Tetrahedron, 1966, Vol. 22, pp. 3001 to 3005. Pergamon Press Ltd. Printed in Northern Ireland

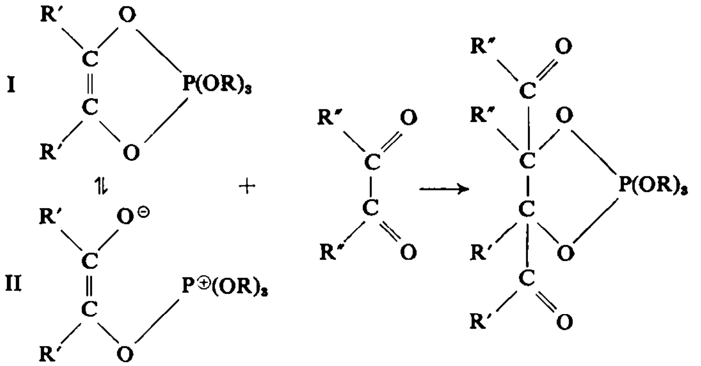
A DESAURIN FROM A CYCLIC PHOSPHORANE

A. J. KIRBY
University Chemical Laboratory, Cambridge

(*Received* 9 *February* 1966)

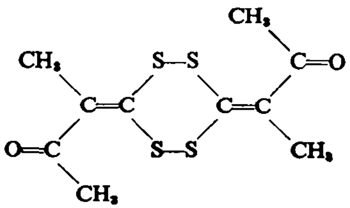
Abstract—The 1 : 1 adduct from diacetyl and trimethyl phosphite reacts with carbon disulphide to give the 1,2,4,5-tetrathiin (IV). This is converted successively into the 1,2,4-trithiole (VII) and the 1,3-dithiete or desaurin (VIII) by removal of sulphur using triethyl phosphite. The unusual UV spectra of these compounds may be due to conjugation through sulphur in VII and VIII.

RAMIREZ has shown[1] that the cyclic unsaturated phosphoranes (I) obtained from the addition of trialkyl phosphites to α-diketones, behave in their reactions with electrophiles as expected for the acyclic form II. Carbonyl compounds in particular attack the double bond, to give saturated cyclic phosphoranes (III).



III

When I ($R = R' = CH_3$) is dissolved or made in carbon disulphide, the solution slowly becomes deep red, and after a few days at room temperature large yellow crystals appear. The elucidation of the structure of this compound, as IV, is described in the following communication.[2]



IV

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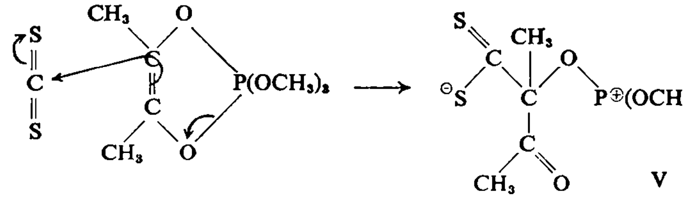
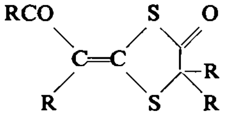
[1] F. Ramirez, *Pure Appl. Chem.* **9**, 337 (1964).

[2] N. W. Alcock and A. J. Kirby, *Tetrahedron* **22**, 3007 (1966).

There is little doubt that the reaction involves electrophilic attack on carbon by carbon disulphide. The alternative initial loss of trimethyl phosphate would be



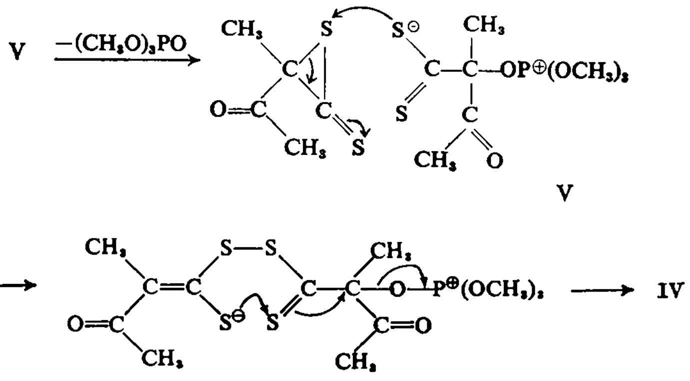
expected to lead to dimethyl ketene, by a Wolff-type rearrangement. In fact the reactions of α-diazoketones with carbon disulphide appear to involve the addition of the ketene formed in this way, to a molecule of the initial 1:1 product with carbon disulphide. Benzoylphenyldiazomethane, for example, gives VI (R = Ph)[3]: and acetylmethyldiazomethane under the same conditions gave a compound with analysis and NMR spectrum consistent with structure VI (R = CH_3). Diaryldiazomethanes,



VI

on the other hand, give compounds containing the tetrathiin ring as in IV.[4]

The further conversion of V into IV can be rationalized by an intramolecular displacement of trimethyl phosphate by sulphur, followed by attack of a second molecule of V on the thiolactone produced.

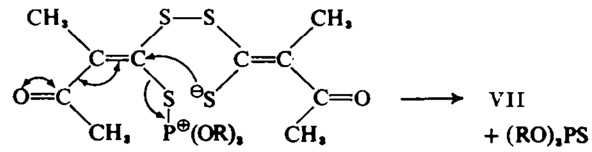


The compound IV shows negligible nucleophilic reactivity. It can be recrystallized from refluxing methyl iodide, and recovered from concentrated sulphuric acid. In refluxing toluene, however, it loses one atom of sulphur, to form a second compound, $C_{10}H_{12}S_3O_2$, with IR and NMR spectra closely similar to those of IV. There is little doubt that this is the trithiole VII; especially as the conversion can be carried out at room temperature using triethyl phosphite. The removal of an atom of sulphur

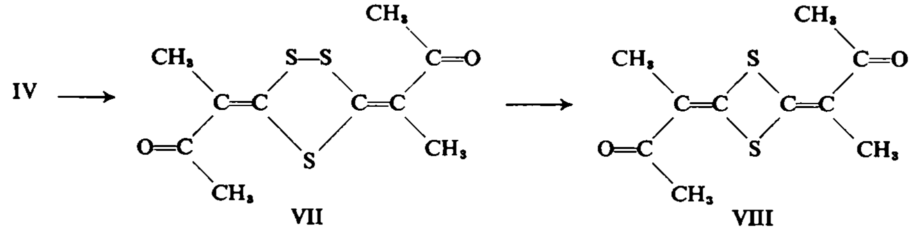
[3] P. Yates and B. G. Christensen, *Chem. Ind.* (*London*) 1441 (1958).

[4] A. Schoenberg, E. Frese and K. H. Brosowski, *Chem. Ber.* **95**, 3077 (1962).

from a disulphide by a trialkyl phosphite is well known.[5] In this case intramolecular displacement of triethylphosphorothionate can account for the formation of the symmetrical monosulphide by an ionic mechanism.



Compound VII itself loses an atom of sulphur on refluxing in triethyl phosphite, and is converted into a third compound, $C_{10}H_{12}S_2O_2$. This is the desaurin (VIII) which has not previously been prepared, but has an UV spectrum almost identical to that of the desaurin obtained from benzyl methyl ketone and carbon disulphide.[3] (λ_{max} 373 (ε_{max} 30,800) and 249 (ε_{max} 1560) in $CHCl_3$.)



Like IV and VII, VIII is a yellow, highly crystalline compound. Evidently the four-membered ring is the most stable of the three. The molecular ion of the desaurin, (VIII) for example, is much more prominent than the parent molecular ion in the mass spectrum of VII; and IV is converted into VII on heating.

The 1,3-dithiete ring is formally a 6 π-electron system, and like the 1,2-dithiete[6] shows remarkable stability. Its properties in VIII, however, are not qualitatively different from those of the rings containing three and four atoms of sulphur.

UV spectra

Compounds IV, VII and VIII all show a band near 240 mμ, in the position expected for the π–π^* transition of an $\alpha\beta$-unsaturated ketone; but the spectrum is increasingly dominated by a strong band at 340–370 mμ, which doubles and triples in intensity as first one and then two sulphur atoms are removed from IV.

This behaviour is unexpected if the transition involves two insulated unsaturated ketone chromophores, and suggests that delocalization may occur through sulphur in VII and VIII. Previous attempts to demonstrate this phenomenon have been inconclusive, and it has been pointed out that conjugated systems with a single linking sulphur atom are not normally coplanar.[7] Compounds VII and VIII are presumably

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[5] C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.* **81**, 1243 (1959).
R. G. Harvey, H. I. Jacobson and E. V. Jensen, *J. Amer. Chem. Soc.* **85**, 1618 (1963).

[6] C. G. Krespan, B. C. McKusick and T. L. Cairns, *J. Amer. Chem. Soc.* **83**, 3434 (1961).

[7] R. C. Passerini, in N. Kharasch (ed.), *Organic Sulphur Compounds*, Vol. I, Pergamon Press, London, 1961.

TABLE 1. UV SPECTRA IN 95% ETHANOL

	λ_{max}	ε_{max}	λ_{max}	ε_{max}
IV	247	11,300	301	11,200
			343	10,900
VII	232	15,200	347	19,800
VIII	241	1,440	359	28,700
		(shoulder)	370	28,700

planar[8] and conjugation through the 3p orbitals of sulphur may be favoured by the geometry of this system. For comparison, VI ($R = CH_3$) has λ_{max} at 243 and 317 mμ, ε_{max} 5,360 and 8,950, respectively.

EXPERIMENTAL

3,6-*Bis*-2-*oxobut*-3-*ylidene*-1,2,4,5-*tetrathiin* (IV)

The 1:1 adduct of trimethyl phosphite is conveniently prepared *in situ*: the purified adduct gives the same results.

An equimolar amount of diacetyl is added slowly, with external cooling, to trimethyl phosphite dissolved in 5 volumes of CS_2. After the exothermic reaction is complete the mixture is set aside at room temp: preferably in the dark, since the product in solution is destroyed by light. After 3–5 days large yellow crystals appear, reaching a maximum of some 20% of the theoretical yield in 10–14 days. The mother liquor showed the bands of trimethyl phosphate in the IR solution spectrum.

The compound was recrystallized from EtOH, m.p. 169–169·5°. (Found: C, 41·1; H, 4·0; S, 43·9. Mol. wt., 289 (ebullioscopic in $CHCl_3$); and 289 (thermistor method in CH_2Cl_2). $C_{10}H_{12}S_4O_2$ requires: C, 41·1; H, 4·1; S, 43·9. Mol. wt., 292.) The IR spectrum shows strong bands at 1640, 1497, 1273 and 972 cm^{-1}, and the NMR spectrum had only two peaks, at 7·66 and 7·75 τ, of equal intensity.

Attempts to prepare homologues

Other α-diketones gave negative results under a variety of conditions. Only $PhCOCOCH_3$, gave a few mg of yellow crystals after several months, with UV maxima at 374 mμ ($\varepsilon = 27{,}700$) and 262 mμ ($\varepsilon = 21{,}400$). This might possibly have been the benzoyl methyl desaurin; since the lower wavelength band differs from that of the acetyl phenyl compound, measured by Yates.[9] However, no satisfactory analysis could be obtained, and the product was destroyed on warming with triethyl phosphite.

3,5-*Bis*-2-*oxobut*-3-*ylidene*-1,2,4-*trithiole* (VII)

1 gm of IV dissolved in 50 ml hot toluene. After refluxing for 2 hr ether was added to the cooled solution, and a pale yellow solid was precipitated. Recrystallization from EtOH to m.p. 185–185·5° gave needles. (Found: C, 46·3; H, 4·25; S, 37·2. Mol. wt. (mass spectral), 260. $C_{10}H_{12}S_3O_2$ requires: C, 46·1; H, 4·6; S, 36·9% Mol. wt., 260.) The spectra were similar to those of IV, with individual bands shifted somewhat: IR peaks were at 1615, 1440, 1278 and 974 cm^{-1}, and the NMR spectrum showed the doublet at 7·7 τ, resolved by only 2 c/s.

Compound IV could also be converted to VII by dissolving in $CHCl_3$ with an excess of triethyl phosphate at room temp. After standing for two days VII crystallized on addition of pentane.

The desaurin, 2,4-*bis*-2-*oxobut*-3-*ylidene*-1,3-*dithiete* (VIII).

Compound IV or VII (1 g) in triethyl phosphite (30 ml) was dissolved by refluxing. After 2 hr the solution was allowed to cool, and VIII crystallized. After washing with ether it was recrystallized from EtOH to m.p. 236–238°.

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[*] An X-ray crystallographic examination of the desaurin VII has been initiated: which will settle both this point, and the interesting question of the bond-angles about sp^2-hydrized carbon in the four-membered ring.

The same bands appear in the spectra as before, shifted now to 1651, 1530, 1274 and 966 cm^{-1} in the IR, and better resolved in the NMR at 7·94 and 8·22 τ. The UV spectra of IV, VII and VIII are recorded in Table 1.

Reaction of carbon disulphide with 2-*diazo*-3-*butanone*

2–3 ml of crude 2-diazo-3-butanone, prepared from AcCl and diazoethane in ether, were dissolved in 10 volumes of CS_2 and refluxed for 36 hr. The solution was concentrated to a small volume and cooled overnight. About 50 mg of a pale yellow crystalline compound was obtained. Filtered, washed with ether, and recrystallized from EtOH, this was almost colourless, with m.p. 126°. The NMR spectrum showed 4 peaks of equal intensity, at 7·57, 8·00, 8·14 and 8·36 τ. This contrasts with VIII, which has only two NMR peaks, but is consistent with VI ($R = CH_3$). (Found: C, 50·0; H, 5·5; S, 30·6. $C_9H_{12}O_2S_2$ requires: C, 50·0; H, 5·4; S, 29·7%.)