an oil separated. The mixture was extracted with ether, and the ether solution was dried and concentrated under reduced pressure to give the lactones. 5-Allyloxy-2,2-diphenyl-4-pentanolactone, b.p. 195–200°/1 mm.

Anal. Calc'd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54.
Found: C, 77.70; H, 6.56.

5-Chloro-2,2-diphenyl-4-pentanolactone m.p. 89–90° (from ethanol).

Anal. Calc'd for $C_{17}H_{15}ClO_2$: C, 71.20; H, 5.27; Cl, 12.37.
Found: C, 71.25; H, 5.31; Cl, 12.18.

5-(Diphenylcyano)-methyl-2,2-diphenyl-4-pentanolactone, m.p. 139–140° (from ethanol).

Anal. Calc'd for $C_{31}H_{25}NO_2$: C, 83.94; H, 5.68; N, 3.16.
Found: C, 83.90; H, 5.97; N, 3.14, 3.16.

5-Diethylamino-2,2-diphenyl-4-pentanolactone hydrochloride. The isolation of this compound required that the water solution be made basic and extracted with ether. The product was obtained by treating the dried ether solution with alcoholic hydrogen chloride, m.p. 203–204° (from ethanol-ether).

Anal. Calc'd for $C_{21}H_{26}ClNO_2$: Cl, 9.85. Found: Cl, 9.76.

Mixture m.p. with previously prepared authentic sample, 203–204°.

Reaction of 5-chloro-2,2-diphenyl-4-pentanolactone with morpholine. A mixture of 7.3 g. of the chlorolactone and 30 ml. of morpholine was refluxed for 4 hours and then concentrated at reduced pressure. Addition of anhydrous ether precipitated 3 g. of morpholine hydrochloride. Benzene was added to the ether layer, and the mixture was washed five times with water. The organic layer was dried over magnesium sulfate and then was treated with alcoholic hydrogen chloride. The yield of 5-morpholino-2,2-diphenylpentanolactone hydrochloride (4) melting at 237–239° (with decomposition) was 7.6 g.

A mixture of this compound and that prepared by Craig (4) shows no depression of m.p.

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SUMMARY

The reactions of diphenylacetonitrile with epichlorohydrin, N,N-diethylepihydrinamine, and allyl glycidyl ether to give the corresponding imidolactones are reported.

Two products are isolated from the action of epichlorohydrin on diphenylacetonitrile, one of which is the result of two moles of diphenylacetonitrile reacting with one mole of epichlorohydrin.

The imidolactones are hydrolyzed to the lactones.

BETHLEHEM, PENNA.

BIBLIOGRAPHY

(1) EASTON, GARDNER, AND STEVENS, *J. Am. Chem. Soc.*, **69**, 2941 (1947).
(2) SCHULTZ, ROBB, AND SPRAGUE, *J. Am. Chem. Soc.*, **69**, 2454 (1947).
(3) ATTENBORROW, ELKS, HEMS, AND SPEYER, *J. Chem. Soc.*, 517 (1949).
(4) CRAIG, WILL, MACKO, DACANAY, FELLOWS, AND ULLYOT, *J. Am. Chem. Soc.*, **73**, 1339 (1951).
(5) GILMAN, SHERMAN, PRICE, ELDERFIELD, MAYNARD, REITSEMA, TOLMAN, MASSIE, JR., MARSHALL, AND YOLDMAN, *J. Am. Chem. Soc.*, **68**, 1291 (1946).