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Received February 20, 1996

The reactions of 1,1-disubstituted ethenes with 2,4-pentanedione in the presence of manganese(III) acetate and atmospheric oxygen yielded 4-acetyl-6,6-diaryl-3-methyl-1,2-dioxan-3-ols. The latter gave 4-(2-hydroperoxy-2,2-diarylethyl)-3,5-dimethylpyrazoles by the reaction with hydrazines in methanol-acetic acid (1:1 v/v) at 50° in 15-77% yields, or 4-(2-hydroxy-2,2-diarylethyl)-3,5-dimethylpyrazoles by the reaction with hydrazines in methanol in 2-78% yields. The acid-catalyzed reaction of 4-(2-hydroperoxy-2,2-diarylethyl)-3,5-dimethylpyrazoles yielded 4-(aroylmethyl)-3,5-dimethylpyrazoles (15-55%) and 4-(2,2-diarylethyl)-3,5-dimethylpyrazoles (9-29%).

J. Heterocyclic Chem., 33, 1291 (1996).

Introduction.

We recently reported the manganese(II) or manganese(III) acetate-mediated free-radical cyclization of alkenes with 1,3-diones [1-3], acetoacetamides [1,4], or β -keto esters [5] and atmospheric oxygen that gave 1,2-dioxan-3-ols in good yields. It was also found that the reaction of alkenes with barbituric acid and oxygen in the presence of manganese(II) acetate gave 5,5-bis(2-hydroperoxyalkyl)barbituric acid [6]. We have been interested in the formation of compounds bearing a hydroperoxyl group since a 2-hydroperoxy-2,2-diarylethyl group has a potential utility of forming carbonyl groups by the acid-catalyzed reaction. In fact, the acid-catalyzed decomposition of 6-aryl-1,2-dioxan-3-ols yielded substituted furans which could be formally derived *via* 1,4-dicarbonyl compounds [7]. 4-Acetyl-6,6-diaryl-3-methyl-1,2-dioxan-3-ols have a partial ketal structure of 1,3-dicarbonyl moiety

that can be transformed into a pyrazole ring bearing a 2-hydroperoxy-2,2-diarylethyl group as a substituent by the reaction with hydrazine and hydrazine derivatives. Pyrazoles have attracted attention because of their bacteriostatic, bacteriocidal, and fungicidal properties [8-13]. We describe the facile syntheses of 4-(2-hydroperoxyethyl)-3,5-dimethylpyrazoles and 4-(2-hydroxyethyl)-3,5-dimethylpyrazoles by the reactions of 4-acetyl-6-aryl-3-methyl-1,2-dioxan-3-ols with hydrazine, and hydrazine derivatives in this paper.

Results and Discussion.

Preparations of 4-(2-Hydroperoxy-2,2-diarylethyl)-3,5-dimethylpyrazoles **3** and 4-(2-Hydroperoxy-2,2-diarylethyl)-3,5-dimethylisoxazoles **7**.

When the reaction of 4-acetyl-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (**1a**) with methylhydrazine (**2a**) was carried out in acetic acid at 50°, the products were 4-(2-hydro-

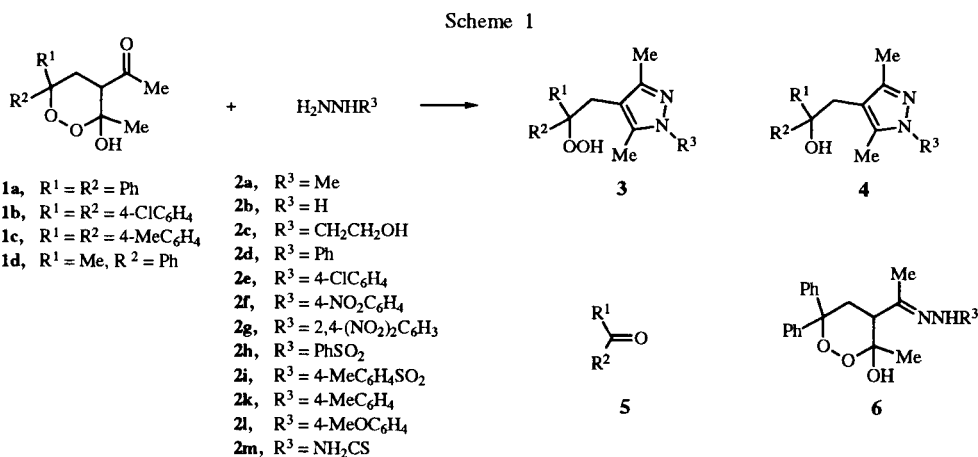


Table 1
Reaction of 4-Acetyl-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (**1a**) with Methylhydrazine (**2a**)

| Entry | Molar ratio [a] | Solvent | Temp °C | Time hours | Product composition (yield/%) [b] | | | |
|-------|-----------------|----------------|---------|------------|-----------------------------------|------------|------------|-----------|
| | | | | | 1a | 3aa | 4aa | 5a |
| 1 | 1:2 | AcOH | 50 | 4 | 25 | 52 | | 18 |
| 2 | 1:2 | MeOH | 50 | 4 | | | 74 | 16 |
| 3 | 1:2 | MeCN | 60 | 4 | | 17 | 67 | 9 |
| 4 | 1:1 | MeOH:AcOH(1:1) | 50 | 4 | 51 | 40 | | 6 |
| 5 | 1:2 | MeOH:AcOH(1:1) | 50 | 3 | 22 | 66 | | 9 |
| 6 | 1:2 | MeOH:AcOH(1:1) | 40 | 4 | 37 | 45 | | 5 |
| 7 | 1:2 | MeOH:AcOH(1:1) | 50 | 4 | 6 | 73 | | 8 |
| 8 | 1:2 | MeOH:AcOH(1:1) | 60 | 4 | | 59 | | 26 |
| 9 | 1:2 | MeOH:AcOH(1:1) | 50 | 5 | | 77 | | 11 |
| 10 | 1:2 | MeOH:AcOH(1:1) | 50 | 6 | | 67 | | 14 |
| 11 | 1:3 | MeOH:AcOH(1:1) | 50 | 4 | | 68 | | 13 |
| 12 | 1:2 | MeOH:AcOH(9:1) | 50 | 4 | | 50 | 35 | 7 |
| 13 | 1:2 | MeOH:AcOH(1:9) | 50 | 4 | 33 | 47 | | 9 |

[a] **1a**:**2a**. [b] Isolated yield (based on 1,2-dioxan-3-ol **1a** used).

peroxy-2,2-diphenylethyl)-1,3,5-trimethylpyrazole (**3aa**) and benzophenone (**5a**) (Scheme 1 and Table 1, entry 1). The reaction was also conducted in methanol, but it gave 4-(2-hydroxy-2,2-diphenylethyl)-1,3,5-trimethylpyrazole (**4aa**) (entry 2). When acetonitrile was used as a solvent, it yielded a mixture of **3aa** and **4aa** (entry 3). It was found that a mixed solvent of acetic acid and methanol is the best for the formation of **3aa**.

Yields of **3aa** varied depending on the molar ratio of **1a**:**2a**. The maximum yield for **3aa** was attained when the molar ratio was 1:2 (entry 9). The yields were also dependent on the reaction temperature and reaction time, for which we found that the reaction temperature of 50° and the reaction time of 5 hours were satisfactory because higher temperature and prolonged reaction time reduced the yields (entries 8, 10).

The structures of the products were determined on the basis of ¹H nmr, ¹³C nmr, ir spectra, and elemental analyses. The ¹³C nmr spectrum of **3aa** in deuteriochloroform showed methyl carbon signals at $\delta = 35.5, 11.3, \text{ and } 9.2$, a methylene carbon at $\delta = 31.3$, a quaternary carbon bearing a hydroperoxy group at $\delta = 89.8$, and aromatic and other sp² carbons at $\delta = 144.7, 143.2, 138.9, 128.0, 127.7, 127.3, \text{ and } 110.3$. The signal at $\delta = 89.8$ is characteristic to all 4-(2-hydroperoxy-2,2-diaryethyl)-3,5-dimethylpyrazoles.

Then, the generality of the reactions were examined by using hydrazine (**2b**), (2-hydroxyethyl)hydrazine (**2c**), phenylhydrazine (**2d**), (4-chlorophenyl)hydrazine (**2e**), (4-nitrophenyl)hydrazine (**2f**), (2,4-dinitrophenyl)hydrazine (**2g**), phenylsulfonylhydrazide (**2h**), 4-methylphenylsulfonylhydrazide (**2i**), hydroxylamine (**2j**), 4-acetyl-6,6-bis(4-chlorophenyl)-3-methyl-1,2-dioxan-3-ol (**1b**), 4-acetyl-6,6-bis(4-methylphenyl)-3-methyl-1,2-dioxan-3-ol (**1c**), and 4-acetyl-3,6-dimethyl-6-phenyl-1,2-dioxan-3-ol (**1d**) (Table 2). The reaction of **1a** with **2f** afforded **3af** together with a hydrazone **6af**, while the reaction of **1a** and

2g gave the corresponding hydrazone **6ag** alone (entries 18, 19). The reactions of **1a**, **1b**, and **1c** with phenylhydrazine (**2d**) were carried out in methanol at room temperature that gave better yields for **3** (entries 16, 24, 27).

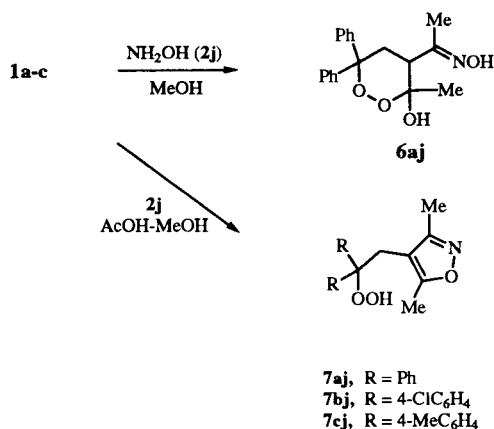
When the reactions of **1a** with hydrazines bearing the electron-donating substituent such as 4-methylphenyl- (**2k**) and 4-methoxyphenyl group (**2l**) were examined, they did not give hydroperoxides, but yielded 4-(2-hydroxy-2,2-diphenylethyl)-3,5-dimethylpyrazoles

Table 2
Reaction of 4-Acetyl-6,6-diaryl-3-methyl-1,2-dioxan-3-ols **1a-c** with Hydrazines **2a-i** or Hydroxylamine (**2j**) [a]

| Entry | Substrate | Reagent | Product (yield/%) [b] | |
|--------|-----------|-----------|-----------------------|-----------------|
| 9 | 1a | 2a | 3aa (77) | 5a (11) |
| 14 | 1a | 2b | 3ab (77) | |
| 15 | 1a | 2c | 3ac (68) | |
| 16 [c] | 1a | 2d | 3ad (55) | |
| 17 | 1a | 2e | 3ae (15) | |
| 18 | 1a | 2f | 3af (58) | 6af (42) |
| 19 | 1a | 2g | | 6ag (50) |
| 20 | 1a | 2h | 3ah (63) | |
| 21 | 1a | 2i | 3ai (70) | |
| 22 | 1b | 2a | 3ba (55) | |
| 23 | 1b | 2b | 3bb (76) | |
| 24 [c] | 1b | 2d | 3bd (47) | |
| 25 | 1c | 2a | 3ca (64) | |
| 26 | 1c | 2b | 3cb (61) | |
| 27 [c] | 1c | 2d | 3cd (52) | |
| 28 | 1d | 2a | 3da (77) | |
| 29 [d] | 1a | 2j | | 6aj (67) |
| 30 | 1a | 2j | | 7aj (68) |
| 31 | 1b | 2j | | 7bj (60) |
| 32 | 1c | 2j | | 7cj (72) |

[a] The reaction was carried out in methanol-acetic acid (1:1 v/v) at a molar ratio of **1a**:**2** = 1:2 at 50° for 5 hours unless otherwise stated. [b] Isolated yield (based on the amount of **1** used). [c] The reaction was carried out in methanol at 23° for 5 hours. [d] The reaction was carried out in methanol at 50° for 4 hours.

Scheme 2



(*vide infra*). It was demonstrated that the change of solvent system has again a remarkable effect on the reaction product: in methanol the reaction of **1a** with hydroxylamine (**2j**) gave an oxime **6aj** (entry 29), but the reaction product from **1a** and **2j** in acetic acid-methanol was 4-(2-hydroperoxy-2,2-diphenylethyl)-3,5-dimethylisoxazole (**7aj**). The reactions of **1b** and **1c** similarly yielded the corresponding isoxazoles **7bj** and **7cj**, respectively (Scheme 2 and entries 30-32).

Preparation of 4-(2-Hydroxy-2,2-diarylethyl)-3,5-dimethylpyrazoles **4**.

When the reaction of **1a** with **2a** was carried out in methanol at 50°, the major product was found to be 4-(2-hydroxy-2,2-diphenylethyl)-1,3,5-trimethylpyrazole (**4aa**) (entry 2), indicating that the reduction of the hydroperoxyl group occurred. The yields did not vary much under the reaction conditions except for the molar ratio of **1a:2a** for which the ratio of 1:2 was found to be the best.

The structure of **4aa** was again determined by ¹³C nmr. The spectrum exhibited a signal at $\delta = 77.8$ due to the sp³ carbon bearing the hydroxyl group that is characteristic to all other 4-(2-hydroxy-2,2-diarylethyl)-3,5-dimethylpyrazoles.

The reaction was examined for other hydrazines **2b-f**, **h**, **i**, and **k-m**, hydroxylamine (**2j**), and also for 4-acetyl-6,6-bis(4-chlorophenyl)-3-methyl-1,2-dioxan-3-ol (**1b**) and 4-acetyl-6,6-bis(4-methylphenyl)-3-methyl-1,2-dioxan-3-ol (**1c**). The reaction of **1a** with **2b** gave 4-(2-hydroperoxy-2,2-diphenylethyl)-3,5-dimethylpyrazole (**3ab**) in the reactions both in methanol and in boiling ethanol. With hydrazines **2d** and **2e** the reactions of **1a** yielded a mixture of **3** and **4** even in the reaction in boiling ethanol (Table 3, entries 38, 39), while the reactions of **1a** with **2h** and **2i** gave only **3ah** and **3ai**, respectively, in poor yields (entries 41, 42). The reaction of **1a** with **2l** did not give the product in the reaction in methanol at 50°, but it yielded the corresponding alcohol **4al** in boiling ethanol (entry 44). The reactions of (4-nitrophenyl)hydrazine (**2f**) and (2,4-dinitrophenyl)hydrazine (**2g**) with **1a** gave intractable mixtures under forcing reaction conditions, and were not further examined.

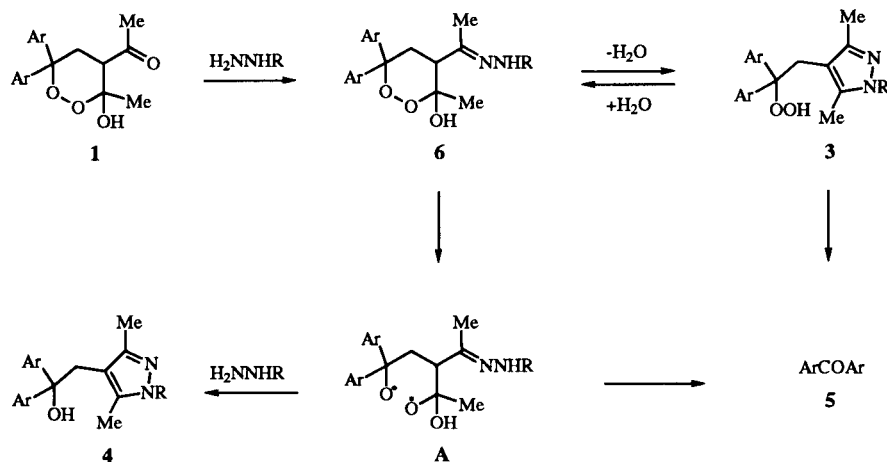
Table 3

Reactions of 4-Acetyl-6,6-diaryl-3-methyl-1,2-dioxan-3-ols **1a-c**, 4-(2-Hydroperoxy-2,2-diphenylethyl)-1,3,5-trimethylpyrazole (**3aa**), and 3-Methyl-4-[1-(4-nitrophenylhydrazono)ethyl]-6,6-diphenyl-1,2-dioxan-3-ol (**6af**) with Hydrazines **2** [a]

| Entry | Substrate | Reagent | Solvent | Temp °C | Time hours | Product (yield/%) [b] |
|-------|------------|-----------|---------|---------|------------|--|
| 2 | 1a | 2a | MeOH | 50 | 4 | 4aa (74) 5a (16) |
| 33 | 1a | 2b | MeOH | 50 | 4 | 3ab (52) 5a (15) |
| 34 | 1a | 2b | EtOH | reflux | 1 | 3ab (50) |
| 35 | 1a | 2c | MeOH | 50 | 3 | 4ac (67) 5a (16) |
| 36 | 1a | 2c | MeOH | 50 | 4 | 4ac (78) 5a (20) |
| 37 | 1a | 2c | MeOH | 50 | 5 | 4ac (72) 5a (25) |
| 38 | 1a | 2d | EtOH | reflux | 0.5 | 3ad (26) 4ad (47) [c] 5a (11) |
| 39 | 1a | 2e | EtOH | reflux | 0.5 | 3ae (15) 4ae (29) 5a (40) |
| 40 | 1a | 2f | EtOH | reflux | 2 | 4af (2) 5a (20) 6af (33) |
| 41 | 1a | 2h | PrOH | reflux | 2.5 | 3ah (10) |
| 42 | 1a | 2i | EtOH | reflux | 3 | 3ai (30) |
| 43 | 1a | 2k | MeOH | 50 | 1 | 4ak (50) 5a (13) |
| 44 | 1a | 2l | EtOH | reflux | 0.5 | 4al (32) 5a (23) |
| 45 | 1a | 2m | EtOH | reflux | 3 | 4ab (36) 5a (15) 4am (26) |
| 46 | 1b | 2a | MeOH | 50 | 4 | 4ba (60) 5b (30) |
| 47 | 1b | 2c | MeOH | 50 | 4 | 4bc (64) 5b (24) |
| 48 | 1c | 2a | MeOH | 50 | 4 | 4ca (72) 5c (19) |
| 49 | 1c | 2c | MeOH | 50 | 4 | 4cc (74) 5c (14) |
| 50 | 3aa | 2a | MeOH | reflux | 2 | 4aa (14) 5a (75) |
| 51 | 6af | 2a | EtOH | reflux | 5 | 4af (17) 5a (20) |

[a] The reaction was carried out at a molar ratio of the substrate: **2** = 1:2. [b] Isolated yield (based on the amount of **1**, **3aa**, or **6af** used). [c] Calculated from ¹H nmr.

Scheme 3



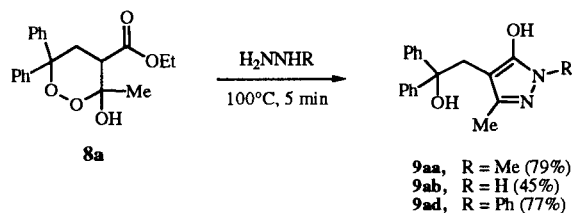
It is interesting to note that the reaction of **1a** with thiosemicarbazide (**2m**) gave 4-(2-hydroxy-2,2-diphenylethyl)-3,5-dimethylpyrazole (**4ab**) and 1-aminothiocarbonyl-4-(2-hydroxy-2,2-diphenylethyl)-3,5-dimethylpyrazole (**4am**). The product **4ab** was formed with a loss of an aminothiocarbonyl group (entry 45). As the reactions of **1a** with **2b** yielded only the hydroperoxide **3ab** both in methanol at 50° and in boiling ethanol (entries 33, 34), the reaction of **1a** with **2m** is useful for synthesizing **4ab**.

It is known that when hydrazines are warmed with hydroperoxides rapid decomposition of the hydroperoxides occurs to provide the corresponding alcohols [14]. However, when **3aa** was warmed with **2a** in methanol at 50°, **3aa** was recovered quantitatively. After being heated in the presence of **2a** in boiling methanol for 2 hours, **3aa** afforded **4aa** (14%) and **5a** (75%) (entry 50). The formation of a large amount of **5a** may indicate that the reaction pathway from **3aa** to **4aa** is not likely to be important, but the thermal decomposition of a hydrazone **6** leads to a cleavage of the oxygen-oxygen bond forming a radical such as **A** which is either reduced to **4** or further decomposed to give **5** (Scheme 3). It was observed that when compound **6af** was dissolved in deuteriochloroform for measuring the nmr spectra, it gradually changed to the spectrum of a mixture of **6af** and **3af**. This showed that **6af** and **3af** are in equilibrium. When **6af** was treated with hydrazine in boiling ethanol, **4af** was obtained (entry 51). These observations could support our proposed mechanism for the formation of **3** and **4** as shown in Scheme 3. As it was previously reported that triphenylphosphine reduced **1a** to give 3-acetyl-2-methyl-5,5-diphenyl-4,5-dihydrofuran [2], the reactions of **3ab** and **3af** with this reagent in diethyl ether gave **4ab** (23%) and **4af** (80%) together with **5a** (75 and 11%), respectively.

Preparation of 4-(2-Hydroxy-2,2-diphenylethyl)-3-methyl-1-phenyl-5-pyrazolones **9**.

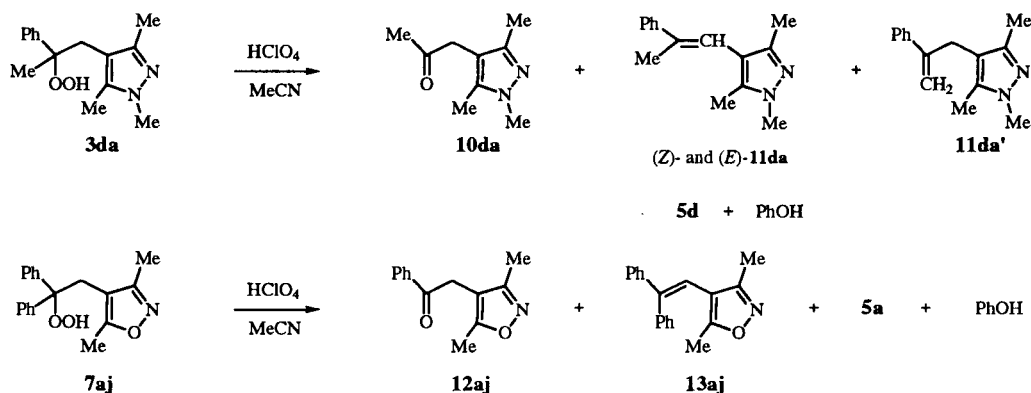
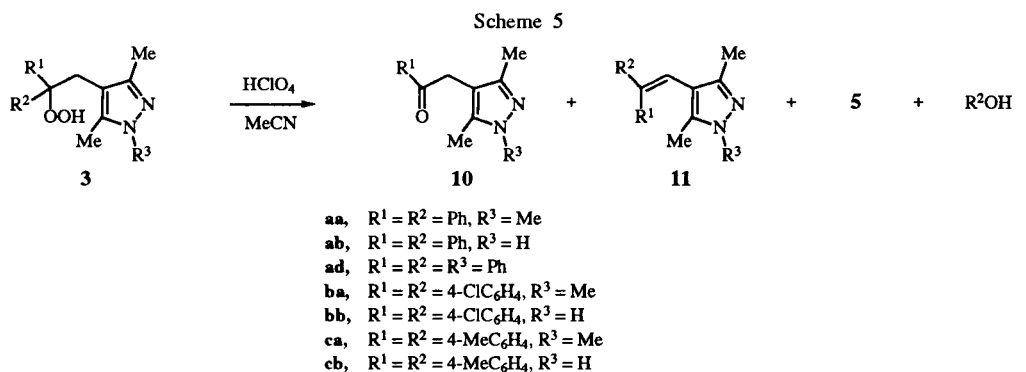
It is known that β -keto esters are also reactive towards hydrazines and give 2-pyrazolin-5-one derivatives [15], therefore, the reaction of 1,2-dioxane-3-ol bearing an ester function at the C-4 position was examined. The reaction of ethyl 3-hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate (**8a**) with phenylhydrazine (**2d**) at room temperature gave no products, but the reaction at 100° without solvent yielded 4-(2-hydroxy-2,2-diphenylethyl)-3-methyl-1-phenyl-5-pyrazolone (**9ad**) (Scheme 4). The ir spectrum of **9ad** showed a broad absorption at $\nu = 3000 \text{ cm}^{-1}$, but no carbonyl absorption at a region of $\nu = 1600\text{--}1700 \text{ cm}^{-1}$, indicating that the compound could be of an enol form. The structure was confirmed on comparison with the ^{13}C nmr spectra of **9ad** and an authentic sample of 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone. The latter showed a similar spectrum to that of **9ad** as to the 5-pyrazolone rings. The ir spectrum of 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone also showed only one hydrogen bonded carbonyl absorption at $\nu = 1606 \text{ cm}^{-1}$.

Scheme 4



Similarly, methylhydrazine (**2a**) and hydrazine (**2b**) were also allowed to react with **8a** at 100° that gave the corresponding 5-pyrazolones **9aa** and **9ab**, respectively.

The Acid-Catalyzed Decomposition of 4-(2-Hydroperoxy-2,2-diarylethyl)-3,5-dimethylpyrazoles **3** and 4-(2-Hydroperoxy-2,2-diphenylethyl)-3,5-dimethylisoxazole (**7aj**).



We reported that the treatment of 4-acetyl-6-aryl-3-methyl-1,2-dioxan-3-ols with strong acid yielded substituted furans [7]. It seems that the hydroperoxyl group at benzylic position facilitates a facile aryl migration from carbon to oxygen giving a carbonyl compound and a phenol. When **3aa** was treated with perchloric acid in acetonitrile, three products were obtained: benzophenone (**5a**), 4-(benzoylmethyl)-1,3,5-trimethylpyrazoles (**10aa**)

and 1,3,5-trimethyl-4-(2,2-diphenylethenyl)pyrazoles (**11aa**) (Scheme 5 and Table 4). The reaction was examined by changing the molar ratio of substrate and perchloric acid as well as the reaction time and the reaction temperature to achieve complete conversion of the substrate. The optimum yields of **10aa** and **11aa** were attained when the reaction was performed at the 1:2 molar ratio of the substrate and perchloric acid heating under reflux for 30

Table 4

Acid-Catalyzed Decomposition of 4-(2-Hydroperoxy-2,2-diarylethyl)-3,5-dimethylpyrazoles **3** and 4-(2-Hydroperoxy-2,2-diphenylethyl)-3,5-dimethylisoxazole (**7aj**) [a]

| Entry | Substrate | Molar ratio [b] | Temp °C | Time hours | Recovered 3/% | Product (yield/%) [c] | | |
|-------|------------|-----------------|---------|------------|---------------|-----------------------|------------------|---------------------|
| 52 | 3aa | 1:2 | 50 | 0.5 | 37 | 5a (9) | 10aa (28) | 11aa (15) |
| 53 | 3aa | 1:2 | 50 | 2 | 22 | 5a (12) | 10aa (42) | 11aa (21) |
| 54 | 3aa | 1:2 | reflux | 0.5 | | 5a (9) | 10aa (49) | 11aa (27) |
| 55 | 3aa | 1:4 | 50 | 2 | 9 | 5a (21) | 10aa (46) | 11aa (21) |
| 56 | 3aa | 1:6 | 50 | 2 | | 5a (30) | 10aa (49) | 11aa (14) |
| 57 | 3aa | 1:8 | 50 | 2 | | 5a (13) | 10aa (41) | 11aa (14) |
| 58 | 3ab | 1:2 | reflux | 0.5 | | 5a (47) | 10ab (15) | 11ab (27) |
| 59 | 3ad | 1:2 | reflux | 0.5 | | 5a (9) | 10ad (55) | 11ad (29) |
| 60 | 3ba | 1:2 | reflux | 0.5 | | 5b (22) | 10ba (40) | 11ba (13) |
| 61 | 3bb | 1:2 | reflux | 0.5 | | 5b (19) | 10bb (27) | |
| 62 | 3ca | 1:2 | reflux | 0.5 | | 5c (14) | 10ca (54) | 11ca (28) |
| 63 | 3cb | 1:2 | reflux | 0.5 | | 5c (25) | 10cb (27) | 11cb (29) |
| 64 | 3da | 1:2 | 50 | 1.5 | | 5d (13) | 10da (42) | 11da (9) [d] |
| 65 | 7aj | 1:2 | reflux | 0.5 | | 5a (13) | 12aj (52) | 13aj (27) |

[a] The reaction was carried out in acetonitrile. [b] The substrate: perchloric acid. [c] Isolated yield (based on the amount of pyrazole **3** or **7aj** used). [d] A mixture of (Z)- and (E)-**11da** and **11da'** in a molar ratio of 1:1.7 based on ¹H nmr.

minutes (entry 54). In the reactions at a higher acid concentration and prolonged reaction time the ratio of **10aa** and **11aa** was improved in favor of **10aa**, but it gave a considerable amount of benzophenone (**5a**) in the expense of **11aa** (entries 53, 55-57). The acid catalyzed decomposition of other 4-(2-hydroperoxy-2,2-diarylethyl)-3,5-dimethylpyrazoles **3** were examined and the results are listed in Table 4. Phenols were also obtained in the reaction, but their yields were not listed in the Table because of its considerable loss during the work-up procedure. The reaction of **3da** with perchloric acid gave acetophenone (**5d**), 1,3,5-trimethyl-4-(2-oxopropyl)pyrazole (**10da**), (*Z*)- and (*E*)-1,3,5-trimethyl-4-(2-phenyl-1-propenyl)pyrazole (**11da**) and 1,3,5-trimethyl-4-(2-phenyl-2-propenyl)pyrazole (**11da'**). The presence of **10da** in the products indicates that the phenyl group preferentially migrated during the acid-catalyzed decomposition (entry 64). Products **11da** and **11da'** could not be separated. The ¹H nmr spectrum of the mixture exhibited the presence of a methylene group (=CH₂) at δ = 4.83 and 5.33, and a vinylic hydrogen at δ = 6.57. Gas chromatography of the mixture showed three peaks all having the same molecular ions (m/z = 226) and the same fragmentation patterns in their mass spectra.

The acid-catalyzed decomposition of **7aj** also yielded 4-(benzoylmethyl)-3,5-dimethylisoxazole (**12aj**) and 3,5-dimethyl-4-(2,2-diphenylethyl)isoxazole (**13aj**) in moderate yields (Entry 65).

In conclusion, convenient preparations of 4-(2-hydroperoxy-2,2-diarylethyl)-3,5-dimethylpyrazoles, 4-(2-hydroxy-2,2-diarylethyl)-3,5-dimethylpyrazoles, and 4-(aroylmethyl)-3,5-dimethylpyrazoles from readily available materials are reported. The reactions are easily carried out giving products in moderate yields and should be applicable to the other classes of heterocycles.

EXPERIMENTAL

Measurements.

All of the ¹H and ¹³C nmr spectra were taken with a JNM PMX-60SI (60 MHz) and a JNM EX-90FT nmr (90 MHz for ¹H and 22.5 MHz for ¹³C) spectrometer with tetramethylsilane being used as the internal standard. Chemical shifts are shown in δ values (ppm). The ir spectra were measured on a JASCO A-102 ir spectrometer and expressed in ν values (cm⁻¹). Mass spectra were taken with a JMS-LX1000, and a Shimadzu QP2000GF mass spectrometer at an ionizing voltage of 70 eV. All of the melting points were determined with a Yanagimoto micromelting-point apparatus MP-J3. Elemental analyses were performed by the Instrumental Analysis Center, Kumamoto University and the Microanalytical Center, Kyushu University, Fukuoka.

Materials.

The preparations of 6-substituted and 6,6-disubstituted 1,2-dioxan-3-ols **1a**, **1b**, **1c**, **1d**, and **8a** have been reported in previous papers [1,2,5]. Methylhydrazine (**2a**) (Tokyo Kasei), hydrazine hydrate (**2b**) (Wako), (2-hydroxyethyl)hydrazine (**2c**) (Tokyo Kasei), phenylhydrazine hydrochloride (**2d**) (Wako), (4-chlorophenyl)hydrazine hydrochloride (**2e**) (Tokyo Kasei), (4-nitrophenyl)hydrazine hydrochloride (**2f**) (Tokyo Kasei), (2,4-dinitrophenyl)hydrazine (**2g**) (Wako), benzenesulfonylhydrazide (**2h**) (Tokyo Kasei), *p*-toluenesulfonylhydrazide (**2i**) (Tokyo Kasei), hydroxylamine hydrochloride (**2j**) (Tokyo Kasei), (4-methylphenyl)hydrazine hydrochloride (**2k**) (Wako), (4-methoxyphenyl)hydrazine hydrochloride (**2l**) (Tokyo Kasei), and 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone (Tokyo Kasei) were used as received.

Reactions of 4-Acetyl-6-aryl-3-methyl-1,2-dioxan-3-ols **1a-d** with Hydrazine (**2b**), Hydrazine Derivatives **2a**, **2c-i**, or Hydroxylamine (**2j**) in Methanol-Acetic Acid.

The general procedure for the reaction of 4-acetyl-6-aryl-3-methyl-1,2-dioxan-3-ols **1a-d** with hydrazine, hydrazine derivatives, or hydroxylamine in methanol-acetic acid was as follows. A solution of a 1,2-dioxan-3-ol (1 mmole) and a hydrazine or a hydrazine hydrochloride (2 mmoles) in a 1:1 mixture of methanol-acetic acid (v/v, 10 ml) was stirred at a temperature and for the period of time shown in Table 1. The reaction was quenched by adding water (60 ml) and the mixture was then extracted with benzene. After removing the benzene, the resulting products were separated on tlc (Wakogel B10) while eluting with a mixture of hexane-ethyl acetate (1:1 v/v). The products were further purified for analytical samples by recrystallization from appropriate solvents. The yields are listed in Tables 1 and 2. Specific details are given below.

Products.

4-(2-Hydroperoxy-2,2-diphenylethyl)-1,3,5-trimethylpyrazole (**3aa**).

This compound was obtained as colorless microcrystals from chloroform-hexane, mp 166-167°; ir (chloroform): ν = 3520-3200cm⁻¹; ¹H nmr (60 MHz, deuteriochloroform): δ = 1.63 (3H, s), 1.73 (3H, s), 3.40 (2H, s), 3.50 (3H, s), 7.28 (11H, br s); ¹³C nmr (22.5 MHz, deuteriochloroform): δ = 147.7, 143.2, 138.9, 128.0, 127.7, 127.3, 110.3, 89.8, 35.5, 31.3, 11.3, 9.22.

Anal. Calcd. for C₂₀H₂₂N₂O₂: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.25; H, 6.94; N, 8.94.

4-(2-Hydroperoxy-2,2-diphenylethyl)-3,5-dimethylpyrazole (**3ab**).

This compound was obtained as colorless microcrystals from chloroform-hexane, mp 158-159°; ir (potassium bromide): ν = 3480-3200 cm⁻¹; ¹H nmr (60 MHz, deuteriochloroform): δ = 1.73 (6H, s), 3.44 (2H, s), 5.67 (2H, br s), 7.37 (10H, s); ¹³C nmr (22.5 MHz, deuteriochloroform): δ = 144.6, 143.0, 128.0, 127.9, 127.5, 109.6, 90.2, 31.0, 10.5.

Anal. Calcd. for C₁₉H₂₀N₂O₂: C, 74.00; H, 6.54; N, 9.08. Found: C, 73.93; H, 6.57; N, 8.99.

1-(2-Hydroxyethyl)-4-(2-hydroperoxy-2,2-diphenylethyl)-3,5-dimethylpyrazole (**3ac**).

This compound was obtained as colorless microcrystals from diethyl ether, mp 125-126°; ir (chloroform): ν = 3500-3200 cm⁻¹; ¹H nmr (90 MHz, deuteriochloroform): δ = 1.68 (3H, s), 1.70 (3H, s), 3.39 (2H, s), 3.73-3.83 (4H, m), 5.71 (1H, br s),

7.21 (11H, br s); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 148.6, 143.0, 139.3, 128.0, 127.7, 127.4, 110.5, 90.0, 61.6, 49.8, 31.1, 11.5, 9.1.

Anal. Calcd. for $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_3$: C, 71.57; H, 6.86; N, 7.95. Found: C, 71.54; H, 6.93; N, 8.07.

4-(2-Hydroperoxy-2,2-diphenylethyl)-3,5-dimethyl-1-phenylpyrazole (**3ad**).

This compound was obtained as colorless microcrystals from chloroform-hexane, mp 138-140°; ir (chloroform): ν = 3628-3200 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 1.65 (3H, s), 1.90 (3H, s), 3.40 (2H, s), 7.40 (15H, m), 8.30 (1H, br s); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 150.0, 142.7, 140.2, 139.0, 128.8, 128.1, 127.9, 127.7, 127.0, 125.0, 112.1, 90.5, 31.1, 11.7, 10.7.

Anal. Calcd. for $\text{C}_{25}\text{H}_{24}\text{N}_2\text{O}_2$: C, 78.10; H, 6.29; N, 7.29. Found: C, 77.80; H, 6.35; N, 7.63.

1-(4-Chlorophenyl)-4-(2-hydroperoxy-2,2-diphenylethyl)-3,5-dimethylpyrazole (**3ae**).

This compound was obtained as colorless cubes from chloroform-hexane, mp 158-159°; ir (chloroform): ν = 3616-3200 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 1.65 (3H, s), 1.80 (3H, s), 3.43 (2H, s), 7.20 (14H, m), 8.50 (1H, br s); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 150.3, 142.8, 139.0, 138.4, 132.5, 128.9, 127.9, 127.7, 127.5, 125.9, 112.6, 90.0, 31.0, 11.5, 10.6.

Anal. Calcd. for $\text{C}_{25}\text{H}_{23}\text{ClN}_2\text{O}_2 \cdot 1/4\text{H}_2\text{O}$: C, 70.91; H, 5.59; N, 6.62. Found: C, 70.45; H, 5.51; N, 7.02.

4-(2-Hydroperoxy-2,2-diphenylethyl)-3,5-dimethyl-1-(4-nitrophenyl)pyrazole (**3af**).

This compound was obtained as pale yellow cubes from chloroform-hexane, mp 122-124°; ir (chloroform): ν = 3520-3200, 1598, 1340 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 1.82 (6H, s), 3.48 (2H, s), 7.25 (10H, s), 7.41-8.28 (4H, m), 8.10 (1H, br s); ^{13}C nmr (22.5 MHz, deuteriochloroform) δ = 152.1, 145.4, 145.0, 142.7, 139.4, 127.9, 127.7, 124.6, 123.7, 114.7, 90.0, 30.9, 11.7, 11.4.

Anal. Calcd. for $\text{C}_{25}\text{H}_{23}\text{N}_3\text{O}_4$: C, 69.92; H, 5.40; N, 9.78. Found: C, 69.70; H, 5.49; N, 9.71.

1-Benzenesulfonyl-4-(2-hydroperoxy-2,2-diphenylethyl)-3,5-dimethylpyrazole (**3ah**).

This compound was obtained as colorless cubes from chloroform-hexane, mp 164-165°; ir (chloroform): ν = 3512-3200, 1372, 1183 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 1.77 (3H, s), 2.00 (3H, s), 3.40 (2H, s), 6.47 (1H, br s), 7.10-8.10 (15H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 155.5, 143.1, 142.0, 138.7, 133.7, 129.2, 128.0, 127.8, 127.7, 127.5, 116.8, 90.1, 30.4, 12.1, 10.9.

Anal. Calcd. for $\text{C}_{25}\text{H}_{24}\text{N}_2\text{O}_4\text{S}$: C, 66.90; H, 5.40; N, 6.20. Found: C, 66.96; H, 5.42; N, 5.90.

4-(2-Hydroperoxy-2,2-diphenylethyl)-3,5-dimethyl-1-(4-methylbenzenesulfonyl)pyrazole (**3ai**).

This compound was obtained as colorless microcrystals from chloroform-hexane, mp 154-155°; ir (chloroform): ν = 3280, 1372, 1173 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 1.75 (3H, s), 1.97 (3H, s), 2.45 (3H, s), 3.35 (2H, s), 6.45 (1H, br s), 7.18-7.90 (14H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 155.2, 144.8, 143.0, 142.0, 135.8, 129.8, 128.0, 127.9, 127.7, 127.5, 116.5, 90.2, 30.4, 21.7, 12.1, 10.9.

Anal. Calcd. for $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_4\text{S}$: C, 67.51; H, 5.67; N, 6.06. Found: C, 67.70; H, 5.54; N, 5.76.

4-[2-Hydroperoxy-2,2-bis(4-chlorophenyl)ethyl]-1,3,5-trimethylpyrazole (**3ba**).

This compound was obtained as colorless microcrystals from chloroform-hexane; mp 176-177°; ir (chloroform): ν = 3624-3200 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 1.67 (3H, s), 1.77 (3H, s), 3.40 (2H, s), 3.57 (3H, s), 6.30 (1H, br s), 7.25 (8H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 147.5, 141.0, 138.7, 133.7, 129.4, 128.0, 109.6, 89.4, 35.7, 31.3, 11.4, 9.3.

Anal. Calcd. for $\text{C}_{20}\text{H}_{20}\text{Cl}_2\text{N}_2\text{O}_2 \cdot 1/2\text{H}_2\text{O}$: C, 60.01; H, 5.29; N, 7.00. Found: C, 59.71; H, 5.32; N, 7.16.

4-[2-Hydroperoxy-2,2-bis(4-chlorophenyl)ethyl]-3,5-dimethylpyrazole (**3bb**).

This compound was obtained as colorless microcrystals from chloroform-hexane, mp 153-155°; ir (chloroform): ν = 3472-3200 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 1.66 (6H, s), 3.32 (2H, s), 7.14 (8H, m), 9.63 (2H, br s); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 144.3, 141.2, 133.3, 129.6, 127.8, 109.2, 88.9, 31.2, 10.4.

Anal. Calcd. for $\text{C}_{19}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_2$: C, 60.49; H, 4.81; N, 7.43. Found: C, 60.11; H, 4.82; N, 7.40.

4-[2-Hydroperoxy-2,2-bis(4-chlorophenyl)ethyl]-3,5-dimethyl-1-phenylpyrazole (**3bd**).

This compound was obtained as colorless cubes from chloroform, mp 146-147°; ir (chloroform): ν = 3610-3200 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 1.73 (3H, s), 1.83 (3H, s), 3.45 (2H, s), 6.30 (1H, br s), 7.25 (13H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 149.0, 140.3, 138.8, 138.4, 133.0, 128.8, 128.2, 127.2, 126.6, 124.2, 111.0, 88.6, 30.4, 10.9, 10.1.

Anal. Calcd. for $\text{C}_{25}\text{H}_{22}\text{Cl}_2\text{N}_2\text{O}_2$: C, 66.23; H, 4.89; N, 6.18. Found: C, 66.07; H, 4.75; N, 6.34.

4-[2-Hydroperoxy-2,2-bis(4-methylphenyl)ethyl]-1,3,5-trimethylpyrazole (**3ca**).

This compound was obtained as colorless microcrystals from chloroform-hexane, mp 166-167°; ir (chloroform): ν = 3508-3200 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 1.60 (3H, s), 1.77 (3H, s), 2.30 (6H, s), 3.33 (2H, s), 3.50 (3H, s), 7.11 (9H, s); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 147.7, 140.3, 138.7, 136.9, 128.4, 127.9, 110.4, 89.7, 35.6, 31.3, 21.0, 11.3, 9.30.

Anal. Calcd. for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_2 \cdot 1/4\text{H}_2\text{O}$: C, 74.44; H, 7.52; N, 7.89. Found: C, 74.63; H, 7.37; N, 8.11.

4-[2-Hydroperoxy-2,2-bis(4-methylphenyl)ethyl]-3,5-dimethylpyrazole (**3cb**).

This compound was obtained as colorless microcrystals from chloroform-hexane, mp 108-110°; ir (chloroform): ν = 3472-3200 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 1.67 (6H, s), 2.30 (6H, s), 3.35 (2H, s), 6.95-7.50 (10H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 144.3, 140.3, 136.9, 128.4, 128.0, 109.7, 89.8, 31.0, 21.0, 10.4.

Anal. Calcd. for $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_2 \cdot 1/4\text{H}_2\text{O}$: C, 73.98; H, 7.24; N, 8.22. Found: C, 74.31; H, 7.18; N, 8.35.

4-[2-Hydroperoxy-2,2-bis(4-methylphenyl)ethyl]-3,5-dimethyl-1-phenylpyrazole (**3cd**).

This compound was obtained as colorless cubes from diethyl ether, mp 173-174°; ir (chloroform): $\nu = 3600\text{-}3200\text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 1.77$ (3H, s), 1.80 (3H, s), 2.30 (6H, s), 3.43 (2H, s), 7.10-7.33 (14H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 149.9, 144.0, 139.8, 139.1, 137.2, 128.8, 128.5, 127.9, 127.0, 124.9, 112.4, 90.2, 31.0, 21.0, 11.5, 10.7$.

Anal. Calcd. for $\text{C}_{27}\text{H}_{28}\text{N}_2\text{O}_2$: C, 78.61; H, 6.85; N, 6.79. Found: C, 78.44; H, 6.84; N, 7.02.

4-(2-Hydroperoxy-2-phenylpropyl)-1,3,5-trimethylpyrazole (3da).

This compound was obtained as colorless cubes from chloroform-hexane, mp 112-113°; ir (chloroform): $\nu = 3536\text{-}3200\text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 1.67$ (6H, s), 1.85 (3H, s), 2.68 (2H, s), 3.48 (3H, s), 7.24 (5H, s), 8.30 (1H, br s); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 146.9, 144.0, 138.1, 127.8, 126.8, 126.0, 110.8, 86.6, 35.8, 35.3, 21.8, 11.4, 9.1$.

Anal. Calcd. for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_2$: C, 69.21; H, 7.74; N, 10.76. Found: C, 69.49; H, 7.81; N, 11.01.

Benzophenone (5a).

This compound had mp 47-49° (from ethanol).

3-Methyl-4-[1-(4-nitrophenylhydrazino)ethyl]-6,6-diphenyl-1,2-dioxan-3-ol (6af).

This compound was obtained as pale yellow cubes from chloroform-hexane, mp 120-122°; ir (chloroform): $\nu = 3630\text{-}3200, 1600, 1329\text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 1.30$ (3H, s), 2.03 (3H, s), 2.80 (3H, m), 4.10 (1H, br s), 7.30-8.25 (15H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 149.9, 149.3, 143.6, 141.1, 140.3, 128.6, 128.4, 128.0, 127.4, 126.8, 126.6, 126.1, 125.7, 112.0, 85.7, 48.1, 33.3, 24.4, 14.4$.

3-Methyl-4-[1-(2,4-dinitrophenylhydrazino)ethyl]-6,6-diphenyl-1,2-dioxan-3-ol (6ag).

This compound was obtained as orange cubes from benzene-hexane, mp 175-177°; ir (chloroform): $\nu = 3552\text{-}3292, 1609, 1327$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 1.30$ (3H, s), 2.20 (3H, s), 2.90 (3H, m), 3.67 (1H, br s), 7.35-8.45 (13H, m), 9.20 (1H, s); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 156.1, 144.9, 143.5, 140.9, 138.3, 130.1, 128.6, 128.5, 128.1, 127.5, 126.8, 125.6, 123.4, 116.6, 99.9, 85.8, 48.7, 32.8, 24.4, 14.8$.

Anal. Calcd. for $\text{C}_{25}\text{H}_{24}\text{N}_4\text{O}_7$: C, 60.97; H, 4.91; N, 11.38. Found: C, 60.87; H, 4.87; N, 11.14.

4-[1-(Hydroxyimino)ethyl]-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (6aj).

This compound was obtained as colorless needles from diethyl ether-hexane, mp 156-157°; ir (chloroform): $\nu = 3592\text{-}3150, 1600\text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 1.25$ (3H, s), 1.98 (3H, s), 2.75 (3H, m), 4.50 (1H, br s), 6.10 (1H, br s), 7.30-7.60 (10H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 157.9, 143.6, 141.0, 128.5, 128.3, 127.9, 127.3, 126.8, 125.8, 100.1, 85.9, 45.9, 32.9, 24.1, 13.0$.

Anal. Calcd. for $\text{C}_{19}\text{H}_{21}\text{NO}_4$: C, 69.71; H, 6.47; N, 4.28. Found: C, 69.42; H, 6.27; N, 4.10.

4-(2-Hydroperoxy-2,2-diphenylethyl)-3,5-dimethylisoxazole (7aj).

This compound was obtained as colorless microcrystals from chloroform-hexane, mp 174-176°; ir (chloroform): $\nu = 3290\text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 1.70$ (3H, s), 1.92 (3H, s), 3.37 (2H, s), 7.30 (10H, s), 7.90 (1H, br s); ^{13}C nmr

(22.5 MHz, deuteriochloroform): $\delta = 167.7, 160.9, 142.4, 128.0, 127.6, 127.5, 108.2, 89.5, 29.5, 10.5, 9.4$.

Anal. Calcd. for $\text{C}_{19}\text{H}_{19}\text{NO}_3$: C, 73.76; H, 6.19; N, 4.53. Found: C, 73.34; H, 6.09; N, 4.30.

4-[2-Hydroperoxy-2,2-bis(4-chlorophenyl)ethyl]-3,5-dimethylisoxazole (7bj).

This compound was obtained as colorless cubes from chloroform, mp 186-188°; ir (chloroform): $\nu = 3620\text{-}3200\text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 1.73$ (3H, s), 1.95 (3H, s), 3.35 (2H, s), 7.25-7.50 (8H, m), 8.30 (1H, br s); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 167.8, 160.9, 141.3, 133.6, 129.3, 128.0, 108.2, 88.0, 29.7, 10.8, 9.8$.

Anal. Calcd. for $\text{C}_{19}\text{H}_{17}\text{Cl}_2\text{NO}_3$: C, 60.33; H, 4.53; N, 3.70. Found: C, 60.03; H, 4.34; N, 3.75.

4-[2-Hydroperoxy-2,2-bis(4-methylphenyl)ethyl]-3,5-dimethylisoxazole (7cj).

This compound was obtained as colorless cubes from diethyl ether-hexane, mp 126-127°; ir (chloroform): $\nu = 3696\text{-}3200\text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 1.67$ (3H, s), 1.93 (3H, s), 2.30 (6H, s), 3.33 (2H, s), 7.11 (8H, m), 7.97 (1H, br s); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 167.8, 161.1, 139.6, 137.4, 128.7, 127.5, 108.6, 89.4, 29.6, 21.0, 10.7, 9.5$.

Anal. Calcd. for $\text{C}_{21}\text{H}_{23}\text{NO}_3$: C, 74.75; H, 6.87; N, 4.15. Found: C, 74.69; H, 6.65; N, 4.14.

Reactions of 4-Acetyl-6-aryl-3-methyl-1,2-dioxan-3-ols **1a-c**, 4-(2-Hydroperoxy-2,2-diphenylethyl)-1,3,5-trimethylpyrazole (**3aa**), and 3-Methyl-4-[1-(4-nitrophenylhydrazino)ethyl]-6,6-diphenyl-1,2-dioxan-3-ol (**6af**) with Hydrazine (**2b**) or Hydrazine Derivatives **2a, c-f, h, i, k-m** in an Alkanol.

The general procedure for the reaction of 4-acetyl-6-aryl-3-methyl-1,2-dioxan-3-ols **1a-c** with hydrazine (**2b**), hydrazine derivatives **2a, c-f, h, i, k-m** in an alkanol was as follows. A solution of a 1,2-dioxan-3-ol (1 mmole) and a hydrazine or a hydrazine hydrochloride (2 mmoles) in a solvent (10 ml) was stirred at a temperature and for the period of time shown in Tables 1-3. The reaction was quenched by adding water (60 ml) and the mixture was then extracted with benzene. After removing the benzene, the resulting products were separated on tlc (Wakogel B10) while eluting with a mixture of hexane-diethyl ether (1:4 v/v). The products were further purified for analytical samples by recrystallization from appropriate solvents. The yields are listed in Tables 1-3. Specific details are given below.

Products.

4-(2-Hydroxy-2,2-diphenylethyl)-1,3,5-trimethylpyrazole (**4aa**).

This compound was obtained as colorless microcrystals from chloroform-hexane, mp 169-171°; ir (chloroform): $\nu = 3552\text{-}3200\text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 1.61$ (3H, s), 1.72 (3H, s), 2.65 (1H, br s), 3.32 (2H, s), 3.56 (3H, s), 7.18-7.38 (10H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 147.5, 147.0, 138.5, 127.8, 126.7, 126.2, 109.4, 77.8, 37.0, 35.7, 11.6, 9.3$.

Anal. Calcd. for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}$: C, 78.40; H, 7.24; N, 9.14. Found: C, 78.52; H, 7.33; N, 9.20.

4-(2-Hydroxy-2,2-diphenylethyl)-3,5-dimethylpyrazole (**4ab**).

This compound was obtained as colorless microcrystals from chloroform-diethyl ether, mp 204-205°; ir (potassium bromide): $\nu = 3416\text{-}3220\text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 1.69$

(6H, s), 3.35 (2H, s), 4.70 (2H, br s), 7.21-7.37 (10H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 147.1, 144.6, 128.1, 126.9, 126.5, 109.1, 78.2, 36.7, 10.8.

Anal. Calcd. for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}$: C, 78.05; H, 6.89; N, 9.58. Found: C, 77.78; H, 6.84; N, 9.52.

1-(2-Hydroxyethyl)-4-(2-hydroxy-2,2-diphenylethyl)-3,5-dimethylpyrazole (**4ac**).

This compound was obtained as colorless needles from ethanol, mp 128-129°; ir (chloroform): ν = 3556-3200 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 1.63 (3H, s), 1.73 (3H, s), 2.70 (1H, br s), 3.33 (2H, s), 3.85 (1H, br s), 3.90 (4H, s), 7.20-7.50 (10H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 148.4, 147.0, 139.1, 128.0, 126.9, 126.4, 109.8, 78.1, 61.5, 50.0, 36.9, 11.9, 9.3.

Anal. Calcd. for $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_2$: C, 74.97; H, 7.19; N, 8.33. Found: C, 74.69; H, 7.18; N, 8.41.

4-(2-Hydroxy-2,2-diphenylethyl)-3,5-dimethyl-1-phenylpyrazole (**4ad**).

This compound was obtained as colorless cubes from chloroform-hexane, mp 156-157°; ir (chloroform): ν = 3696-3200 cm^{-1} ; ^1H nmr (90 MHz, deuteriochloroform): δ = 1.65 (3H, s), 1.90 (3H, s), 2.45 (1H, br s), 3.41 (2H, s), 7.33-7.36 (15H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 149.8, 147.0, 140.0, 138.9, 128.9, 128.1, 127.2, 127.0, 126.5, 124.8, 111.7, 78.3, 37.1, 12.1, 10.9.

Anal. Calcd. for $\text{C}_{25}\text{H}_{24}\text{N}_2\text{O} \cdot 1/4\text{H}_2\text{O}$: C, 80.51; H, 6.62; N, 7.51. Found: C, 80.76; H, 6.77; N, 7.69.

1-(4-Chlorophenyl)-4-(2-hydroxy-2,2-diphenylethyl)-3,5-dimethylpyrazole (**4ae**).

This compound was obtained as colorless cubes from chloroform-hexane, mp 150-151°; ir (chloroform): ν = 3610-3250 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 1.70 (3H, s), 1.90 (3H, s), 2.50 (1H, br s), 3.45 (2H, s), 7.45 (14H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 150.1, 146.8, 138.7, 138.4, 132.5, 128.9, 127.9, 126.9, 126.4, 125.7, 112.2, 78.2, 36.8, 11.9, 10.8.

Anal. Calcd. for $\text{C}_{25}\text{H}_{23}\text{ClN}_2\text{O}$: C, 74.52; H, 5.75; N, 6.95. Found: C, 74.60; H, 5.53; N, 6.92.

4-(2-Hydroxy-2,2-diphenylethyl)-1-(4-nitrophenyl)-3,5-dimethylpyrazole (**4af**).

This compound was obtained as pale yellow cubes from chloroform-hexane, mp 167-168°; ir (chloroform): ν = 3616-3200, 1598, 1341 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 1.77 (3H, s), 1.87 (3H, s), 2.40 (1H, br s), 3.40 (2H, s), 7.40-8.37 (14H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 151.9, 146.8, 145.6, 145.1, 139.1, 128.2, 127.3, 126.6, 124.7, 123.7, 114.5, 78.6, 36.8, 12.1, 11.6.

Anal. Calcd. for $\text{C}_{25}\text{H}_{23}\text{N}_3\text{O}_3$: C, 72.62; H, 5.61; N, 10.16. Found: C, 72.83; H, 5.69; N, 10.19.

4-(2-Hydroxy-2,2-diphenylethyl)-1-(4-methylphenyl)-3,5-dimethylpyrazole (**4ak**).

This compound was obtained as colorless microcrystals from chloroform-hexane, mp 128-129°; ir (chloroform): ν = 3552-3250 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 1.62 (3H, s), 1.90 (3H, s), 2.35 (3H, s), 2.50 (1H, br s), 3.43 (2H, s), 7.25-7.50 (14H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 149.5, 147.0, 138.9, 137.5, 137.1, 129.5, 128.1, 127.0, 126.5, 124.8, 111.3, 78.2, 37.2, 21.1, 12.1, 10.8.

Anal. Calcd. for $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}$: C, 81.64; H, 6.85; N, 7.32. Found: C, 81.66; H, 6.87; N, 7.33.

4-(2-Hydroxy-2,2-diphenylethyl)-1-(4-methoxyphenyl)-3,5-dimethylpyrazole (**4al**).

This compound was obtained as colorless cubes from chloroform-hexane, mp 177-178°; ir (chloroform): ν = 3552-3200 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 1.60 (3H, s), 1.89 (3H, s), 2.55 (1H, br s), 3.40 (2H, s), 3.80 (3H, s), 6.83-7.40 (14H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 158.8, 149.3, 147.0, 139.1, 133.1, 128.0, 127.0, 126.5, 126.4, 114.1, 111.0, 78.2, 55.5, 37.1, 12.0, 10.6.

Anal. Calcd. for $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_2 \cdot 1/3\text{H}_2\text{O}$: C, 77.21; H, 6.65; N, 6.93. Found: C, 76.78; H, 6.56; N, 6.79.

1-Aminothiocabonyl-4-(2-hydroxy-2,2-diphenylethyl)-3,5-dimethylpyrazole (**4am**).

This compound was obtained as colorless plates from chloroform-hexane, mp 194-195°; ir (chloroform): ν = 3528, 3384, 1225; ^1H nmr (60 MHz, deuteriochloroform): δ = 2.10 (3H, s), 2.30 (3H, s), 2.31 (1H, s), 3.65 (2H, s), 7.40-7.55 (10H, m), 8.70 (2H, br s); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 178.3, 156.8, 146.3, 145.5, 128.4, 127.5, 125.7, 109.1, 89.6, 46.2, 15.2, 14.3.

Anal. Calcd. for $\text{C}_{20}\text{H}_{21}\text{N}_3\text{OS}$: C, 68.35; H, 6.02; N, 11.96. Found: C, 68.18; H, 5.88; N, 11.75.

4-[2-Hydroxy-2,2-bis(4-chlorophenyl)ethyl]-1,3,5-trimethylpyrazole (**4ba**).

This compound was obtained as colorless cubes from chloroform-hexane, mp 150-151°; ir (chloroform): ν = 3540-3200 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 1.70 (3H, s), 1.77 (3H, s), 2.75 (1H, br s), 3.30 (2H, s), 3.65 (3H, s), 7.35 (8H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 147.5, 145.3, 138.6, 138.0, 128.2, 127.8, 109.0, 77.3, 37.0, 35.9, 11.9, 9.6.

Anal. Calcd. for $\text{C}_{20}\text{H}_{20}\text{Cl}_2\text{N}_2\text{O} \cdot 1/4\text{H}_2\text{O}$: C, 63.25; H, 5.44; N, 7.38. Found: C, 63.37; H, 5.32; N, 7.38.

1-(2-Hydroxyethyl)-4-[2-hydroxy-2,2-bis(4-chlorophenyl)ethyl]-3,5-dimethylpyrazole (**4bc**).

This compound was obtained as colorless needles from chloroform-hexane, mp 158-159°; ir (chloroform): ν = 3620-3195; ^1H nmr (60 MHz, deuteriochloroform): δ = 1.70 (3H, s), 1.80 (3H, s), 2.50 (1H, br s), 3.30 (2H, s), 3.60 (1H, br s), 3.93 (4H, s), 7.30 (8H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 148.3, 145.2, 139.0, 133.2, 128.2, 127.8, 109.2, 77.5, 61.6, 50.0, 36.8, 12.1, 9.5.

Anal. Calcd. for $\text{C}_{21}\text{H}_{22}\text{Cl}_2\text{N}_2\text{O}_2$: C, 62.22; H, 5.47; N, 6.91. Found: C, 62.12; H, 5.35; N, 6.67.

4-[2-Hydroxy-2,2-bis(4-methylphenyl)ethyl]-1,3,5-trimethylpyrazole (**4ca**).

This compound was obtained as colorless cubes from chloroform-hexane, mp 153-154°; ir (chloroform): ν = 3548-3200 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 1.67 (3H, s), 1.75 (3H, s), 2.30 (6H, s), 2.75 (1H, br s), 3.30 (2H, s), 3.63 (3H, s), 7.07-7.40 (8H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 147.6, 144.3, 138.6, 136.2, 128.5, 126.2, 109.7, 77.6, 37.0, 35.7, 20.8, 11.7, 9.4.

Anal. Calcd. for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}$: C, 79.01; H, 7.84; N, 8.38. Found: C, 78.76; H, 7.99; N, 8.34.

1-(2-Hydroxyethyl)-4-[2-hydroxy-2,2-bis(4-methylphenyl)ethyl]-3,5-dimethylpyrazole (**4cc**).

This compound was obtained as colorless microcrystals from chloroform-hexane, mp 140-142°; ir (chloroform): $\nu = 3612-3195\text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 1.65$ (3H, s), 1.73 (3H, s), 2.30 (6H, s), 2.75 (1H, br s), 3.30 (2H, s), 3.73 (1H, br s), 3.90 (4H, s), 7.00-7.45 (8H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 148.5, 144.3, 139.0, 136.5, 128.7, 126.3, 110.0, 78.0, 61.7, 49.9, 36.9, 21.0, 12.0, 9.4$.

Anal. Calcd. for $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_2 \cdot 1/4\text{H}_2\text{O}$: C, 74.87; H, 7.78; N, 7.59. Found: C, 74.39; H, 7.69; N, 7.51.

4,4'-Dichlorobenzophenone (**5b**).

This compound had mp 145-146° (from benzene-hexane).

4,4'-Dimethylbenzophenone (**5c**).

This compound had mp 92-94° (from ethanol).

Reduction of **3ab** and **3af** with Triphenylphosphine.

A mixture of **3ab** (77 mg) and triphenylphosphine (66 mg) in anhydrous diethyl ether (10 ml) was stirred at room temperature for 6 hours. The solvent was removed and the residue was triturated with 2M hydrochloric acid. The mixture was then extracted with benzene (3 x 10 ml). After the benzene being removed, the residue was separated by tlc to give **4ab** (17 mg, 23%) and **5a** (34 mg, 75%) which were identified with authentic samples. Compounds **4af** (119 mg, 80%) and **5a** (23 mg, 11%) were similarly obtained from **3af** (156 mg).

The Reaction of Ethyl 3-Hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate (**8a**) with Hydrazine (**2b**) or Hydrazine Derivatives **2a**, **2d**.

The general procedure for the reaction of ethyl 3-hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate (**8a**) with hydrazine (**2b**) or hydrazine derivatives **2a** or **2d** was as follows. A mixture of ethyl 3-hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate (**8a**) (1 mmole) and a hydrazine (5 mmoles) was heated at 100° for 5 minutes. The precipitate was collected and recrystallized from methanol to afford 4-(2-hydroxy-2,2-diphenylethyl)-3-methyl-5-pyrazolone **9**. Yields are listed in Scheme 4.

Products.

4-(2-Hydroxy-2,2-diphenylethyl)-1,3-dimethyl-5-pyrazolone (**9aa**).

This compound was obtained as colorless microcrystals from methanol, mp 265-266°; ir (potassium bromide): $\nu = 3456-2924, 1560\text{ cm}^{-1}$; ^1H nmr (60 MHz, DMSO- d_6): $\delta = 1.90$ (3H, s), 2.40-2.80 (1H, br s), 3.18 (2H, s), 3.23 (3H, s), 3.40-3.80 (1H, br s), 7.15-7.70 (10H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 159.0, 148.4, 144.5, 127.6, 125.9, 125.8, 100.5, 78.5, 36.6, 30.4, 10.5$.

Anal. Calcd. for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2$: C, 74.00; H, 6.54; N, 9.08. Found: C, 74.05; H, 6.61; N, 9.16.

4-(2-Hydroxy-2,2-diphenylethyl)-3-methyl-5-pyrazolone (**9ab**).

This compound was obtained as colorless microcrystals from methanol, mp 167-168°; ir (potassium bromide): $\nu = 3700-2000, 1568\text{ cm}^{-1}$; ^1H nmr (60 MHz, DMSO- d_6): $\delta = 1.80$ (3H, s), 2.30 (1H, br s), 3.10 (1H, br s), 3.23 (2H, s), 7.20-7.70 (11H, m); ^{13}C nmr (22.5 MHz, DMSO- d_6): $\delta = 162.5, 147.8, 141.1, 127.4, 125.9, 98.3, 78.3, 35.6, 10.0$.

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.60; H, 6.24; N, 9.57.

4-(2-Hydroxy-2,2-diphenylethyl)-3-methyl-1-phenyl-5-pyrazolone (**9ad**).

This compound was obtained as colorless needles from methanol, mp 195-196°; ir (potassium bromide): $\nu = 3625-3052, 1565\text{ cm}^{-1}$; ^1H nmr (60 MHz, DMSO- d_6 + deuteriochloroform): $\delta = 1.87$ (3H, s), 3.10 (1H, br s), 3.30 (2H, s), 4.90 (1H, br s), 7.10-7.70 (15H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 162.0, 147.6, 147.4, 136.6, 128.7, 127.7, 126.4, 126.2, 125.3, 120.1, 102.0, 78.4, 36.1, 11.0$.

Anal. Calcd. for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_2$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.48; H, 6.00; N, 7.52.

Acid-Catalyzed Decomposition of 4-(2-Hydroperoxy-2,2-diarylethyl)-3,5-dimethylpyrazoles **3** and 4-(2-Hydroperoxy-2,2-diphenylethyl)-3,5-dimethylisoxazole (**7aj**).

The general procedure for the acid-catalyzed decomposition of 4-(2-hydroperoxy-2,2-diarylethyl)-3,5-dimethylpyrazoles **3** and 4-(2-hydroperoxy-2,2-diphenylethyl)-3,5-dimethylisoxazole (**7aj**) was as follows. A solution of a **3** or **7aj** (1 mmole) in acetonitrile (15 ml) containing perchloric acid (1-8 mmoles) was heated at a temperature shown in Table 4 for 0.5-2 hours. After being diluted with water (30 ml), the reaction mixture was extracted with a mixture of benzene and diethyl ether (3:1 v/v, total 60 ml). The organic layer was separated and washed with water. After removing the solvent, the resulting products were separated on tlc (Wakogel B10) while eluting with a mixture of ethyl acetate and hexane (1:1 v/v). The yields are listed in Table 4. Specific details are given below.

Products.

Acetophenone (**5d**).

This compound had mp 18-20°.

4-(Benzoylmethyl)-1,3,5-trimethylpyrazole (**10aa**).

This compound was obtained as a colorless liquid; ir (chloroform): $\nu = 1686\text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 2.14$ (6H, s), 3.70 (3H, s), 4.00 (2H, s), 7.24-8.04 (5H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 197.1, 146.1, 137.3, 136.8, 133.1, 128.6, 128.3, 109.0, 35.9, 34.2, 12.0, 10.0$; ms: m/z (relative intensity) = 228 (15, M⁺), 124 (15), 123 (100), 105 (6), 77 (13).

Anal. Calcd. for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}$: M, 228.1263. Found: m/z = 228.1281.

4-(Benzoylmethyl)-3,5-dimethylpyrazole (**10ab**).

This compound was obtained as colorless needles from diethyl ether-hexane, mp 111-112°; ir (chloroform): $\nu = 3472, 1691\text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 2.15$ (6H, s), 4.03 (2H, s), 7.20 (1H, s), 7.30-8.10 (5H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 197.2, 143.0, 136.8, 133.1, 128.6, 128.3, 108.5, 33.7, 11.1$.

Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}$: C, 72.87; H, 6.59; N, 13.08. Found: C, 72.69; H, 6.55; N, 12.90.

4-(Benzoylmethyl)-3,5-dimethyl-1-phenylpyrazole (**10ad**).

This compound was obtained as a colorless liquid; ir (chloroform): $\nu = 1692$ (C=O); ^1H nmr (60 MHz, deuteriochloroform): $\delta = 2.20$ (6H, s), 4.10 (2H, s), 7.30-8.25 (10H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 196.9, 148.3, 140.0, 137.6, 136.8, 133.2, 129.0, 128.7, 128.3, 127.3, 124.9, 111.0, 34.1, 12.2, 11.3$; ms: m/z (relative intensity) = 290 (12, M⁺), 185 (100), 143 (12), 105 (8), 77 (18).

Anal. Calcd. for $C_{19}H_{18}N_2O$: M, 290.1419. Found: *m/z* = 290.1439.

4-[(4-Chlorobenzoyl)methyl]-1,3,5-trimethylpyrazole (**10ba**).

This compound was obtained as a colorless liquid; *ir* (chloroform): $\nu = 1681$; 1H nmr (60 MHz, deuteriochloroform): $\delta = 2.13$ (6H, s), 3.72 (3H, s), 4.00 (2H, s), 7.33-8.07 (4H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 196.0, 139.6, 135.1, 131.4, 131.2, 129.7, 129.0, 108.7, 35.9, 34.2, 11.3, 9.9$; *ms*: *m/z* (relative intensity) = 262 (5, M^+), 139 (6), 123 (100), 111 (9).

Anal. Calcd. for $C_{14}H_{15}^{35}ClN_2O$: M, 262.0873. Found: *m/z* = 262.0916.

4-[(4-Chlorobenzoyl)methyl]-3,5-dimethylpyrazole (**10bb**).

This compound was obtained as colorless needles from diethyl ether, mp 105-106°; *ir* (chloroform): $\nu = 3460, 1681$ cm^{-1} ; 1H nmr (60 MHz, deuteriochloroform): $\delta = 2.15$ (6H, s), 3.97 (2H, s), 7.36-8.00 (4H, m), 10.30 (1H, s); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 195.9, 142.8, 139.5, 135.0, 129.7, 128.9, 108.1, 33.7, 11.0$.

Anal. Calcd. for $C_{13}H_{13}ClN_2O \cdot 1/2H_2O$: C, 60.59; H, 5.48; N, 10.87. Found: C, 60.43; H, 5.02; N, 10.66.

4-[(4-Methylbenzoyl)methyl]-1,3,5-trimethylpyrazole (**10ca**).

This compound was obtained as a colorless liquid; *ir* (chloroform): $\nu = 1676$ cm^{-1} ; 1H nmr (60 MHz, deuteriochloroform): $\delta = 2.12$ (6H, s), 2.40 (3H, s), 3.70 (3H, s), 3.98 (2H, s), 7.25-8.00 (4H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 196.8, 146.0, 143.9, 137.3, 134.3, 129.3, 128.4, 109.2, 35.9, 34.0, 21.6, 12.0, 9.9$; *ms*: *m/z* (relative intensity) = 242 (20, M^+), 123 (100), 119 (33), 91 (25), 65 (18), 56 (69), 42 (20).

Anal. Calcd. for $C_{15}H_{18}N_2O$: M, 242.1419. Found: *m/z* = 242.1428.

4-[(4-Methylbenzoyl)methyl]-3,5-dimethylpyrazole (**10cb**).

This compound was obtained as a colorless liquid; *ir* (chloroform): $\nu = 3472, 1675$ cm^{-1} ; 1H nmr (60 MHz, deuteriochloroform): $\delta = 2.17$ (6H, s), 2.40 (3H, s), 4.00 (2H, s), 7.30-8.10 (5H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 196.7, 144.0, 143.0, 134.3, 129.3, 128.4, 108.9, 33.5, 21.6, 11.1$; *ms*: *m/z* (relative intensity) = 228 (13, M^+), 123 (60), 119 (100), 109 (92), 91 (28), 65 (11).

Anal. Calcd. for $C_{14}H_{16}N_2O$: M, 228.1263. Found: *m/z* = 228.1280.

1,3,5-Trimethyl-4-(2-oxopropyl)pyrazole (**10da**).

This compound was obtained as a colorless liquid; *ir* (chloroform): $\nu = 1704$ cm^{-1} ; 1H nmr (60 MHz, deuteriochloroform): $\delta = 2.07$ (3H, s), 2.13 (6H, s), 3.40 (2H, s), 3.70 (3H, s); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 206.3, 145.9, 137.2, 109.1, 39.4, 35.9, 28.7, 11.8, 9.7$; *ms*: *m/z* (relative intensity) = 166 (8, M^+), 123 (100), 56 (27), 43 (10).

Anal. Calcd. for $C_9H_{14}N_2O$: M, 166.1106. Found: *m/z* = 166.1118.

1,3,5-Trimethyl-4-(2,2-diphenylethenyl)pyrazole (**11aa**).

This compound was obtained as colorless cubes from hexane, mp 105-106°; 1H nmr (60 MHz, deuteriochloroform): $\delta = 1.71$ (3H, s), 1.92 (3H, s), 3.61 (3H, s), 6.61 (1H, s), 7.19-7.31 (10H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 146.3, 143.9, 142.6, 141.1, 136.9, 130.6, 128.2, 128.2, 128.1, 127.3, 126.9, 119.9, 115.6, 35.8, 12.5, 10.2$; *ms*: *m/z* (relative intensity) = 288 (100, M^+), 273 (8), 197 (30), 182 (22), 144 (15), 135 (19), 109 (7), 91 (10).

Anal. Calcd. for $C_{20}H_{20}N_2$: C, 83.29; H, 6.99; N, 9.71. Found: C, 82.93; H, 6.84; N, 9.69.

3,5-Dimethyl-4-(2,2-diphenylethenyl)pyrazole (**11ab**).

This compound was obtained as colorless needles from diethyl ether, mp 190-191°; *ir* (chloroform): $\nu = 3472$ cm^{-1} ; 1H nmr (60 MHz, deuteriochloroform): $\delta = 1.82$ (6H, s), 6.70 (1H, s), 7.20-7.30 (11H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 143.9, 142.8, 141.0, 130.6, 128.1, 128.0, 127.3, 126.8, 119.4, 114.8, 11.5$.

Anal. Calcd. for $C_{19}H_{18}N_2$: C, 83.17; H, 6.61; N, 10.21. Found: C, 82.92; H, 6.68; N, 10.13.

3,5-Dimethyl-4-(2,2-diphenylethenyl)-1-phenylpyrazole (**11ad**).

This compound was obtained as a colorless liquid; 1H nmr (60 MHz, deuteriochloroform): $\delta = 1.73$ (3H, s), 2.05 (3H, s), 6.70 (1H, s), 7.25-7.55 (15H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 148.5, 143.7, 143.5, 140.9, 139.7, 136.8, 130.6, 128.9, 128.2, 128.2, 128.1, 127.5, 127.1, 127.0, 124.6, 119.3, 117.5, 12.7, 11.9$; *ms*: *m/z* (relative intensity) = 350 (100, M^+), 349 (10), 259 (23), 258 (12), 175 (10), 118 (10), 91 (5), 77 (28).

Anal. Calcd. for $C_{25}H_{22}N_2$: M, 350.1783. Found: *m/z* = 350.1779.

4-[2,2-Bis(4-chlorophenyl)ethenyl]-1,3,5-trimethylpyrazole (**11ba**).

This compound was obtained as colorless needles from chloroform-hexane, mp 139-140°; 1H nmr (60 MHz, deuteriochloroform): $\delta = 1.65$ (3H, s), 1.80 (3H, s), 3.67 (3H, s), 6.67 (1H, s), 7.10-7.25 (8H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 146.0, 141.9, 140.2, 139.1, 133.4, 132.9, 131.9, 129.4, 128.6, 128.4, 120.9, 115.2, 35.9, 12.6, 10.4$.

Anal. Calcd. for $C_{20}H_{18}Cl_2N_2$: C, 67.24; H, 5.08; N, 7.84. Found: C, 67.28; H, 5.08; N, 7.91.

4-[2,2-Bis(4-methylphenyl)ethenyl]-1,3,5-trimethylpyrazole (**11ca**).

This compound was obtained as colorless cubes from chloroform-hexane, mp 124-125°; 1H nmr (60 MHz, deuteriochloroform): $\delta = 1.72$ (3H, s), 1.90 (3H, s), 2.30 (3H, s), 2.35 (3H, s), 3.65 (3H, s), 6.60 (1H, s), 7.07-7.23 (8H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 146.2, 142.5, 141.3, 138.2, 137.0, 136.7, 136.4, 130.4, 128.8, 128.7, 128.1, 118.6, 115.8, 35.8, 21.2, 21.1, 12.5, 10.2$; *ms*: *m/z* (relative intensity) = 316 (100, M^+), 301 (11), 286 (6), 211 (17), 210 (10), 196 (14), 150 (11), 56 (21).

Anal. Calcd. for $C_{22}H_{24}N_2$: C, 83.50; H, 7.64; N, 8.85. Found: C, 83.65; H, 7.77; N, 8.92.

4-[2,2-Bis(4-methylphenyl)ethenyl]-3,5-dimethylpyrazole (**11cb**).

This compound was obtained as colorless microcrystals from diethyl ether-hexane, mp 177-178°; *ir* (chloroform): $\nu = 3472$ cm^{-1} ; 1H nmr (60 MHz, deuteriochloroform): $\delta = 1.83$ (6H, s), 2.30 (3H, s), 2.35 (3H, s), 6.60 (1H, s), 7.07-7.25 (8H, m), 8.07 (1H, s); ^{13}C nmr (22.5 MHz, deuteriochloroform): $\delta = 142.9, 141.2, 138.1, 137.1, 136.5, 130.5, 128.8, 128.7, 128.1, 118.1, 115.2, 21.2, 21.1, 11.6$.

Anal. Calcd. for $C_{21}H_{22}N_2$: C, 83.40; H, 7.33; N, 9.26. Found: C, 83.29; H, 7.17; N, 9.39.

1,3,5-Trimethyl-4-(2-phenyl-1-propenyl)pyrazole (**11da**).

This compound was obtained as a colorless liquid; 1H nmr (60 MHz, deuteriochloroform): $\delta = 2.12$ (6H, s), 2.17 (3H, s), 3.73

(3H, s), 6.57 (1H, s), 7.25-7.75 (5H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 146.2, 145.6, 142.7, 137.8, 128.1, 128.0, 125.6, 118.2, 115.5, 35.7, 17.2, 12.5, 10.4; ms: m/z = 226 (M^+), 225, 211, 197, 196, 123, 105, 91, 77, 56.

Anal. Calcd. for $\text{C}_{15}\text{H}_{18}\text{N}_2$: M, 226.1470. Found: m/z = 226.1451.

1,3,5-Trimethyl-4-(2-phenyl-2-propenyl)pyrazole (**11da'**).

This compound was obtained as a colorless liquid; ^1H nmr (60 MHz, deuteriochloroform): δ = 2.00 (3H, s), 2.07 (3H, s), 3.50 (2H, s), 3.67 (3H, s), 4.83 (1H, m), 5.33 (1H, m), 7.25-7.75 (5H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 146.1, 141.4, 136.6, 136.3, 127.2, 126.9, 125.8, 112.8, 112.5, 35.6, 29.2, 11.6, 9.4; ms: m/z = 226 (M^+), 225, 211, 197, 196, 123, 105, 91, 77, 56.

Anal. Calcd. for $\text{C}_{15}\text{H}_{18}\text{N}_2$: M, 226.1470. Found: m/z = 226.1451.

4-(Benzoylmethyl)-3,5-dimethylisoxazole (**12aj**).

This compound was obtained as colorless needles from diethyl ether, mp 125-126 $^\circ$; ir (chloroform): ν = 1692 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 2.17 (3H, s), 2.30 (3H, s), 4.00 (2H, s), 7.30-8.10 (5H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 195.4, 166.3, 160.0, 136.3, 133.6, 128.8, 128.2, 107.4, 32.4, 11.2, 10.3.

Anal. Calcd. for $\text{C}_{13}\text{H}_{13}\text{NO}_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.59; H, 6.20; N, 6.35.

3,5-Dimethyl-4-(2,2-diphenylethenyl)isoxazole (**13aj**).

This compound was obtained as colorless cubes from diethyl ether, mp 107-108 $^\circ$; ^1H nmr (60 MHz, deuteriochloroform): δ = 1.85 (3H, s), 1.97 (3H, s), 6.50 (1H, s), 7.25-7.95 (10H, m); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ = 159.6, 146.3, 142.8, 139.9, 137.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.6, 115.3, 113.2, 11.6, 10.6.

Anal. Calcd. for $\text{C}_{19}\text{H}_{17}\text{NO}$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.86; H, 6.24; N, 5.29.

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