Reaction of 4-Arylmethylene-3-phenylisoxazolones and 4-Arylmethylene-1,3-diphenylpyrazolones with Enamines and Nucleophilic Heterocycles

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4-Arylmethylene-3-phenylisoxazolones (1) and 4-arylmethylene-1,3-diphenylpyrazolones (2) were treated with enamines (8), 3-phenylisoxazol-5(4*H*)-one (4), 1,3-diphenylpyrazol-5(4*H*)-one (6), and 2-phenyloxazol-5(4*H*)-one (3). The enamines were β-alkylated to give 1 : 1 adducts (9) and (10). The reaction of (1) with (6) and (2) with (4) gave symmetrical benzylidenedi-isoxazolones and -pyrazolones (7). 2-Phenyloxazol-5(4*H*)-one with (1) gave 4-benzylidene-2-phenyloxazolone (5) by transfer of the benzylidene group and with (2), a 1 : 1 adduct (19) isolated as the corresponding ethyl hippurate derivative (20).

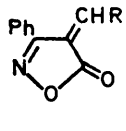
THE activated exocyclic double bond of the arylmethylene compounds (1) and (2) undergoes addition reactions with certain nucleophiles.[1] The reaction of enamines with 2-phenyloxazol-5(4*H*)-one (3),[2] 3-phenylisoxazol-5(4*H*)-one (4),[3] and 4-benzylidene-2-phenyloxazolone (5)[4] has been described. It is known[1] that the 4-arylmethylene compounds (1; R = Ph) and (2; R = Ph) add to the 4-unsubstituted heterocycles (4) and (6) respectively to give bridged compounds (7; X = O or NPh).

When treated with enamines in chloroform at room temperature both arylmethylene compounds (1) and (2) readily formed stable 1 : 1 adducts which have been formulated as (9) and (10) respectively.

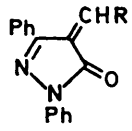
The i.r. spectra of compounds (9) and (10) (Table) appear to have the absorption due to the OH group obscured by the C–H stretching absorption at *ca.* 2800—3050 cm^{-1} except in a few cases [*i.e.* (9c, f, and g)]. The isoxazolone and pyrazolone portions of (9) and (10) could not be in the form of their carbonyl tautomers as the absorption in the 1600—1800 region is much too low.[5,6] The OH form would be favoured by hydrogen bonding to the nitrogen atom of the enamine. The

[1] P. Pastour, *Compt. rend.*, 1957, **244**, 2243; E. Ehsan, S. Ali, N. Ahmed, and Karimullah, *Pakistan J. Sci. Ind. Res.*, 1967, **10**, 228.
[2] A. M. Knowles, A. Lawson, G. V. Boyd, and R. A. Newberry, *J. Chem. Soc.* (*C*), 1971, 598.
[3] A. M. Knowles and A. Lawson, *J.C.S. Perkin I*, 1972, 1240.
[4] K. K. Prasad, D. S. Iyengar, and R. V. Venkataratnam, *Tetrahedron Letters*, 1972, 2865.
[5] A. J. Boulton and A. R. Katritzky, *Tetrahedron*, 1961, **12**, 41.
[6] F. W. Maine and A. R. Katritzky, *Tetrahedron*, 1964, **20**, 299.

pyrazolone adducts (10) show no absorption in the region 1620—1680 cm^{-1} normally associated with enamines;[7]



(1)



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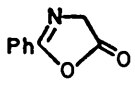

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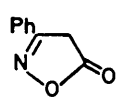

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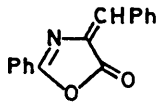

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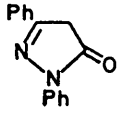

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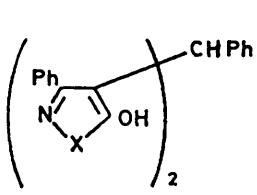

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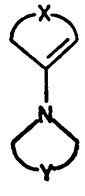
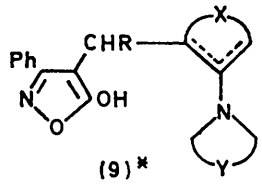


(8)

this is possibly due to a strong hydrogen bond on the nitrogen atom inhibiting conjugation.

Hydrolysis of adducts (9a) and (9b) with aqueous sodium hydroxide in both cases rapidly produced the ketone (11) and the corresponding free base, pyrrolidine or perhydroazepine respectively. The isoxazolone carbonyl absorption now appeared in (11) at 1780 cm^{-1}, together with a ketonic peak at 1690 cm^{-1}. In the i.r. spectrum of the sodium salt of (11) the ketonic peak remained but the isoxazolone absorption was at 1620 cm^{-1}.[8] Mild neutral hydrolysis of adducts (10) likewise proceeded readily, but gave the corresponding cycloalkanones and the benzylamine derivatives (12), which

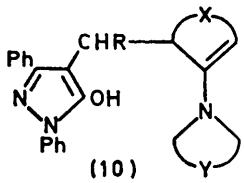
(10) may possibly be due to the weakness of the carbon–carbon bond giving rise to an equilibrium mixture con-



(9)*

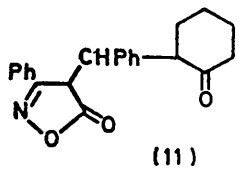
	R	X	Y
a;	Ph	$[CH_2]_3$	$[CH_2]_2$
b;	Ph	$[CH_2]_3$	$[CH_2]_4$
c;	*p*-$MeOC_6H_4$	$[CH_2]_3$	$[CH_2]_2$
d;	PhCH:CH	$[CH_2]_3$	$[CH_2]_2$
e;	*p*-$NO_2C_6H_4$	$[CH_2]_3$	$[CH_2]_2$
f;	*p*-MeC_6H_4	$[CH_2]_3$	$[CH_2]_2$
g;	Ph	$CH_2CHMeCH_2$	$[CH_2]_2$

* The dotted line in (9) indicates that the position of the double bond is not known.



(10)

	R	X	Y
a;	Ph	$[CH_2]_3$	$[CH_2]_2$
b;	Ph	$[CH_2]_3$	$[CH_2]_3$
c;	Ph	$[CH_2]_3$	$[CH_2]_4$
d;	Ph	$[CH_2]_3$	CH_2OCH_2
e;	*p*-$MeOC_6H_4$	$[CH_2]_3$	$[CH_2]_2$
f;	Furyl	$[CH_2]_3$	$[CH_2]_2$



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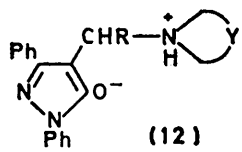


(12)

taining small amounts of the starting materials (2) and (8). The enamine (8) would hydrolyse to the correspond-

Enamine–arylmethylene compound adducts

Product	Yield (%)	M.p. (°C) *	Found (%) C	H	N	Required (%) C	H	N	$\nu_{max.}$ (cm^{-1}) [b]
(9a)	94	163—165	77·8	7·1	6·9	78·0	7·0	7·0	1640, 1660m
(9b)	92	108—109	78·6	7·55	6·4	78·5	7·55	6·55	1605—1640br
(9c)	80	130—132	75·2	7·3	6·6	75·3	7·0	6·5	1625, 1660m, 3300
(9d)	85	202—203	78·7	7·2	6·75	78·85	7·1	6·55	1630, 1650
(9e)	87	183—185	69·9	5·95	8·5	70·1	6·1	8·35	1600m
(9f)	39	115—117	78·0	7·0	6·5	78·5	7·3	6·75	1620, 1640sh, 3200
(9g)	24	131—133	78·1	7·0	6·5	78·25	7·3	6·75	1620, 1645sh, 3350
(10a)	98	158—159	80·9	6·8	9·0	80·8	7·0	8·85	1600, 1570m
(10b)	95	166—168	81·1	7·0	8·45	81·0	7·2	8·6	1600, 1570m
(10c)	94	129—130	81·2	7·3	8·3	81·1	7·4	8·35	1600, 1570m
(10d)	66	185—188	78·0	6·5	8·8	78·2	6·75	8·55	1600, 1570m
(10e)	54	132—133	78·3	7·1	8·4	78·4	7·0	8·3	1600, 1575m
(10f)	57	132—135	77·5	6·5	8·9	77·4	6·7	9·05	1605, 1575m

* All decomposition points. [b] All peaks are strong unless otherwise stated.

have also been prepared by the addition of the corresponding secondary amines to arylmethylenepyrazolones (2).[9]

This unexpected mode of hydrolysis of the adducts

ing ketone and amine, the latter then reacting with the arylmethylenepyrazolone (2) to form the compounds (12). This mechanism requires the assumption that the rate of hydrolysis of the free enamine is much greater than that of the enamine system in the adducts (10),

[7] S. K. Malhotra and J. V. Paukstelis, in 'Enamines,' ed. A. G. Cook, Marcel Dekker, New York, 1969, pp. 39 and 178.

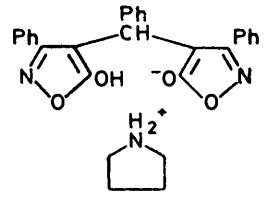
[8] R. Jacquier, C. Petrus, F. Petrus, and J. Verdacci, *Bull. Soc. chim. France*, 1970, 2690.

[9] A. Mustafa, W. Asker, A. F. A. Shalaby, S. A. Khattab, and Z. E. Selim, *J. Amer. Chem. Soc.*, 1959, **81**, 6007.

which is reasonable if the conjugated enamine character has been influenced in the adducts by hydrogen bonding. Acid hydrolysis of adducts (9) and (10) yielded a mixture containing benzaldehyde. This finding also suggests a weak carbon–carbon linkage.

Periodicity of behaviour of 4-benzylidene-3-phenylisoxazolone (1; R = Ph) towards enamines of different ring size was indicated by the production of adducts (9a) and (9b) in high yield from 1-(pyrrolidin-1-yl)-1-hexamethyleneamino-cyclohexene, whereas no products at all were obtained from 1-piperidino- or 1-morpholino-cyclohexene or 1-(pyrrolidin-1-yl)cyclopentene. This steric effect has been noted by Stork *et al.*[10] who found that pyrrolidin-1-yl enamines were considerably easier to alkylate than the piperidino-analogues, despite their having similar base strengths. That the reaction takes place for a 6-membered cycloalkene ring but not for a 5-membered one can also be explained on steric grounds.[10] The low base strength of the morpholine enamine may also be a contributing factor in its failure to react with (1; R = Ph). On the other hand 4-benzylidene-1,3-diphenylpyrazolone (2; R = Ph), while insensitive to variation in the amine portion of the enamine, still failed to react with 1-(pyrrolidin-1-yl)cyclopentene. Another difference in reactivity was noted in the action of 1-(pyrrolidin-1-yl)cyclohexene on the furylmethylene derivatives where the pyrazolone compound (2; R = furyl) reacted but the isoxazolone (1; R = furyl) did not.

Reaction of adduct (9a) with 3-phenylisoxazol-5(4*H*)-one (4) yielded the bis-isoxazolone salt (13). This contrasts with the reaction of adduct (10a) with 1,3-diphenylpyrazol-5(4*H*)-one (6) which produced the benzylamine derivative (12; R = Ph, Y = $[CH_2]_2$) and 4-cyclohexylidene-1,3-diphenylpyrazolone (14). Both of these reactions require fission of the carbon–carbon bond present in the original adduct.



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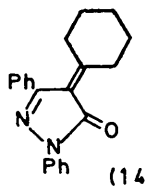
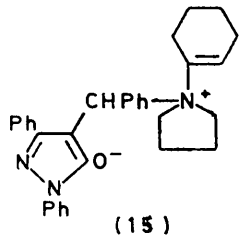


(14)

That the pyrazolone adducts (10) had a more labile carbon–carbon bond could be demonstrated by pyrolysis under high vacuum. The adduct (10a) gave only the enamine (8; X = $[CH_2]_3$, Y = $[CH_2]_2$) as a distillate, whereas the adduct (9a) distilled unchanged.

The properties of adducts (10) prompt speculation as to whether *N*-alkylation of the enamines to yield compounds (15) or (16) had taken place. These structures, however, are not in keeping with the following features. (i) The n.m.r. spectra of adduct (10a) and its hydrogenated derivative (17) both showed doublets at τ *ca.* 5·8, corresponding to the methine group, and a broad band at *ca.* 7·0 corresponding to the α-CH_2 of the pyrrolidine group. The latter would be expected at τ *ca.* 6·0 if the nitrogen atom had carried a positive charge.[11,12] (ii) All known Michael additions to enamines involve *C*-alkylation due to the reversibility of *N*-alkylation reactions.[13] The vinylic hydrogen in (10a) did not appear in the region τ 3·1—7·0, as was to be expected of normal enamines;[14] it was therefore assumed to be obscured by the aromatic absorption at τ 2·0—3·1. This would again suggest that a conjugated enamine function is not present.



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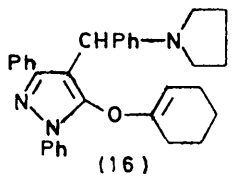

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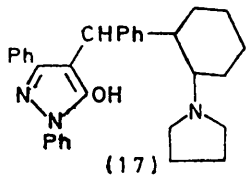

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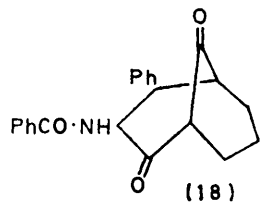


(18)

The formation of adducts (9) and (10) is related to the reaction of 1-(pyrrolidin-1-yl)cyclohexene with 4-benzylidene-2-phenyloxazolone (5) when a bicyclononanedione (18) was obtained.[4] Mechanisms proposed for the formation of (18) involve Michael-type adduct formation analogous to that for (9) and (10) and *C*-acylation of the enamine by the oxazolone so produced. This latter β-acylation of enamines by oxazolone has no precedent.

4-Benzylidene-2-phenylisoxazolone (1; R = Ph) reacted with 2-phenyloxazol-5(4*H*)-one (3) in pyridine to give 4-benzylidene-2-phenyloxazolone (5) as the major product. The expected 3-phenylisoxazol-5(4*H*)-one (4) was detected by t.l.c. but not isolable since the residue after removal of (5) was a mixture containing also the bridged compound (8; X = O).[1] A basic solvent was necessary since no reaction occurred in either toluene or dioxan. This reaction, which involves a transfer of the benzylidene group from one heterocycle to the other no doubt results from the breakdown of a bridged intermediate analogous to that postulated for the pyrazolone derivative (19) below.

When 4-benzylidene-1,3-diphenylpyrazolone (2; R = Ph) was treated with 2-phenyloxazol-5(4*H*)-one (3) in pyridine, a crystalline product could only be isolated after addition of ethanol. We assume that an adduct (19) was first formed but only crystallised when converted

[10] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkoviz, and R. Terrel, *J. Amer. Chem. Soc.*, 1963, **85**, 207.

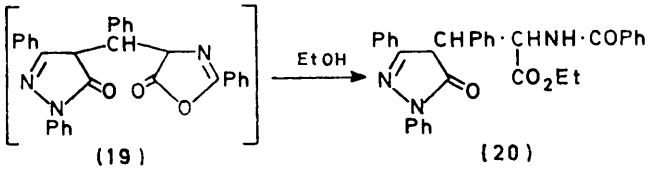
[11] J. A. Elvidge, in ' Nuclear Magnetic Resonance for Organic Chemists,' ed. D. W. Mathieson, Academic Press, London, 1967, p. 179.

[12] Ref. 7, pp. 46 and 179.

[13] M. E. Kuehne, in ref. 7, p. 359.

[14] S. K. Malhotra, in ref. 7, p. 42.

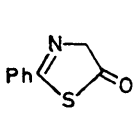
into the substituted ethyl hippurate (20) by opening of the oxazolone ring with ethanol. As expected, the same product (20) was obtained from the reaction between 4-benzylidene-2-phenyloxazolone (5) and 1,3-diphenylpyrazol-5(4*H*)-one (6).



(19) (20)

Transfer of a benzylidene group was also involved when 4-benzylidene-2-phenylisoxazolone (1; R = Ph) was treated with 1,3-diphenylpyrazol-5(4*H*)-one (6) or when 4-benzylidene-1,3-diphenylpyrazolone (2; R = Ph) was treated with 3-phenylisoxazol-5(4*H*)-one (4) in pyridine, since the same mixture of bridged compounds (7; X = O) and (7; X = NPh) was obtained in both cases. The bis-pyrazolone (7; X = NPh) was isolated and the bis-isoxazolone (7; X = O) identified by its i.r. spectrum.

When 2-phenylthiazol-5(4*H*)-one (22) was treated with 4-benzylidene-1,3-diphenylpyrazolone (2; R = Ph) in pyridine, 4-benzylidene-2-phenylthiazolone (23) and the bis-pyrazolone (7; X = NPh) were formed, the yields of both products being high when a 2 : 1 (stoicheiometric) ratio of benzylidenepyrazolone to thiazolone was used. 4-Benzylidene-3-phenylisoxazolone (1; R = Ph) also reacted with 2-phenylthiazol-5(4*H*)-one (22) to give the thiazolone (23) but the corresponding bis-isoxazolone (7; X = O), though not isolable, was detected in the i.r. spectrum of the residual oil.



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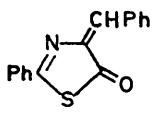

(23)

There was no reaction between 4-benzylidene-2-phenyloxazolone (5) and either 3-phenylisoxazol-5(4*H*)-one (4) or 2-phenyloxazol-5(4*H*)-one (3).

EXPERIMENTAL

I.r. spectra were determined for KBr discs; n.m.r. spectra were measured at 100 MHz.

Preparation of Adducts (9) *and* (10).—*General procedure.* The arylmethylene-isoxazolone (1) [15] or -pyrazolone (2) [16] was suspended or dissolved in chloroform and an equimolar amount of freshly distilled enamine (3) [10] added. The mixture became warm and the characteristic colour of the unsaturated isoxazolone (1) (yellow) or pyrazolone (2) (red) quickly disappeared. The resultant solution was left at room temperature for *ca.* 15 min, evaporated to dryness, and absolute ethanol added to obtain the *product* (see the Table), which was recrystallised from dimethylformamide–ethanol as white or off-white microcrystals. The crude material was pure enough for most purposes.

Hydrolysis of 5-Hydroxy-3-phenyl-4-α-[2-(pyrrolidin-1-yl)-cyclohex-1(or 2)-enyl]benzylisoxazole (9a).—Compound (9a) (5·0 g) was stirred at room temperature with 3N-sodium hydroxide (30 ml). After 20 min the suspension, which smelt of pyrrolidine, was made acid with 3N-hydrochloric acid and extracted with chloroform. The extract was evaporated to dryness and the crude solid, crystallised from ethanol–water, gave *4-α-(2-oxocyclohexyl)benzyl-3-phenylisoxazol-5(4H)-one* (11) (1·8 g, 42%), m.p. 165—167° (from benzene), $\nu_{max.}$ 1780 and 1690 cm^{-1} (Found: C, 76·3; H, 6·0; N, 4·05. $C_{22}H_{21}NO_3$ requires C, 76·05; H, 6·1; N, 4·05%); *m/e* 347.

Hydrolysis of 5-Hydroxy-1,3-diphenyl-4-α-[2-(pyrrolidin-1-yl)cyclohex-2-enyl]benzylpyrazole (10a).—Compound (10a) [τ ($CDCl_3$) 2·0—3·0(m), 4·75 (1H, d) 7·05 (4H, m), and 7·8—8·4 (12H, m)] (1·0 g) was dissolved in dioxan (20 ml) on a steam-bath and a few drops of water were added. After *ca.* 1 min 5-hydroxy-1,3-diphenyl-4-α-(pyrrolidin-1-yl)benzylpyrazole (12; Y = $[CH_2]_2$), (0·8 g, 97%), m.p. 242—246° (decomp.) (from Me_2NCHO–EtOH), $\nu_{max.}$ 2500—2800br, 1605, and 1575 cm^{-1}, separated out (Found: C, 79·2; H, 6·3; N, 10·5. Calc. for $C_{26}H_{25}N_3O$: C, 78·95; H, 6·35; N, 10·6%). This material was identical with a specimen prepared from pyrrolidine and 4-benzylidene-1,3-diphenylpyrazol-5(4*H*)-one.[9]

Reaction of Compound (9a) *with 3-Phenylisoxazol-5(4H)-one* (4).—Compound (9a) (4·0 g) and the isoxazolone (4) (1·6 g) were dissolved in pyridine (20 ml) and left for 4 h. The solution was evaporated and ethanol added to the residue to give pyrrolidinium 4-[α-(5-hydroxy-3-phenylisoxazol-4-yl)benzyl]-3-phenylisoxazol-5-olate (13) (1·1 g, 23%), m.p. 198—200° (decomp.) (from Me_2N·CHO–EtOH) (Found: C, 72·2; H, 5·5; N, 8·6. Calc. for $C_{29}H_{28}N_3O_4$: C, 72·3; H, 5·65; N, 8·7%). When this compound was dissolved in 3N-sodium hydroxide and the solution was made acid with 3N-hydrochloric acid, 3,3′-diphenyl-4,4′-benzylidenedi-(isoxazol-5-ol) (7; X = O) identical with an authentic sample,[17] was precipitated.

Reaction of Compound (10a) *with 1,3-Diphenylpyrazol-5(4H)-one* (6).—Compound (10a) (3·6 g) and the pyrazolone (6) (1·8 g) were dissolved in pyridine (15 ml). After 4 h., the solution was evaporated and ethanol added to give compound (12) (2·9 g, 97%). Pyrrolidine (0·5 ml) was added to the mother liquor which after evaporation and addition of ethyl acetate slowly gave *pyrrolidinium 4-(cyclohex-1-enyl)-1,3-diphenylpyrazol-5-olate* (0·2 g, 9%), m.p. 154° (from EtOAc), $\nu_{max.}$ 1540, 1600, and 2300—3000br (Found: C, 77·3; H, 7·5; N, 10·85. $C_{25}H_{30}N_3O$ requires C, 77·5; H, 7·55; N, 10·85%). The same product could also be prepared by the action of 1,3-diphenylpyrazol-5(4*H*)-one (6) on 1-(pyrrolidin-1-yl)cyclohexene (3; X = $[CH_2]_3$, Y = $[CH_2]_2$), as in the reaction with 3-phenylisoxazol-5(4*H*)-one (4).[3]

5-Hydroxy-1,3-diphenyl-4-{α-[2-(pyrrolidin-1-yl)cyclohexyl]benzyl}pyrazole (17).—Compound (10a) (20 g) was dissolved in glacial acetic acid (120 ml) and hydrogenated at atmospheric pressure using Adam's catalyst (0·5 g) for 30 min, when hydrogen uptake had ceased (*ca.* 1020 ml H_2). The solution was filtered, evaporated, and the residue dissolved in ethanol to give the *product* (17) (15·4 g, 77%), m.p. 213—215° (from dioxan), $\nu_{max.}$ 1603 cm^{-1}, τ ($CDCl_3$) 1·9—2·9 (16H, m), 5·85 (1H, d, C*H*Ph), 7·1—7·4 (6H, m), and 8·0—8·8 (12H, m) (Found: C, 80·4; H, 7·2; N, 9·0. $C_{32}H_{35}N_3O$ requires C, 80·45; H, 7·4; N, 8·8%).

Reaction of 4-Arylmethylene Compounds with Nucleophilic Heterocycles.—General procedure. The starting materials were dissolved in anhydrous pyridine. After *ca.* 4 h, the

[15] A. Wahl and A. Meyer, *Bull. Soc. chim. France*, 1908, **3**, 955.
[16] L. Knorr and C. Klotz, *Ber.*, 1887, **20**, 2545.
[17] A. M. Knowles and A. Lawson, *J.C.S. Perkin I*, 1973, 537.

solution was evaporated, and the residue dissolved in hot ethanol and left to cool.

(*a*) 4-Benzylidene-3-phenylisoxazol-5(4*H*)-one (1; R = Ph) (5·0 g) and 2-phenyloxazol-5(4*H*)-one (3) (3·2 g) gave 4-benzylidene-2-phenyloxazol-5(4*H*)-one (5) (3·5 g, 70%), m.p. 167° (lit.,[18] 167—168°), i.r. spectrum identical with that of an authentic sample,[18] and 3-phenylisoxazol-5(4*H*)-one (4) detected in the mother liquors by t.l.c.

(*b*) 4-Benzylidene-1,3-diphenylpyrazol-5(4*H*)-one (2; R = Ph) (3·2 g) and the oxazolone (3) (1·6 g) gave 4-(2-*benzamido*-2-*ethoxycarbonyl*-1-*phenylethyl*)-5-*hydroxy*-1,3-*diphenylpyrazole* (20) (3·2 g, 60%), m.p. 237—240° (decomp.) (from butan-2-one), $\nu_{max.}$ 1605m, 1630, 1730, and 3050br cm^{-1}, τ [$(CD_3)_2SO$] 2·1—2·8 (m, aromatic, OH, NH), 4·8 (dd, C*H*NH), 5·3 (d, C*H*Ph), 6·1 (q, CH_2), and 9·15 (t, CH_3) (Found: C, 74·6; H, 5·6; N, 7·7. $C_{33}H_{29}N_3O_4$ requires C, 74·55; H, 5·5; N, 7·9%).

(*c*) The benzylideneoxazolone (5) (2·5 g) and 1,3-diphenylpyrazol-5(4*H*)-one (6) (2·4 g) also gave (20) (3·3 g, 62%).

(*d*) The benzylidenepyrazolone (2; R = Ph) (1·6 g) and the isoxazolone (4) (0·8 g) gave 1,1′,3,3′-tetraphenyl-4,4′-benzylidenedi(pyrazol-5-ol) (7; X = NPh) (0·3 g, 50%), m.p. 218—219° (lit.,[16] 220°) (from EtOAc) (Found: C, 79·3; H, 5·05; N, 10·0. Calc. for $C_{31}H_{23}N_3O_3$: C, 79·3; H, 5·05; N, 10·1%) and a mother liquor showing two components on a t.l.c. plate and the presence of (7; X = NPh) and pyridinium 4-[α-(5-hydroxy-3-phenylisoxazol-4-yl)benzyl]-3-phenylisoxazol-5-olate [17] (by i.r. spectrum after evaporation).

(*e*) The benzylideneisoxazolone (1; R = Ph) (1·4 g) and the pyrazolone (6) (1·3 g) also gave (7; X = NPh) (0·3 g, 16%).

(*f*) The benzylidenepyrazolone (2; R = Ph) (3·05 g) and 2-phenylthiazol-5(4*H*)-one (22) [19] (0·85 g) gave (7; X = NPh) (1·9 g, 76%) as an ethanol-insoluble residue and 4-benzylidene-2-phenylthiazol-5(4*H*)-one (23) (1·2 g, 94%), m.p. 129—131° (from EtOH) (lit.,[19] 130—132°) (Found: C, 72·5; H, 4·25; N, 5·3; S, 11·8. Calc. for $C_{16}H_{11}NOS$: C, 72·4; H, 4·2; N, 5·3; S, 12·1%) from the filtrate on standing.

(*g*) The benzylideneisoxazolone (1; R = Ph) (0·8 g) and the thiazolone (22) (0·6 g) gave (23) (0·6 g, 65%).

[3/2130 *Received*, 18*th October*, 1973]

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