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THE EFFECT OF NITRO GROUPS ON OXIDATIVE CYCLISATION OF CHALCONES BY THALLIUM(III) NITRATE(TTN)

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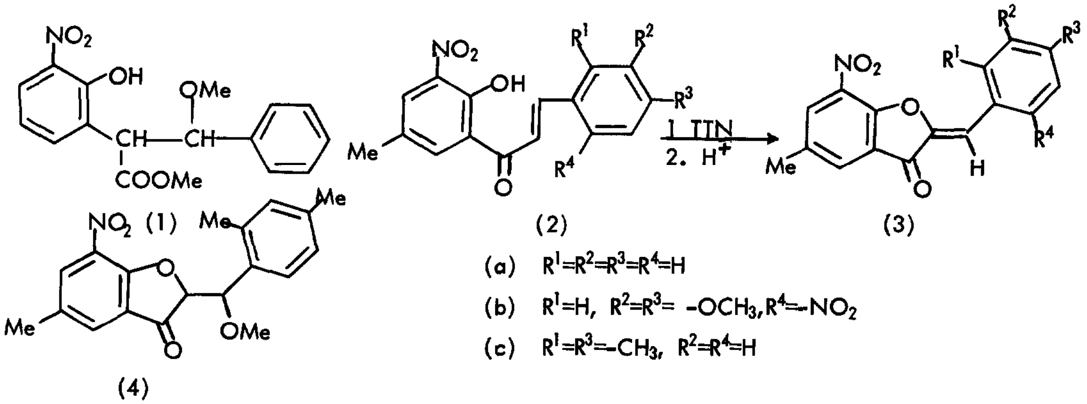
ABSTRACT 2'-Hydroxy-3'-nitrochalcones on oxidation with thallium(III) nitrate do not give rearranged intermediates that can give isoflavones, instead cyclisation gives benzylidenebenzofuran-3(2H)-one derivatives.

Chalcones are normally oxidised with thallium(III) nitrate (TTN) with rearrangement providing easy access to a variety of compounds[1,2] including isoflavones. In the preparation of isoflavone from 2'-hydroxychalcone by means of TTN we isolated a nitro derivative(1) as a minor product.[3] The nitro group might have been introduced first, and then modified the reaction course, or it might have been introduced only after the abnormal reaction had occurred.

We have therefore investigated the reaction of 2'-hydroxy-3'-nitro chalcones (2a-c) in methanol with 2 mol. equivalents of thallium(III) nitrate. After 72h, the precipitated thallium(1) nitrate was separated and the traces of unreacted chalcone removed by passing the solution (CH_2Cl_2) through a small column of basic alumina. The intermediate obtained was heated with methanolic hydrochloric acid (10%) for 4h to give single product in each case. The infrared spectra of these products revealed carbonyl absorption around 1705 cm^{-1}. The U.V. and ^1H n.m.r. data[4] confirmed the compounds to be aurone derivatives (3a-c) and the configuration is believed to be (Z) on the basis of chemical shifts of 2',6' protons[5-7] and their i.r. spectra.[7]

In one case, (2c), we have isolated an intermediate after 10h with possible structure (4), m.p. 145-155°C, IR(KBr) ν ($Cm.^{-1}$) 1737, 1630, 1584 and 1527, NMR δ (220MHz,$CDCl_3$) 8.22(1H,d,H-4), 7.78(1H,d,H-6), 7.51(1H,d,H-6') 7.15(1H,dd, H-5'), 7.02(1H,d,H-3'),5.09(1H,d,-CH),4.75(1H,d,-CH),3.11(3H,s,-OCH_3), 2.46, 2.39 and 2.34(3xCH_3) which upon warming with acid or in contact with alkali in cold gave readily the product (3c).

This appears to be the only example in extensively studied chalcone oxidation reactions[2] where thallium(III) nitrate induces cyclisation without rearrangement just like other oxidising agents.[6] Furthermore, we observed this oxidative cyclisation only in case



(1) (2) (3) (4)

(a) $R^1=R^2=R^3=R^4=H$

(b) $R^1=H$, $R^2=R^3=-OCH_3, R^4=-NO_2$

(c) $R^1=R^3=-CH_3$, $R^2=R^4=H$

of 3'-nitrosubstituent, 5'-nitro and 4-nitro chalcones did not give aurones under similar conditions. It is also clear that in the formation of (1) nitration was not the first step in the reaction.

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4. 3a 54% yield, M^+ 281, $C_{16}H_{11}NO_4$, m.p. 235-236° C(MeOH),IR(KBr) ν (Cm.$^{-1}$) 1704, 1645, 1614 and 1582,UV λmax.(MeOH) 245(ϵ16,660),332(25,800) and 380nm(11,900),NMR δ (220MHz,$CDCl_3$) 8.26(1H,d,H-4),8.05(2H,q,H-2',6'),7.91 (1H,d,H-6),7.50(3H,m,H-3',4',5') and 7.03(1H,s,=CH).

   3b 19% yield, M^+ 386,$C_{18}H_{14}N_2O_8$, m.p. 300°C(MeOH),IR(KBr) ν (Cm^{-1}) 1707, 1648, 1620 and 1586; UV λmax. (CH_2Cl_2) 254, 318(inf.), 368 and 406nm,NMR δ (220MHz,TFA)· 8.48-7.88(5H,ArH and =CH),4.28 and 4.11(6H,2x-OCH_3) and 2.60(3H,-CH_3).

   3c 86% yield, M^+ 309, $C_{18}H_{15}NO_4$, m.p. 227-228°C (MeOH), IR(KBr) ν(Cm^{-1}) 1709, 1644, 1622 and 1583, UV λmax.(MeOH) 249(ϵ 18,000),344(20,900) and 388nm(16,550), NMR δ(220MHz,$CDCl_3$): 8.37(1H,d,H-6'),8.24(1H,d,H-4),7.90 (1H,d,H-6),7.25-7.08(3H,H-3',5' and =CH),2.50,2.49 and 2.37(3x-CH_3). 3a-c gave satisfactory microanalysis.
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