OXIDATIVE CLEAVAGE OF THE NITROFURYL GROUP ACCOMPANYING THE NITRATION OF 2-(2-FURYL)IMIDAZO[1,2-a]PYRIMIDINES

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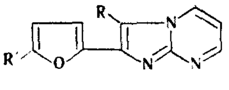
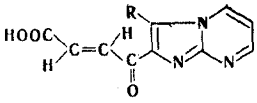
We have found that, depending on the conditions, 2-(2-furyl)imidazo[1,2-a]pyrimidine (I) gives different reaction products on treatment with a nitrating mixture. The action of an equimolar amount of 70% HNO_3 on a solution of I in a mixture of 95% H_2SO_4 and glacial acetic acid at 5-10°C leads to 5-nitro derivative II (89%); however, when I is added to a mixture of nitric and sulfuric acids, 3,5'-dinitro derivatives III, 2-(trans-3-carboxyacryloyl)imidazo[1,2-a]pyrimidine (V), and more profound oxidation products are formed in addition to II.



I-IV



V, VI

I R=R'=H; II R=H, R'=NO_2; III R=R'=NO_2; IV R=Br, R'=NO_2;
V R=H; VI R=Br

Since II is converted under the same conditions not only to nitro derivative III but also to keto acid V, whereas 3-bromo-2-(5-nitro-2-furyl)imidazo[1,2-a]pyrimidine is converted to bromo keto acid VI, it may be concluded that the trans-acylacrylic acids are formed as a result of oxidative cleavage of the nitrofuryl group. This case is of fundamental significance for the explanation of the frequently observed low yields of hetarylnitrofurans when nitration is the final step. Up until now, only nonoxidative cleavage of 2-nitrofuran to give monomethyl fumarate and methyl trans-formylacrylate under the influence of sodium methoxide was known [1].

The yields of II, III, and V, which were precipitated after neutralization of the reaction mixtures to pH 3, were (according to the PMR spectra) 16, 20, and 6%, respectively, when the reaction was carried out with 2 moles of HNO_3 (at 0-5°C for 2 h), and were 6, 14, and 12% under the influence of 5 moles of HNO_3 (at 25-30°C for 3 h). In the case of the reaction of IV with 2 moles of HNO_3 at 20-25°C for 2 h, bromo keto acid VI was obtained in 79% yield, and 10% of the starting compound was regenerated.

Nitro derivatives II-IV were isolated by elution with ethyl acetate and a column filled with silica gel and were recrystallized from dimethylformamide (DMF). Keto acids V and VI were removed from the start of the column by dissolving in DMF and were isolated by the addition of ether and recrystallized from DMF—ether. Their structures were confirmed by the results of elementary analysis and the PMR (d_6-DMSO, Bruker WH-90 spectrometer) and IR spectra. The following data were obtained for the compounds obtained [the compounds, empirical formulas, melting points, and PMR spectral data (δ, in parts per million) are given]: II, $C_{10}H_6N_4O_3$, 300°C, 7.15 (dd, J_{67} = 4.1 Hz, J_{56} = 7.0 Hz, 6-H), 7.30 and 7.84 (two d, J = 4.1 Hz, 3'-H, 4'-H), 8.50 (1H, s, 3-H), 8.55 (dd, 7-H), 9.03 (dd, J_{57} = 2 Hz, 5-H); III, $C_{10}H_5N_5O_5$, 284-285°C, 7.68 (dd, J_{56} = 7.0 Hz, J_{67} = 4.1 Hz, 6-H), 7.93 (2H, s, 3'-H, 4'-H), 9.08 (dd, J_{57} = 2.0 Hz, 7-H), 9.80 (dd, 5-H); V, $C_{10}H_7N_3O_3$, 300°, 6.85 and 7.85 (two d, J = 15.8 Hz, trans-CH═CH), 7.17 (dd, J_{56} = 6.7 Hz, J_{67} = 4.0 Hz, 6-H), 8.66 (s, 3-H), 8.76 (dd, J_{57} = 2.0 Hz, 7-H), 9.02 (dd, 5-H); VI, $C_{10}H_6BrN_3O_3$, 300°, 6.83 and 8.14 (two d, J = 16.1 Hz, trans-CH═CH), 7.31 (dd, J_{56} = 6.7 Hz, J_{67} = 4.2 Hz, 6-H), 8.79 (dd, J_{57} = 2.0 Hz, 7-H), 8.91 (dd, 5-H). IR spectra of keto acids V and VI (in mineral oil): 1725 and, respectively, 1718 (COOH), 1670 and 1675 (C═O), and 977 and 983 cm^{-1} (trans-CH═CH).

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SYNTHESIS OF TELLURAXANTHENE

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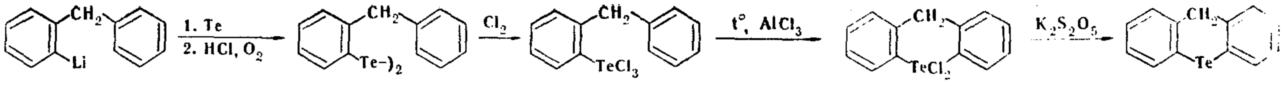
We have obtained the previously unknown telluraxanthene (I) by intramolecular electrophilic cyclization of 2-trichlorotelluriodiphenylmethane (II) in the presence of aluminum chloride and subsequent reduction.



III II IV I

Ditelluride III was obtained in 78% yield by reaction of 2-lithiodiphenylmethane (from 2-bromodiphenylmethane and lithium) in ether with powdered tellurium and subsequent treatment of the resulting lithium tellurophenoxide with hydrochloric acid in air; the product was obtained as large red crystals with mp 101°C (from petroleum ether). PMR spectrum in deuteroacetone: 4.17 (s, 2H, CH_2) and 6.95-8.07 ppm (m, 9H, aromatic protons). Compound II was obtained in almost quantitative yield when chlorine was passed with cooling into a solution of III in methylene chloride; the product was obtained as slightly yellowish crystals with mp 199-200°C (from glacial acetic acid). Large colorless plates of 10,10-dichlorotelluraxanthene (IV), with mp 250-270°C (dec., from chlorobenzene), were obtained in 80% yield when equimolar amounts of II and aluminum chloride were heated in o-dichlorobenzene at 50-70°C for 3-4 h. Treatment of a suspension of IV in water with potassium metabisulfite gave colorless needles of telluraxanthene, with mp 151°C (from petroleum ether), in almost quantitative yield. PMR spectrum in deuteroacetone: 3.93 (s, 2H, CH_2) and 6.90-7.93 ppm (m, 8H, aromatic protons).

The results of elementary analysis of I-IV were in agreement with the calculated values.

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