

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

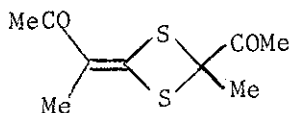
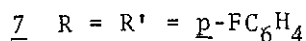
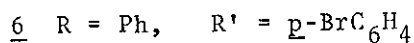
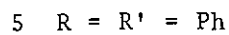
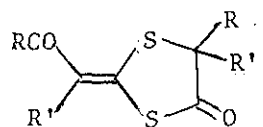
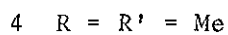
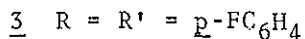
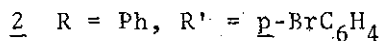
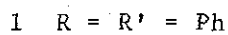
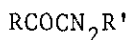
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The major determining factor of the course of the reactions of α -diazoketones $\text{RCOCHN}_2\text{R}'$ with carbon disulfide is the nature of R' . When $\text{R}' = \text{Ph}$, 1,3-dithiolanes are the sole products; when $\text{R}' = \text{Me}$, both 1,3-dithiolanes and 1,3-dithietanes are formed; when $\text{R}' = \text{H}$, a 1,2,3-thiadiazole is formed.

Reaction of the α -diazoketones 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 -diazoketones and the products they form with carbon disulfide.

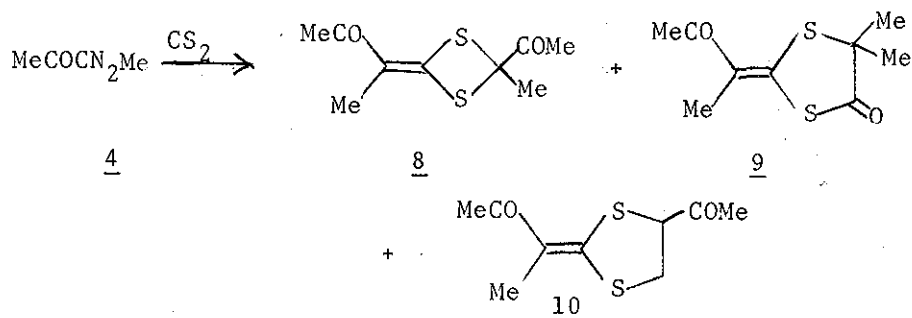
*Dedicated to Professor R.B. Woodward on the occasion of his sixtieth birthday.



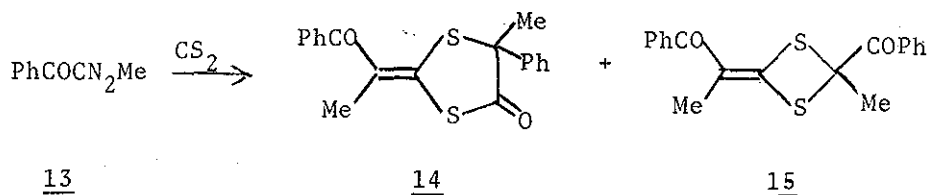
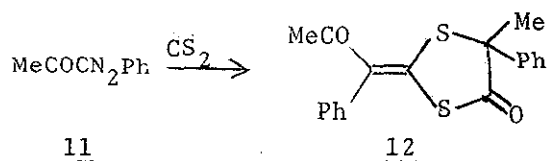
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The diazo ketones were heated in boiling carbon disulfide until reaction was complete, as vouchsafed by i.r. spectroscopy; the reaction times varied from 1 day to 18 weeks. The products were identified by elemental analysis and spectroscopic data; 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.



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.



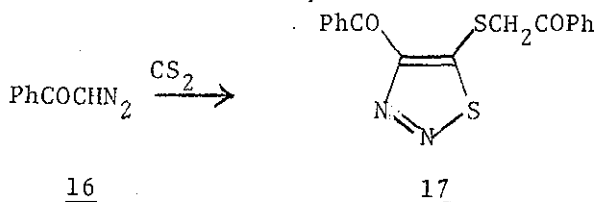
TABLE

SPECTROSCOPIC DATA FOR REACTION PRODUCTS

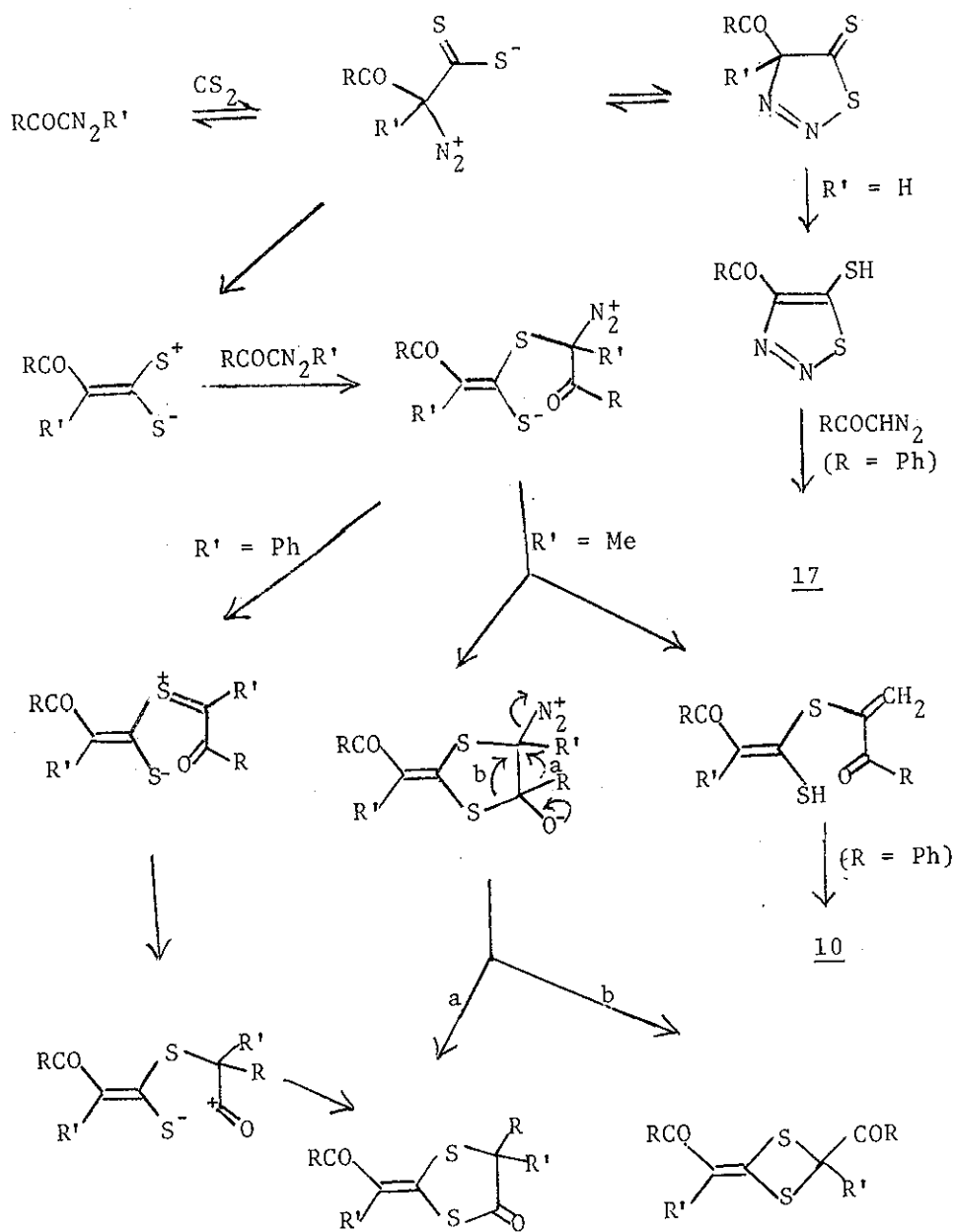
M.p.	$\lambda_{\text{max}}^{\text{CHCl}_3}, \mu$	$\lambda_{\text{max}}^{\text{MeOH}}, \text{nm}(\epsilon)$	$\text{H}_\delta^{\text{CDCl}_3}, \text{ppm}$
<u>5</u> 154-155°	5.86	254 (16,500),	7.0-7.6(m)
	6.17(w)	347 (12,400)	
<u>8</u> 124-125°	5.84,	242 (9400),	1.82(s,3H), 2.04(s,3H),
	6.06	316 (16,900)	2.18(s,3H), 2.60(s,3H)
<u>9</u> 98-99°	5.88,	261 (5300),	1.60(s,6H), 2.13(s,3H),
	6.06	315 (12,100)	2.27(s,3H)
<u>10</u> 87-88°	5.86,	277 (sh, 4900),	2.14(s,3H), 2.24(s,3H),
	6.15	320 (13,900)	2.30(s,3H), 3.28(dd,1H), ^a
			3.75(dd,1H), ^b 4.35(dd,1H) ^c
<u>12</u> 64-66°	5.90,	265 (6200),	2.01(s,3H), 2.04(s,3H),
	6.08	322 (15,900)	7.2-7.7(m,10H)
<u>14</u> 101-102°	5.88,	257 (10,200),	1.98(s,3H), 2.16(s,3H),
	6.16(w)	333 (9600)	7.2-7.8(m,10H)
<u>15</u> 100-101°	5.95,	255 (24,300),	1.91(s,3H), 2.44(s,3H),
	6.19	340.5 (18,100)	7.2-8.0(m,10H)
<u>17</u> 158-159°	5.92,	248 (19,700),	4.53(s,2H), 7.2-7.6(m,6H),
	6.12	319 (11,700)	7.8-8.4(m,4H)

^a $\underline{J} = 10, 5 \text{ Hz}$ ^b $\underline{J} = 10, 3.5 \text{ Hz}$ ^c $\underline{J} = 5, 3.5 \text{ Hz}$

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 17⁷ was isolated in low yield.



Thus the major determining factor of the course of the reactions of α -diazo ketones $\text{RCOCN}_2\text{R}'$ with carbon disulfide is the nature of R' . When $\text{R}' = \text{Ph}$, 1,3-dithiolanes are the sole products; when $\text{R}' = \text{Me}$, reaction proceeds much more slowly and both 1,3-dithiolanes and 1,3-dithietanes are formed; when $\text{R}' = \text{H}$, 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

We thank the National Research Council of Canada for support of this work.

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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