The Reaction between Feist's Ester and Dimethyl Acetylenedicarboxylate

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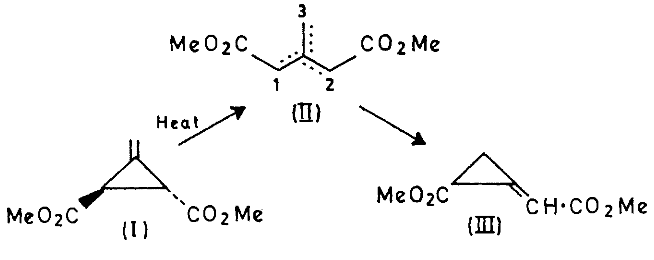
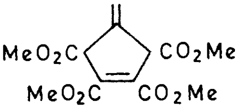
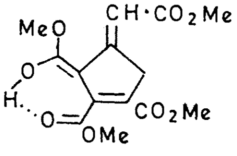
Summary Feist's ester reacts with dimethyl acetylenedicarboxylate at 180—190° to give a 1 : 1-adduct, which has been shown by *X*-ray crystallographic analysis to be methyl 2-hydroxy-5-methoxy-3,4-dimethoxycarbonylphenylacetate (VI).

PARTIAL racemisation accompanies the thermal rearrangement of optically active Feist's ester (I) to (III), and the reaction has therefore been considered to proceed, in part, through a planar intermediate (II) of the trimethylenemethane (2-methylenetrimethylene) type.[1] Since the parent species, $C(CH_2)_3$, generated in other ways, can be trapped by cycloaddition,[2] there exists the possibility of trapping the species (II) by carrying out the thermal rearrangement of Feist's ester (I) in the presence of an appropriate reagent. However, when Feist's ester was heated at *ca.* 200° with furan, cyclopentadiene, and anthracene, the sole products were Diels–Alder adducts of (I) and (III).[3] Use of dimethyl acetylenedicarboxylate as trapping agent seemed to us more likely to succeed for two reasons: (i) unwanted side-reactions of the acetylene with (I) and (III) should, as thermal [2 + 2] cycloadditions, be unfavourable;[4] and (ii) concerted cycloaddition of the acetylene across C(1) and C(2) of the species (II) (highest filled molecular orbital antisymmetric to reflection in the vertical plane) to give the methylenecyclopentene (IV) is symmetry-allowed.†

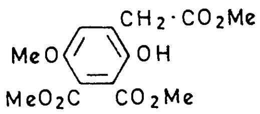




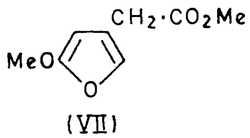
(IV)



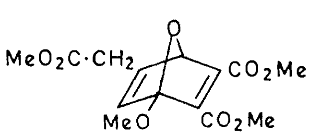
(V)



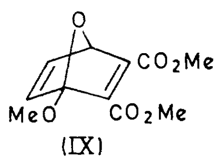
(VI)



(VII)



(VIII)



(IX)

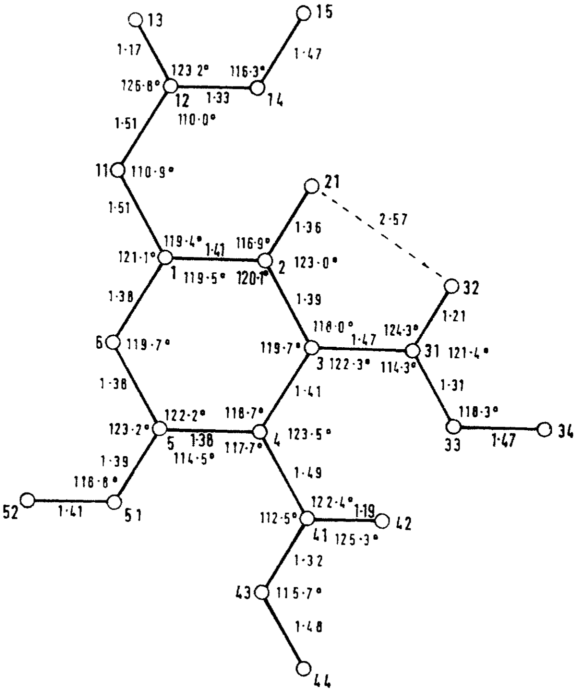


FIGURE. *Molecular dimensions of the adduct* (VI).

When Feist's ester (1 mol.) and dimethyl acetylenedicarboxylate (2 mol.) were heated together at 180—190° for 1 hr., a crystalline 1 : 1-adduct, m.p. 137—138°, was obtained in 30% yield. No other adducts were detected, the remainder of the material being reactants, polymer, rearrangement products of Feist's ester, and, when the reaction was carried out without exclusion of air, 2-methoxy-3,4,5-trimethoxycarbonylfuran derived from the acetylene.[7] The adduct was shown *not* to have the structure (IV) by its n.m.r. spectrum which, in addition to signals for four methoxy-groups, contained a two-proton singlet at τ 6·39 and one-proton singlets at τ 2·87 and $-0{\cdot}84$. The low-field proton was exchangeable with D_2O, and corresponded to a hydroxy-group, which was further shown to be intramolecularly hydrogen-bonded (ν_{max} 3160 cm^{-1} unaffected by dilution) and weakly acidic (slow methylation by diazomethane). Whilst the evidence was not inconsistent with structure (V) containing an enolised ester group[8] and corresponding to an adduct formed, contrary to prediction,

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† Contrast the behaviour of cyclopropanones, which undergo 1,4-addition across conjugated dienes,[5] probably *via* their oxyallyl tautomers (highest filled orbital symmetric).[6]

across C(1) and C(3) of the species (II), *X*-ray analysis established the phenolic structure (VI).

Crystal data for methyl 2-hydroxy-5-methoxy-3,4-dimethoxycarbonylphenylacetate (VI), $C_{14}H_{16}O_8$: *M* 312·27; monoclinic, $a = 10{\cdot}45 \pm 0{\cdot}01$, $b = 12{\cdot}32 \pm 0{\cdot}01$, $c = 12{\cdot}34 \pm 0{\cdot}02$ Å, $\gamma = 76{\cdot}25 \pm 0{\cdot}1°$; $D_m = 0{\cdot}882 \pm 0{\cdot}001$ gcm^{-3} (by flotation), $Z = 4$, $D_c = 0{\cdot}867$ g cm^{-3}; space group $P2_1/n(C^5_{2h}$, No. 14); Mo-K_α radiation, $\mu = 7{\cdot}8$ cm^{-1}, Hilger and Watts linear diffractometer, 1534 independent reflections, layers *hk*0—*hk*13, crystal size 0·3 × 0·5 × 0·5 mm.

A trial structure was obtained from an *E* synthesis compiled from 507 reflections phased by direct methods. The structure was refined by full-matrix least-squares analysis, assuming anisotropic thermal motion. Convergence was reached at $R = 0{\cdot}088$. Hydrogen atoms were not located.

The Figure shows the molecular dimensions. The benzene ring and the individual ester groups are planar. The torsional angles about C(1)–C(11), C(3)–C(31), C(4)–C(41), and C(5)–C(51) are 108·72, 174·13, 93·02, and 177·60°, respectively. The hydroxy-group forms a short (2·57 Å) hydrogen bond to O(32).

A plausible route to the phenol (VI) involves the isomerisation of (I) or (III) to the furan (VII), for which several possible mechanisms can be envisaged, followed by Diels–Alder addition of dimethyl acetylenedicarboxylate to give (VIII). In support of the route (VII) → (VIII) → (VI), we find that the acetylenic ester reacts readily with 2-methoxyfuran at room temperature to give dimethyl 1-methoxy-7-oxabicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylate (IX), which rearranges very readily on heating to dimethyl 3-hydroxy-6-methoxyphthalate. Experiments are currently under way to investigate the suggested route further, in particular to detect the furan (VII) as a pyrolysis product of Feist's ester. Preliminary studies show that the pyrolysis gives at least 15 products in addition to *syn*- and *anti*- (III); clearly the reaction is much more complicated than has previously been thought.

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[1] E. F. Ullman, *J. Amer. Chem. Soc.*, 1959, **81**, 5386; 1960, **82**, 505; *cf.* E. F. Ullman and W. J. Fanshawe, *ibid.*, 1961, **83**, 2379. *Non-planar* acyclic species may also be involved in methylenecyclopropane rearrangements, *cf.* J. J. Gajewski, *J. Amer. Chem. Soc.*, 1968, **90**, 7178.

[2] R. G. Doerr and P. S. Skell, *J. Amer. Chem. Soc.*, 1967, **89**, 3062; P. S. Skell and R. G. Doerr, *ibid.*, p. 4688; A. C. Day and J. T. Powell, *Chem. Comm.*, 1968, 1241; P. Dowd, G. Sengupta, and K. Sachdev, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, New Jersey, 1968, Organic Division, paper 147.

[3] R. C. Cookson, B. Halton, I. D. R. Stevens, and C. T. Watts, *J. Chem. Soc.* (*C*), 1967, 928.

[4] R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, 1965, **87**, 2046; *Accounts Chem. Res.*, 1968, **1**, 17.

[5] R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *J. Chem. Soc.* (*C*), 1967, 473 and refs. therein; N. J. Turro, S. S. Edelson, J. R. Williams, and T. R. Darling, *J. Amer. Chem. Soc.*, 1968, **90**, 1926, 5947 and earlier refs.

[6] R. Hoffmann, *J. Amer. Chem. Soc.*, 1968, **90**, 1475.

[7] C. F. Huebner, E. Donoghue, L. Dorfman, F. A. Stuber, N. Danieli, and E. Wenkert, *Tetrahedron Letters*, 1966, 1185; E. Winterfeldt and G. Giesler, *Angew. Chem. Internat. Edn.*, 1966, **5**, 579; E. Winterfeldt, *ibid.*, p. 741; *cf.* E. LeGoff and R. B. LaCount, *Tetrahedron Letters*, 1967, 2333.

[8] *Cf.* J. K. van der Baan and F. Bickelhaupt, *Chem. Comm.*, 1968, 1661. The condensation products of malononitrile and β-keto-esters were reported to contain enolic ester groups. However, the suggestion has recently been retracted (*idem, ibid.*, 1970, 326).