

1,3-CYCLOADDITION REACTIONS OF 'CARBONYL YLIDES' RESULTING  
FROM THE MILD THERMOLYSIS OF  $\Delta^3$ -1,3,4-OXADIAZOLINES\*.

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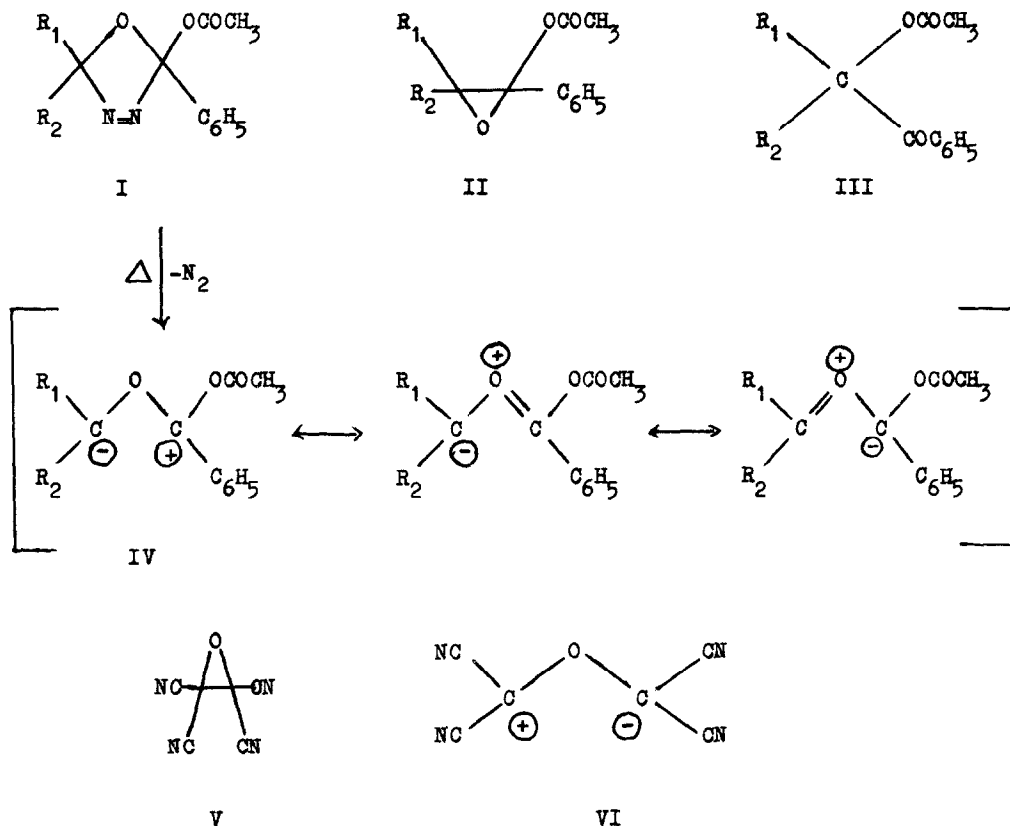
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One route to transient and reactive 1,3-dipoles is through the pyrolysis of suitable heterocyclic compounds as has been well illustrated by Huisgen and coworkers by their elegant work involving 2,5-diphenyltetrazole (1) and N-phenyl-C-methylsydnone (2) as the source of a 'nitrile imine' and an 'azomethine imine' respectively (3).

A recent publication by Hoffmann and Luthardt (4) on the preparation of  $\Delta^3$ -1,3,4-oxadiazolines of the type I and their thermal breakdown to the compounds of the type II and III stimulated us to explore whether the intermediates in the primary decomposition of the oxadiazolines (II) could be the 1,3-dipolar 'carbonyl ylides' (IV) and, if so, whether they could be trapped by reactive dipolarophiles as in the case of tetracyanoethyleneoxide (V) the many facile addition reactions of which (5) can be rationalised on the basis of its ability to exist as the 'carbonyl ylide' (VI) under suitable conditions (6).

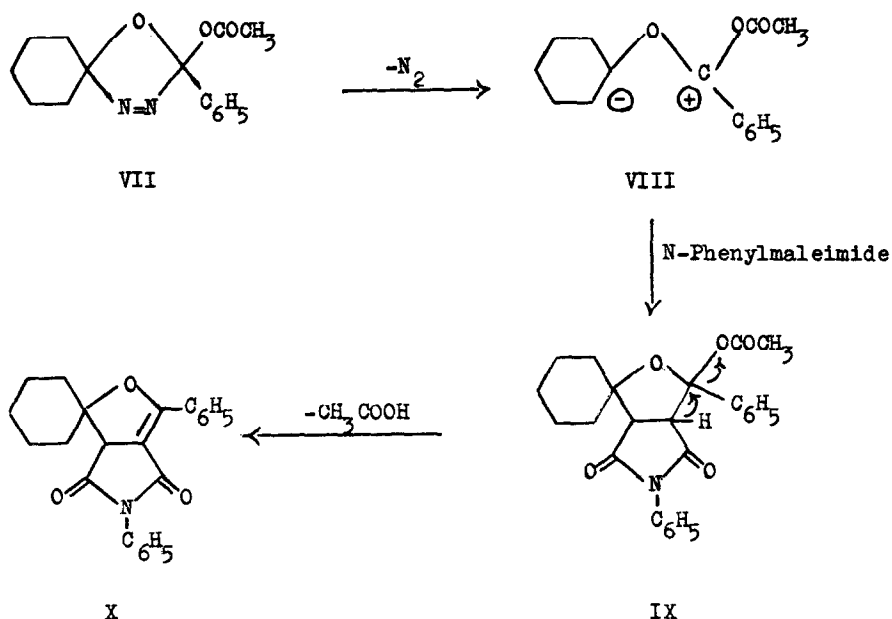
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Accordingly, 2-acetyl-5,5-pentamethylene-2-phenyl- $\Delta^3$ -1,3,4-oxadiazoline (VII) was prepared by the method of Hoffmann and Luthardt (4) and decomposed in the presence of a molar equivalent of N-phenylmaleimide in anhydrous benzene medium. Vigorous evolution of nitrogen took place even at 60-65° and the product isolated, after the decomposition was complete, was not the expected IX (molecular formula  $C_{19}H_{25}NO_5$ ) but one which analysed for  $C_{17}H_{21}NO_3$  [ $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$  330  $\mu$  ( $\epsilon = 15,780$ ), 244  $\mu$  ( $\epsilon = 10,810$ ) 226  $\mu$  ( $\epsilon = 16,300$ ) and 206  $\mu$  ( $\epsilon = 25,830$ )]. A comparison of the molecular formulas of expected compound (IX) with that of the one actually obtained immediately revealed that the latter could, in all probability, have resulted from the former by

the loss of the elements of acetic acid and that it could have the structure X.

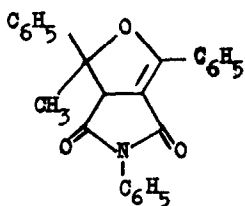


The infrared and NMR spectra of the product are consistent with this structure (X). The former, in nujol, exhibits a pair of strong absorptions at 1758 and 1692  $\text{cm}^{-1}$  corresponding to an  $\alpha, \beta$ -unsaturated five-membered cyclic imide function (7) and a strong absorption at 1628  $\text{cm}^{-1}$  indicative of a styrene type of double bond (7) while the latter (8) carries signals at  $\delta$  8.45 - 7.23 ppm (multiplet corresponding to ten aromatic protons),  $\delta$  4.24 ppm (one proton singlet) and  $\delta$  2.35 - 1.34 ppm (multiplet corresponding to ten alicyclic protons).

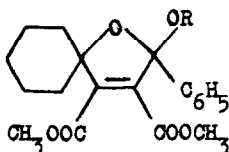
That acetic acid was indeed eliminated during the course of the reaction was confirmed by the vapour phase chromatographic examination of the mother liquor obtained after the removal of X. It is evident, then, that IX which should have been the primary product resulting from the 1,3-dipolar addition

of the 'carbonyl ylide' (VIII) to N-phenylmaleimide had split off the elements of acetic acid spontaneously to yield X, the driving force of the reaction being the formation of the double bond in conjugation with the phenyl group on one side and the carbonyl function on the other.

Other N-phenylmaleimides afforded similar derivatives (see Table) of the novel 3-oxa-7-azabicyclo[3,3,0]octane system. Likewise structure XI could be assigned to the product obtained by the thermolysis of 2-acetyl-2,5-diphenyl-5-methyl- $\Delta^3$ -1,3,4-oxadiazoline (II;  $R_1 = C_6H_5$ ,  $R_2 = CH_3$ ) in the presence of N-phenylmaleimide and this is borne out by its molecular formula ( $C_{25}H_{19}NO_3$ ), infrared spectrum in nujol (similar to that of X with strong absorption at 1765, 1710 and 1650  $cm^{-1}$ ) and NMR spectrum (8) which carries signals at  $\delta$ 8.44 - 7.17 ppm (multiplet corresponding to the fifteen aromatic protons),  $\delta$ 4.68 ppm (one proton singlet) and  $\delta$ 1.74 ppm (singlet corresponding to the three protons of the methyl group).



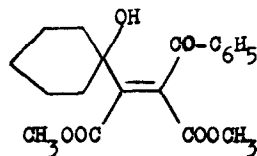
XI



XII

a : R = COCH<sub>3</sub>

b : R = H



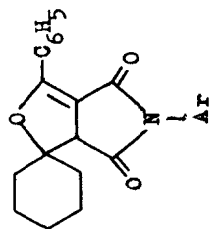
XIII

The thermal decomposition of VII in the presence of dimethyl acetylene-dicarboxylate was rather unusual. The product, isolated in good yield, analysed for  $C_{19}H_{22}O_6$  which is short of that of the expected compound (XIIa) by  $C_2H_2O$ . Its ultraviolet spectrum (in methanol) has maxima at 226  $m\mu$  ( $\epsilon = 8,190$ ) and 206  $m\mu$  ( $\epsilon = 16,700$ ) and an inflection at 218  $m\mu$  ( $\epsilon = 8,849$ ) and its

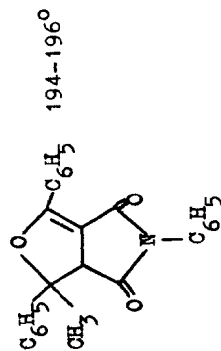
infrared spectrum (in nujol) exhibits absorptions at  $3500\text{ cm}^{-1}$  (strong),  $1738\text{ cm}^{-1}$  (strong),  $1706\text{ cm}^{-1}$  (strong),  $1655\text{ cm}^{-1}$  (moderate),  $1288\text{ cm}^{-1}$  (strong) and  $1142\text{ cm}^{-1}$  (strong). The last two of the infrared absorptions, in conjunction with usual ester carbonyl absorptions (at  $1738$  and  $1706\text{ cm}^{-1}$ ), are indicative of the presence of a substituted maleate or a fumarate moiety (7) while the absorption at  $3500\text{ cm}^{-1}$  clearly suggests the presence of a hydroxyl function in the molecule. This is confirmed by its NMR spectrum (8) which carries signals at  $\delta 7.77 - 7.26$  ppm (multiplet corresponding to five aromatic protons),  $\delta 3.85$  ppm (three proton singlet corresponding to ester methyl protons),  $\delta 3.66$  ppm (three proton singlet corresponding to ester methyl protons),  $\delta 3.53$  ppm (singlet corresponding to one exchangeable proton) and  $\delta 2.21 - 1.41$  ppm (multiplet corresponding to ten alicyclic protons). These analytical and spectral data are consistent with the hemiketal structure XIIb for this product. The possibility of it existing in the open keto form XIII seems to be remote in that such a compound might dehydrate readily and in that the infrared spectrum is not quite consistent with it.

The mechanism of formation of XIIb seems, at present, to be obscure. The likelihood that XIIa which is first formed gets readily hydrolysed to XIIb was precluded by the use of anhydrous materials and strict exclusion of moisture during the reaction. The other attractive possibility is the extrusion of the elements of ketene during the decomposition of VII for which a mechanism can easily be envisaged. But attempts to trap ketene, if it is formed at all, with suitable reagents have thus far not been successful.

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<u>Ar</u>	<u>M. P.</u>	<u>Yield</u>	<u>Mol. Formula</u>	<u>C</u>	<u>H</u>	<u>N</u>
	189-91°	51%	C <sub>23</sub> H <sub>21</sub> NO <sub>3</sub>	Calc. 76.86 Found 77.21	5.89 5.90	3.90 3.60
	149-152°	48%	C <sub>24</sub> H <sub>23</sub> NO <sub>4</sub>	Calc. 74.02 Found 74.16	5.95 6.27	3.60 3.70
	188-189°	37%	C <sub>23</sub> H <sub>20</sub> N <sub>2</sub> O <sub>5</sub>	Calc. 68.80 Found 68.07	4.99 5.04	6.93 7.36
	202-205°	55%	C <sub>24</sub> H <sub>23</sub> NO <sub>3</sub>	Calc. 77.19 Found 77.00	6.21 6.47	3.75 4.03



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