Acenaphtho[5,6-*cd*]thiapyran

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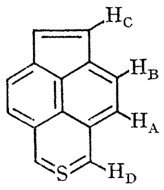
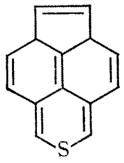
Summary An unusual sulphoxide dehydration reaction has been used to prepare deep blue solutions of the reactive nonclassical sulphur heterocycle acenaphtho[5,6-*cd*]-thiapyran (I).

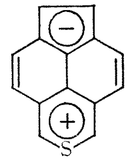
WE reported[1] the generation of acenaphtho[5,6-*cd*]thiapyran (I) by dehydration of the sulphoxide (II) in refluxing acetic anhydride. Under these conditions it was not possible to obtain spectroscopic data on (I); however, its existence as a transient reaction intermediate was demonstrated by trapping the heterocycle with *N*-phenylmaleimide.† Stable highly substituted derivatives of (I), [(III)[2] and (IV)[3]] have since been prepared, and compound (IV) has been extremely useful with respect to chemical examination of these heterocycles. Unfortunately, the extensive ring substitution of (III) and (IV) has precluded the obtaining of meaningful n.m.r. data pertaining to the possible presence in these systems of a peripheral π-electron ring-current.‡ We have studied alternative methods of dehydrating the sulphoxide (II) in the hope that the unsubstituted heterocycle (I) could be generated under conditions which would allow at least its spectroscopic characterization.



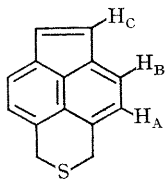
(Ia)



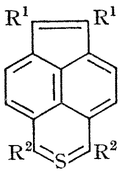
(Ib)



(Ic)



(II)



(III) $R^1=Br^2$, $R^2=Ph$
(IV) $R^1=R^2=Ph$

We have found that relatively stable intense deep blue solutions of heterocycle (I) may be prepared by reaction of the sulphoxide (II) with methylmagnesium bromide under light-shielded and rigorously degassed conditions.§ A variety of organic solvents including benzene, ether, and chloroform may be used in this reaction. Solutions of (I) react with *N*-phenylmaleimide to give the same bright yellow Diels–Alder adduct (75% yield) previously obtained from sulphoxide (II) and the dienophile in refluxing acetic anhydride.[1] All attempts to isolate (I), including low-temperature chromatography, have resulted only in the formation of a light yellow polymer.

Freshly prepared benzene solutions of (I) show visible absorption maxima at: $\lambda_{\max}$ 515 (ϵ 886), 590 (807), and 635 nm (605) with tailing to 690 nm.¶ Consistently reproducable n.m.r. spectra of the heterocycle could be obtained from

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† The validity of the conclusion that heterocycle (I) was involved in adduct formation has been challenged recently by W. G. Salmond, *Quart. Rev.*, 1968, **22**, 253. The experiments here indicate that our original supposition concerning the intermediacy of (I) in the Diels–Alder reaction was correct.

‡ The n.m.r. spectra of some analogous *peri*-fused acenaphthylene-derived heterocycles have been reported recently by P. Flowerday and M. J. Perkins, *Tetrahedron Letters*, 1968, 1261. The data obtained by these authors indicates that a ring current is present in the peripheral π-electron system of these heterocycles.

§ A similar dehydration reaction of sulphoxides with phenyl-lithium has been described by R. H. Schlessinger, G. S. Ponticello, A. G. Schultz, I. S. Ponticello, and J. M. Hoffman, jun., *Tetrahedron Letters*, 1968, 3963 (also see ref. 2). Stable solutions of (I) could not be formed using this base.

¶ Aged solutions of (I) gave the same absorption maxima but with diminished ϵ values.

solutions of (I) in deuteriochloroform. These spectra showed resonance for the naphthalene protons (H_A and H_B) as a well defined AB quartet centred at δ 8·00 and 8·70 (J_{AB} 8 Hz). Sharp singlet resonance for both the H_C and H_D protons of (I) were observed at δ 8·19 and 8·69, respectively. The n.m.r. spectrum of sulphoxide (II) gave resonance for the H_A and H_B protons as a quartet centred at δ 7·31 and 7·64 (J_{AB} 7·3 Hz) while a sharp singlet was observed for the H_C protons at δ 7·01.

The H_A, H_B, and H_C protons of heterocycle (I) are strongly deshielded relative to the comparable protons of sulphoxide (II). This clearly suggests that a diamagnetic peripheral π-electron ring-current is present in the heterocycle. In addition, a somewhat greater AB coupling constant (0·73 Hz) is observed for (I), which implies increased double-bond character between the carbon atoms bearing these protons. The latter result may be consistent with the supposition that structures (Ib) and (Ic) contribute to ground-state of the heterocycle.[1] Very similar n.m.r. behaviour recently has been reported for acenaphtho[5,6-*cd*]-1,2,6-thiadiazine.‡

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[1] R. H. Schlessinger and I. S. Ponticello, *Tetrahedron Letters*, **1967**, 4057.

[2] I. S. Ponticello and R. H. Schlessinger, *J. Amer. Chem. Soc.*, 1968, **90**, 4190.

[3] J. M. Hoffman, jun., and R. H. Schlessinger, *J. Amer. Chem. Soc.*, 1969, **91**, 3953.