# An Ester Migration in the Rearrangement of a Diels–Alder Adduct of a Furan and a Phenyl Migration in the Rearrangement of Methyl 3,3,5-Triphenylpyrazole-4-carboxylate

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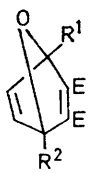
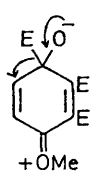
Methyl 5-methoxyfuran-2-carboxylate reacts with dimethyl acetylenedicarboxylate to give trimethyl 3-hydroxy-6-methoxybenzene-1,2,4-tricarboxylate, identified from its spectra and its conversion into diethyl 2,5-dihydroxyterephthalate. The thermal rearrangement of methyl 3,3,5-triphenyl-3*H*-pyrazole-4-carboxylate proceeds by a phenyl, and not by an ester, migration.

FURANS, behaving as dienes, undergo Diels–Alder addition reactions with ease across the 2- and 5-positions, and the adduct obtained from furan and maleic anhydride, when treated with boiling hydrobromic acid, aromatises to give phthalic acid.[1] In the case of the adduct (1), from 2,5-dimethylfuran and dimethyl acetylenedicarboxylate, a migration of a methyl group is necessary for aromatisation. This takes place [2] to give the phthalate (6) in the presence of aluminium chloride, and similar shifts occur in the pyrrole series.[3]



(1) $R^1 = R^2 = Me$
(2) $R^1 = CO_2Me$, $R^2 = OMe$



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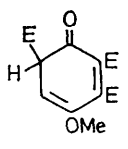
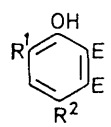


(4)

$E = CO_2Me$



(5) $R^1 = CO_2Me$, $R^2 = OMe$
(6) $R^1 = R^2 = Me$

Heating methyl 5-methoxyfuran-2-carboxylate with dimethyl acetylenedicarboxylate gave a 1 : 1 adduct [4] which had none of the properties expected of structure (2). It gave a purple colour with ferric chloride, and did not couple with diazotised aromatic amines or react with bromine in aqueous dioxan. Its n.m.r. spectrum showed signals for four *O*-methyl groups, one aromatic proton, and an exchangeable proton at low field; no O–H signal was detected in the i.r. spectrum because of strong hydrogen bonding,[5] and the u.v. spectrum showed a benzenoid chromophore. These data are consistent with structure (5). Treatment with diazomethane methylated the hydroxy-group and the product gave no colour with ferric chloride; however alkaline hydrolysis and attempted decarboxylation with soda-lime to give 1,4-dimethoxybenzene failed, probably because demethylation occurred during decarboxylation. Hydrolysis by hydrogen bromide in acetic acid gave 2,5-dihydroxyterephthalic acid, identified by comparison of the diethyl ester with an authentic sample. The structure of the adduct therefore can only be (5), or the isomer with the hydroxy- and methoxy-groups interchanged. Irradiation at the frequency of one of the methoxy-resonances in the n.m.r. spectrum caused a sharpening of the aromatic proton resonance, as occurs [6] for an *ortho*-proton. A nuclear Overhauser effect experiment showed a 30% enhancement of the aromatic proton signal, confirming that this proton must be *ortho* to the methoxy-group.

The formation of (5) is envisaged as involving a Diels–Alder reaction leading to (2) followed by ring

[1] A. P. Dunlop and F. N. Peters, 'The Furans,' A.C.S. Monograph No. 119, Reinhold, New York, 1953.
[2] A. W. McCulloch, B. Stanovnick, D. G. Smith, and A. C. McInnes, *Canad. J. Chem.*, 1969, **47**, 4319.
[3] R. C. Bansal, A. W. McCulloch, and A. C. McInnes, *Canad. J. Chem.*, 1970, **48**, 1472.
[4] G. W. Brown, Ph.D. Thesis, Southampton, 1964.
[5] M. St. C. Flett, *J. Chem. Soc.*, 1948, 1441.
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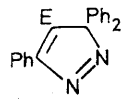
opening to (3), ester migration to (4), and tautomerisation to (5). A number of ester 1,2-shifts, where the ester group moves with its bonding electrons to a positive centre, are known,[7] but it is interesting that in this case the shift occurs in preference to oxiran formation, which would lead to a resorcinol derivative.

van Alphen [8] prepared the pyrazole (7) from diphenyldiazomethane and methyl phenylpropiolate, but he considered the addition to have occurred in the opposite sense. The correct interpretation was provided by Hüttel *et al.*,[9] who extended van Alphen's experiments on the rearrangement of (7). Heating at 100° was



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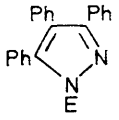
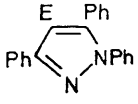
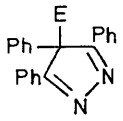


(8)



(9)



(10)

thought to give methyl 3,4,5-triphenylpyrazole-1-carboxylate (8), but at 190° a mixture of 3,4,5-triphenylpyrazole and the pyrazole (9) was formed. Compound (9) could be formed by a [1,5]-sigmatropic shift of a phenyl group, and the 1-carboxylate (8), identified only by hydrolysis and decarboxylation to 3,4,5-triphenylpyrazole, would necessarily be formed by a methoxycarbonyl migration. An alternative explanation to the ester shift is that a phenyl migration to carbon occurs, giving the 4*H*-pyrazole (10), for this on hydrolysis and decarboxylation could yield 3,4,5-triphenylpyrazole by several possible pathways.

In our hands pyrolysis of (7) at 100, 150, and 200° gave approximately the same proportions of the pyrazole (9) and the ' 1-carboxylate ', which we consider to have structure (10) and to be formed by a phenyl migration. The u.v. spectrum of this compound in methanol [$\lambda_{max.}$ 208 (ε 19,800), 232infl (5600), and 325 nm (16,500)] resembles that of benzaldehyde azine [$\lambda_{max.}$ MeOH) 217 (17,900), 303 (37,800), 309infl (34,000), and 324infl nm (17,200)],[10] which has the same chromophore although the conjugation is not the same because of the different preferred steric arrangements, and is unlike those of (9), 3,4,5-triphenylpyrazole, and other pyrazoles [11] (long wavelength band *ca.* 240 nm) which should be similar to that expected for structure (8). There are, however, two convincing reports of ester shifts in the pyrazole series, involving the migration of a 2-ester group of a 3-methyl-3*H*-pyrazole in preference to the methyl group to the adjacent carbon [12] and nitrogen [11] atoms.

## EXPERIMENTAL

The instruments and general procedures used have been described.[13]

*Methyl 5-Methoxyfuran-2-carboxylate.*—Methyl 5-bromofuran-2-carboxylate [14] in a solution of sodium (11·4 g) in dry methanol (195 ml) containing a trace of copper(I) chloride was refluxed for 1 h and the solvent was removed *in vacuo*. The residue and ether (300 ml) were shaken rapidly with ice-cold aqueous 2N-hydrochloric acid, and the combined ether layer and further extracts were washed with saturated aqueous sodium hydrogen carbonate, dried, and distilled to give the ester (11·9 g), b.p. 128—130° at 19 mmHg, m.p. 49—51° (lit.,[14] m.p. 50—52°, for a less convenient pressure-bottle preparation); τ ($CCl_4$) 3·05 (d, 3-H), 4·87 (d, $J_{3,4}$ 4 Hz, 4-H), 6·10 (OMe), and 6·28 (OMe).

*Trimethyl 3-Hydroxy-6-methoxybenzene-1,2,4-tricarboxylate* (5).—Dimethyl acetylenedicarboxylate (2·07 g) and the foregoing furan (2·07 g) were heated at 100° for 24 h; the mixture was cooled and triturated with ether, and the *phenol* crystallised as prisms (1·07 g; from ethanol), m.p. 121° (Found: C, 51·9; H, 4·2. $C_{13}H_{14}O_8$ requires C, 52·35; H, 4·7%); $\nu_{max.}$ (Nujol) 1740, 1675, 1620, and 1375 $cm^{-1}$; $\lambda_{max.}$ (MeOH) 210 (ε 23,400), 355 (5600), and 410infl nm (2300); τ ($CDCl_3$) 2·49 (s, ArH), −1·08 (s, OH), and 6·04, 6·12, 6·12, and 6·21 (4 OMe). Irradiation at τ 6·12 caused sharpening of the ArH signal and a nuclear Overhauser effect.

*Diethyl 2,5-Dihydroxyterephthalate.*—(i) The ester (5) (0·39 g) was refluxed for 5 h with hydrobromic acid (48%; 20 ml) and acetic acid (20 ml), and the solvent was removed *in vacuo*. The residual 2,5-dihydroxyterephthalic acid (0·26 g) crystallised from methanol as a pale yellow solid which sublimed at *ca.* 295° (Found: C, 48·6; H, 3·0. Calc. for $C_8H_6O_6$: C, 48·5; H, 3·1%). It reduced Fehling's solution and ammoniacal silver nitrate, gave a brown dye with benzenediazonium chloride and alkali, and gave a blue colour with ferric chloride. Hydrogen chloride was passed through a refluxing ethanolic solution (50 ml) of this acid (0·1 g) for 2 h; removal of solvent and recrystallisation of the residue from ethanol gave the ester (0·06 g) as yellow plates, m.p. 131—133° (lit.,[15] 133°); τ ($CDCl_3$) 2·60 (ArH), −0·99 (OH), 5·63 (q, $CH_3{\cdot}CH_2$), and 8·61 (t, $CH_3{\cdot}CH_2$) (*J* 7 Hz); $\nu_{max.}$ (Nujol) 3290, 1676, and 1490 $cm^{-1}$.

(ii) Diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate [16] (1·0 g) in chloroform (75 ml) was treated slowly with bromine (0·62 g).[17] The solution was washed with water, dried, and evaporated and the residue was recrystallised to give the ester (0·53 g), identical (m.p., mixed m.p., and i.r. spectrum) with the sample prepared in (i).

*Methyl 3,3,5-Triphenyl-3H-pyrazole-4-carboxylate* (7).—This was prepared as described [8] in 52% yield; m.p. 98—102° (lit.,[8] 102°), $\nu_{max.}$ (Nujol) 1830, 1730, 1720, and 1640 $cm^{-1}$; τ ($CDCl_3$) 6·40 (OMe), 2·43—2·85 (m, 13 ArH), and 1·82—2·03 (m, 2 ArH).

[7] R. M. Acheson, *Accounts Chem. Res.*, 1971, **4**, 177.
[8] J. van Alphen, *Rec. Trav. chim.*, 1943, **62**, 485.
[9] R. Hüttel, K. Franke, H. Martin, and J. Riedel, *Chem. Ber.*, 1960, **93**, 1433.
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This compound (500 mg) was rearranged by heating at 100° for 20 h. Addition of methanol gave methyl 1,3,5-triphenylpyrazole-4-carboxylate (9) (360 mg) as needles (from methanol), m.p. 126—130° (lit.,[9] 141°), $\nu_{max.}$ (Nujol) 1720 and 1595 $cm^{-1}$; $\tau$ ($CDCl_3$) 6·50 (OMe), 2·86 (s, 5 ArH), 2·77 (s, 5 ArH), 2·52—2·88 (m, 3 ArH), and 2·17—2·43 (m, 2 ArH); $\lambda_{max.}$ (MeOH) 210 (ε 40,800) and 238 nm (30,400).

The filtrate yielded methyl 3,4,5-triphenyl-4*H*-pyrazole-4-carboxylate (10) as crystals (100 mg) (from methanol), m.p. 198—201° (lit.,[9] 191°), $\nu_{max.}$ (Nujol) 1745, 1600, and 1580 $cm^{-1}$; $\tau$ ($CDCl_3$) 6·45 (OMe), 2·50—2·90 (m, 15 ArH), and 2·10—2·40 (m, 2 ArH); $\lambda_{max.}$ 208 (ε 19,800), 232infl (5100), and 325 nm (16,400).

A preparative t.l.c. work-up for a similar reaction, and for reactions at 150° for 5 h and 200° for 2 h, gave similar results and showed no additional products.

3,4,5-*Triphenylpyrazole*.—Sulphuric acid (1·0 g) was added at 0° to the pyrazole (7) (500 mg). Much frothing ensued and after 0·5 h addition of water and recrystallisation of the precipitate from methanol gave 3,4,5-triphenylpyrazole (200 mg), m.p. 265—266°, $\nu_{max.}$ (Nujol) 3220 (NH), 1605, and 1590 $cm^{-1}$; $\tau$ [$(CD_3)_2SO$] 2·70 (s, ArH); $\lambda_{max.}$ (MeOH) 210 (ε 29,900) and 244 nm (26,800).

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