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A Route for the Synthesis of Substituted Dioxene Derivatives*

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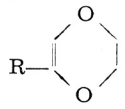
In our work on muscarine, certain quaternary ammonium salts with the substituted 1,4-dioxane nucleus were necessary for studies on biological activity. For this purpose we followed a new synthetic route for the preparation of substituted 1,4-dioxene derivatives, according to the reaction scheme I—IV.

$R.CO_2H$ (I) $R.COCHN_2$ (II) $R.COCH_2OCH_2CH_2OH$ (III)



IV

As an example for this synthesis a description is now given of the preparation of 2-phthalimidomethyl-1,4-dioxene-(2) (IV). ($R = C_6H_4(CO)_2NCH_2$ in I—IV).

The diazoketone II was suspended in 1,2-ethanediol and converted, with catalytic quantities of boron trifluoride-diethyl ether complex[1] into 1-(2′-hydroxyethoxy)-3-phthalimidopropanone (III). A benzene solution of this compound, on treating with phosphorus pentoxide, afforded 2-phthalimidomethyl-1,4-dioxene-(2) (IV). The scope of this reaction is being investigated.

EXPERIMENTAL

All melting points are uncorrected.

1-(2′-Hydroxyethoxy)-3-phthalimidopropanone (III)

A suspension of 1-diazo-3-phthalimidopropanone[3] (4.6 g., 0.02 mole) in 1,2-ethanediol (20 ml.) and borontrifluoride-diethyl ether complex (0.1 ml.) was heated to 50—60°. After half an hour the foaming ceased, and the clear yellowish solution was poured into a tenfold quantity of water and left overnight at 0°. The crude *1-(2′-hydroxyethoxy)-3-phthalimidopropanone* was collected and dried, yield 3.3 g. (63%), m. p. 85—102°. The sample for analysis was dissolved in benzene and passed through a column of alumina (1 : 10). After removing the solvent by evaporation, the residue was recrystallized three times from dichloromethane-petroleum ether;

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white needles were obtained, with the m. p. 132—135° (sintering at 110°). Before analysis the substance was fused at 180°/0.05 mm. for a short time.

Anal. 3.99 mg. subst.: 0.195 ml. N_2 (15°C, 745 mm.)
$C_{13}H_{13}NO_5$ (263.24) calc'd.: N 5.32%
found: N 5.68%

2-*Phthalimidomethyl-1,4-dioxene-(2)* (IV)

A solution of pure 1-(2'-hydroxyethoxy)3-phthalimidopropanone (III, 1 g.) in benzene (40 ml.) was shaken with phosphorus pentoxide (2 g.) at room temperature for 24 hours. The suspension was filtered, evaporated to dryness, and the thus obtained crude 2-*phthalimidomethyl*-1,4-*dioxene*-(2), yield 0.77 g. 83%), m. p. 145—153°, recrystallized from dichloromethane-petroleum ether and sublimed at 140°/0.01 mm.; white prisms, m. p. 164—165°.

Anal. 9.68 mg. subst.: 22.63 mg. CO_2, 4.26 mg. H_2O
$C_{13}H_{11}NO_4$ (245.22) calc'd.: C 63.67; H 4.52%
found: C 63.81; H 4.92%

The substance gave a strong positive test for unsaturation with bromine in tetrachloromethane.

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IZVOD

Sinteza supstituiranih derivata dioksena

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Na primjeru 1-diazo-3-ftalimidopropanona pokazano je, da se iz diazoketona sa 1,2-etandiolom mogu prirediti, preko 1-(2'-oksietoksi)-ketona III, supstituirani diokseni IV.

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