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REACTION OF NITROSOBENZENE WITH 1,2,3,4-TETRACHLORO-5,5-ETHYLENEDIOXYCYCLOPENTADIENE

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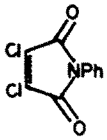
Abstract—The reaction of nitrosobenzene with 1,2,3,4-tetrachloro-5,5-ethylenedioxycyclopentadiene gives rise to N-phenyldichloromaleimide 1 and the unsaturated trichloro-hydroxy-ester-lactam 2.

The dienophilic behaviour of nitrosobenzene is well known.[1,2] Attempted diene addition of 1,2,3,4 - tetrachloro - 5,5 - ethylenedioxycyclopentadiene[3] in toluene at −5° to +10° (reaction time up to 3 weeks) gave a complex mixture of products from which two crystalline compounds could be isolated. The first was identified as N-phenyldichloromaleimide 1,[4,5] and the second product, $C_{13}H_{10}Cl_3NO_4$, could be assigned structure 2 on the evidence detailed below.

In the mass spectrum, the base peak at *m/e* 242 resulted from the loss of 107 m.u. from the parent ion [*m/e* 349 (^{35}Cl)]. The obvious conclusion, that this corresponded to the loss of C_6H_5NO, was shown to be incorrect by identification of the fragment of *m/e* 242 as $C_{10}H_6Cl_2NO_2$ (by mass-matching); thus the fragment lost from the parent ion was $C_3H_4ClO_2$. The PMR spectrum of the product indicated the presence of five aromatic protons, and a single OH or NH proton (exchangeable with deuterium); additionally, it showed that the four remaining protons were contained in a 1,2-disubstituted ethane system. The mass spectral fragment of *m/e* 107 could therefore be formulated as $-CO_2CH_2CH_2Cl$. The IR spectrum confirmed the presence of OH or NH, and suggested that the compound also contained C=C and at least two different C=O groups. Reaction with acetic anhydride in pyridine (or isopropenyl acetate in the presence of sulphuric acid) gave an acetyl-derivative; diazomethane in ether–methanol yielded a methyl-derivative. Permanganate oxidation led to 2-chloroethyl oxanilate 3, which on hydrolysis with aqueous trifluoroacetic acid gave oxanilic acid 4, identical with an authentic sample.

This evidence is accommodated by either of the structures 2 or 5.† A decision between these alternatives was then made on the following grounds. When the compound was treated with methyl iodide, no reaction occurred in the absence of silver oxide, but in its presence there resulted a Me-derivative identical with the product obtained by means of diazomethane. This behaviour is as expected for a hydroxy-ester (Ref. 7), but is not typical of an amino-compound; moreover, the chemical shift (τ 6.62) of the Me protons in the PMR spectrum of the methylated product was indicative of CH_3O- rather than $CH_3\overset{|}{N}Ph$.[8] Finally, and most conclusively, the PMR spectrum of the parent compound in trifluoroacetic acid was consistent with the formation of the trifluoroacetate 6, but not with that of the salt 7.

The production of compounds 1 and 2 from nitrosobenzene and 1,2,3,4 - tetrachloro - 5,5 - ethylenedioxycyclopentadiene is most readily explained by assuming the initial formation of the Diels–Alder adduct 8. One possible way in which this might give rise to the observed products is outlined in Scheme 1. Cleavage of the bridge via the dipolar intermediate 9 could lead either to 10 (see Ref. 9) or to 11 (see Ref. 3). In either case fission of the N–O bond (see Ref. 10) would then produce an acid chloride, which would be expected to recyclize to give 12 and 13 respectively. Attack of water could then furnish the observed products. This mechanistic scheme is of course purely speculative, and alternative paths may readily be devised.



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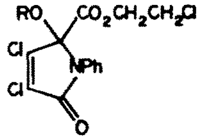
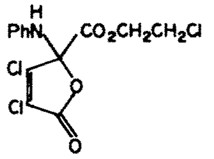


2 R = H
6 R = CF_3CO
14 R = CH_3CO
15 R = CH_3

$PhNHCOCO_2R$

3 R = CH_2CH_2Cl
4 R = H



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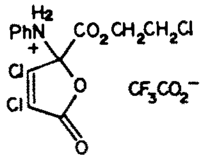

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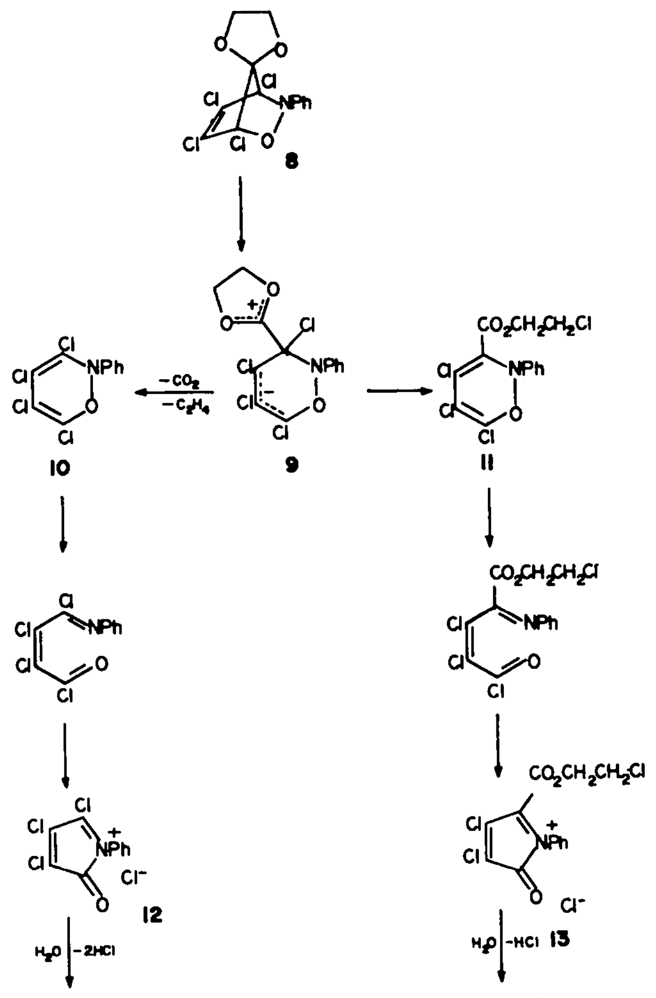
†α-Hydroxy-esters are known to be methylated by diazomethane;[6] the α-amino-ester 5 might behave similarly.



Scheme 1.

EXPERIMENTAL

Unless stated otherwise, IR spectra were determined for Nujol mulls, and PMR spectra were measured at 100 MHz in $CDCl_3$.

Reaction of nitrosobenzene with 1,2,3,4 - *tetrachloro* - 5,5 - *ethylenedioxycyclopentadiene.* (This reaction was somewhat capricious, and optimum conditions were not established). A mixture of nitrosobenzene (2.7 g) and the tetrachloro-ketal[3] (6.5 g) in toluene (30 ml) was kept at 6° for 19 days. The resulting soln was decanted from a small amount of tar and chromatographed using a silica column made up with light petroleum (b.p. 40–60°). Elution with ether–CCl_4 (1:1) gave crystalline material which was extracted with cold MeOH. The insoluble portion (0.71 g) was 1.[4,5] identical with a sample prepared from dichloromaleic anhydride and aniline in refluxing xylene (see Ref. 11).

The MeOH-soluble material was then rechromatographed on a dry silica column.[12] Elution with MeOH–CH_2Cl_2 (1:10) afforded 2 (1.18 g), m.p. 117–118° from CCl_4. (Found: C, 44.5; H, 2.9; Cl, 30.1; N, 4.3; *M* (mass spectrum), 349 (^{35}Cl). $C_{13}H_{10}Cl_3NO_4$ requires: C, 44.5; H, 2.9; Cl, 30.35; N, 4.0%; *M*, 349 (^{35}Cl)]; IR ν_{max} 3340, 1773, 1711, 1691, 1634 cm^{-1}; ν_{max} (CCl_4) 3490, 3340, 1774, 1745, 1710, 1690, 1635 cm^{-1}; λ_{max} (EtOH) 226, 271 nm (ϵ 6750, 2330); τ 2.55–2.85 (5H), 5.14 (s, 1H, exchangeable with D), 5.55–5.75 (2H), 6.4–6.6 (2H); τ (CF_3CO_2H) 2.4–2.75 (5H), 5.3–5.55 (2H), 6.2–6.4 (2H).

The derivative 14 (prepared with Ac_2O in pyridine at room temp. or with isopropenyl acetate in refluxing benzene in the presence of a catalytic quantity of conc. HSO_4) had m.p. 102.5–103.5° from CCl_4 tetrachloride. (Found: C, 45.9; H, 3.0; Cl, 27.1; N, 3.7. $C_{15}H_{12}Cl_3NO_5$ requires: C, 45.9; H, 3.1; Cl, 27.1; N, 3.6%); ν_{max} 1770, 1730, 1641 cm^{-1}; τ 2.5–2.85 (5H), 5.55–5.75 (2H), 6.4–6.6 (2H), 7.90 (s, 3H).

The derivative 15 (prepared with diazomethane in ether–MeOH, or with MeI in the presence of dry Ag_2O)[7] had m.p. 93–94° from light petroleum, b.p. 60–80°. (Found: C, 46.3; H, 3.3; Cl, 28.9; N, 3.9. $C_{14}H_{12}Cl_3NO_3$ requires: C, 46.1; H, 3.3; Cl, 29.2; N, 3.8%); ν_{max} 1776, 1729, 1641 cm^{-1}; τ 2.35–2.85 (5H), 5.55–5.75 (2H), 6.45–6.65 (2H), 6.62 (s, 3H).

Permanganate oxidation of 2. Powdered $KMnO_4$ (1.92 g) was added in portions during 30 min to a refluxing soln of 2 (1.44 g) in dry acetone (50 ml). The solvent was evaporated and the residue was treated with SO_2aq. The resulting solid was collected, washed with water, and dried to give 3 (0.48 g), m.p. 134–136° from benzene-light petroleum, b.p. 40–60°. (Found: C, 53.3; H, 4.6; Cl, 15.4; N, 6.6. $C_{10}H_{10}ClNO_3$ requires: C, 52.8; H, 4.4; Cl, 15.6; N, 6.2%); ν_{max} 3350, 1742, 1717, 1707 sh cm^{-1}; τ 1.2 (br s, 1H, exchangeable with D), 2.24–2.9 (5H), 5.3–5.5 (2H), 6.05–6.3 (2H).

Treatment of 3 with 50% aqueous trifluoroacetic acid under reflux overnight gave 4, identical with an authentic specimen prepared by hydrolysis of ethyl oxanilate.[13]

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