Diels–Alder Reactions of 2-Arylfurans

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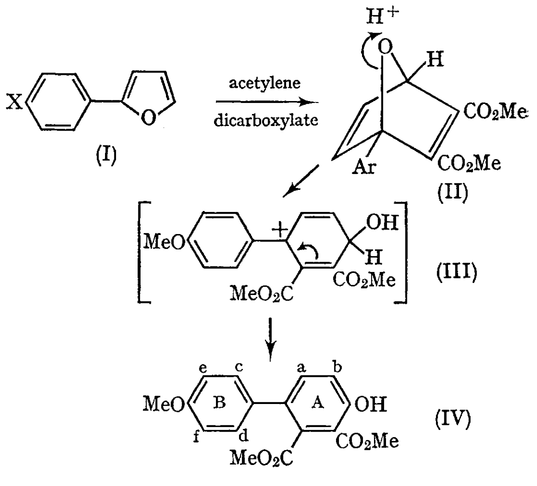
A GROUP of 2-arylfurans (I; X = Cl, H, Me, or OMe) has been prepared in 30—40% yield by a modified Gomberg synthesis,[1] in which stabilised diazonium salts[2] derived from the corresponding amines were decomposed in a large excess of furan. The products were characterised by i.r. and ^1H n.m.r. spectra, and by analysis; they underwent uncatalysed addition of tetracyanoethylene and of dimethyl acetylenedicarboxylate. The initial rate of addition of the latter was followed through the intensity of the arylfuran ultraviolet absorption (2810—2830 Å); the following second-order constants were obtained at 30°.

TABLE

Substituent in (I)	Rate (10^2k; l./mole/min.$^{-1}$)	Hammett constant (σ)
MeO	2·2	−0·27
Me	1·3	−0·17
H	0·6	zero
Cl	0·14	0·23

The relative insensitivity of the rate to variation of the substituent is in accord with a concerted rather than a two-step mechanism.[3] A Hammett plot of log k/σ afforded a straight line of slope −2·27.



The methoxylated adduct (II) was characterised by its infrared and ^1H n.m.r. spectra; on warming in acetic acid it rearranged, presumably by a mechanism of type (III), to dimethyl 3-hydroxy-4′-methoxydiphenyl-1,2-dicarboxylate (IV). This product was insoluble in cold alkali and gave no diazo-coupling, however, its infrared spectrum was typical of a salicylic ester having peaks at: 3200 w (bonded OH); 1740 (free CO_2Me); 1680 cm.$^{-1}$ (bonded CO_2Me). The low-field absorption (τ $-0{\cdot}83$) typified the bonded phenolic proton in the ^1H n.m.r. spectrum of (IV), whilst the ring A protons formed an AB system centred at τ 2·84, $J_{ab} = 9{\cdot}0$ c./sec. The spectrum of the ring B protons was closely approximate to two coincident AB systems centred at τ 3·03 having J_{ce}, $J_{df} = 9$ c./sec.

The diphenyl derivative (IV) was obtained in 35% yield from 4-methoxyaniline and the route may therefore be of wider synthetic interest. A preliminary account of related work[4] on disubstituted furans has appeared.

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