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SULFUR HETEROCYCLES FROM THE REACTION OF α-DIAZO KETONES WITH CARBON DISULFIDE

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The major determining factor of the course of the reactions of α-diazo ketones $RCOCN_2R'$ with carbon disulfide is the nature of R'. When R' = Ph, 1,3-dithiolanes are the sole products; when R' = Me, both 1,3-dithiolanes and 1,3-dithietanes are formed; when R' = H, a 1,2,3-thiadiazole is formed.

Reaction of the α-diazo ketones 1 and 2 with boiling carbon disulfide gives the 1,3-dithiolane derivatives 5[1,2] and 6,[3] respectively, and spectroscopic evidence suggests strongly that 3 gives the analogous product 7.[4] In striking contrast, a product of analogous elemental composition formed from 4 has been shown to be the 1,3-dithietane derivative 8.[5] We now report on an investigation of the relationship between the structures of α-diazo ketones and the products they form with carbon disulfide.

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*Dedicated to Professor R.B. Woodward on the occasion of his sixtieth birthday.

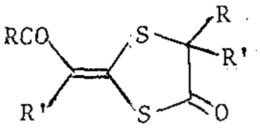
$RCOCN_2R'$

1 R = R' = Ph

2 R = Ph, R' = *p*-BrC$_6$H$_4$

3 R = R' = *p*-FC$_6$H$_4$

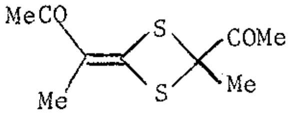
4 R = R' = Me



5 R = R' = Ph

6 R = Ph, R' = *p*-BrC$_6$H$_4$

7 R = R' = *p*-FC$_6$H$_4$



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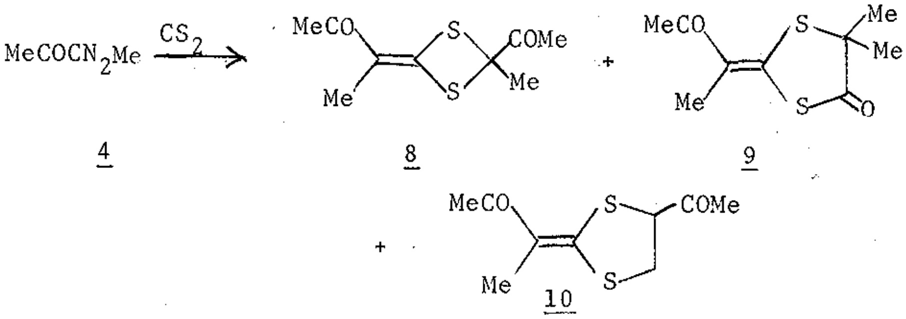
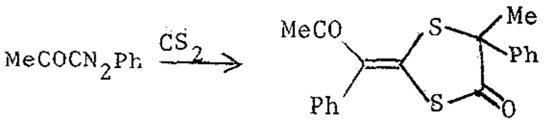
The diazo ketones were heated in boiling carbon disulfide until reaction was complete, as vouchsafed by i.r. spectroscopy; the reaction times varied from 1 day to 18 weeks. The products were identified by elemental analysis and spectroscopic data; distinction between the 1,3-dithiolane and 1,3-dithietane series was made most readily on the basis of mass spectrometry.[6]

Re-examination of the reaction of 4 revealed that, while 8 is the major product (50%), the 1,3-dithiolane 9 is also formed together with a third isomeric product, 10. Re-examination of the reaction of 1, however, gave no evidence for the formation of a product other than 5. The reaction of 1 was much more rapid than that of 4.

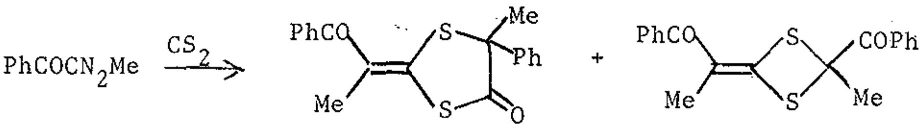


4 8 9 10

To determine whether the difference between the reactions of 1 and 4 is associated with the replacement of an individual phenyl group by a methyl group, the reactions of 11 and 13 were examined. The former gave the 1,3-dithiolane 12 as the only product detected, while the latter reacted very much more slowly to give both the 1,3-dithiolane 14 and the 1,3-dithietane 15. It was established that compounds 14 and 15 are not interconverted in boiling carbon disulfide.



11 12



13 14 15

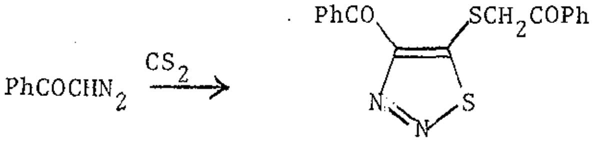
TABLE

SPECTROSCOPIC DATA FOR REACTION PRODUCTS

	M.p.	$\lambda_{max}^{CHCl_3}$, μ	λ_{max}^{MeOH}, nm(ε)	$\delta_H^{CDCl_3}$, ppm
5	154-155°	5.86 6.17(w)	254 (16,500), 347 (12,400)	7.0-7.6(m)
8	124-125°	5.84, 6.06	242 (9400), 316 (16,900)	1.82(s,3H), 2.04(s,3H), 2.18(s,3H), 2.60(s,3H)
9	98-99°	5.88, 6.06	261 (5300), 315 (12,100)	1.60(s,6H), 2.13(s,3H), 2.27(s,3H)
10	87-88°	5.86, 6.15	277 (sh, 4900), 320 (13,900)	2.14(s,3H), 2.24(s,3H), 2.30(s,3H), 3.28(dd,1H),[a] 3.75(dd,1H),[b] 4.35(dd,1H)[c]
12	64-66°	5.90, 6.08	265 (6200), 322 (15,900)	2.01(s,3H), 2.04(s,3H), 7.2-7.7(m,10H)
14	101-102°	5.88, 6.16(w)	257 (10,200), 333 (9600)	1.98(s,3H), 2.16(s,3H), 7.2-7.8(m,10H)
15	100-101°	5.95, 6.19	255 (24,300), 340.5 (18,100)	1.91(s,3H), 2.44(s,3H), 7.2-8.0(m,10H)
17	158-159°	5.92, 6.12	248 (19,700), 319 (11,700)	4.53(s,2H), 7.2-7.6(m,6H), 7.8-8.4(m,4H)

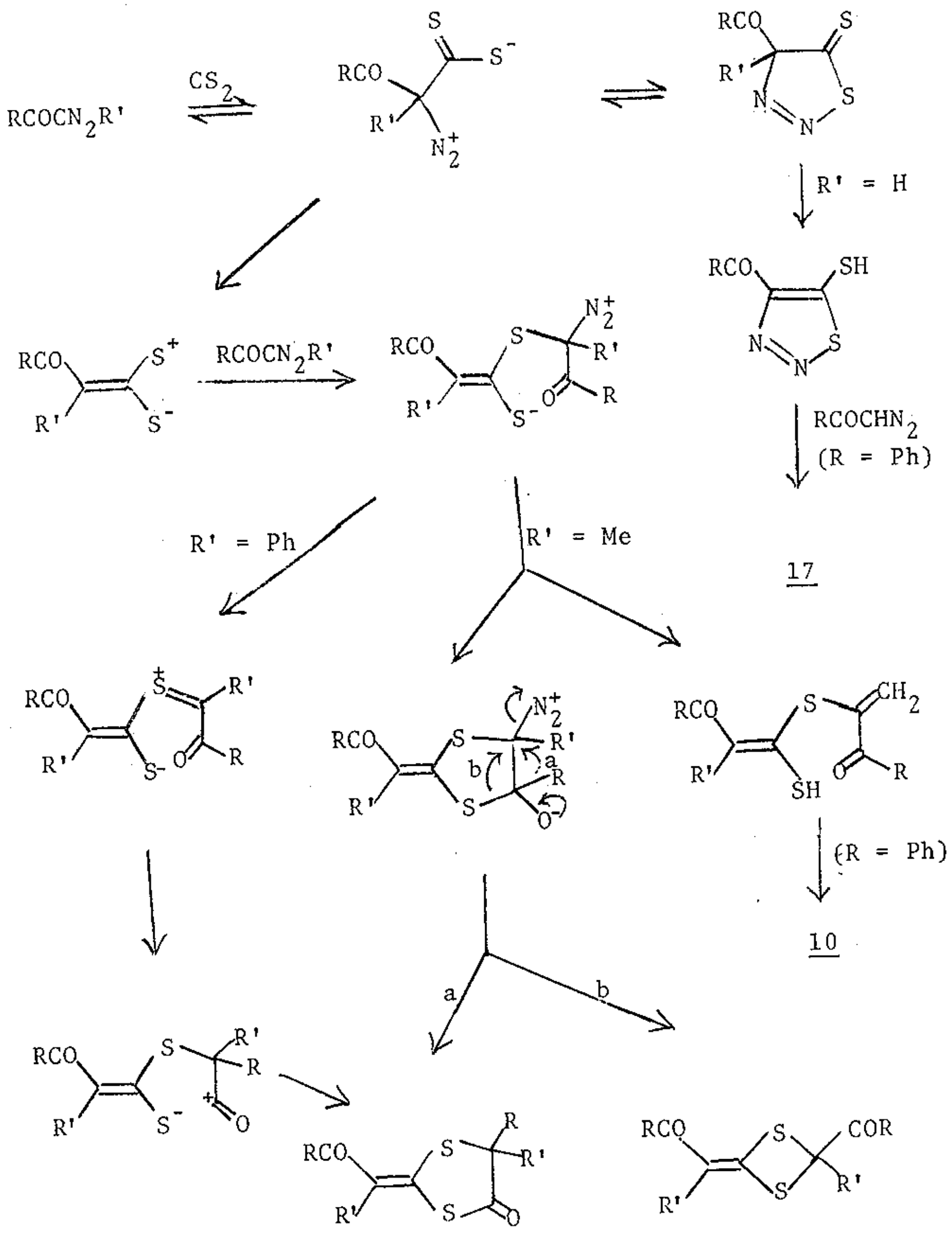
[a] J = 10, 5 Hz [b] J = 10, 3.5 Hz [c] J = 5, 3.5 Hz

Reaction of the α-diazo ketone 16 bearing no substituent on the diazo carbon atom proceeded more slowly yet (18 weeks); a complex product mixture was formed from which the 1,2,3-thiadiazole 17[7] was isolated in low yield.



16 17

Thus the major determining factor of the course of the reactions of α-diazo ketones $RCOCN_2R'$ with carbon disulfide is the nature of R'. When R' = Ph, 1,3-dithiolanes are the sole products; when R' = Me, reaction proceeds much more slowly and both 1,3-dithiolanes and 1,3-dithietanes are formed; when R' = H, reaction is exceedingly slow and a 1,2,3-thiadiazole is formed. The following reaction scheme is proposed to account for these observations.



SCHEME

ACKNOWLEDGMENT

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REFERENCES and NOTES

1 P. Yates, B.G. Christensen, and L.L. Williams, *Can. J. Chem.*, 1971, **49**, 1691.

2 For **5** and analogous 1,3-dithiolanes no configurational assignment is implied, except in the case of **6**.

3 K. Dichmann, D. Bichan, S.C. Nyburg, and P. Yates, *Tetrahedron Lett.*, 1971, 3649.

4 J.E. Baldwin and J.A. Kapecki, *J. Org. Chem.*, 1969, **34**, 724.

5 J.A. Kapecki, J.E. Baldwin, and I.C. Paul, *J. Amer. Chem. Soc.*, 1968, **90**, 5800; A.J. Kirby, *Tetrahedron*, 1966, **22**, 3001.

6 This will be discussed in a subsequent publication; other spectroscopic data are given in the Table.

7 Cf. P. Demaree, M.-C. Doria, and J.M. Muchowski, *Can. J. Chem.*, 1977, **55**, 243.

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