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1*H*-INDENO[1,2-*c*]THIOPHENES AND 1*H*-INDENO[1,2-*c*]FURANS

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Isobenzofulvenes are active components in cycloaddition reactions of varying order.[1-3] While these reactions have been governed strictly by frontier orbital control, it occured to us that some of the non-allowed reactions, would be of more synthetic value. We have now developed a method of obtaining products formally derived from the thermally forbidden [10+2] cycloaddition reaction, *via* a 1,3-migration of the initially formed [8+2] adducts. This has lead to a synthesis of indeno[1,2-*c*]thiophenes and indeno[1,2-*c*]furans. These classes of heterocyclic compound have received essentially no attention in the literature to this time.

Reaction of 7-isopropylidenebenzonorbornadiene(1a) with 3,6-di(2'-pyridyl)*s*-tetrazine (2) in the presence of an equivalent of thiophosgene yielded the 1:1 adduct (5a)[4], which results from the capture of the 8,8-dimethylisobenzofulvene by the thione π-system of thiophosgene[5].

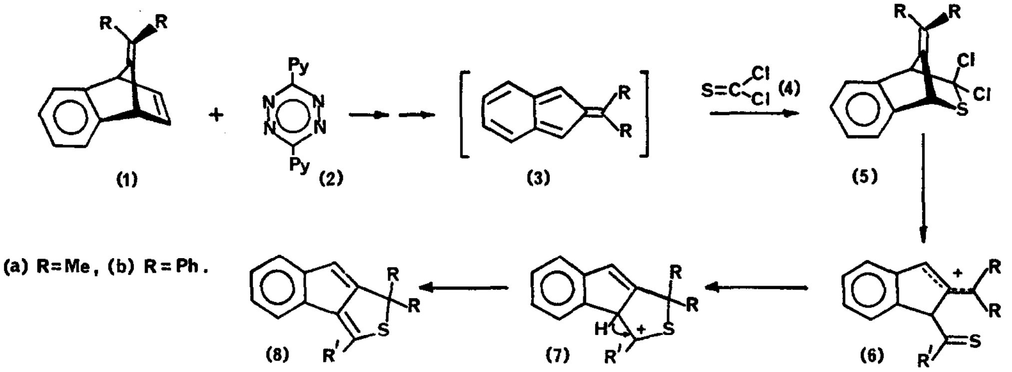

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Table 1. Summary of u.v. data

(8) R'=Cl				(11)		(10)	
λ max	ε	λ max	ε	λ max	ε	λ max	ε
235^+	11770	286^+	7900	247	8600	238	12650
239	12670	292^+	8890	257	7320	243^+	12080
248	10450	294^+	10200	276^+	3840	263^+	5120
275^+	7410	348	12840	287^+	4260	300^+	1490
283	9050	359^+	12010	313	5260		

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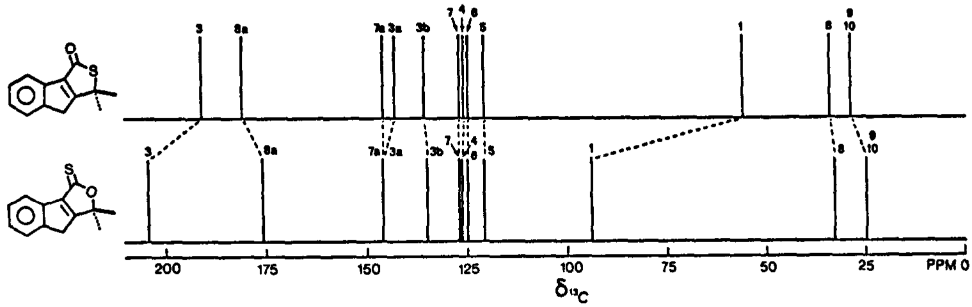


Figure 1. ^{13}C-n.m.r. chemical shifts of (10) and (11).

Infra-red spectroscopy distinguished between these isomers, as only the oxothiophene (10) displayed a carbonyl stretching frequency (ν=1695 cm^{-1}). The ^{13}C-n.m.r. spectra are also diagnostic since the thione carbon resonance is typically at lower field ($\Delta\delta$=12.91) than that of the related carbonyl carbon resonance.[10] In this respect the thiolactone grouping is similar to heterocyclic thiolactams.[11] Additionally, the C-1 resonance of (11) is 38.33 p.p.m. downfield from the corresponding resonance in (10), due to attachment to ring oxygen and ring sulphur atoms respectively.[12]

A ring-opened species related to (9) is presumed to be the common intermediate involved in the formation of (10) and (11). This ambident nucleophile can cyclise on sulphur or oxygen, the proportion of each product depending on the hydrolysis conditions used. Conditions for the interconversion of these isomers are presently being investigated and will be reported, together with the results of other heterodienophilic reactions with isobenzofulvenes, in due course.

The p.m.r. spectrum of this product displayed two singlet methyl resonances (δ1.74, 1.78) and two doublet methine resonances. The lower field methine resonance (δ5.12) is assigned to H-8, adjacent to the sulphur atom, and the other (δ4.72) to H-1, where long range coupling ($^4J_{1,8}$=1.5Hz) accounts for the observed multiplicity. A similar adduct (5b)[4] was obtained from 8,8-diphenylisobenzofulvene (3b).

Rearrangement of the [8+2] adduct (5a) was achieved by treatment with mild acid[6,7] (or even chromatography on silica gel) which initiated a ring-opening, ring-closure reaction to form, ultimately, 1*H*-indeno[1,2-*c*]thiophene (8a;R'=Cl)[4], m.p. 39-40°C. The diphenyl compound (8b;R'=Cl)[4], m.p. 161-2°C, was produced in an analogous fashion. The u.v. spectrum of (8a;R'=Cl), c.f. table 1, has a long wavelength absorption which is consistent with the presence of a modified benzofulvene chromophore.[8] The p.m.r. spectrum of (8a;R'=Cl) confirms the presence of two equivalent methyl groups (singlet, 6H,δ1.74) and an indenyl vinylic proton (singlet, 1H,δ6.25).

Reaction of 8,8-dimethylisobenzofulvene (3a) with thiophosgene in the presence of ethanol leads to the formation of the oily ethoxy compound (8a;R'=OEt), the p.m.r. spectrum of which is reported in table 2. This result suggests that ethyl chlorothionoformate may be involved and that other thiones could participate, thereby extending the synthetic value of the reaction.[9]

Treatment of the initial adduct (5a), with aqueous ethanolic hydrochloric acid, formed two new isomeric products (m/e=216). These are assigned the oxo-thiophene structure (10)[4], m.p. 66-7°C, and the thiono-furan structure (11)[4], m.p. 83-4°C. (See table 1 for u.v. spectra).

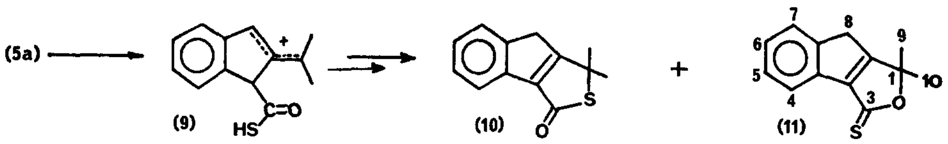
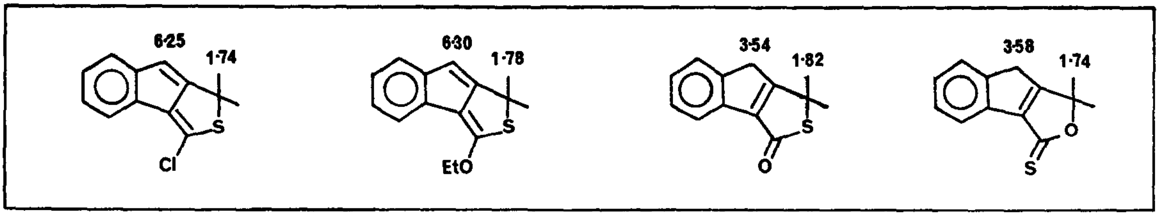


Table 2. Summary of p.m.r. data (δppm in $CDCl_3$)



References and Footnotes

1. P.L. Watson and R.N. Warrener, *Aust. J. Chem.*, 1973, 26, 1725.

2. M.N. Paddon-Row, P.L. Watson and R.N. Warrener, *Tetrahedron Lett.*, 1973, 1033.

3. M.N. Paddon-Row and R.N. Warrener, *Tetrahedron Lett.*, 1974, 3797.

4. Satisfactory combustion analysis or accurate mass measurement has been carried out on this new compound.

5. For other examples of thiophosgene acting as a dienophile see H. Allgeier and T. Winkler, *Tetrahedron Lett.*, 1976, 215 and references cited therein.

6. Simple alicyclic α,α-dichloro-thioethers yield the thiolactone on treatment with acid, see H.J. Reich and J.E. Trend, *J. Org. Chem.*, 1973, 38, 2637.

7. Halogen has been observed to act as a leaving group in an α,α-dibromothioether, as an alternative to hydrolysis to the thiolactone mentioned in ref. 6, see Y. Gaoni, *Tetrahedron Lett.*, 1976, 2167. Compare, however, G. Markl and R. Fuchs, *Tetrahedron Lett.*, 1972, 4691.

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9. 1,1'-Carbonothionylbis-1*H*-imidazole forms a 1:1 adduct of type (5a) with 8,8-dimethylisobenzofulvene (3a), while carbon disulphide is too unreactive to compete with the the [10+8] self-dimerisation of (3a)[1].

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