Reactions of Arynes in the Synthesis of 2*H*-Chromens†

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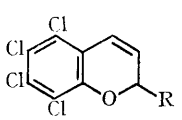
ALTHOUGH $\alpha\beta$-unsaturated carbonyl compounds normally react readily with nucleophiles, as in Michael reactions, they could, in principle, function as the nucleophilic species in the presence of a very strong electrophile. Reactions of arynes with $\alpha\beta$-unsaturated carbonyl compounds, or suitable derivatives, should provide a novel approach to the synthesis of heterocyclic ring systems. Tetrachlorobenzyne may be generated by the aprotic diazotisation of tetrachloroanthranilic acid, and displays the normal high electrophilicity of the tetrahalogenobenzynes in reactions with arenes.[1]

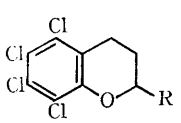
Experiment has confirmed this reasoning and we find that acrolein and crotonaldehyde react with tetrachlorobenzyne to give 5,6,7,8-tetrachloro-2*H*-chromen (Ia; R = H, 17%), and its 2-methyl derivative (Ib; R = Me, 34%), respectively.

The structures of the adducts (I) were confirmed by analytical and spectroscopic data, and by reduction to the chromans (II).



(I)

(a; R=H)
(b; R=Me)

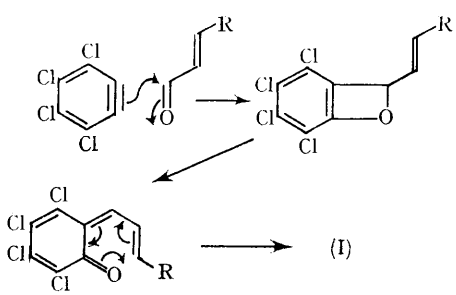


(II)

(a; R=H)
(b; R=Me)

The ^{1}H n.m.r. spectra of compounds (I) were analysed by first-order methods for comparison with the data for 2*H*-chromen,[2] and 4*H*-chromen.[3] The ^{1}H n.m.r. spectra of the chromans (II), in particular (IIb), were found to indicate the structure. Spin–spin decoupling experiments prove that the multiplet at lowest field in (IIb) is spin–spin coupled to the methyl group. The u.v. spectra of compounds (Ia and b) show the presence of the styrene-type chromophore.

The Scheme shows a possible mechanism for the production of our compounds in which we postulate an electrocyclic ring closure of the type which Ollis and Sutherland[4] suggested may occur in the biosynthesis of the 2,2-dimethylchromen system.



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† Previous Paper in the "Aryne Chemistry" series, J. D. Cook, B. J. Wakefield, H. Heaney, and J. M. Jablonski, *J. Chem. Soc.* (*C*), in the press.

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[2] J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 1964, 981.
[3] W. E. Parham and L. D. Huestis, *J. Amer. Chem. Soc.*, 1962, **84**, 813.
[4] W. D. Ollis and I. O. Sutherland, "Chemistry of Natural Phenolic Compounds", Pergamon Press, Oxford, 1961, p. 84.