A Study on *m*-Chloroperbenzoic Acid and Lead Tetraacetate Oxidation of some 1-Aroyl-4,5-dihydro-4,4-dimethyl-5-methylene-1*H*-pyrazoles

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1-Aroyl-4,5-dihydro-5-methylene-1*H*-pyrazoles **1** are converted upon oxidation with *m*-chloroperbenzoic acid to the pyrazolones **2**. The same aroyl enamides **1** are also oxidized with LTA to form the acetoxy derivatives **7** and **8**. The reaction mechanisms are discussed.

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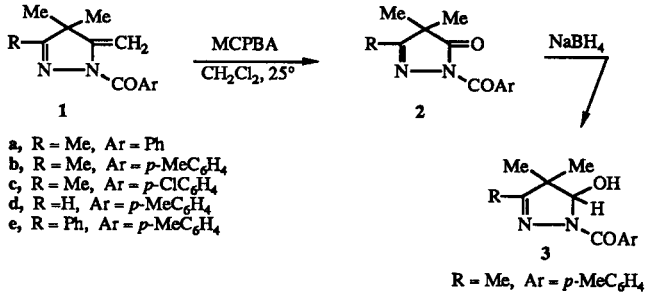
The reaction of the exomethylene double bond of heterocyclic compounds with peracids leading to the formation of epoxides [1,2,3] has been studied. On the other hand, attempted epoxidation with peracids of enol ethers [4,5] and enamides (acyl enamines) [6] usually results in bond cleavage. Lead tetraacetate has been reported to introduce a β-acetoxy group in steroidal enamides [7] with the reaction occuring through the diacetoxy derivative [8]. The lead tetraacetate oxidation of *N*-acylbenzylidene isoquinoline enamides has been studied extensively [9]. The obtained products are *Z*-β-acetoxy-substituted enamides, pyrazolones or benzoin esters depending on the solvent, the substitution on the benzylidene aromatic ring and on the type of carbonyl function in the enamide. Recently the LTA oxidative rearrangement of 1-methyleneisoquinoline enamides to 3-benzazepin-2-ones has been reported [10].

It looked therefore interesting to investigate the behaviour of the 1-aroyl-4,5-dihydro-5-methylene-1*H*-pyrazoles **1** towards peracids and LTA, due to the possibility of compounds **1** to behave either as heterocyclic compounds containing an exomethylene double bond or as pyrazole enamides.

When the 1-aroyl-5-methylene-4,5-dihydro-1*H*-pyrazoles **1a-e** were allowed to react with a large excess of *m*-chloroperbenzoic acid a product was isolated in good yield, whose analytical and spectral data (Table 1) corroborated with the structure of pyrazolone **2** (Scheme 1). Additional proof for the formation of pyrazolones **2** was the sodium borohydride reduction of **2b** to the hydroxy-derivative **3**. This hydroxy-derivative **3** was also independently isolated during the preparation of the unknown 4,5-dihydro-4,4-dimethyl-5-methylene-1-(*p*-toluoyl)-1*H*-pyrazole (**1d**), which was synthesized by the reaction of α-acetylisobutyralde-

Scheme 1



1

a, R = Me, Ar = Ph
b, R = Me, Ar = *p*-MeC$_6$H$_4$
c, R = Me, Ar = *p*-ClC$_6$H$_4$
d, R =H, Ar = *p*-MeC$_6$H$_4$
e, R = Ph, Ar = *p*-MeC$_6$H$_4$

2

3

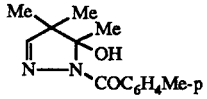
R = Me, Ar = *p*-MeC$_6$H$_4$

Table 1

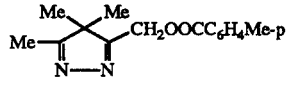
Physical, Spectral and Analytical Data for 1-Aroyl-4,4-dimethylpyrazolones 2

Compound	Yield %	Mp °C [a]	IR (Nujol) cm^{-1}		^{1}H-NMR (deuteriochloroform) ppm	Formula (Molecular Weight)	Analysis % Calcd./Found C	H	N	MS, m/e (Relative Intensity, %)
2a	33	61-63	1760	1690	1.27 (s, 6H, CMe_2), 2.08 (s, 3H, Me), 7.21-7.62 (m, 3H, ArH), 7.66-7.95 (m, 2H, ArH)	$C_{13}H_{14}N_2O_2$ (230.26)	67.81 67.85	6.13 6.02	12.17 12.10	230 (M^+, 13), 188 (7), 105 (100)
2b	38	107-109	1770	1680	1.31 (s, 6H, CMe_2), 2.08 (s, 3H, Me), 2.39 (s, 3H, p-Me), 7.22 (d, J = 8.5 Hz, 2H, ArH), 7.67 (d, J=8.5 Hz, 2H, ArH)	$C_{14}H_{16}N_2O_2$ (244.28)	68.83 69.08	6.60 6.68	11.43 11.33	244 (M^+, 89), 202 (10), 119 (100)
2c	48	95-97	1770 1760	1670	1.31 (s, 6H, CMe_2), 2.08 (s, 3H, Me), 7.40 (d, J=8.5 Hz, 2H, ArH), 7.74 (d, J=8.5 Hz, 2H, ArH)	$C_{13}H_{13}ClN_2O_2$ (264.71)	58.99 58.98	4.95 5.10	10.58 10.34	266/264 (M^+, 50), 224/222 (14) 141/139 (100)
2d	83	93-95	1775	1670	1.34 (s, 6H, CMe_2), 2.38 (s, 3H, p-Me), 7.37 (s, 1H, CH), 7.38 (d, J=8.5 Hz, 2H, ArH), 7.75 (d, J=8.5 Hz, 2H, ArH)	$C_{13}H_{14}N_2O_2$ (230.26)	67.81 67.92	6.13 6.16	12.17 12.02	230 (M^+, 15), 202 (4), 119 (87), 91 (100)
2e	75	155-157	1760 1740	1690	1.60 (s, 6H, CMe_2), 2.44 (s, 3H, p-Me), 7.28 (d, J=8.5 Hz, 2H, ArH), 7.38-7.52 (m, 3H, ArH), 7.70-7.94 (m, 4H, ArH)	$C_{19}H_{18}N_2O_2$ (306.35)	74.49 74.42	5.92 5.81	9.15 9.08	306 (M^+, 10), 119 (100), 91 (40)

[a] From ether-petroleum ether.



4

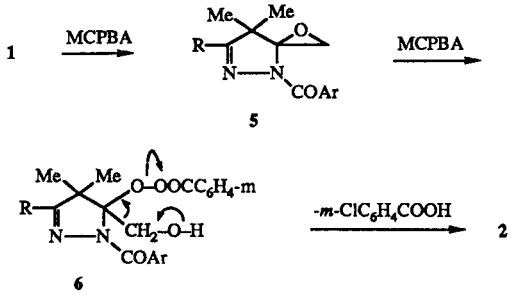


9

hyde with *p*-toluic hydrazide in boiling toluene, whereupon the two hydroxy-derivatives **3** and **4** were isolated in 9% and 33% respectively in addition to a small amount (2%) of **1d**. Thermolysis of **4** at 150° gave **1d** in 45% yield.

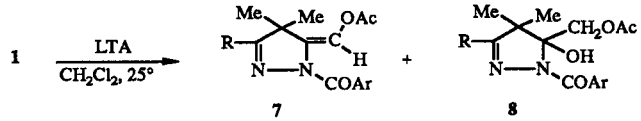
The formation of pyrazolones **2** can best be accomodated by a mechanism analogous to that already proposed for the oxidation of enamides [6] and enol ethers [5]. The initially formed epoxide **5** is opened by *m*-chloroperbenzoic acid to the perester **6** from which by fragmentation the pyrazolone **2** is formed (Scheme 2).

Scheme 2



Next the oxidation of the 1-aroyl-4,5-dihydro-5-methylene-1*H*-pyrazoles **1** with LTA was investigated (Scheme 3). Oxidation of **1a**, **1c** and **1d** in methylene chloride gave the β-acetoxy enamides **7a**, **7c** and **7d** and the 5-hydroxy-5-acetoxymethylpyrazoles **8a**, **8c** and **8d** respectively, whereas compound **1b** furnished the 5-hydroxy-5-acetoxymethylpyrazole **8b** as a sole product in almost quantitative yield.

Scheme 3



a, R = Me, Ar = Ph
b, R = Me, Ar = *p*-MeC_6H_4
c, R = Me, Ar = *p*-ClC_6H_4
d, R = H, Ar = *p*-MeC_6H_4
e, R = Ph, Ar = *p*-MeC_6H_4

Finally by the oxidation of the 3-phenyl-substituted compound **1e** the enamide **7e** was isolated along with the decomposition product 3,3-dimethyl-4-phenyl-2,4-butanedione.

However, when oxidation of **1b** was carried out in acetic acid in addition to **8b** a second product, identified through its spectral properties as the pyrazole **9** was isolated, whereas from the oxidation of **1a** and **1c** in acetic acid the same products, namely **7a** and **8a**, and **7c** and **8c**, were again isolated.

The analytical and spectral data of **7**, **8** and **9** are given in Table 2.

In many respects the LTA oxidation in methylene chloride of the enamides **1** described in this article resembles the LTA oxidation of the *N*-benzoylbenzylidene-isoquinoline enamides [9,10] and also of enol ethers and esters [11] which proceeds through diacetoxylation of the double bond (Scheme 4).

Scheme 4

So addition of LTA to the enamide double bond in **1** generates the organolead derivatives **10**, which can either be converted to the diacetoxy intermediate **11**, or fragmented to the carbonium ion **12**. From **11** by elimination

Scheme 4

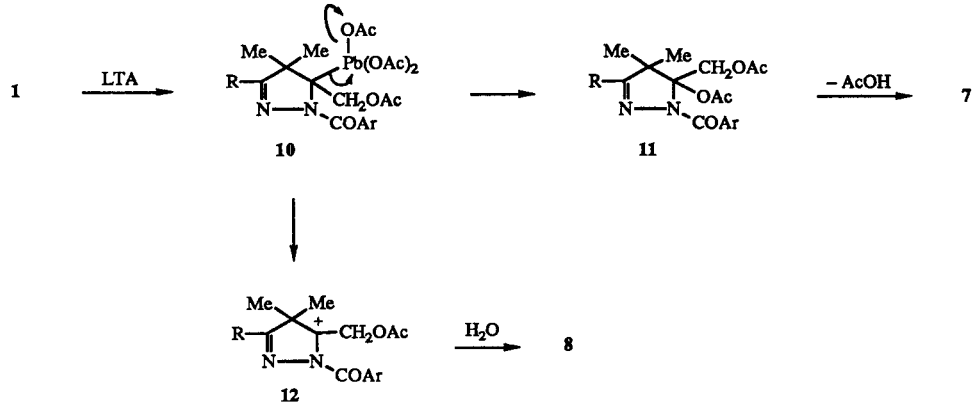


Table 2

Physical, Spectral and Analytical Data for Compounds 7, 8 and 9

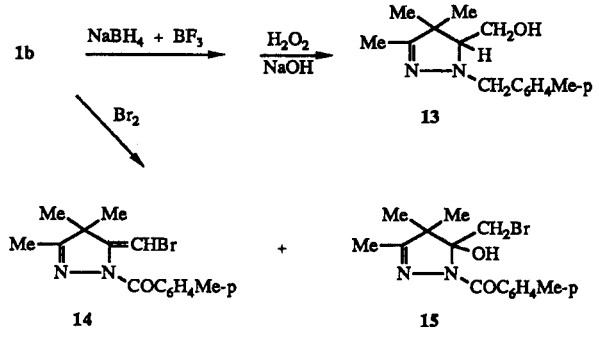
Compound	Yield %	Mp °C	IR (Nujol) cm^{-1}		^1H-NMR (deuteriochloroform) ppm	Formula (Molecular Weight)	Analysis % Calcd./Found C	H	N	MS, m/e (Relative Intensity, %)
7a	36	104-106 [a]	1770	1640	1.47 (s, 6H, CMe_2), 1.92 (s, 3H, Me), 2.18 (s, 3H, OOCMe), 7.21-7.58 (m, 3H, ArH), 7.67-7.88 (m, 2H, ArH), 8.74 (s, 1H, C=CH)	$C_{16}H_{18}N_2O_3$ (286.32)	67.11 67.31	6.34 6.51	9.78 9.88	286 (M^+,8), 244 (4), 227 (2), 105 (100)
7c	19	163-165 [a]	1760	1640	1.47 (s, 6H, CMe_2), 1.95 (s, 3H, Me), 2.19 (s, 6H, OOCMe), 7.35 (d, J = 10.0 Hz, 2H, ArH), 7.75 (d, J = 10.0 Hz, 2H, ArH), 8.73 (s, 1H, C=CH)	$C_{16}H_{17}ClN_2O_3$ (320.77)	59.91 60.11	5.34 5.48	8.73 8.87	322/320 (M^+,50), 280/278 (25), 263/261 (2) 141/139 (100)
7d	10	154-156 [a]	1750	1640	1.50 (s, 6H, CMe_2), 2.16 (s, 3H, OOCMe), 2.35 (s, 3H, p-Me), 7.19 (d, J = 9.0 Hz, 2H, ArH), 7.65 (d, J = 9.0 Hz, 2H, ArH), 8.73 (s, 1H, C=CH)	$C_{16}H_{18}N_2O_3$ (286.32)	67.11 67.31	6.34 6.22	9.78 9.63	286 (M^+,2), 227 (1), 119 (68) 91 (100)
7e	15	152-154 [a]	1750	1640	1.79 (s, 6H, CMe_2), 2.22 (s, 3H, OOCMe), 2.39 (s, 3H, p-Me), 7.12-7.47 (m, 5H, ArH), 7.67-7.95 (m, 4H, ArH), 8.82 (s, 1H, C=CH)	$C_{22}H_{22}N_2O_3$ (362.41)	72.91 72.75	6.12 6.01	7.73 7.89	362 (M^+,1), 303 (3), 119 (100)
8a	45	oil	3410 1630 [b]	1745	1.25 (s, 6H, CMe_2), 1.90 (s, 3H, Me), 2.04 (s, 3H, OOCMe), 4.64 (s, 2H, CH_2), 7.40-8.20 (m, 5H, ArH)	$C_{16}H_{20}N_2O_4$ (304.34)	63.14 63.39	6.62 6.45	9.21 9.39	304 (M^+,-), 231 (18), 105 (100)
8b	96	121-123 [c]	3480 1640	1730	1.22 (s, 6H, CMe_2), 1.91 (s, 3H, Me), 2.02 (s, 3H, OOCMe), 2.36 (s, 3H, p-Me), 4.62 (s, 2H, CH_2), 5.40 (br s, 1H, OH), 7.19 (d, J = 9.0 Hz, 2H, ArH), 7.73 (d, J = 9.0 Hz, 2H, ArH)	$C_{17}H_{22}N_2O_4$ (318.36)	64.13 64.15	6.97 6.88	8.80 8.70	318 (M^+,-), 245 (23), 119 (100)
8c	49	119-121 [c]	3410 1650	1740	1.21 (s, 6H, CMe_2), 1.90 (s, 3H, Me), 2.00 (s, 3H, OOCMe), 4.63 (s, 2H, CH_2), 5.36 (br s, 1H, OH), 7.34 (d, J = 10.0 Hz, 2H, ArH), 7.78 (d, J = 10.0 Hz, 2H, ArH)	$C_{16}H_{19}ClN_2O_4$ (338.78)	56.72 56.50	5.65 5.88	8.27 8.36	340/338 (M^+,0.5) 267/265 (66), 141/139 (100)
8d	17	88-90 [c]	3460 1640	1740	1.28 (s, 6H, CMe_2), 2.04 (s, 3H, OOCMe), 2.38 (s, 3H, p-Me), 4.58 (d, J = 12.0 Hz, 1H, CH_2), 4.78 (d, J = 12.0 Hz, 1H, CH_2), 6.71 (s, 1H, CH), 7.20 (d, J = 8.0 Hz, 2H, ArH), 7.68 (d, J = 8.0 Hz, 2H, ArH)	$C_{16}H_{20}N_2O_4$ (304.34)	63.14 63.28	6.62 6.50	9.21 9.00	304 (M^+,0.5), 231 (44), 119 (100)
9		[d]	1720		1.26 (s, 6H, CMe_2), 2.17 (s, 3H, Me), 2.40 (s, 3H, p-Me), 5.30 (s, 2H, CH_2), 7.23 (d, J = 8.0 Hz, 2H, ArH), 7.85 (d, J = 8.0 Hz, 2H, ArH)	$C_{15}H_{18}N_2O_2$ (258.31)		[d]		258 (M^+,12), 230 (3), 214 (12), 199 (6), 136 (27) 119 (100)

[a] From ether-petroleum ether. [b] Neat. [c] From ethanol. [d] Mp and elemental analysis not possible because of partial decomposition.

of acetic acid **7** is formed, whereas from **12** compound **8** is obtained. The possibility of formation of **8** by addition of water to the acetoxyenamide **7** was excluded by an independed experiment, whereupon **7** remained unchanged after standing in methylenechloride, ethanol, or ethanol-water solution.

Finally, the hydroboration of **1b** resulted to the reduction of the amide carbonyl and also to anti-Markownikoff water addition to the exomethylene double bond and the formation of the pyrazole derivative **13**, whereas by bromination the two monobromo derivatives **14** and **15**, parallels to **7** and **8** respectively, are formed (Scheme 5).

Scheme 5



In summary, the 5-methylene-1*H*-pyrazoles **1** behave as heterocyclic enamides by the oxidation with MCPBA and LTA. So the *m*-chloroperbenzoic acid oxidation of **1** instead of epoxidation results in bond cleavage and formation of pyrazolones **2**, whereas LTA oxidation leads to the formation of acetoxylated products. The LTA oxidations proceed through a common intermediate. Partitioning of this intermediate then leads to the observed products **7** and **8**.

EXPERIMENTAL

All melting points are uncorrected. The ir spectra were taken as nujol mulls on a Perkin-Elmer model 297 spectrometer. The ^{1}H-nmr spectra were recorded in deuteriochloroform on a Varian A 60-A (60 MHz) or on a Bruker AW 80 (80 MHz) spectrometer reported as δ value (ppm) relative to tetramethylsilane as an internal standard. Mass spectra were recorded at 70 eV on a Hitachi Perkin Elmer mass spectrometer. Analysis were performed with a Perkin Elmer 240 B analyser.

1-Aroyl-4,5-dihydro-3,4,4-trimethyl-5-methylene-1*H*-pyrazoles **1a-c** and 4,5-dihydro-4,4-dimethyl-5-methylene-3-phenyl-1-(*p*-toluoyl)-1*H*-pyrazole (**1e**) were prepared as described [12,13].

Reaction of α-Acetylisobutyraldehyde with *p*-Toluic Hydrazide.

To a solution of α-acetylisobutyraldehyde (1.14 g, 10 mmoles) in toluene (25 ml), *p*-toluic hydrazide (1.65 g, 11 mmoles) was added and the reaction mixture was refluxed for 5 hours. The solvent was then removed under vacuum and the residue was subjected to silica gel column chromatography. Elution with petroleum ether-ethyl acetate (5:1) gave in order of elution:

(a) 4,5-Dihydro-4,4-dimethyl-5-methylene-1-(*p*-toluoyl)-1*H*-pyrazole (**1d**).

Compound **1d** was obtained in 2% yield (50 mg) mp 101-103° (ether-*n*-hexane); ir (Nujol): ν 1665 (C=O) cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.26 (s, 6H, CMe_2) 2.37 (s, 3H, *p*-Me), 4.70 and 6.12 (two s, 2H, $C=CH_2$), 6.89 (s, 1H, 3-H), 7.20 (d, J = 9.0 Hz, 2H, ArH), 7.65 (d, J = 9.0 Hz, 2H, ArH); ms: (m/e) 228 (M$^+$, 8), 119 (100), 91 (31).

Anal. Calcd. for $C_{14}H_{16}N_2O$: C, 73.65; H, 7.06; N, 12.27. Found: C, 73.66; H, 6.92; N, 12.41.

(b) 4,5-Dihydro-5-hydroxy-4,4,5-trimethyl-1-(*p*-toluoyl)-1*H*-pyrazole (**4**).

This compound was obtained in 33% yield (850 mg) mp 130-132° (ethanol); ir (Nujol): ν 3420 (OH), 1640 (C=O) cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.15 and 1.22 (two s, 2 x 3H, CMe_2), 1.75 (s, 3H, 5-Me), 2.36 (s, 3H, *p*-Me), 3.73 (br s, 1H, OH), 6.73 (s, 1H, 3-H), 7.18 (d, J = 9.0 Hz, 2H, ArH), 7.70 (d, J = 9.0 Hz, 2H, ArH); ms: (m/e) 246 (M$^+$, 27), 119 (100), 91 (69).

Anal. Calcd. for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.36; N, 11.37. Found: C, 68.20; H, 7.18; N, 11.13.

(c) 4,5-Dihydro-5-hydroxy-3,4,4-trimethyl-1-(*p*-toluoyl)-1*H*-pyrazole (**3**).

This compound was obtained in 9% yield (210 mg) mp 109-111° (ethanol); ir (Nujol): ν 3250 (OH), 1630 (C=O) cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.11 and 1.19 (two s, 2 x 3H, CMe_2), 1.86 (s, 3H, 3-Me), 2.33 (s, 3H, *p*-Me), 4.86 (br s, 1H, OH), 5.61 (s, 1H, 5-H), 7.23 (d, J = 9.0 Hz, 2H, ArH), 7.81 (d, J = 9.0 Hz, 2H, ArH); ms: (m/e) 246 (M$^+$, 34), 119 (100), 91 (75).

Anal. Calcd. for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.36; N, 11.37; Found: C, 68.17; H, 7.11; N, 11.20.

Thermolysis of 4,5-Dihydro-5-hydroxy-4,4,5-trimethyl-1-(*p*-toluoyl)-1*H*-pyrazole (**4**) to 4,5-Dihydro-4,4-dimethyl-5-methylene-1-(*p*-toluoyl)-1*H*-pyrazole (**1d**).

A sample of **4** (246 mg, 1 mmole) was heated in an oil bath at 170° for 4 hours and was then subjected to column chromatography (silica gel, petroleum ether-ethyl acetate 7:1) to give the 5-methylene-1*H*-pyrazole **1d**, 103 mg (45%), mp 101-103° (ether-*n*-hexane).

General Procedure for MCPBA Oxidation of 1-Aroyl-4,5-dihydro-4,4-dimethyl-5-methylene-1*H*-pyrazoles **1**. Preparation of 1-Aroyl-4,5-dihydro-4,4-dimethyl-5-oxo-1*H*-pyrazoles **2**.

To a stirred suspension of *m*-chloroperbenzoic acid (12 mmoles) in methylene chloride (14 ml) a solution of the 5-methylenepyrazole **1** (4 mmoles) in methylene chloride (4 ml) was added at room temperature and the reaction mixture was stirred for 1 hour. During the course of the reaction MCPBA dissolved and the *m*-chlorobenzoic acid precipitated. This was then filtered off, the resulting solution was washed with 10% sodium bicarbonate, water and dried. The solvent was evaporated under vacuum and the residue was subjected to silica gel column chromatography. Elution with petroleum ether:ethyl acetate (5:1) gave products **2**. The results are summarized in Table 1.

Sodium Borohydride Reduction of 4,5-Dihydro-3,4,4-trimethyl-5-oxo-1-(*p*-toluoyl)-1*H*-pyrazole (**2b**).

Methanol (2 ml) was added dropwise at room temperature over a period of 3 hours to a stirred solution of the 5-oxopyrazole **2b** (122 mg, 0.5 mmole) and sodium borohydride (228 mg, 6 mmoles) in *t*-butyl alcohol (4 ml). After complete disappearance of the starting material, water (5 ml) was added and the reaction mixture was extracted with methylene chloride. The organic solution was dried (sodium sulfate) and evaporated under vacuum to give the 4,5-dihydro-5-hydroxy-3,4,4-trimethyl-1-(*p*-toluoyl)-1*H*-pyrazole (**3**) 63 mg (51%), mp 109-111° (ethanol).

General Procedure for LTA Oxidation of 1-Aroyl-4,5-dihydro-4,4-dimethyl-5-methylene-1*H*-pyrazoles **1** in Methylene Chloride.

The 5-methylenepyrazole **1** (1.0 mmole) was dissolved in methylene chloride (30 ml). To this solution dry LTA (488 mg) was added and the mixture was stirred at room temperature for 2 hours. The reaction mixture was diluted with water and then extracted with methylene chloride. The organic layer was washed with dilute sodium bicarbonate, dried (sodium sulfate) and the solvent was evaporated. The residue was subjected to silica gel column chromatography using as elution solvents petroleum ether-ethyl acetate 5:1. The 5-(acetoxymethylene)-1-aroyl-4,5-dihydro-4,4-dimethyl-1*H*-pyrazole (**7**) was eluted first and the 5-acetoxymethyl)-1-aroyl-4,5-dihydro-5-hydroxy-4,4-dimethyl-1*H*-pyrazole (**8**) was eluted second.

General Procedure for the Lead Tetraacetate Oxidation 4,5-Dihydro-4,4-dimethyl-5-methylene-1-phenyl-1*H*-pyrazole (**1a**) in Acetic Acid.

Dry lead tetraacetate (2.4 mmoles) was suspended in acetic acid (15 ml). The 5-methylenepyrazole **1a** (2.0 mmoles) was then added to this magnetically stirred suspension and the reaction

mixture was stirred at room temperature for 3 hours during which time a clear dark red solution resulted. The solution was diluted with water and then extracted with methylene chloride. The extracts were washed with sodium bicarbonate solution, dried (sodium sulfate) and the solvent was evaporated under vacuum. The residue was chromatographed (silica gel, petroleum ether-ethyl acetate 5:1) to give **7a** in 40% yield and **8a** in 14% yield.

Lead Tetraacetate Oxidation of **1b** in Acetic Acid.

The procedure described above was followed to give **8b** in 17% yield and **9** in 30% yield.

Lead Tetraacetate Oxidation of **1c** in Acetic Acid.

The procedure described above was followed to give **7c** in 35% yield and **8c** in 11% yield.

Hydroboration Oxidation of **1b**.

To a magnetically stirred mixture of **1b** (100 mg, 0.4 mmole) and sodium borohydride (38 mg, 1 mmole) in diglyme (1 ml) a solution of boron trifluoride etherate (0.11 ml) in diglyme (1 ml) was added dropwise under nitrogen over a period of 1.5 hours at room temperature. The mixture was made basic with sodium hydroxide (6 *N*, 1 ml), oxidized at 50-64° with hydrogen peroxide (30%, 0.1 ml) and acidified with hydrochloric acid. The reaction mixture was extracted with dichloromethane, the solvent was evaporated and the residue was subjected to alumina column chromatography using as elution solvents petroleum ether-ethyl acetate 4:1 to give 4,5-dihydro-5-hydroxymethyl-3,4,4-trimethyl-1-(4-methylbenzyl)-1*H*-pyrazole (**13**), 53 mg (52%), oil; ir (Nujol): ν 3300 (OH) cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 0.97 and 1.05 (two s, 2 x 3H, CMe_2), 1.79 (s, 3H, Me-C=N), 2.29 (s, 3H, *p*-Me), 2.73 (t, J = 5.0 Hz, 1H, CH), 2.80 (br s, 1H, OH), 3.64 (d, J = 5.0 Hz, 2H, CH_2), 4.12 (s, 2H, NCH_2), 7.10 (d, J = 9.0 Hz, 2H, ArH), 7.23 (d, J = 9.0 Hz, 2H, ArH); ms: (m/e) 246 (M^+, 30), 215 (100).

Anal. Calcd. for $C_{15}H_{22}N_2O$: C, 73.13; H, 9.00: N, 11.37. Found: C, 73.31; H, 8.88; N, 11.19.

Bromination of **1b**.

To a magnetically stirred solution of **1b** (1 g, 4 mmoles) in carbon tetrachloride (25 ml) of a solution of bromine (0.2 ml) in carbon tetrachloride (5 ml) was added at 0° and the reaction mixture was stirred for 30 minutes. The solvent was evaporated and the remainder was subjected to silica gel column chromatography. Elution with petroleum ether-ethyl acetate (15:1) gave in order of elution:

(a) 5-(Bromomethylene)-4,5-dihydro-3,4,4-trimethyl-1-(*p*-toluoyl)-1*H*-pyrazole (**14**).

This compound was obtained in 8% yield (95 mg) mp 126-128°; ir (Nujol): ν 1640 (C=O) cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.53 (s, 6H, CMe_2), 1.87 (s, 3H, Me-C=N), 2.36 (s, 3H, *p*-Me), 7.16 (d, 2H, J = 9.0 Hz, ArH), 7.64 (d, 2H, J = 9.0 Hz, ArH), 7.73 (s, 1H, CHBr); ms: (m/e) 322/320 (M^+, 10), 241 (100).

Anal. Calcd. for $C_{15}H_{17}BrN_2O$: C, 56.09; H, 5.33; N, 8.72. Found: C, 56.20; H, 5.22; N, 8.85.

(b) 5-(Bromomethyl)-4,5-dihydro-5-hydroxy-3,4,4-trimethyl-1-(*p*-toluoyl)-1*H*-pyrazole (**15**).

This compound was obtained in 55% yield (750 mg) mp 112-114°; ir (Nujol): ν 3440 (OH), 1630 (C=O) cm^{-1}; ^{1}H-nmr (deuteriochloroform): 1.20 and 1.41 (two s, 2 x 3H, CMe_2), 1.95 (s, 3H, Me-C=N), 2.34 (s, 3H, *p*-Me), 3.90 (d, 1H, J = 11.0 Hz, CH_2), 4.04 (d, 1H, J = 11.0 Hz, CH_2), 4.68 (br s, 1H, OH), 7.23 (d, 2H, J = 9.0 Hz, ArH), 7.79 (d, 2H, J = 9.0 Hz, ArH); ms: (m/e) 340/338 (M^+, 6), 245 (33), 119 (100).

Anal. Calcd. for $C_{15}H_{19}BrN_2O_2$: C, 53.11; H, 5.64; N, 8.26. Found: C, 53.35; H, 5.59; N, 8.35.

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