

Reactions of Dimethylsulphoxonium Methylide with Benzo-4-pyrone Derivatives

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THE reactions of dimethylsulphoxonium methylide with a variety of compounds including those containing carbonyl groups,¹ electron-deficient carbon-carbon double bonds,² carbon-nitrogen multiple bonds,³ aromatic systems,⁴ and 1,3-dipoles⁵ yield products that originate from nucleophilic attack by the methylide. We now report the reactions† of a variety of benzo-4-pyrone derivatives (I) with dimethylsulphoxonium

methylide (II) and, from the structural relations between the products obtained, it is possible to comment upon the mechanism of cyclopropane formation by the addition of (CH_2) from the methylide to activated carbon-carbon double bonds.

The reaction of 7-methoxyisoflavone (Ia, see Table) with dimethylsulphoxonium methylide (II) gave as the major product the cyclopropane

† A preliminary investigation of this reaction was carried out by Miss C. A. Rhodes, Ph.D. thesis, Sheffield 1965.

derivative (IIIa). The structure of this product was established by its spectroscopic properties

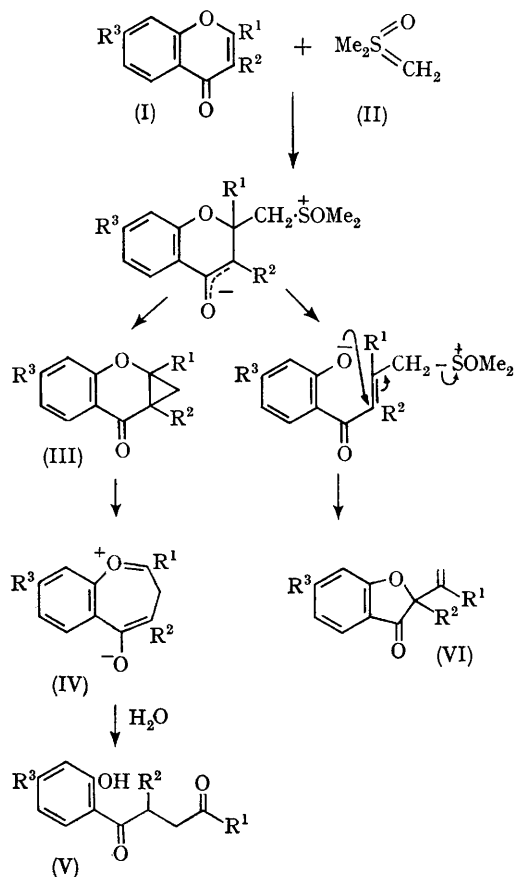


FIGURE. The reactions of benzo-4-pyrone (I) with dimethylsulphoxonium methylide (II). The substituents R^1 , R^2 , and R^3 are identified in the Table.

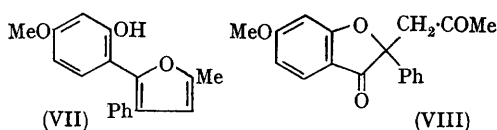
(ν_{max} 1660 cm^{-1} ; the n.m.r. spectrum showed an ABX system to be associated with cyclopropanon protons, τ_{A} 8.14, τ_{B} 8.30, τ_{X} 5.36, $J_{\text{AB}} = 7.0$, $J_{\text{AX}} = 7.0$, and $J_{\text{BX}} = 4.8$ c./sec.), its catalytic reduction to give *trans*-7-methoxy-2-methylisoflavanone, and its acid-catalysed transformation to give the aldehyde (Va), m.p. 102°. The other product from the reaction of 7-methoxyisoflavone (Ia) and dimethylsulphoxonium methylide was shown to be the 2-phenyl-2-vinylcoumaran-3-one (VIa) from its spectroscopic properties (ν_{max} 1700 cm^{-1} ; the n.m.r. spectrum showed an ABX system to be associated with the vinyl protons, τ_{A} 4.45, τ_{B} 4.68, τ_{X} 3.68, $J_{\text{AB}} = 1.4$, $J_{\text{AX}} = 17.0$,

and $J_{\text{BX}} = 10.0$ c./sec.) and its catalytic reduction to give the corresponding 2-ethyl-2-phenylcoumaran-3-one, m.p. 133°; the presence of an ethyl group in this dihydro-derivative was clearly demonstrated by its n.m.r. spectrum (A_2X_3 system, τ_{A} 7.82, τ_{X} 9.12, $J_{\text{AX}} = 7.0$ c./sec.).

On the other hand, the reaction of flavone (Ig) with dimethylsulphoxonium methylide gave the diketone (Vg) in high yield which was identified by its spectroscopic properties (ν_{max} 1635 and 1680 cm^{-1} ; the n.m.r. spectrum showed a 4-proton singlet associated with $-\text{CH}_2-\text{CH}_2-$ group and chelated hydroxyl, $\tau = 2.10$). The methyl ether of the diketone (Vg) was synthesised directly and by alkaline hydrolysis of ethyl 2-(2'-methoxyphenacyl)benzoylacetate.

The generality of these reactions is indicated by the results summarised in the Table. Thus, reactions involving the isoflavones (Ia), (Ib), (Ic), and (Id) give cyclopropanes (III) and/or coumaran-3-ones (VI), whereas the flavones (Ig), (Ih), and (Ij) give diketones (V) which probably result from the hydrolysis during work-up of the initially formed cyclopropanes (III). The formation, (III) \rightarrow (V), of the diketones (V) may be represented as involving hydration of the dipolar intermediate (IV). It may be noted that the physical properties of the cyclopropanes (III) show that the valence tautomer (IV) does not make a significant contribution to a possible valence tautomeric equilibrium [(III) \rightleftharpoons (IV)].

The reactions leading to the simultaneous formation of the products (III) and (VI) may be rationalised in terms of the general scheme shown in the Figure. This proposal involves a two-stage process for the reactions of the methylide. The first stage requires β -nucleophilic attack by the dimethylsulphoxonium methylide to give an intermediate enolate anion. This enolate anion either gives the cyclopropane (III) by direct displacement of dimethyl sulphoxide or it undergoes β -elimination to give a phenolate anion which cyclises by an allylic displacement of dimethylsulphoxide to give a coumaran-3-one (VI). These results suggest that cyclopropane formation by the Corey reagent,^{1,2} dimethylsulphoxonium methylide, is probably not a concerted process.



During these studies an interesting autoxidation reaction was encountered. Mild acid-catalysed

TABLE

The products^a (III, V, and VI) from the reaction^b of benzo-4-pyrones (I) with dimethylsulphoxonium methyllide (II).

	Substituents in formulae (I, III, V, and VI)			Yield % ^c (m.p.)		
	R ¹	R ²	R ³	(III)	(V)	(VI)
(Ia)	H	Ph	OMe	58 (122°)	—	18 (oil)
(Ib)	H	2'-(OMe)C ₆ H ₄	OMe	74 (122°)	—	4 (121°)
(Ic)	H	2'-(OH)C ₆ H ₄	OMe	—	—	63 (156°)
(Id)	H	2'-(OH),4'-(OMe)C ₆ H ₄	OMe	—	—	55 (140°—142°)
(Ie)	Me	H	H	—	50 (50°)	—
(If)	Me	Ph	OMe	86 (144°)	—	—
(Ig)	Ph	H	H	—	86 (107°)	—
(Ih)	2'-(OMe)C ₆ H ₄	H	H	—	72 (71°)	—
(Ij)	4'-(OMe)C ₆ H ₄	H	H	—	83 (124°)	—

^a All the products indicated in this Table gave analytical data and ultraviolet, infrared, nuclear magnetic resonance, and mass spectra in accord with the proposed structures.

^b Reactions in dimethylsulphoxide solution at room temperature.

^c The percentage yields given refer to isolated products.

hydrolysis of the cyclopropane (III_f) gave the diketone (V_f) which was converted by longer treatment with acid into the aryl-furan (VII).

Exposure of a chloroform solution of this furan (VII) to air gave the diketone (VIII).

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⁴ V. J. Traynelis and J. V. McSweeney, *J. Org. Chem.*, 1966, **31**, 243.

⁵ G. Gaudiano, A. Umani-Ronchi, P. Bravo, and M. Acampara, *Tetrahedron Letters*, 1966, 3477; 1967, 107.