CHEMISTRY OF 2-METHYLENE-2,3-DIHYDRO-3-PYRANONES. 7.* REACTION OF 5-ARYL-2-ACYLMETHYLENE-2,3-DIHYDRO-3-FURANONES WITH HYDRAZINE HYDRATE

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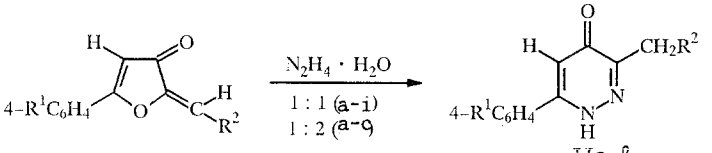
5-Aryl-2-acylmethylene-2,3-dihydro-3-furanones are recyclized by the action of hydrazine hydrate with the formation of 3-substituted 6-aryl-1H-4-pyridazinones, 3-alkoxycarbonylacetyl-5-aryl-4-methylpyrazoles, or 5-aryl-3-(3-oxo-2,3-dihydro-1H-5-pyrazolyl)pyrazoles, depending on the structure of the starting materials and the ratio of the reactants. The last-named are also obtained by the hydrazinolysis of the known 2-alkoxycarbonylmethyl-2-hydroxy-1,5-diaryl-2,3-dihydro-3-pyrrolones.

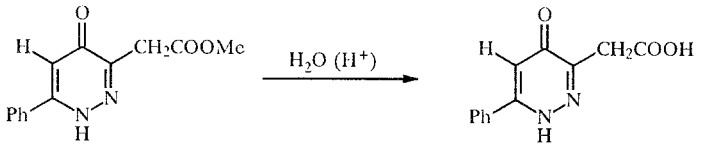
It has been established previously that substituted 2-arylidene-2,3-dihydro-3-furanones are recyclized by hydrazine hydrate with the formation of 3 arylacetylpyrazoles [2-4]. In addition, our results have shown that compounds with structures close to that of 5-aryl-2-acylmethene-2,3-dihydro-3-furanones react with hydrazine hydrate to form different compounds — 6-aryl-1H-4-pyridazinones [5, 6].

In a continuation of our studies of the recyclization reactions of 5-aryl-2-acylmethylene-2,3-dihydro-3-furanones under the action of nucleophilic reagents (arylamines [7-9] and o-phenylenediamine [5, 10, 11]), we have studied the reaction of 2-alkoxycarbonyl- and 2-cyanomethylene-5-aryl-2,3-dihydro-3-furanones (Ia-i) with hydrazine hydrate. We have established that the reaction of equimolar quantities of the reactants in ethanol at room temperature leads to the formation of 3-substituted 6-aryl-1H-4-pyridazinones (IIa-i) in yields of 67-79% (Table 1).

Heating the methyl furanones Ia-c with a twofold excess of hydrazine hydrate for 3-4 h in ethanol gives 6-aryl-3-hyrazinocarbonylmethyl-1H-4-pyridazinones (IIj-*l*) in 52-65% yield (Table 1). These same compounds were obtained in yields of 81-89% by the hydrazinolysis of the corresponding pyridazines IIa-c under similar conditions. The pyridazinone IIa was hydrolyzed on boiling 2 h in dioxane with the addition of 10% hydrochloric acid to give 3-carboxymethyl-6-phenyl-1H-4-pyridazinone (IIm) and heating this briefly in ethanol (during crystallization) led again to the formation of the ester IIf.



Ia-i IIa-l



IIa II m

I, IIa,f, i, IIj, R^1 = H; I, II b,g, II k R^1 = Me; I, IIc, II l R^1 = MeO; I, IId R^1 = Br; I, IIe,h R^1 = Cl; I, II[a]—e R^2 = COOMe, f—h R^2 = COOEt, i R^2 = CN; II j—l R^2 = $CONHNH_2$

The IR spectra of crystals of compounds IIa-m have intense broad bands for the stretching vibrations of carbonyl $C_{(4)}$=O, C=C, and C=N of the pyridazinone at 1575-1655 cm^{-1}, and vibrations of the $N_{(1)}H$ group of the ring at 3215-3315 cm^{-1}

*For Communication 6, see [1].

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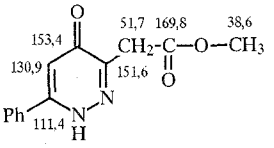
TABLE 1. Physicochemical and Spectroscopic Characteristics of Compounds IIa-m and III

Compound	Empirical formula	mp °C (decomp.)	IR spectrum, ν, cm^{-1}, crystals	PMR spectrum, δ, ppm, DMSO-D_6	Yield, %
IIa	$C_{13}H_{12}N_2O_3$	217...218	3280...3300 (NH), 3090...3130 (C-H), 1741 ($COOCH_3$), 1585...1512 ($C_{(4)}$=O, C=N, C=C)	3,62 (3H, s, CH_3O); 3,67 (2H, s, CH_2); 6,62 (1H, s, CH); 7,53...7,80 (5H, m, C_6H_5); 13,40 (1H, br, NH)	75
IIb	$C_{14}H_{14}N_2O_3$	229...230	3280...3305 (NH), 3090...3135 (C-H), 1747 ($COOCH_3$), 1590...1615 ($C_{(4)}$=O, C=N, C=C)	2,37 (3H, s CH_3); 3,63 (5H, s CH_3O, CH_2); 6,60 (1H, C, CH); 7,36, 7,70 (4H, d.d C_6H_4); 13,20 (1H, br, NH)	72
IIc	$C_{14}H_{14}N_2O_4$	222...223	3260...3280 (NH), 3085...3120 (C-H), 1742 ($COOCH_3$), 1575...1605 ($C_{(4)}$=O, C=N, C=C)	3,63 (5H,s, CH_3O, CH_2); 3,82 (3H, s, CH_3O); 6,58 (1H,s, CH); 7,07, 7,83 (4H,d , C_6H_4); 13,35 (1H, br, NH)	70
IId	$C_{13}H_{11}BrN_2O_3$	251...252	3260...3290 (NH), 3090...3120 (C-H), 1752 ($COOCH_3$), 1580...1605 ($C_{(4)}$=O, C=N, C=C)	3,65 (5H, s, CH_3O, CH_2); 6,68 (1H, s CH); 7,80 (4H, s, C_6H_4); 13,50 (1H,br., NH)	67
IIe	$C_{13}H_{11}ClN_2O_3$	247...248	3280...3310 (NH), 3080...3110 (C-H), 1738 ($COOCH_3$), 1575...1605 ($C_{(4)}$=O, C=N, C=C)	3,62 (3H,s , CH_3O); 3,65 (2H,s , CH_2); 6,66 (1H,s , CH); 7,60 (4H, d.d C_6H_4); 13,48 (1H, br, NH)	71
IIf	$C_{14}H_{14}N_2O_3$	200...201	3215...3245 (NH), 3070...3125 (C-H), 1742 ($COOC_2H_5$), 1580...1600 ($C_{(4)}$=O, C=N, C=C)	1,17 (3H, t, CH_3); 3,62 (2H,s CH_2); 4,09 (2H, q , CH_2O); 6,60 (1H, s CH); 7,55...7,85 (5H, m, C_6H_5); 13,40 (1H,br., NH)	75
IIg	$C_{15}H_{16}N_2O_3$	204...205	3265...3280 (NH), 3090...3135 (C-H), 1749 ($COOC_2H_5$), 1585...1610 ($C_{(4)}$=O, C=N, C=C)	1,18 (3H, t, CH_3); 2,35 (3H, s, CH_3); 3,61 (2H, s CH_2); 4,09 (2H, q , CH_2O); 6,62 (1H, s, CH); 7,32, 7,78 (4H, d.d C_6H_4); 13,40 (1H, br, NH)	74
IIh	$C_{14}H_{13}ClN_2O_3$	231...232	3280...3315 (NH), 3095...3135 (C-H), 1753 ($COOC_2H_5$), 1580...1610 ($C_{(4)}$=O, C=N, C=C)	1,19 (3H, t, CH_3); 3,65 (2Hs , CH_2); 4,12 (2H, q , CH_2O); 6,68 (1H, s, CH); 7,62, 7,90 (4H, d.d, C_6H_4); 13,45 (1H,br , NH)	68
IIi	$C_{12}H_9N_3O$	273...274	3220...3240 (NH), 3085...3110 (C-H), 2270 (C≡N), 1595...1625 ($C_{(4)}$=O, C=N, C=C)	4,06 (2H, s CH_2); 6,72 (1H,s , CH); 7,60...7,85 (5H, m C_6H_5); 13,70 (1H, br, NH)	79
IIj	$C_{12}H_{12}N_4O_2$	319...320	3320...3335 (NHCO), 3230...3250 (NH), 3090...3130 (C-H), 1625...1640 (CONH, $C_{(4)}$=O)	3,47 (2H, s, CH_2); 6,60 (1H,s , CH); 7,45...7,80 (5H,m , C_6H_5); 9,15 (1H, br, NH); 13,10 (1H, br, NH)	60*
IIk	$C_{13}H_{14}N_4O_2$	323...324	3302...3310 (NHCO), 3210...3230 (NH), 3080...3120 (C-H), 1640...1655 (CONH, $C_{(4)}$=O)	2,36 (3H,s , CH_3); 3,42 (2H, s , CH_2); 6,58 (1H,s , CH); 7,36, 7,72 (4H, d.d, C_6H_4); 9,20 (1H,br , NH); 13,00 (1H,br , NH)	65*
IIℓ	$C_{13}H_{14}N_4O_3$	309...310	3310...3338 (NHCO), 3260...3285 (NH), 3110...3130 (C-H), 1640...1650 (CONH, $C_{(4)}$=O)	3,48 (2H, s, CH_2); 3,82 (3H, s, CH_3O); 6,57 (1H, c, CH); 7,06, 7,84 (4H,d.d., C_6H_4); 9,25 (1H, br, NH); 12,95 (1H,br , NH)	52*
IIm	$C_{12}H_{10}N_2O_3$	282...283	3210...3230 (NH), 3085...3130 (C-H), 1738 (COOH), 1575...1615 ($C_{(4)}$=O, C=N, C=C)	3,62 (2H, s, CH_2); 6,68 (1H,s , CH); 7,55...7,90 (5H, m, C_6H_5); 13,60 (2H, br, NH, OH)	87
III	$C_{18}H_{12}Br_2N_2O_2$	280...281	3320...3450 (NH), 1637 ($C_{(4)}$=O), 1560, 1580...1590 (4-BrC_6H_4CO chelate C=N, C=C)	6,70 (1H, s, $C_{(5)}H$); 7,70...8,05 (9H, m, CH, 2C_6H_4); 13,42...13,72 (2H, br, 2NH)	67

*Yield shown for products of hydrazinolysis of methylenefuranones Ia-c.

(Table 1), and these, taken together with the absence of bands for exolic hydroxyl in the higher frequency region show that these compounds cannot have the structure of the isomeric 4-hydroxypyridazinones, the formation of which would be expected as a result of this reaction. The position of the signal of the $N_{(1)}H$ proton in the PMR spectrum of compounds IIa-i at 13.25-13.70 ppm also agrees with that for the known 3-arylmethyl-5,6,7,8-tetrahydro-1H-4-cinnolones (12.7 ppm [12]) and 6-aryl-3-methyl-5-ethoxycarbonyl-1H-4-pyridazinones (12.9-13.3 ppm [13]). Furthermore, the presence of a long-wave maximum at 279-286 nm (log ε 4.10-4.35) in the UV spectra of compounds IIa-i, corresponding to the analogous maximum of the 1H-4-cinnolones (275-281 nm [12]), together with the 3,6-disubstituted 1H-4-pyridazinones reported in the literature (270-280 nm [13] and 277 nm [14]) but having a bathochromic shift relative to the maximum of the substituted 4-hydroxy-(methoxy)pyridazinones (254-260 nm [14, 15]) enables us to reject the 4-hydroxypyridazinone structure.

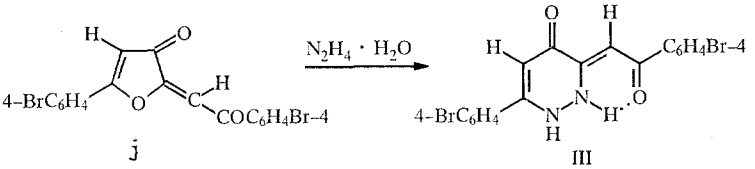
In the ^{13}C NMR spectrum of the pyridazinone IIa there are signals for the carbon atoms with chemical shifts, as follows:



and also signals corresponding to the benzene ring at 127.1, 129.2, 19.1, and 130.9 ppm, which is in agreement with the structure of compounds II.

The mass spectrum of compound IIf has molecular and fragment ion peaks with m/z as follows (relative intensities %): 258 (81 $M^{+\cdot}$), 213 (57 $[M-OC_2H_5]^{+\cdot}$), 212 (94 $[M-C_2H_5OH]^{+\cdot}$), 186 (100 $[M-COOC_2H_4]^{+\cdot}$), 185 (15 $[M-COOC_2H_5]^{+\cdot}$), 157 (15 $[185-CO]^{+\cdot}$), 145 (78 $[C_6H_5-C(=NH)-CHCO]^{+\cdot}$ — retrodiene splitting), 103 (12 $[C_6H_5CN]^{+\cdot}$), 102 (13 $[C_6H_5-C\equiv CH]^{+\cdot}$), 68 (11 $NC-CH_2C\equiv O^+$).

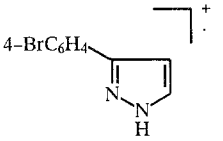
The high intensity of the molecular ion peak and the manner of its splitting are in agreement with literature data for the mass fragmentation of 1H-4-pyridazinones [16]. The presence in the mass spectrum of fragment peaks with m/z 145 and 68 together with the absence of peaks with m/z 141 $[N\equiv C-COCH_2COOC_2H_5]^{+\cdot}$ and 69 $[CH_3COC\equiv N]^{+\cdot}$ provide evidence in favor of the structure which we have proposed for compound IIa-h and enable us to exclude the alternative structure of 3-alkoxycarbonylacetyl-5-arylpyrazoles.



Ij III

The reaction of 2-p-bromobenzoylmethylene-5-p-bromophenyl-2,3-dihydro-3-furanone (Ij) with hydrazine hydrate in ethanol leads, after heating for 2 h, to the formation of the tautomeric 3-p-bromobenzoylmethylene-6-p-bromophenyl-2,3-dihydro-1H-4-pyridazinone (III) in 67% yield (Table 1).

In the IR spectrum of pyridazinone III (Table 1) there are intense bands for $C_{(4)}=O$ carbonyl stretching vibrations at 1637 cm^{-1} (at 1616-1639 cm^{-1} in the spectra of 1-phenyl-2,3-dihydro-1H-4-pyridazinones [14]), and for the carbonyl of the p-bromobenzoyl fragment at 1580-1590 cm^{-1}, the vibrational frequency of this being reduced on account of the involvement of the hydrogen atom of the NH group in intramolecular hydrogen bonding with the formation of a chelate ring. Bromine-containing fragment ions with m/z 224 ($4\text{-}BrC_6H_4COCH=C=O^{+\cdot}$) and 222 are absent from the mass spectrum of compound IIIa, from which one can reject the alternative structure 3-p-bromobenzoylacetyl-5-p-bromophenylpyrazole, the formation of which is possible as a result of recyclization.



It seems that the recyclization of 5-aryl-2-acylmethylene-2,3-dihydro-3-furanones under the action of hydrazine hydrate is associated with nucleophilic attack by the hydrazine on the carbon in position 2 of the furanone ring of I with the intermediate formation of 5-aryl-1-acyl-2-hydrazino-3-hydroxy-1,3-pentadiene-5-ones and their subsequent retrocyclization leading to 3-substituted 6-aryl-1H-4-pyridazinones II or the tautomeric form III.

TABLE 2. Physicochemical and Spectroscopic Characteristics of Compounds IVa-c, Va-g

Compound	Empirical formula	mp, °C (decomp.)	IR spectrum, ν, cm^{-1}, crystals	PMR spectrum, δ, ppm, DMSO-d_6	Yield, %
IVa	$C_{14}H_{14}N_2C_3$	125...126	3220...3240 (NH); 1717 ($COOCH_3$); 1695 (CO); 1595, 1508 (C=N, C=C)	2,42 (3H, s, CH_3); 3,75 (3H, s CH_3O); 4,11 (2H, s, CH_2); 7,50...7,75 (5H, m, C_6H_5); 12,90 (1H, br, NH)*	67
IVb	$C_{15}H_{16}N_2O_3$	136...137	3190...3215 (NH); 1707 ($COOCH_3$); 1682 (CO); 1515, 1615 (C=N, C=C)	2,34 (6H, s, $2CH_3$); 3,63 (3H, s, CH_3O); 4,02 (2H, s CH_2); 7,20, 7,50 (4H, d.d, C_6H_4); 12,70 (1H, br, NH)*	69
IVc	$C_{16}H_{18}N_2O_4$	121...122	3195...3220 (NH); 1705 ($COOC_2H_5$); 1681 (CO); 1516, 1613 (C=N, C=C)	1,21 (3H, t, CH_3); 2,36 (3H, s, CH_3); 3,87 (3H, s, CH_3O); 4,06 (2H, s, CH_2); 7,00, 7,60 (4H, d.d, C_6H_4); 12,75 (1H, br NH)*	73
Va	$C_{12}H_{10}N_4O$	325...326	3310...3320 (NHCO); 3160...3180, 3200...3230 (NH); 1627 (CONH)	5,88 (1H, s, CH); 6,98 (1H, s, $C_{(4)}H$); 7,30...7,90 (5H, m, C_6H_5); 11,80 (2H, br, 2NH)	68
Vb	$C_{13}H_{12}N_4O$	329...330	3300...3315 (NHCO); 3160...3170, 3200...3220 (NH); 1626 (CONH)	2,27 (3H, s, CH_3); 5,86 (1H, s, CH); 6,91 (1H, s, $C_{(4)}H$); 7,20, 7,76 (4H, d.d, C_6H_4); 11,78 (2H, br, 2NH)	62
Vc	$C_{13}H_{12}N_4O_2$	316...317	3290...3310 (NHCO); 3150...3170, 3190...3220 (NH); 1630 (CONH)	3,76 (3H, s, CH_3); 5,90 (1H, s, CH); 6,90 (1H, s, $C_{(4)}H$); 6,98, 7,75 (4H, d.d, C_6H_4); 11,75 (2H, br, 2NH)	67
Vd	$C_{12}H_9ClN_4O$	319...320	3300...3320 (NHCO); 3140...3160, 3180...3215 (NH); 1630 (CONH)	5,88 (1H, s, CH); 7,00 (1H, s, $C_{(4)}H$); 7,50, 7,92 (4H, d.d, C_6H_4); 11,90 (2H, br, 2NH)	71
Ve	$C_{13}H_{12}N_4O$	322...323	3270...3300 (NHCO); 3150...3170, 3180...3200 (NH); 1623 (CONH)	2,24 (3H, s, CH_3); 5,77 (1H, s, CH); 7,40...7,70 (5H, m, C_6H_5); 11,60 (2H, br, 2NH)	63 †
Vf	$C_{14}H_{14}N_4O$	323...324	3260...3290 (NHCO); 3150...3160, 3190...3210 (NH); 1625 (CONH)	2,21 (3H, s, CH_3); 2,34 (3H, s, CH_3); 5,74 (1H, s, CH); 7,15, 7,55 (4H, d.d, C_6H_4); 11,65 (2H, br, 2NH)	61 †
Vg	$C_{14}H_{14}N_4O_2$	315...316	3280...3300 (NHCO); 3160...3170, 3180...3215 (NH); 1632 (CONH	2,21 (3H, s, CH_3); 3,78 (3H, s, CH_3O); 5,73 (1H, s, CH); 7,00, 7,55 (4H, d.d, C_6H_4); 11,55 (2H, br 2NH)	65 †

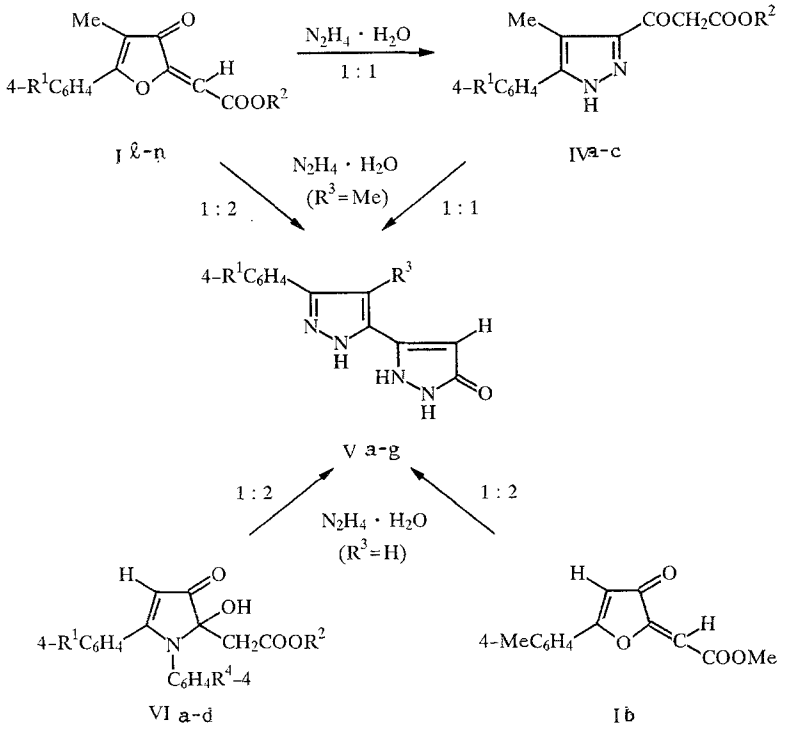
*Spectrum run in acetone-d_6.

†Yields are shown for products of hydrazinolysis of methylenefuranones I*l*-n.

In a study of the hydrazinolysis of 5-aryl-2-acylmethylene-2,3-dihydro-3-furanones we unexpectedly found that the reaction of compounds with structures similar to 2-alkoxycarbonylmethylene-5-aryl-4-methyl-2,3-dihydro-3-furanones (*Il*-n) with an equimolar quantity of hydrazine hydrate in ethanol at bp for 15-20 min led to the formation of different nitrogen-containing heterocycles — 3-alkoxycarbonylacetyl-5-aryl-4-methylpyrazoles (IVa-c) [17] (Table 2).

Heating methylenefuranones *Il*-n with a twofold excess of hydrazine hydrate or 3-alkoxycarbonyl acetyl-5-aryl-4-methylenepyrazoles IVa-c with an equimolar quantity of hydrazine hydrate in ethanol for 30-60 min results in the formation of 5-aryl-4-methyl-3-(3-oxo-2,3-dihydro-1H-5-pyrazolyl)pyrazoles (Ve-g) [17, 18] in yields of 61-65% or 73-82%, respectively (Table 2). 5-Aryl-3-(3-oxo-2,3-dihydro-1H-5-pyrazolyl)pyrazoles unsubstituted at the 4-position (Va-d) in their turn are recyclized by the action of a twofold excess of hydrazine hydrate to form compounds which we have prepared previously [8] — 2-alkoxycarbonylmethyl-2-hydroxy-1,5-diaryl-2,3-dihydro-3-pyrrolones (VIa-d) [19] or 2-methoxycarbonylmethylene-5-p-tolyl-2,3-dihydro-3-furanone (Ib).

The spectroscopic characteristics of the compounds IVa-c and Va-g which we prepared are given in Table 2. The characteristics for compounds IVa-c correspond to the proposed structure and agree well with those for the known 4-substituted 3-arylacetyl-5-methylpyrazoles [2, 3]. In the PMR spectra of compounds IVa-c, run in deuteroacetone, there are singlets for the two methylene protons at 4.02-4.11 ppm and a broad downfield signal for the ring aminogroup protons of the pyrazole at 12.70-12.90 ppm (for comparison, in the spectrum of 4-acetyl-3-phenylacetyl-5-methylpyrazole δNH = 12.80 ppm [3]), and from this, taken with the absence of a signal for an enol hydroxyl proton, one can exclude the possible H-chelate tautomeric structure of a 3-alkoxycarbonylacetyl fragment. The compounds IVa-c which we prepared have the following absorptions in the UV [λ_{max} nm (log ε)]: 210-211 (4.10-4.18) and 244-251 (4.41-4.43). These are in agreement with the spectroscopic data for 3-phenylacetyl-4-ethoxycarbonyl-5-methylpyrazole [213 (4.20), 235 (4.37)] [2] and also testify to the absence of enolization of the β-ketoester fragment. The insignificant bathochromic shift which is observed in the long-wave band of the spectra of compounds Va-g (247-259 nm) apparently results from the presence of a second pyrazole ring, and this again is consistent with literature results [20].



Il, IVa, Va, d, VIa: R^1 = H; Im, IVb, Vb, f, VIb: R^1 = Me; In, IVc, Vc, g, VIc: R^1 = MeO; Vd, VId: R^1 = Cl; *Il*, m, IVa, b, VIb-d: R^2 = Me; In, IVc, VIa: R^2 = Et; Va-d: R^3 = H; Ve-g: R^3 = Me; VIb, d: R^4 = Me; VIa: R^4 = MeO

In the mass spectrum of compound IVa there are molecular and fragment ion peaks with m/z as follows (relative intensity %): 258 (53 $M^{+\cdot}$), 227 (20 $[M-OCH_3]^{+\cdot}$), 226 (95 $[M-CH_3OH]^{+\cdot}$), 185 (70 $[M-CH_2COOCH_3]^{+\cdot}$), 157 (17 $[M-COCH_2COOCH_3]^{+\cdot}$), 128 (100 $CH_3OCOCH_2COC{\equiv}N^+H$), 127 (17 $CH_3OCOCH_2COCN^{+\cdot}$), 104 (22 $C_6H_5{\equiv}N^+H$), 103 (12 $C_6H_5CN^{+\cdot}$).

The presence in the mass spectrum of fragment ion peaks with m/z 127 and 128, together with the absence of peaks for methyl cyanoacetate (99) and the cyanoacetyl ion (68), lead to the conclusion that the compounds obtained do not have the 3-alkoxycarbonylmethyl-6-aryl-1H-4-pyridazinone structure. In the mass spectrum of compound Va the molecular ion peak has maximum intensity; this is consistent with literature data and provides evidence of the considerable stability of pyrazole derivatives to electron bombardment [21]. Fragmentation of the 5-phenyl-3-cyanopyrazole (m/z 169) formed by splitting of the stable ion is impeded and takes place primarily at the N—N bond of the heterocycles; this is in good agreement with known results [21].

The formation of pyrazoles IV is apparently the result of initial attack of the electrophilic center at the $C_{(5)}$ atom of compounds *Il*-n with subsequent recyclization of the intermediate 6-aryl-6-hydrazino-5-methyl-3,4-dioxo-5-hexenoic acid esters. When a twofold excess of hydrazine hydrate is used, further heterocyclization occurs with the participation of the β-ketoester fragment of compounds IV to form pyrazolylpyrazoles V, the acid catalyst apparently facilitating hydration of the 2-exoethylene bond which leads to transfer of the electrophilic center in compounds Ib from the $C_{(2)}$ to the $C_{(5)}$ ring carbon. Recyclization of the 3-pyrrolones VI under the action of excess hydrazine hydrate is probably the result of reaction of the latter with the uncyclized oxo-tautomeric forms of compounds VI — esters of 6-aryl-6-arylamino-3,4-dioxo-5-hexenoic acid — with subsequent heterocyclization.

EXPERIMENTAL

Infrared spectra were run on a UR-20 instrument as mulls in mineral oil. UV spectra were recorded on a Specord UV-Vis spectrophotometer in ethanol at a concentration of 10^{-4} mmole/liter. PMR spectra were run on an RYa-2310 (60 MHz) instrument in DMSO-D_6 and in acetone-D_6 with HMDS as internal standard. Carbon-13 NMR spectra were obtained on a Bruker HX-90 (90 MHz) in $CDCl_3$ with TMS as internal standard. A Varian MAT-311 instrument was used for recording mass spectra with direct injection of the sample, ionization energy 70 eV, and vaporizer at 120-200°C. The homogeneity of the compounds was confirmed on Silufol UV-254 plates in either 3:2 benzene—ether or 10:9:1 benzene—ether—acetone with visualization by either iodine or UV light.

The characteristics of the compounds prepared are set out in Tables 1 and 2.

Results of elemental analyses corresponded to those calculated.

3-Substituted 6-Aryl-1H-4-pyridazinones (IIa-i, IIIa, b). To a suspension of 0.01 mole 2-alkoxycarbonyl-, cyano-, or p-halobenzoylmethylene-5-aryl-2,3-dihydro-3-furanones Ia-k [7, 22, 23] in 100-150 ml ethanol was added with stirring 0.5 ml 70% aqueous hydrazine. For starting materials Ia-i, after 2 h the precipitate was filtered off and crystallized from acetone (IIa, b, f, i) or ethanol (IIc-e, g, h). For the methylenefuranone Ij the mixture was heated at bp for 2 h and then the precipitate filtered off and crystallized from 1:1 DMF-ethanol to yield compound III. IR spectrum of compound IIf (in $CHCl_3$, cm^{-1}): 3410 (NH), 1715 ($COOC_2H_5$), 1590-1605 (C=O, C=N, C=C). Mass spectrum of compound III, m/z (I, %):* 446 (20), 418 (15), 223 (5), 183 (100), 182 (12), 155 (27).

6-Aryl-3-hydrazinocarbonylmethyl-1H-4-pyridazinones (IIj-*l*). To a suspension of 0.01 mole 5-aryl-2-methoxycarbonylmethylene-2,3-dihydro-3-furanones Ia-c in 100 ml ethanol was added with stirring 1.0 ml 70% hydrazine solution (method **A**), or to a suspension of 0.01 mole 6-aryl-3-methoxycarbonylmethyl-1H-4-pyridazinones IIa-c in 100 ml ethanol was added 0.5 ml 70% hydrazine solution (method **B**) and the mixture heated at bp 3-4 h. The precipitate was filtered off and crystallized from ethanol to yield compounds IIj-*l*.

3-Carboxymethyl-6-phenyl-1H-4-pyridazinone (IIm). To a solution of 2.44 g (0.01 mole) 3-methoxycarbonyl-6-phenyl-1H-4-pyridazinone IIa in 100 ml dioxane was added 10 ml 10% hydrochloric acid and the mixture heated 2 h at bp. The solvent was evaporated and the product crystallized from water to yield 2.0 g (87%) compound IIm. On crystallizing IIm from ethanol, 6-phenyl-3-ethoxycarbonylmethyl-1H-4-pyridazinone IIf was obtained in 94% yield.

3-Alkoxycarbonylacetyl-5-aryl-4-methylpyrazoles (IVa-c). To a solution of 0.01 mole 2-alkoxycarbonylmethylene-5-aryl-4-methyl-2,3-dihydro-3-furanones *Il*-n [7, 22] in 100-150 ml ethanol was added 0.5 ml 70% hydrazine solution and the mixture heated at bp 15-20 min. The solvent was evaporated and the product crystallized from ethanol to yield compounds IVa-c.

5-Aryl-3-(3-oxo-2,3-dihydro-1H-5-pyrazolyl)pyrazoles (Va-g). A. To a solution of 0.01 mole 2-alkoxycarbonylmethylene-5-aryl-4-methyl-2,3-dihydro-3-furanones *Il*-n in 100-150 ml ethanol was added 1.0 ml 70% hydrazine solution and the mixture heated at bp 40-60 min. The precipitate was filtered off and crystallized from acetone or ethanol to yield compounds Ve-g.

B. To a solution of 0.01 mole 3-alkoxycarbonylacetyl-5-aryl-4-methylpyrazoles IVa-c in 50 ml ethanol was added 0.5 ml 70% hydrazine solution and the mixture heated at bp 30-40 min. Further treatment was as in method **A**.

*Mass numbers of ions containing ^{79}Br are given.

C. To a solution of 0.01 mole 2-alkoxycarbonylmethyl-2-hydroxy-1,5-diaryl-2,3-dihydro-3-pyrrolones VIa-d [8] in 100 ml ethanol was added 1.0 ml 70% hydrazine and the mixture heated at bp 2-3 h. The precipitate was filtered off and crystallized from ethanol or toluene to yield compounds Va-d.

D. To a suspension of 0.01 mole methylenefuranone Ib [7, 22] in 100 ml ethanol was added 3 ml hydrochloric acid, the mixture heated to 60-70°C, and then 1.0 ml 70% hydrazine solution added with stirring and the mixture heated at bp 30 min. Further treatment was as in method **A**. Compound Vb was obtained in 33% yield. UV spectra of compounds Va-g, λ_{max}, nm ($\log \varepsilon$): 210-214 (4.06-4.47), 247-259 (4.24-4.65). Mass spectrum of compound Va, m/z (I, %): 226 (100), 169 (67), 104 (5), 103 (4), 102 (4). Mass spectrum of compound Vg, m/z (I, %): 270 (100), 213 (27), 212 (9), 198 (9), 170 (5), 169 (5), 146 (10), 137 (22), 130 (5), 129 (7), 115 (9).

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