Reaction of 2-Dimethylaminomethylene-1,3-diones with Dinucleophiles. I. Synthesis of 1,5-Disubstituted 4-Acylpyrazoles

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Received May 3, 1982

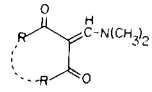
Reaction of open-chain and cyclic *sym*-1,3-diones with *N,N*-dimethylformamide dimethyl acetal gave, generally in high yield, a series of *sym*-2-dimethylaminomethylene-1,3-diones which reacted with phenylhydrazine and methylhydrazine to afford, generally in satisfactory yield, a number of 1,5-disubstituted 4-acylpyrazoles. The applications and limits of this new pyrazole synthesis are presented and discussed.

J. Heterocyclic Chem., **19**, 1355 (1982).

2-Alkoxymethylene-1,3-diones I and 2-anilinomethylene-1,3-diones II, available from 1,3-diones III plus trialkoxymethanes by reaction with acetic anhydride (1) and aniline (2,3), respectively, are useful synthons for the construction of heterocylic systems; less used were 2-hydroxymethylene-1,3-diones, available from I or II by often tedious hydrolytic procedures (4). For example, the reaction of the highly electrophilic extra-chain carbon atom of I and II with the most nucleophilic site of dinucleophiles such as hydrazines, hydroxylamine, amidines or guanidine, followed by ring closure *via* interaction of a carbonyl group with the other nucleophilic site, led to a number of acyl substituted heterocycles such as pyrazoles (5,6,7), isoxazoles (8) and pyrimidines (9,10,11,12), respectively. However, the utilization of I and II meets with some limitations. For example, compounds I are not available in the case of cyclic 1,3-diones (2), whereas in the case of II the reaction with the dinucleophile (*e.g.* phenylhydrazine) should be carried out in two steps (7,25) or did not lead to the heterocycle [*e.g.* hydroxylamine (13)]. In pursuing our continuing study on the polar cycloaddition of ketenes and sulfenes to *N,N*-disubstituted heterocylic enaminones (14), we became interested in the availability of heterocylic ketones such as 1,5,6,7-tetrahydroindazol-4-ones, 6,7-dihydro-1,2-benzoisoxazol-4(5*H*)-ones and 7,8-dihydroquinazolin-5(6*H*)-ones. Following a suggestion from a procedure used for similar compounds in the 1,5-benzodiazepine field (18), we found that the reaction of both open-chain and cyclic *sym*-2-dimethylaminomethylene-1,3-diones IV with hydrazines, hydroxylamine and amidines or guanidine led to 4-acyl-

Table I

sym-2-Dimethylaminomethylene-1,3-diones IVa-i



Formula Number	R or R⌒R	Reflux Time (hours)	Yield %	Bp/mm or Mp °C	Molecular Formula	Analyses % Calcd./Found C	H	N
IVa	-CH_3	1	86	115-120/0.4; 59-61 (a)	$C_8H_{13}NO_2$	61.91 62.16	8.44 8.52	9.02 8.88
IVb	-$CH(CH_3)_2$	6	78	71 (b)	$C_{12}H_{21}NO_2$	68.21 68.50	10.02 10.13	6.63 6.59
IVc	-$C(CH_3)_3$	40	18	120-125/0.4; 81-83	$C_{14}H_{25}NO_2$	70.25 70.14	10.53 10.52	5.85 5.72
IVd	-C_6H_5	2	46	120 (c)	$C_{18}H_{17}NO_2$	77.40 77.48	6.13 6.23	5.01 4.99
IVe	-$(CH_2)_2$-	-(g)	88	94 (b)	$C_8H_{11}NO_2$	62.73 62.89	7.24 7.42	9.14 9.04
IVf	-(CH_2)-	1	90	118 (d)	$C_9H_{13}NO_2$	64.65 64.36	7.84 7.99	8.38 8.23
IVg	-CH_2-$C(CH_3)_2$-CH_2-	1	91	93 (e)	$C_{11}H_{17}NO_2$	67.66 67.90	8.78 8.60	7.17 6.97
IVh	-CH_2-$CH(C_6H_5)$-CH_2-	1	98	137 (d)	$C_{15}H_{17}NO_2$	74.05 74.38	7.04 7.17	5.76 5.65
IVi	*o*-C_6H_4	1	83	147 (c) (f)	$C_{12}H_{11}NO_2$	71.63 71.50	5.51 5.68	6.96 6.90

(a) Reference (20), mp 61-63°, 28% yield. (b) From anhydrous diethyl ether. (c) From 95% ethanol. (d) From ethyl acetate. (e) From anhydrous diethyl ether-petroleum ether, reference (15) mp 92-93.50, reference (20) mp 83-87°. (f) Reference (21) mp 144-145°; the compound has been prepared by our procedure in 62% yield (16). (g) Reaction carried out at 0°, see Experimental.

Table II

UV, IR and NMR Spectral Data of Compounds IVa-i

Compound No.	UV λ max nm (log ε)	IR, cm^{-1} (Chloroform)	NMR, δ (Deuteriochloroform)
IVa	275 (3.96) 298 (4.00)	1660, 1620, 1585	2.32 (s, 2 CH_3CO), 3.01 (s, 2 CH_3N), 7.48 (near s, =CHN)
IVb	283 sh (4.07) 294 (4.11)	1665, 1620, 1585	1.12 (d, J = 7.2, 4 CH_3), 2.8-3.3 (m, 2 CH), 2.99 (s, 2CH_3N), 7.41 (near s, = CHN)
IVc	294 (4.15)	1665, 1620, 1583	1.27 (near s, 6 CH_3), 2.91 (mc, 2 CH_3N), 7.34 (near s, = CHN)
IVd	243.5 (4.20) 309 (4.25)	1643, 1583, 1565	3.01 (s, 2 CH_3N), 7.00-7.45(m, C_6H_5 + =CHN), 7.55-7.85 (m, C_6H_5)
IVe	242 (4.12) 284 sh (3.80) 313 (4.05)	1703, 1625, 1602	2.54 (s, 2 CH_2), 3.46 (s, CH_3N), 3.79 (s, CH_3N), 7.48 (near s, =CHN)
IVf	257 (4.09) 284 sh (3.66) 321 (3.94)	1663, 1590	1.65-2.20 (m, CH_2-5), 2.48 (near t, J = 6, CH_2-4 + CH_2-6), 3.20 (s, CH_3N), 3.42 (s, CH_3N), 8.08 (near s, = CHN)
IVg	259 (4.05) 284 sh (3.68) 321 (3.89)	1665, 1592	1.07 (s, 2 CH_3-5), 2.38 (s, CH_2-4 + CH_2-6), 3.23 (s, CH_3N), 3.44 (s, CH_3N), 8.07 (near s, =CHN)
IVh	260 (4.29) 278 sh (4.12) 320 (3.74)	1663, 1590	2.6-2.9 (m, CH_2-4 + CH_2-6), 3.15-3.80 (m, CH-5), 3.25 (s, CH_3N), 3.42 (s, CH_3N), 7.31 (near s, C_6H_5), 8.10 (near s, = CHN)
IVi	227 (4.06) 237 (4.08) 250 sh (3.88) 285 (3.73) 295 (4.02) 326 sh (4.11) 335 (4.18)	1708, 1650	3.35 (s, CH_3N), 3.78 (s, CH_3N), 7.53 (near s, =CHN), 7.55-7.90 (m, 4 Har)

pyrazoles, 4-acylisoxazoles and 5-acylpyrimidines, generally in one step and in satisfactory yield.

In this paper we wish to report the reaction of IVa-i with phenyl- and methylhydrazine to give 1,5-disubstituted 4-acylpyrazoles Va-i and VIa-d, f-i. Synthons IVa-i (Tables I and II) were prepared in good yield by refluxing a solution of 1,3-diones IIIa-d, f-i in *N,N*-dimethylformamide dimethyl acetal (in the case of IIIe the reaction was carried out at 0°); the poor yield of IVc is evidently due to the strong steric hindrance of the starting 1,3-dione IIIc. The nmr spectra of cyclic derivatives IVe-i (Table II) show two singlets for the dimethylamino group, a feature that is due to hindered rotation [*cf.* (20)].

Oddly enough, this reaction has been rarely used in the past in the case of 1,3-diones (15,16,20), even though it has been successfully employed for a number of ketones (17).

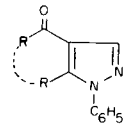
It can be noted that synthons IV present in the mesomeric structure VIII a stabilization of the positive charge better than II, a fact that is decisive for their improved reactivity.

The reaction of IVa-i with phenylhydrazine was best carried out in refluxing 1-butanol-acetic acid mixture (18), with the following results. Synthons IVa-d,f-h afforded pyrazoles Va-d,f-h as sole products, generally in good yield except Vc owing to steric hindrance (Tables III and IV). In the reaction conditions, cyclopentane derivatives IVe,i gave only the phenylhydrazino derivatives IXb and X (Table VII), which were best prepared by carrying out the reaction at 0° and were cyclized to the corresponding pyrazoles Ve,i by refluxing in toluene in the presence of a catalytic amount of *p*-toluenesulfonic acid. We have already observed this reluctance to undergo cyclization of $O{=}\overset{|}{C}\text{-}\overset{|}{C}{=}CH\text{-}NR_2$ groups incorporated in a cyclopentane moiety (19); other cases will be reported on later.

With methylhydrazine, preliminary experiments carried out with IVa in the same conditions as with phenylhydrazine showed that an inseparable 1:1 mixture of pyrazoles VIa and VIIa was formed, as determined by nmr spectra.

Table III

5-Substituted 4-Acyl-1-phenylpyrazoles Va-i



Formula Number	R or R R	Reflux Time (hours)	Yield %	Bp/mm or Mp °C	Molecular Formula	Analyses % Calcd./Found C	H	N
Va	-CH_3	2	78	103 (a) (e)	$C_{12}H_{12}N_2O$	71.98 71.90	6.04 6.00	13.99 14.04
Vb	-$CH(CH_3)_2$	1	100	130/0.4	$C_{16}H_{20}N_2O$	74.97 75.16	7.86 8.09	10.93 10.92
Vc	-$C(CH_3)_3$	2	33	140-150/0.7	$C_{18}H_{24}N_2O$	76.02 76.26	8.51 8.68	9.85 9.60
Vd	-C_6H_5	3	100	153 (a) (f)	$C_{22}H_{16}N_2O$	81.46 81.40	4.97 4.91	8.64 8.64
Ve	-$(CH_2)_2$-	-(i)	62	162 (b)	$C_{12}H_{10}N_2O$	72.71 72.66	5.09 5.22	14.13 13.99
Vf	-$(CH_2)_3$-	2	90	140 (a) (g)	$C_{13}H_{12}N_2O$	73.57 73.81	5.70 5.70	13.20 13.41
Vg	-CH_2-$C(CH_3)_2$-CH_2-	2	64	120 (c) (h)	$C_{15}H_{16}N_2O$	74.97 74.85	6.71 6.60	11.66 11.79
Vh	-CH_2-CHC_6H_5-CH_2-	1	64	138 (d)	$C_{19}H_{16}N_2O$	79.14 79.29	5.59 5.52	9.72 9.74
Vi	*o*-C_6H_4	-(1)	85	144 (a)	$C_{16}H_{10}N_2O$	78.04 78.23	4.09 4.12	11.37 11.36

(a) From 95% ethanol. (b) From ethyl acetate. (c) From anhydrous diethyl ether-petroleum ether. (d) From anhydrous diethyl ether. (e) Reference (5) mp 107-108°. (f) Reference (22) mp 144-145°. (g) Reference (7) mp 139-140°. (h) Reference (23) mp 100-101°. The calculated C,H,N values were erroneous. (i) Obtained by refluxing a toluene solution of IXa with *p*-toluenesulfonic acid (see Experimental). (1) Obtained by refluxing a toluene solution of X with *p*-toluenesulfonic acid (see Experimental). The compound has been already prepared by this procedure (24).

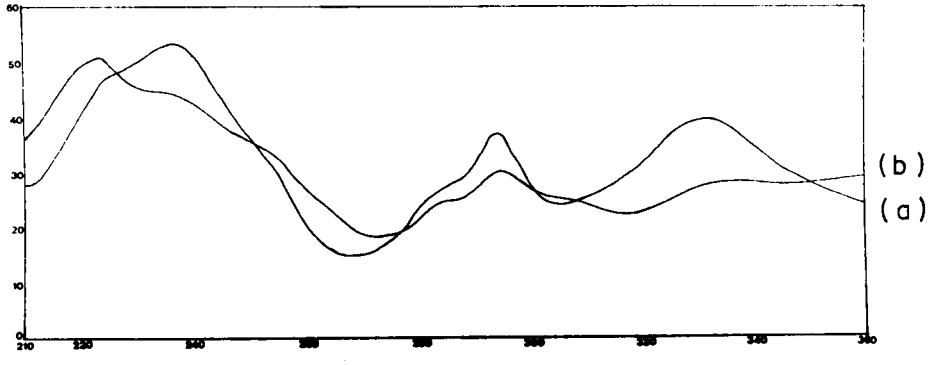


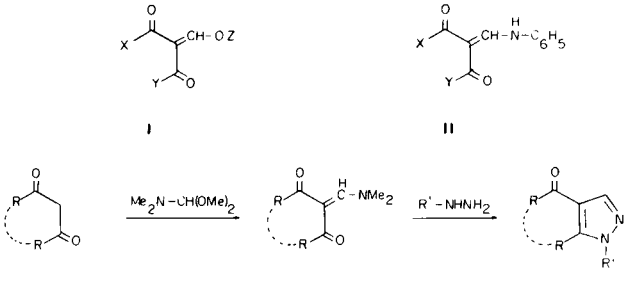
Figure 1. The uv spectra of X (mw = 264.285) in 95% ethanol (c = 0.00492 g/l): (a) initial; (b) after 3 hours.

Table IV

UV, IR and NMR Spectral Data of Compounds IVa-i

Compound No.	UV λ max nm (log ε)	IR, cm⁻¹ (Chloroform)	NMR, δ (Deuteriochloroform)
Va	252 (4.22)	1667, 1542, 1477 1457, 14.03	2.50 (s, CH_3CO), 2.59 (s, CH_3-5), 7.49 (near s, C_6H_5), 8.05 (near s, CH-3)
Vb	250 (4.05)	1675, 1525, 1472 1460, 1412	1.24 [d, J ~ 7, $(CH_3)_2$CH-5), 1.32 (d, J ~ 7, $(CH_3)_2$CHCO], 3.35 (near h, J ~ 7, 2 $CHMe_2$), 7.3-7.7 (m, C_6H_5), 8.06 (near s, CH-3)
Vc	247.5 (3.83)	1670, 1512, 1478 1460, 1395	1.21 [s, $(CH_3)_3$C-5], 1.36 [s, $(CH_3)_3$CCO], 7.45 (mc, C_6H_5), 7.71 (near s, CH-3)
Vd	211 (4.31) 254 (4.17) 270 sh (4.14)	1645, 1537, 1462 1447, 1392	7.28 (near s, C_6H_5), 7.32 (near s, C_6H_5), 7.45-8.00 (m, C_6H_5CO), 8.09 (s, CH-3)
Ve	232 sh (4.21) 249.5 (4.27)	1703, 1532, 1462 1435, 1410	3.0-3.4 (m, 2 CH_2), 7.25-7.75 (m, C_6H_5), 7.78 (s, CH-3)
Vf	254 (4.17)	1675, 1547, 1458 1427, 1410	2.0-2.4 (m, CH_2-6), 2.45 -2.75 (m, CH_2-7), 3.02 (near t, J = 6, CH_2-5), 7.45 (near s, C_6H_5), 8.03 (near s, CH-3),
Vg	295 (4.10)	1675, 1545, 1460 1423, 1408	1.12 (s, 2 CH_3-6), 2.44 (near s, CH_2-7), 2.85 (near s, CH_2-5), 7.53 (near s, C_6H_5), 8.09 (near s, CH-3)
Vh	254.5(4.20)	1670, 1538, 1450 1418, 1403	2.7-3.7 (m, CH_2-5 + CH_2-7 + CH-6),), 7.33 (near s, C_6H_5-6), 7.50 (near s, C_6H_5), 8.13 (near s, CH-3)
Vi	251 (4.30) 286 (3.81) 291 sh (3.79) 323 (3.30)	1762, 1713, 1525, 1460, 1450	7.1-7.9 (m, C_6H_5 + 4 Har), 7.68 (s, CH-3)

In order to obtain pyrazoles VIa-d,f-i (Tables V and VI) we found it more convenient to carry out the reaction in methanol at 0°, followed in general by a reflux period. A sole pyrazole VI was usually formed, generally in high yield, with the exception of open-chain derivatives IVa,c,d, where a mixture of 5-substituted pyrazoles VIa,c,d and isomeric 3-substituted pyrazoles VIIa,c,d, in which the former predominates in the case of a,d, was always formed. From these mixtures, pure pyrazoles VIa and VId could be obtained by crystallization; only the liquid mixture of VIc and VIIc, in which the latter predominates, could not be separated. Once again, the cyclopentane derivative IVe gave only the methylhydrazino compound IXa, which decomposed rather than cyclized by refluxing in toluene or benzene with *p*-toluenesulfonic acid.



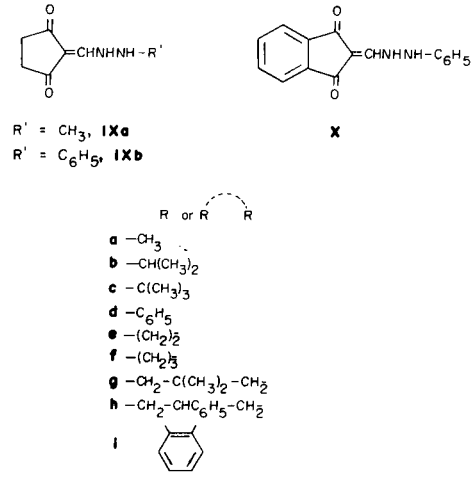
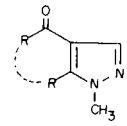


Table V

5-Substituted 4-Acyl-1-methylpyrazoles VIa-d, f-i



Formula Number	R or R R	Reflux Time (hours)	Yield %	Bp/mm or Mp °C	Molecular Formula	Analyses % Calcd./Found C	H	N
VIa	-CH_3	(g)	91	80-85/0.4 (a)	$C_7H_{10}N_2O$	60.85 60.57	7.30 7.04	20.27 20.07
VIb	-$CH(CH_3)_2$	4	94	120/0.4	$C_{11}H_{18}N_2O$	68.00 68.18	9.34 9.27	14.42 14.68
VIc	-$C(CH_3)_3$	3	84	90/0.4 (b)	$C_{13}H_{22}N_2O$	70.23 69.97	9.97 10.07	12.60 12.64
VId	-C_6H_5	4	100	180/0.4 (c)	$C_{17}H_{14}N_2O$	77.84 78.10	5.38 5.50	10.68 10.55
VIf	-$(CH_2)_3$-	1.5	86	94 (d)	$C_8H_{10}N_2O$	63.98 63.95	6.71 6.88	18.65 18.87
VIg	-CH_2-$C(CH_3)_2$-CH_2-	1.5	92	74 (d)	$C_{10}H_{14}N_2O$	67.39 67.14	7.92 8.02	15.72 15.53
VIh	-CH_2-CHC_6H_5-CH_2-	1.5	92	158 (e)	$C_{14}H_{14}N_2O$	74.31 74.08	6.24 6.22	12.38 12.38
VIi	*o*-C_6H_4	0.5	61	162 (f)	$C_{11}H_8N_2O$	71.73 71.80	4.38 4.48	15.21 15.38

(a) The liquid soon solidified, mp 41-42°, and was proven to be a mixture of VIa and VIIa in a 90/10 ratio by nmr data (see Table VI). After many recrystallizations from anhydrous diethyl ether, nmr-pure VIa was obtained, mp 50-51° [reference (5) mp 78-79°]. (b) Isomers mixture VIc/VIIc 31/69, which could not be separated. (c) Isomers mixture VId/VIId 78/22; VId separated from the mixture in 65% yield, mp 61° from anhydrous diethyl ether-petroleum ether. (d) From anhydrous diethyl ether. (e) From ethyl acetate. (f) From 95 % ethanol. (g) Reaction carried out at 0° for 4 hours, see Experimental.

In conclusion, this appears to be an efficient method to prepare 1,5-disubstituted 4-acylpyrazoles in two steps starting from *sym*-1,3-diones, through the facile formation of 2-dimethylaminomethylene-1,3-diones followed by the reaction of these with phenylhydrazine and methylhydrazine. In the latter case, however, the more nucleophilic primary amino group reacts in part with a carbonyl group of open-chain 2-dimethylaminomethylene-1,3-diones even in the cold, giving in nearly all cases a mixture of isomeric pyrazoles.

EXPERIMENTAL

The uv spectra were measured in 95% ethanol with a Hitachi-Perkin-Elmer Model EPS-3T spectrophotometer. The ir spectra were taken on a Perkin-Elmer Model 398 spectrophotometer; nmr spectra were recorded on a Perkin-Elmer Model R12 instrument (60 MHz, TMS as internal standard, J in Hz). Melting points were determined with a Fisher-Johns apparatus.

General Procedure for *sym*-2-Dimethylaminomethylene-1,3-diones (IVa-i).

A solution of *sym*-1,3-dione III (50 mmoles) in *N,N*-dimethylformamide dimethyl acetal (14 ml) was stirred at 0° for 1 hour (IIIe) or refluxed for a certain time (see Table I). The excess acetal was distilled off under reduced pressure and the residue was recrystallized from a suitable solvent or distilled *in vacuo* (Tables I and II).

General Procedure for 5-Substituted 4-Acyl-1-phenylpyrazoles (Va-d) and for 1,5,6,7-Tetrahydro-1-phenylindazol-4-ones (Vf-h).

Phenylhydrazine (2.27 g, 21 mmoles) in 1-butanol (20 ml) was slowly added with stirring to a solution of IV (20 mmoles) in 1-butanol (80 ml) and acetic acid (3 ml). The resulting solution was refluxed for a certain time (see Table III) and evaporated under reduced pressure. The residue was purified by recrystallization from a suitable solvent or by distillation *in vacuo* (Tables III and IV). In the case of Ve and Vi, this procedure gave only the corresponding 2-(2-phenylhydrazino)methylene-1,3-diones IXb and X (Table VII) in low yield. A better yield of IXb and X was obtained by the above described procedure, but carrying out the reaction at 0° and keeping the solution at 0° for 1 hour. The resulting precipitate was filtered and recrystallized.

Table VI

UV, IR and NMR Spectral Data of Compounds VIa-d, f-i

Compound No.	UV λ max nm (log ε)	IR, cm^{-1} (Chloroform)	NMR, δ (Deuteriochloroform)
VIa	246 (3.92)	1667, 1543, 1503 1483, 1445	2.42 (s, CH_3-5), 2.57 (s, CH_3CO), 3.82 (s, CH_3N), 7.83 (near s, CH-3) (a)
VIb	248 (3.92)	1665, 1527, 1488, 1460	1.10 [d, J = 7.2, $(CH_3)_2CH$-5], 1.28 [d, J = 7.2, $(CH_3)_2CHCO$], 3.18 (near h, J = 7.2, $CHMe_2$-5), 3.74 (near h, J = 7.2, $COCHMe_2$), 3.87 (s, CH_3N), 7.81 (near s, CH-3)
VIc (b)	248 (3.67) 300 (2.72)	1678, 1530, 1478 1462	1.27 [near s, $(CH_3)_3C$], 1.40 [mc, 2 $(CH_3)_3CCO$], 3.88 (s, CH_3N), 7.75 (near s, CH-3) (c)
VId	232 (4.10) 252 (4.11) 270 sh (4.02)	1645, 1530, 1478 1450	3.82 (s, CH_3N), 7.42 (near s, C_6H_5-5), 7.25-8.00 (m, C_6H_5CO), 7.91 (s, CH-3) (d)
VIf	247 (3.99)	1673, 1513, 1455	1.90-2.65 (m, CH_2-6 + CH_2-7), 2.86 (near t, J = 5.7, CH_2-5), 3.85 (s, CH_3N), 7.90 (s, CH-3)
VIg	248 (3.95)	1668, 1513, 1452	1.14 (s, 2 CH_3-6), 2.36 (s, CH_2-7), 2.69 (s, CH_2-5), 3.84 (s, CH_3N), 7.87 (s, CH-3)
VIh	247.5 (4.02)	1672, 1512, 1453	2.60-3.15 (m, CH_2-5 + CH_2-7), 3.25-3.75 (m, CH-6), 3.83 (s, CH_3N), 7.34 (mc, C_6H_5), 7.88 (near s, CH-3)
VIi	242 (4.15) 249.5 (4.23) 270 (3.16)	1760, 1714, 1557, 1460	3.99 (s, CH_3N), 7.05-7.65 (m, 4H ar + CH-3)

(a) Extrapolated data of VIIa from the initial mixture VIa/VIIa 90-10: 2.39 (s, CH_3-3), 2.47 (s, CH_3CO), 3.89 (s, CH_3N), 7.89 (s, CH-5). (b) Also present VIIc, see Table V. (c) Extrapolated data of VIIc: 4.04 (s, CH_3N), 7.41 (near s, CH-5). (d) Extrapolated data of VIId from the initial mixture VId/VIId 78/22: 3.95 (s, CH_3N).

General Procedure for 5-Substituted 4-Acyl-1-methylpyrazoles (VIa-d), 1,5,6,7-Tetrahydro-1-methylindazol-4-ones (VIf-h) and 1-Methylindeno-[1,2-*c*]pyrazol-4(1*H*)-one (VIi).

Methylhydrazine (0.92 g, 20 mmoles) in methanol (20 ml) was slowly added with stirring to an ice-cooled solution of IV (20 mmoles) in methanol (80 ml). The resulting solution was stirred at 0° for 4 hours (IVa,e) or refluxed for a certain time (see Table V). With the exception of IVe, the solution was evaporated under reduced pressure and the residue was recrystallized from a suitable solvent or distilled *in vacuo* (Tables V and VI).

In the case of IVe, a crystalline precipitate separated, which was proven to be 2-(2-methylhydrazino)methylenecyclopentane-1,3-dione IXa (Table VII).

The liquids obtained from IVa,c,d were mixtures of 5-substituted pyrazoles VIa,c,d and 3-substituted isomers VIIa,c,d, as shown by their nmr spectra (Table VI); from these mixtures, pure VIa,d could be obtained by crystallization (Table VI).

5,6-Dihydro-1-phenylcyclopentapyrazol-4(1*H*)-one (Ve) and 1-Phenylindeno[1,2-*c*]pyrazol-4(1*H*)-one (Vi).

A solution of IXb or X (10 mmoles) and *p*-toluenesulfonic acid (50 mg) in anhydrous toluene (150 ml) was refluxed in a Dean-Stark apparatus for 3 hours, cooled, washed with 1*N* sodium hydroxide and water, dried (sodium sulfate) and evaporated under reduced pressure. The residue was recrystallized from a suitable solvent (Tables III and IV). Under these conditions, IXa decomposed totally with charring.

Acknowledgement.

The authors wish to thank Dr. E. Sottofattori for the microanalyses, Dr. S. Morasso and Mr. F. Fasce for the uv, ir and nmr spectra.

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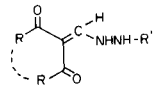
Table VII

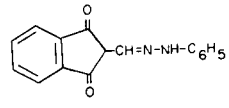
2-[2-(Methyl)(Phenyl)hydrazino]methylene-1,3-diones IXa,b and X



Formula Number	R⌒R	R'	Yield %	Mp, °C	Molecular Formula	Analyses % Calcd./Found C	H	N
IXa	-$(CH_2)_2$-	CH_3	89	156 (a)	$C_7H_{10}N_2O_2$	54.54 54.81	6.54 6.49	18.17 18.15
IXb	-$(CH_2)_2$-	C_6H_5	71	186 (b)	$C_{12}H_{12}N_2O_2$	66.65 66.82	5.59 5.67	12.95 12.94
X	oC_6H_4-	C_6H_5	65	214 (a)	$C_{16}H_{12}N_2O_2$	72.72 72.84	4.58 4.69	10.60 10.46

UV, IR and NMR Spectral Data

	UV λ max nm (log ε)	IR, cm^{-1} (Potassium bromide)	NMR, δ (DMSO-d_6)
IXa	215 (3.72) 252.5 (4.03) 324.5 (4.10)	1683, 1622, 1565	2.36 (s, 2 CH_2), 3.54 (s, CH_3N), 7.18 (near s, =CHN), 7.4-8.1 (m, 2NH; disappears with deuterium oxide)
IXb	232 (4.18) 306 (4.23) 330 sh (4.11)	1692, 1628, 1585	2.46 (s, 2 CH_2), 6.65-7.35 (m, C_6H_5), 7.67 (s, =CHN), 8.40 (broad s, NH; disappears with deuterium oxide), 8.96 (broad s, NH; disappears with deuterium oxide)
X	(c)	1700, 1652, 1625, 1589	6.80-7.65 (m, C_6H_5 + CH), 7.7-7.9 (m, 4H ar + =CH), 8.80 (broad s, NH; disappears with deuterium oxide)

(a) From 95% ethanol. (b) From ethyl acetate. (c) Uv spectrum in ethanol changed with time (Figure 1), a fact that could be ascribed to a tautomerism involving structures such as 

See also the nmr spectrum, where the disappearance of a NH signal can be noted.

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