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A NEW OXIDATIVE ALKOXYLATION REACTION*

THE PREPARATION OF 5-ALKOXY-4,4-DIALKYL-1-ARYL-3-PYRAZOLIDINONES

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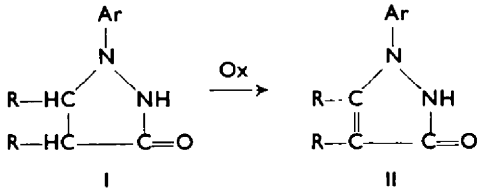
Abstract—A new oxidative alkoxylation method is described. According to this method alkoxy groups are introduced in the 5-position of 4,4-dialkyl-1-aryl-3-pyrazolidinones by oxidation with HgO or SeO_2 in alcohols. The mechanism, the scope and limitations of the reaction are discussed. The 5-alkoxy-4,4-dialkyl-1-aryl-3-pyrazolidinones may be converted to 1-aryl-4,4-dialkyl-5-(1-aryl-3-oxo-4,4-dialkyl-5-alkoxy-5-pyrazolidinyl)-3-pyrazolidinones. The structure of the reaction products was studied by IR and NMR analyses.

IT is known that 1-aryl-3-pyrazolidinones as well as their 4- and or 5-alkyl derivatives I may be oxidized by different oxidizing agents to the corresponding 1-aryl-3-pyrazolinones II.[1–6]



I II

On the other hand Veibel *et al.*[7–10] have shown that 4-alkyl-5-pyrazolinones VI may be oxidized by oxygen or by organic peroxides to 4-alkyl-4-hydroxy-5-pyrazolones VII.

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† In part of the spectrochemical study only.

[1] G. F. Van Veelen and H. Ruysschaert, *Phot. Sci. Eng.* **4**, 129 (1960).
[2] A. J. Axford, *Phot. Eng.* **7**, 23 (1956).
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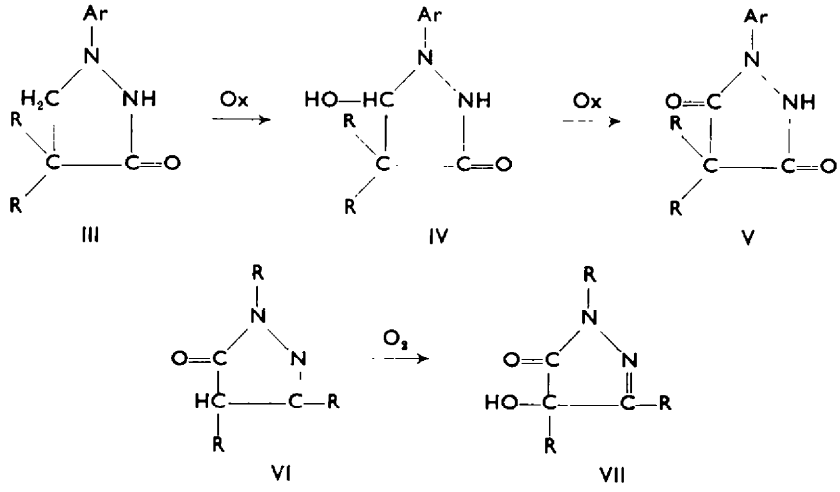
[10] S. Veibel and S. C. Linholt, *Acta Chem. Scand.* **9**, 970 (1955).



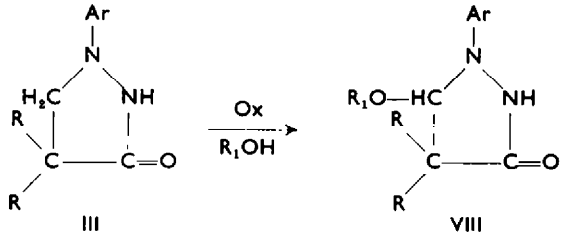
We have been able to show that air oxidation or oxidation with selenium or mercuric oxides in water of 1-aryl-4,4-dialkyl-3-pyrazolidinones III, where no oxidation to a corresponding pyrazolinone can take place, is accompanied by hydrolytic cleavage of the pyrazolidinone ring.

From a complex mixture of reaction products, only small amounts of 4,4-dialkyl-1-aryl-3,5-pyrazolidinediones V (as indicated by the comparison of the IR spectra with the IR spectra of samples prepared independently), probably formed by further oxidation of the 5-hydroxy compounds IV primarily formed, were identified.[11]

If the oxidation is performed in alcoholic medium, hydrolytic cleavage is prevented and well-defined products are obtained, the formulae of which suggest the introduction of an alkoxy group. This was confirmed by carrying out the oxidation in different alcohols. The molecular weight determinations for the methoxy and ethoxy derivatives yielded the values 220 (calc. 220) and 235 (calc. 234) respectively. The IR and NMR spectra* of these reaction products confirm the introduction of an alkoxy group in the 5-position and the preservation of the ring structure.

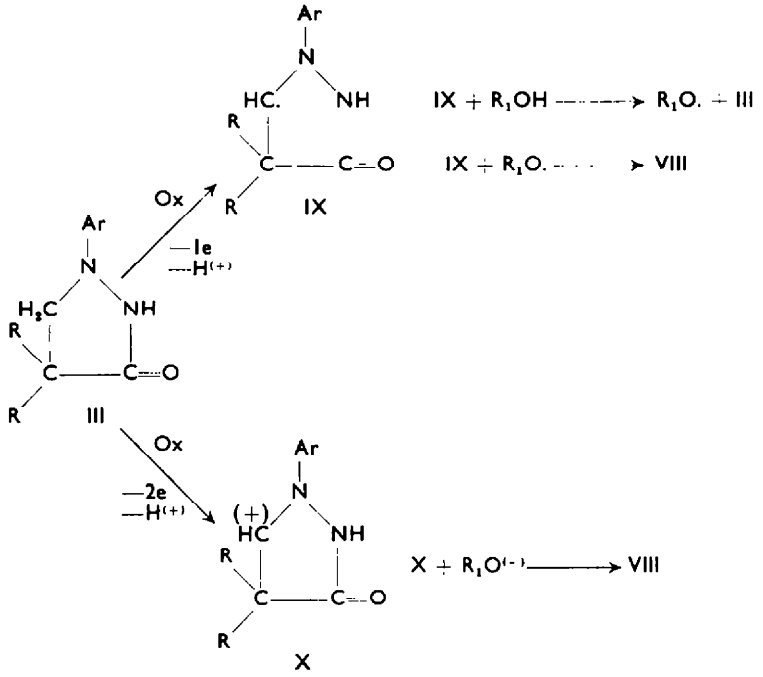
The introduction of an alkoxy group in saturated non-aromatic ring systems by an oxidation reaction, hereinafter called "oxidative alkoxylation," has not been described before. It opens up a convenient route to the preparation of the 5-alkoxy-4,4-dialkyl-1-aryl-3-pyrazolidinones VIII.

These products are not described in the literature, probably because their preparation according to the classical methods is very difficult.



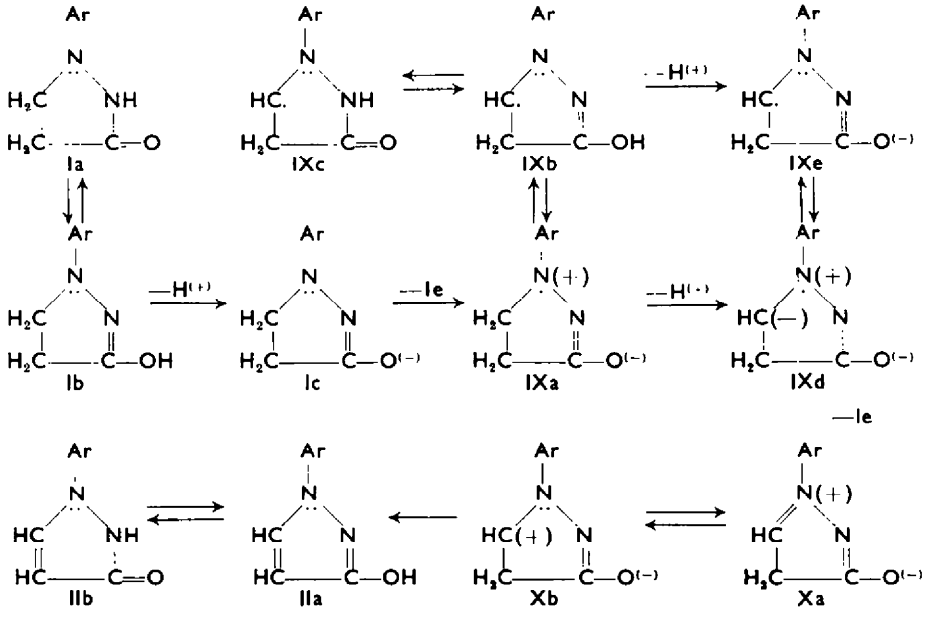
* See Spectrochemical study, p. 2731.

[11] R. Janssen, G. F. Van Veelen and J. F. Willems, Unpublished results.



The introduction of an alkoxy group in the 5-position of a 4,4-dialkyl-1-aryl-3-pyrazolidinone may be due to the initial formation of either a stabilized radical IX or a stabilized carbonium compound X.

The formation of semiquinones IX and carbonium compounds X from 1-aryl-3-pyrazolidinones, which do not carry two alkyl groups on the same carbon atom during oxidation in alkaline medium, namely with silver halide, has often been observed.[12,13]

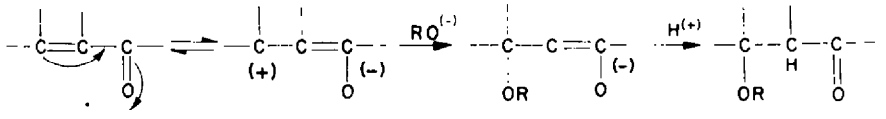


[12] W. E. Lee and T. H. James, *Phot. Sci. Eng.* **6**, 32 (1962).
[13] J. F. Willems and G. F. Van Veelen, *Phot. Sci. Eng.* **6**, 39 (1962).

As a general rule carbonium ions with their great affinity for an electron pair are stabilized by elimination of a proton from the α-carbon atom.

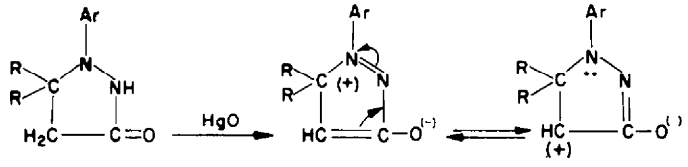
When the carbon atom of the 4-position does not carry two alkyl groups, the carbonium compound Xb isomerizes to the 3-pyrazolinone IIb or the tautomeric 3-hydroxypyrazole structure IIa. This isomerization is impossible in X, since it would require the separation of one of the 4-alkyl groups. Instead, the structure Xb is stabilized by the addition of an alcohol whereby a 5-alkoxy-4,4-dialkyl-3-pyrazolidinone derivative VIII is formed. The possibility that the radical IX pairs with an alkoxy radical (formed from the alcohol and IX) to form VIII, is less likely to occur, since the oxidation of I results always in the formation of II, even in the presence of alcohols.

The addition of an alcohol to structures such as X is similar to the addition of alcohols to α,β-unsaturated carbonyl compounds XI; ketones, acids, esters resulting in the formation of β-alkoxy-carbonyl compounds XIIa e.g. the preparation of β-methoxyethyl methyl ketone by adding methanol to methyl vinyl ketone in the presence of mercuric oxide as a catalyst,[14] as well as the preparation of β-alkoxy-propionic acids (and esters) by adding alcohols to acrylic acid (and esters) with sodium alcoholates as catalysts.[15–18]



XI XIa XII XIIa

In the oxidation of 5,5-dialkyl-1-aryl-3-pyrazolidinones XIII in alcoholic medium with mercuric oxide the product obtained is independent of the alcohol used, since no alkoxy group is introduced. Via a strongly violet colored intermediate product, an alkaline insoluble oxidation product is formed, which contrary to VIII no longer possess any reducing action anymore.



XIII XIV XV

Either the formation of the carbonium structure XV does not occur, or a compound possessing the structure XV cannot be added to alcohols, as in the case of a compound possessing the structure X.

[14] D. B. Killian, G. F. Hennion and J. A. Nieuwland, *J. Amer. Chem. Soc.* **58**, 892 (1936).
[15] C. E. Rehberg, Marion B. Dixon and C. H. Fisher, *J. Amer. Chem. Soc.* **68**, 544 (1946).
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[18] R. H. Hall and E. S. Steen, *J. Chem. Soc.* 2035 (1949).

The oxidative alkoxylations as described in the Experimental occur very smoothly with either mercuric oxide or selenium dioxide, but owing to the difficulties sometimes met in removing the last traces of colloidal selenium, the oxidations with mercuric oxide are generally to be preferred.

The oxidations may be carried out at room temperature as well as at the reflux temperature of the alcohol used. The reactions are promoted by the addition of sodium alcoholates, but oily products are then obtained, the separation and identification of which is very difficult. Ring cleavages also occur, as with the oxidations in aqueous alkaline medium.

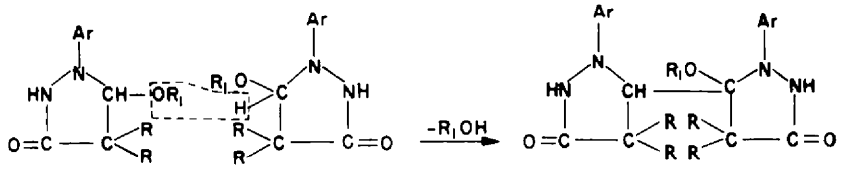
Oxidations carried out in butanol yield unidentified products. The microanalyses indicate that no butoxy group has been introduced. Boiling of the reaction product in methanol results in the formation of the methoxy derivative (VIII; $R_1 = CH_3$).

This observation is supported by the fact that butanol does not add to the α,β-unsaturated carbonyl compounds.[15] The introduction of an isopropoxy group is more difficult than that of an n-propoxy group. Although the oxidative alkoxylations occur very smoothly at room temperature with unbranched alcohols, in the case with 2-propanol, the isolated product had an undefined m.p. which, like the product obtained with butanol, is converted into the corresponding methoxy derivative by recrystallization from methanol. The isopropoxy group is, however, introduced when the oxidation is carried out in boiling 2-propanol. These considerations show that steric factors are of importance in this reaction, as indicated by the Fischer–Taylor–Hirschfelder models.

It is also to be accepted that the oxidation products X of the 4,4-dialkyl-1-aryl-3-pyrazolidinones are relatively stable, since they may be isolated at least in an impure state.

When attempting to purify the 5-alkoxy-4,4-dialkyl-1-aryl-pyrazolidinones VIII by recrystallization from relatively high boiling solvents, an abrupt variation of the m.p. is observed. Microanalysis and molecular weight determinations show that two molecules of VIII are condensed with the elimination of an alcohol molecule. The IR and NMR spectra indicate that an alkoxy group is still present.

The alcohol elimination most probably occurs between the 5-alkoxy group of one VIII molecule and a reactive hydrogen, at the C-5-position of a second VIII molecule.

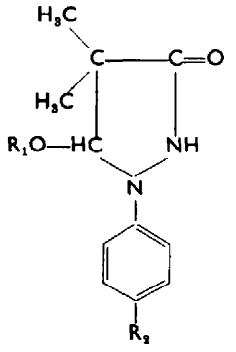


This results in the formation of 1-aryl-4,4-dialkyl-5-(1′-aryl-3′-oxo-4′,4′-dialkyl-5′-alkoxy-5′-pyrazolidinyl)-3-pyrazolidinones XVI. The NMR data could not prove exactly the proposed XVI structure.*

The formation of these products XVI is sometimes observed if the oxidative alkoxylation is carried out at reflux temperature of the alcohol, as in the preparation of the

* See spectrochemical study, p. 2731.

TABLE 1. PREPARATION OF 5-ALKOXY-4,4-DIALKYL-1-ARYL-3-PYRAZOLIDINONES (VIIIa)



VIIIa

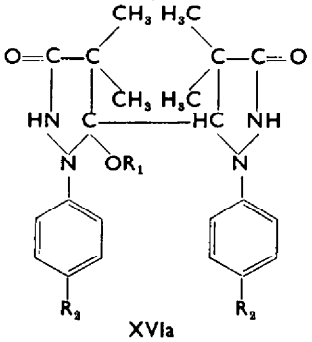
R_2	R_1	Oxidant	Reaction temp	Reaction time hrs	Yield %	Crystallized from	M.p.	Analysis Calc. %	Found %
H	$-CH_3$	HgO	reflux	8	60	methanol	163	C 65·51	65·27
								H 7·33	7·37
		HgO	room	8	32	methanol	163	O 14·54	14·57
								N 12·73	12·54
H	$-C_2H_5$	HgO	reflux	8	51	ethanol/water	166	C 66·72	66·46
								H 7·75	7·88
		HgO	room	8	61	ethanol/water	166	N 11·97	11·77
H	$-(CH_2)_3CH_3$	HgO	reflux	8	51	n-propanol	154	C 67·80	67·76
								H 8·13	8·15
		HgO	room	8	49	n-propanol	154	O 12·90	12·89
								N 11·30	11·13
H	$-HC(CH_3)_2$	HgO	reflux	8	35*	benzene/n-hexane	142	C 67·80	68·09
								H 8·13	7·99
		HgO	room	8	—			O 12·90	12·31
								N 11·30	11·22

R_2	R_1	Oxidant	Reaction temp	Reaction time hrs	Yield %	Crystallized from	M.p.	Analysis Calc. %	Analysis Found %
H	$-CH_2-C_6H_5$	HgO	90°	10	20	ethanol	162	C 73·03	72·31
								H 6·81	6·85
		HgO	room	10	32	ethanol	162	N 9·46	9·26
$-CH_3$	$-CH_3$	HgO	reflux	8	51	methanol	162	C 66·72	66·94
								H 7·75	7·75
		HgO	room	8	79	methanol	162	O 13·68	13·43–13·99
								N 11·97	12·11
		SeO_2	reflux	5	32	benzene/n-hexane	162		
$-CH_3$	$-C_2H_5$	HgO	reflux	8	68*	ethanol	154	C 67·80	67·95
								H 8·13	8·08
		HgO	room	8	56	ethanol	154	N 11·30	10·92
		SeO_2	reflux	5	44	benzene/hexane	154		
$-CH_3$	$-(CH_2)_2CH_3$	HgO	reflux	8	48	n-hexane	113	C 68·76	68·88
								H 8·46	8·22
		HgO	room	8	25	n-hexane	113	O 12·21	12·33
								N 10·69	10·64
		SeO_2	reflux	5	58	n-hexane	113		
$-CH_3$	$-HC(CH_3)_2$	HgO	reflux	8	36†	ethanol	123	C 68·76	68·60
								H 8·46	8·49
		HgO	room	8	—			N 10·69	10·67
$-CH_3$	$-CH_2-C_6H_5$	HgO	90°	10	76	ethanol	190	C 73·61	73·59
								H 7·15	7·02
		HgO	room	10	86	ethanol	190	O 10·32	10·42
								N 9·04	8·90
		SeO_2	90°	5	46	ethanol	190		

* 10% of the corresponding XVI is obtained by further concentration of the filtrate.
† 2% of the corresponding XVI is obtained by further concentration of the filtrate.

isopropoxy compounds (Tables 1 and 2). The 5-n-butoxy derivatives (VIII; R_1 = n-C_4H_9) could not be isolated in the pure state. Condensed compounds (XVI; R_1 = n-C_4H_9) were formed together with the 5-n-butoxy derivatives. Only the condensed compounds remained upon further purification (Table 2).

TABLE 2. PREPARATION OF 1-ARYL-4,4-DIALKYL-5-(1-ARYL-3-OXO-4,4-DIALKYL-5-ALKOXYL-5-PYRAZOLIDINYL-)3-PYRAZOLIDINONES (XVIa).



XVIa

R_2	R_1	Crystallized from	M.p.	Analysis Calc. %	Found %
H	$-CH_3$	n-hexane	170	C 67·70	67·01
				H 6·92	6·75
				O 11·76	11·74
				N 13·73	13·37
H	$-C_2H_5$	acetonitrile/water	175	C 68·30	68·62
				H 7·17	6·91
				O 11·37	11·34
				N 13·28	13·32
H	$-HC(CH_3)_2$	acetonitrile/water	200	C 68·86	68·55
				H 7·40	7·25
				O 11·01	11·38
				N 12·85	12·88
H	$-(CH_2)_3CH_3$	n-hexane/diethyl ether	164	C 69·39	69·10
				H 7·62	7·65
				O 12·45	12·45
H	$-CH_2-C_6H_5$	methylcyclohexane	190	C 71·96	72·34
				H 6·66	6·74
				O 9·92	9·99
				N 11·58	11·28
$-CH_3$	$-CH_3$	methylcyclohexane	180	C 68·86	69·08
				H 7·40	7·89
				O 11·01	10·91
$-CH_3$	$-C_2H_5$	ethanol	195	C 69·39	69·10
				H 7·32	7·55
				N 12·45	12·49
$-CH_3$	$-(CH_2)_2CH_3$	n-hexane	163	C 69·89	70·00
				H 7·82	7·84
				N 12·08	12·06
$-CH_3$	$-HC(CH_3)_2$	n-hexane	180	C 69·89	70·00
				H 7·82	7·81
				N 12·08	12·00

Spectrochemical study

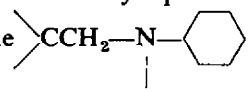
In Fig. 1 the spectra of (1) 1-tolyl-4,4-dimethyl-3-pyrazolidinone (III; R = CH_3; Ar = $-C_6H_5CH_3$), (2) the primary reaction product obtained in methanol (for which structure VIIIa with $R_1 = R_2 = CH_3$ is proposed) and (3) the byproduct (for which structure XVIa with $R_1 = R_2 = CH_3$ is suggested) have been presented.

These spectra, obtained with the solids using the KBr technique were recorded on a Perkin Elmer M21 apparatus equipped with NaCl optics.

The spectrum of III displays a very intense band at 1695 cm^{-1} which can be attributed to an "amide I" vibration. This proves that the 1-aryl-3-pyrazolidinones are present in their lactam form contrary to what is observed in the corresponding unsaturated products which at least in the solid state are present in their tautomeric enolic forms, at least in the solid state.[1,21]

As is normal for a ring structure, the "amide II" band situated near 1550 cm^{-1} in open chain amides is lacking.[22,23] In the IR spectra of the reaction products we find several indications that no ring opening has occurred during the oxidation process. First of all, the frequencies of the "amide I" bands remain practically unchanged and none of the spectra show the "amide II" band, typical for primary or secondary open chain amides. Furthermore, the absorption pattern in the 1700–1450 cm^{-1} region remains practically the same as in the spectrum of III and no supplementary bands are observed. The spectrum of VIIIa contains a very strong absorption at 1080 cm^{-1} which is not present in the spectrum of III. A similar band is observed at 1101 cm^{-1} in the spectrum of XVIa. These bands prove the introduction of an alkoxy group in both reaction products, while aliphatic ethers manifest an intense band in the 1150–1070 cm^{-1} regions due to the asymmetric C—OC stretching mode.[24] Supplementary evidence for the presence of the methoxy group is given by the appearance of a weak band at *circa* 2830 cm^{-1} in the spectra of VIIIa ($R_1 = R_2 = CH_3$) and XVIa ($R_1 = R_2 = CH_3$) which is lacking in the spectrum of the starting product (III). This band is characteristic for the symmetric CH_3 stretching vibration of a CH_3O group.[25] Briefly stated it may be concluded that the IR spectra give sufficient evidence that no ring opening has occurred and that an alkoxy group has been introduced. The study of the spectra of the different reaction products obtained in other media either with 1-phenyl-4,4-dimethyl-3-pyrazolidinone or with 1-tolyl-4,4-dimethyl-3-pyrazolidinone as starting materials generally lead to similar conclusions. An exception, however, has to be made for some products obtained in isopropanol, for which structures VIIIa ($R_1 = -CH(CH_3)_2$; $R_2 - CH_3$) and XVIa ($R_1 = CH(CH_3)_3$; $R_2 = H$) are proposed, showing two carbonyl bands in their IR spectra at *circa* 1720 cm^{-1} and 1680 cm^{-1}. The reason for this undoubling remains unclear.

The NMR spectra of (1) 1-phenyl-4,4-dimethyl-3-pyrazolidinone (III R = CH_3; Ar = C_6H_4), (2) the primary reaction product obtained in methanol (proposed structure VIIIa $R_1 = CH_3$; $R_2 = H$) and (3) the byproduct (proposed structure XVIa $R_1 = CH_3$; $R_2 - H$) are represented in Fig. 2. These spectra were recorded on a Varion A 60 apparatus using 5% solutions in $CDCl_3$.

In the spectrum of III the singlet at τ8·84 has to be ascribed to the 6 protons of the *gem*-methyl groups in the 4 position, which seem to be totally equivalent. Although in open chain structures the CH_2 protons of the  group

absorb between τ-values 6·6 and 7·0, we believe that the 2-proton singlet at τ 6·32 in the spectrum of the starting product likewise must be ascribed to the CH_2 group in the 5-position.[26] The small difference of about 0·3τ is no doubt due to the fact that in this particular case the group makes part of a rigid 5-membered ring. The 5-proton multiplet at *circa* τ2·9 has its origin the spin-spin coupled protons of the aromatic ring. The very broad signal at τ0·25—with an intensity in accordance with 1-proton—is characteristic for the proton of an amidic NH group.[27]

The spectrum of VIIIa shows a supplementary 3-proton singlet at τ6·41. As the literature[26] situates the proton absorption of a methoxy group between τ6·0 and τ6·8, the introduction of a methoxy group is clearly demonstrated. The disappearance of the 2-proton singlet (observed at τ6·32 in the spectrum of III) and the replacement by a 1-proton peak at τ5·50 indicates that the alkoxy group has been introduced in the 5-position. The reduced shielding of the proton is a logical consequence of the direct bonding of the oxygen atom on the CH group. An undoubling of the 6-proton singlet of III at 8·85τ in two 3-proton signals at τ8·85 and τ9·00 respectively points to an unequal environment of the two *gem*-CH_3 groups. This is the case in VIIIa, where one CH_3 group is always much nearer to the oxygen atom of the alkoxy group than the other.

The spectrum of XVIa contains a 3-proton peak at τ8·91, a 6-proton peak at τ8·84 and a 3-proton peak at τ8·70, indicating that here too at least some of the CH_3 groups of the 4-position are no longer equivalent.

Two rather small peaks at τ8·6 and τ9·1 are observed in the same region, the origin of which is difficult to explain. These supplementary peaks may be explained if we take into account that the very compact structure of XVIa inhibits the free rotation of the CH_3 groups around the C—C axes so that—on the average—the individual protons in the methyl groups are no longer equivalent with the result that spin-spin coupling may occur. As in the spectrum of VIIIa the 3-proton singlet at τ6·39 can be assigned to the methoxy group. Only one 3-proton signal is observed in this region, indicating that only one methoxy group is present in the molecule. For the isolated proton in a 5-position of the proposed structure XVIa, a 1-proton singlet is expected in the τ6·00–6·50 region. We find this peak already at τ5·60, too low a position for being considered as good evidence for the proposed structure. Nevertheless it should be noted that this reduced shielding might be due to the extremely crowded structure represented by formula XVIa in which the isolated proton may be influenced not only by the aromatic group but also by the oxygen of the alkoxy group. Finally the NH signal—situated in the region τ0·2–1 in III and VIIIa—has been replaced by two 1-proton peaks at τ4·3 and τ3·4 respectively.

The very broad character suggests that it is probably due to amidic NH groups, although the reason of this very large shift to higher field remains unclear and the assignment of the two peaks remains uncertain.

Briefly summarizing it may be said that the NHR spectra confirm unequivocally the correctness of structure VIIIa ($R_1 = CH_3$, R_2 H). Although the NHR study is not in flagrant contradiction with the proposed structure XVIa ($R_1 = CH_3$, $R_2 =$ H) we find little conclusive evidence in favour of this structure.

The study of the NMR spectra of the reaction products obtained in other media or with 1-tolyl-4,4-dimethyl-3-pyrazolidinone as starting product leads to similar conclusions.

EXPERIMENTAL*

The 4,4-dimethyl-1-phenyl- (mp. 170°),[19] 4,4-dimethyl-1-tolyl- (m.p. 149–150°)[19] and 5,5-dimethyl-1-phenyl-(m.p. 166–168°)[20] 3-pyrazolidinones were prepared as indicated in the literature.

General method for the oxidative alkoxylations

(a) *With mercuric oxide.* 21·6 g (0·1 mole) HgO was added to a solution of 0·1 mole 4,4-dimethyl-1-aryl-3-pyrazolidinone in 200 ml alcohol. After stirring for 8 hr at room temp or at reflux temp, filtering off the Hg precipitate and vacuum concentration of the filtrate to a small volume, the precipitate was filtered off and recrystallized from a suitable solvent (Table 1).

(b) *With selenium dioxide.* 5·5 g (0·05 mole) SeO_2 was added to a solution of 0·1 mole 4,4-dimethyl-1-aryl-3-pyrazolidinone in 200 ml of alcohol. This mixture was refluxed 5 hr with stirring. The Se precipitate was filtered off and the filtrate poured into ice water with rapid stirring. The precipitate was filtered off and recrystallized from a suitable solvent (Table 1).

(c) *Oxidation of 5,5-dimethyl-1-phenyl-3-pyrazolidinone.* 10·8 g (0·05 mole) HgO was added to a solution of 9·5 g (0·05 mole) 5,5-dimethyl-1-phenyl-3-pyrazolidinone in 100 ml methanol. After stirring and refluxing for 5 hr, the Hg precipitate was filtered off, and the violet colored solution poured into ice water with rapid stirring. The precipitate was filtered off and purified by dissolving in tetrachloromethane from which it was precipitated with isopropyl ether, yield: 7 g (74%) of a product with an unsharp m.p. near 180°.

(d) *Oxidation of 4,4-dimethyl-1-phenyl-3-pyrazolidinone in butanol.* 21·6 g (0·1 mole) HgO was added to a solution of 19 g (0·1 mole) 4,4-dimethyl-1-aryl-3-pyrazolidone in 200 ml buranol. After stirring and refluxing for 8 hr, the Hg precipitate was filtered off, the filtrate evaporated to dryness and the residue was crystallized from anhydrous diethyl ether, yield: 5·5 g of a product having an unsharp m.p. near 190°. Recrystallization from methanol yielded 4 g 1-phenyl-4,4-dimethyl-5-methoxy-3-pyrazolidinone, m.p. 163°.

	Calc.	Found	
%N	12·73	12·95,	12·92
C	65·51	65·26	
H	7·33	7·32	

General method for the preparation of 1-aryl-4,4-dialkyl-5-(1-aryl-3-oxo-4,4-dialkyl-5-alkoxy-5-pyrazolidinyl)-3-pyrazolidinones XVI

Compound XIII was boiled 16 hr in a high boiling solvent (generally methylcyclohexane), the solution concentrated, and XVI filtered off and recrystallized from a suitable solvent (Table 2). Table 1 mentions the reactions in which XVI was obtained as a by-product.

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* The m.ps were taken in a Kofler hot bench.

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