Tetrahedron Letters No. 24, pp 2195 - 2198, 1973. Pergamon Press. Printed in Great Britain.

# THE CRYSTAL STRUCTURE OF 2,6-DIPHENYL-4-(4-BROMOPHENYL)-5-NITRO-2,6-DIETHOXY-5,6-DIHYDRO-2H-PYRAN FROM 2,6-DIPHENYL-4-(4-BROMOPHENYL)PYRYLIUM TETRACHLOROFERRATE(III) AND SODIUM NITRITE IN ETHANOL

Christian L. Pedersen and Ole Buchardt (1)
Chemical Laboratory II, The H. C. Ørsted Institute, University of Copenhagen,
Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

Sine Larsen
Chemical Laboratory B, The Technical University of Denmark,
DK-2800 Lyngby, Denmark

Kenneth J. Watson
Chemical Laboratory IV, The H. C. Ørsted Institute, University of Copenhagen,
Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

(Received in UK 16 April 1973; accepted for publication 3 May 1973)

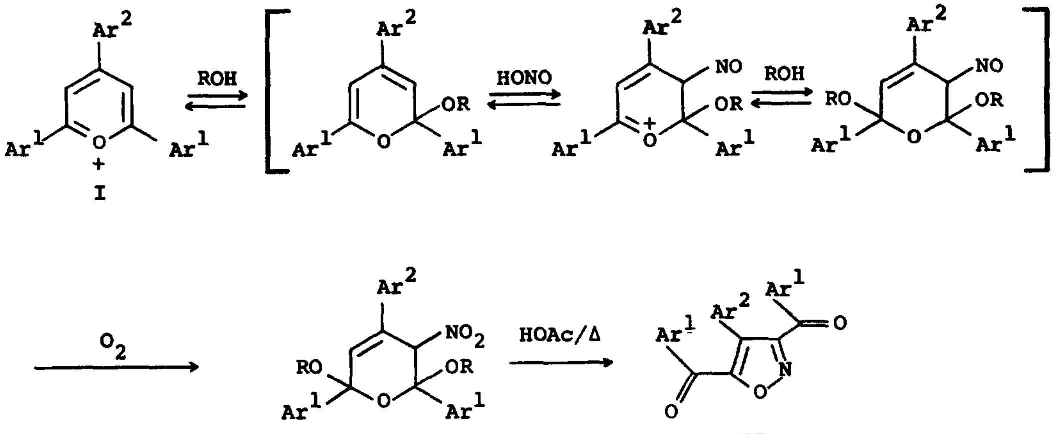
2,4,6-Triaryl pyrylium salts undergo reaction with nitrite and alcohols to form products which correspond to the addition of one mole of nitrite ion and two moles of alcohol in a two-electron oxidation.

$$\mathrm{Pyr}^+ + NO_2^- + 2ROH \xrightarrow[-2H^+ \;\; -2e^-]{} \mathrm{Pyr},\ NO_2,\ 2RO$$

*E.g.*, when 5.00 g 2,4,6-triphenylpyrylium tetrachloroferrate(III) (Ia) was stirred with 1.36 g sodium nitrite in 100 ml 1-propanol for 64 hrs. at ca. 25°, with subsequent removal of 2.26 g Ia and preparative layer chromatography on silica gel, 1.27 g of white crystals, which analyses as $C_{29}H_{31}NO_5$, m.p. 142-43° is obtained. The salient spectroscopic data for this compound are: i.r. (KBr) 1555 $cm^{-1}$ ($-NO_2$); u.v. (96% ethanol $\lambda_{max}$ 248 nm, log $\varepsilon$ 4.10; n.m.r. ($CDCl_3$) 2.0-2.7 $\tau$ (m, 15H), 3.25 $\tau$ (s, 1H), 4.12 $\tau$ (s, 1H), 6.2-7.1 $\tau$ (m, $OCH_2$, 4H), 8.1-8.9 $\tau$ (m, $-\underline{CH}_2-CH_3$, 4H), 8.9-9.4 $\tau$ (m, $-CH_3$, 6H); the mass spectrum is complex and shows no molecular ion.

If the product of the above reaction is boiled in acetic acid a compound with empirical formula $C_{23}H_{15}NO_3$, m.p. 122-23° is formed. I.r. (KBr) 1670 $cm^{-1}$ (CO); u.v. (96% ethanol) $\lambda_{max}$ 263 nm, log ε 4.41, 287 nm (sh), log ε 4.10; n.m.r. signals corresponding to aromatic protons only. This same compound can also be obtained from the reaction of the pyrylium salt and nitrite in acetonitrile or in t-butyl alcohol.

On the basis of this evidence the reaction scheme and the corresponding structures formed were proposed as shown below.[*]



I

II

III

a: $Ar^1 = Ar^2 = Ph$, $R = CH_2CH_2CH_3$ (m.p. 142-143°)

b: $Ar^1 = Ph$, $Ar^2 = 4\text{-Br-Ph}$, $R = CH_2\text{-}CH_3$ (m.p. 151-153°)

To obtain more unambiguous evidence of the structure of compound II and its analogues, compound IIb was prepared and its structure has been determined by X-ray diffraction methods.

Crystals of the compound are monoclinic, space group $P2_1/a$, with unit cell dimensions $a$ = 13.145(10), $b$ = 20.225(15), $c$ = 9.440(8) Å, $\beta$ = 91.61(2)°. There are four molecules in the unit cell. The structure was postulated from a combination of the information obtained by applying direct (2) and Patterson and heavy-atom Fourier methods (2), and this postulate has been refined by full

---

[*] A number of derivatives of II, using various primary and secondary alcohols as well as other 2,4,6-triarylpyrylium salts have been prepared. These results and the mechanistic details will be described in a full paper.

matrix least squares techniques (2) so that the conventional *R* factor for the 2236 diffractometer-measured, independent observed reflections which had $\sin \theta/\lambda < 0.504$ is now 0.11.

The analysis has shown that the product of the reaction described above is 2,6-diphenyl-4-(4-bromophenyl)-5-nitro-2,6-diethoxy-5,6-dihydro-2H-pyran (II, Figure 1) and that the molecules of this substance have the following geometrical features:

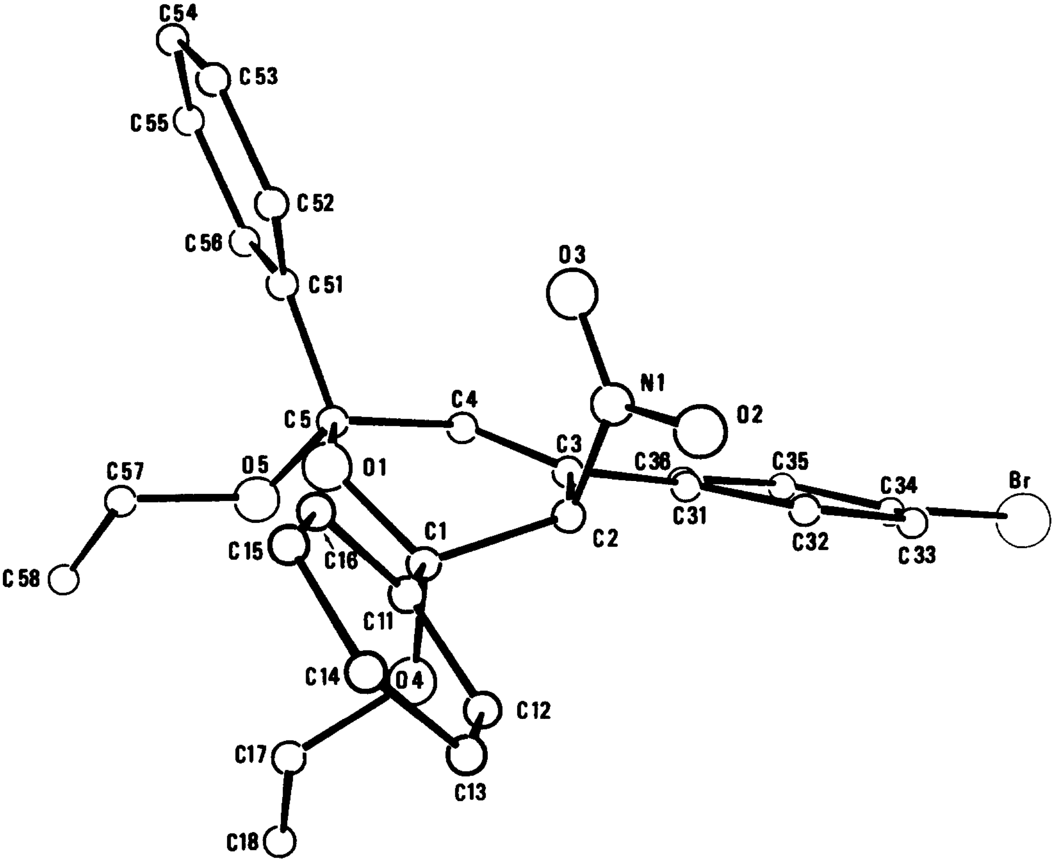


Figure 1

1. Although the double bond is clearly localized between atoms C3 and C4 (C2-C3 is 1.53(2) Å, C3-C4 is 1.32(2) Å, C4-C5 is 1.53(2) Å), five of the six atoms of the central dihydropyran ring are coplanar. C1 is 0.59 Å out of this plane. In addition the "axis" of the 4-(4-bromophenyl) group (i.e. the line through Br, C34 and C31) is only 2.9° from this same plane.

2. The 2- and 6-substituted phenyl groups and the nitro group lie on the same side of the dihydropyran ring, and thus both ethoxy groups extend out to the opposite side.

3. The orientations of the planes through each of the substituent groups are quite irregular with respect to that of the dihydropyran ring, and seem surely to have been determined by intermolecular packing forces, all of which are van der Waals' in character.

4. All the bond lengths and angles correspond to those expected.

## ACKNOWLEDGEMENT

The authors express their gratitude to the Danish National Research Council for Natural Sciences for financial support towards the cost of the diffractomer system.

## REFERENCES

1. To whom correspondence should be directed.
2. J. M. Stewart in Crystallographic Computing (ed. F. R. Ahmed), 1970, Munksgaard, Copenhagen, pp. 71-74; J. M. Stewart, F. A. Kundell and J. C. Baldwin, The X-Ray System, 1970, Computer Science Center, University of Maryland.