

## Heterocycles from Ylides. Part IV.<sup>1</sup> Reactivity of 4-Arylmethylene- $\Delta^2$ -pyrazolin-5-ones with Stabilized Sulphur Ylides

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4-Arylmethylene-1-phenyl- $\Delta^2$ -pyrazolin-5-ones react with carbonyl-stabilized sulphur ylides yielding spiro[cyclopropane-1,4'- $\Delta^2$ -pyrazolin]-5'-ones, identified from spectroscopic data and chemical behaviour.

SULPHUR ylides have found a wide variety of applications in organic synthesis.<sup>2,3</sup> We report the preparation of spiro[cyclopropane-1,4'- $\Delta^2$ -pyrazolin]-5'-one deriva-

tives † from carbonyl-stabilized sulphonium ylides and 4-arylmethylene- $\Delta^2$ -pyrazolin-5-ones.

The reaction of dimethylsulphonium phenacylide (1) with several (*Z*)-4-arylmethylene- $\Delta^2$ -pyrazolin-5-ones (2)

† Some simple derivatives have been reported previously.<sup>4</sup>

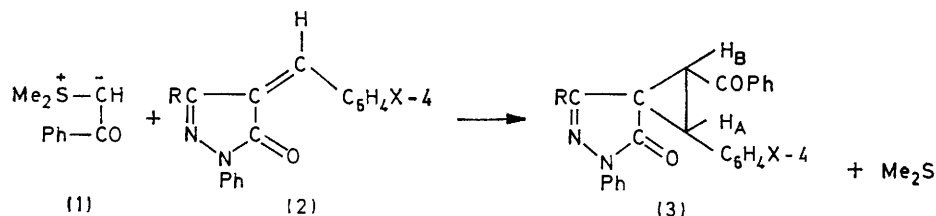
<sup>1</sup> Part III, P. Dalla Croce and D. Pocar, preceding paper.

<sup>2</sup> (a) C. R. Johnson, *Accounts Chem. Res.*, 1973, **6**, 344; (b) B. M. Trast, *ibid.*, 1974, **7**, 85.

<sup>3</sup> C. R. Johnson and C. Schroeck, *J. Amer. Chem. Soc.*, 1973, **95**, 7417.

<sup>4</sup> H. Wamhoff and F. Korte, *Chem. Ber.*, 1966, **99**, 2962.

afforded the spirocyclopropane derivatives (3a—d). Elemental analysis and i.r. data (characteristic cyclopropane bands <sup>5</sup> at 1 015—1 020 cm<sup>-1</sup> and pyrazolinone C=O stretching <sup>6</sup> at 1 680 cm<sup>-1</sup>) confirmed the product structures. The n.m.r. spectra showed an AB splitting pattern for the cyclopropane hydrogen atoms, allowing us to assign to the H<sub>A</sub>H<sub>B</sub> system the *cis*-configuration

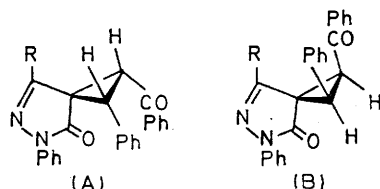


	R	X	M.p. (°C)	Yield (%)	$\delta$		$J_{a,b}$ /Hz
					H <sub>A</sub>	H <sub>B</sub>	
(3a)	Me	H	131—132 <sup>a</sup>	85	4.05	4.25	9.0
(3b)	Ph	H	175—176 <sup>b</sup>	80	4.17	4.62	8.9
(3c)	Me	NO <sub>2</sub>	159—160 <sup>a</sup>	80	3.97	4.18	9.0
(3d)	Me	OMe	147—148 <sup>a</sup>	75	4.12	4.30	9.1

<sup>a</sup> From ethanol. <sup>b</sup> From ethyl acetate.

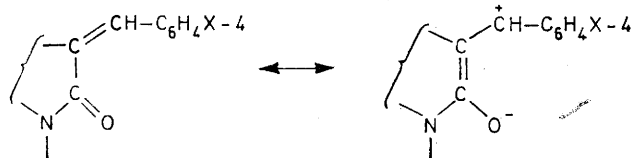
SCHEME 1

on the basis of the coupling constants <sup>7</sup> ( $J$  ca. 9 Hz). The products (3a—d) could therefore have structure (A) or (B).



Molecular models of compounds (3a and b) indicate that in structure (B) there exists a considerable steric interaction between the pyrazoline 3-substituent and the cyclopropane 2- and 3-substituents, whereas structure (A) appears markedly less crowded.

It is known <sup>8</sup> that 4-arylmethylene- $\Delta^2$ -pyrazolin-5-ones show the mesomerism illustrated in Scheme 2. Accordingly, products from 1,2- or 1,4-cycloaddition



SCHEME 2

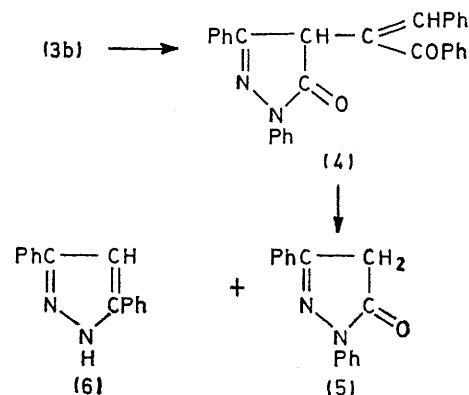
might be expected. However, the reaction gave only 1,2-cycloaddition products. This behaviour is similar to that of stabilized sulphur ylides with  $\alpha\beta$ -unsaturated carbonyl compounds, affording, *via* Michael-type addition, cyclopropane derivatives.<sup>9</sup>

<sup>5</sup> J. D. Graham and M. T. Rogers, *J. Amer. Chem. Soc.*, 1962, **84**, 2149.

<sup>6</sup> R. H. Wiley and P. Wiley, 'Pyrazolones and Derivatives,' Interscience, New York, 1964.

The structure of the spiro[cyclopropanepyrazolin]ones was supported by the following chemical transformation. Treatment of compound (3b) with potassium t-butoxide in dimethyl sulphoxide promoted abstraction of the 3-proton followed by cleavage of the cyclopropane 1,2-bond. This led to 4-( $\alpha$ -benzylidenephenacyl)-1,3-diphenyl- $\Delta^2$ -pyrazolin-5-one (4), which by reaction with

hydrazine in ethanol afforded 1,3-diphenyl- $\Delta^2$ -pyrazolin-5-one (5) and 3,5-diphenylpyrazole (6).



SCHEME 3

The mildness and simplicity of our reaction contribute to the general utility of carbonyl-stabilized sulphur ylides in this regiospecific and stereoselective route to spiro[cyclopropanepyrazolin]ones.

#### EXPERIMENTAL

N.m.r. spectra were measured with a Varian A-60 spectrometer (solvent C<sub>6</sub>D<sub>6</sub>; Me<sub>4</sub>Si internal standard). I.r. spectra were recorded with a Perkin-Elmer 137 Infracord spectrophotometer for ca. 2% solutions in chloroform.

<sup>7</sup> H. Booth, *Progr. NMR Spectroscopy*, 1969, **5**, 167; L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 1969.

<sup>8</sup> G. Cellerino, G. Desimoni, P. P. Righetti, and G. Tacconi, *Gazzetta*, 1973, **103**, 1947.

<sup>9</sup> A. W. Johnson and R. T. Amel, *J. Org. Chem.*, 1969, **34**, 1240.

Elemental analyses for new compounds are available as Supplementary Publication No. SUP 21652 (2 pp.).\*

*4-Arylmethylene-1-phenyl- $\Delta^2$ -pyrazolin-5-ones.*— These were prepared by reported methods<sup>10</sup> from 1-phenyl-3-methyl- or 1,3-diphenyl- $\Delta^2$ -pyrazolin-5-ones and the appropriate aldehyde.

*Preparation of Spiro[cyclopropanepyrzolin]ones (3a—d): General Procedure.*—A solution of dimethylsulphonium phenacylide<sup>9</sup> (1) (0.01 mol) in 1,2-dimethoxyethane (25 ml) was added to a stirred suspension, cooled to  $-20^\circ\text{C}$ , of the 4-arylmethylene-1-phenyl- $\Delta^2$ -pyrazolin-5-one (0.01 mol) in the same solvent (50 ml). The mixture was stirred for 2 h and then the solvent was evaporated off and the residue was crystallized.

*4-( $\alpha$ -Benzylidenephenacyl)-1,3-diphenyl- $\Delta^2$ -pyrazolin-5-one (4).*—A mixture of compound (3b) (1 g) and potassium *t*-butoxide (0.295 g) in dimethyl sulphoxide (30 ml) was kept overnight at room temperature. The solvent was evaporated off under vacuum and the residue taken up with water

(25 ml) and ether (50 ml). The aqueous layer was acidified with acetic acid and the precipitate filtered off. The product was purified from ethanol; yield 0.75 g (75%); m.p.  $130^\circ$ .

*Reaction of the Pyrazolinone (4) with Hydrazine.*—A solution of compound (4) (1 g) in ethanol (50 ml) was treated with hydrazine hydrate (0.14 g) and refluxed for 4 h. Evaporation left an oily residue which was dissolved in ether. Extraction with aqueous 10% sodium hydroxide (20 ml) followed by acidification with hydrochloric acid (2N; 20 ml) afforded 1,3-diphenyl- $\Delta^2$ -pyrazolin-5-one (5) (0.37 g, 70%), m.p.  $134^\circ$ . From the ether layer by conventional work-up, 3,5-diphenylpyrazole (6) was isolated (0.32 g, 65%); m.p.  $198^\circ$ . Both compounds (5) and (6) showed no m.p. depression in admixture with authentic samples.

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\* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1975, Index issue.

<sup>10</sup> G. Desimoni, A. Gamba, P. P. Righetti, and G. Tacconi, *Gazzetta*, 1972, **102**, 491.