Hypervalent Iodine Oxidation of 5-Substituted and 5-Methyl-4-substituted Pyrazol-3(2*H*)-ones. A Facile Synthesis of 2-Alkynoic and 2,3-Allenic Esters

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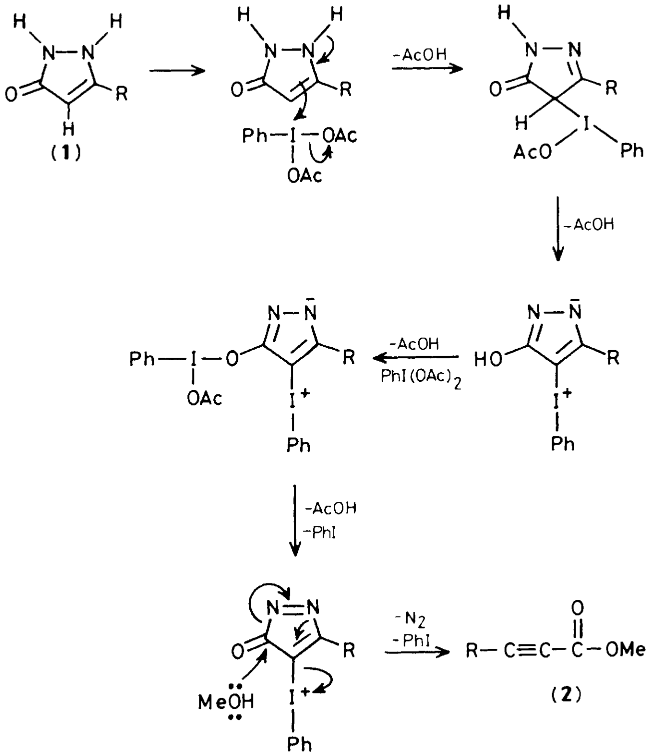
$PhI(OAc)_2$–MeOH causes oxidation of 5-substituted pyrazol-3(2*H*)-ones to the 2-alkynoic methyl ester and 5-methyl-4-substituted pyrazol-3(2*H*)-ones to the 2,3-allenic methyl ester.

(Diacetoxyiodo)benzene, $PhI(OAc)_2$, has been shown to effect oxidative loss of molecular dinitrogen from azines,[1] hydrazine hydrate,[2] and benzophenone hydrazone.[3] The latter reaction suggested to us the possibility of analogous fragmentative loss of N_2 from pyrazol-3(2*H*)-ones to yield the corresponding acetylene derivative. This expectation was encouraged by the fact that $Tl(NO_3)_3$–MeOH has been reported to be effective for this transformation.[4]

Oxidation of (**1a**—**d**) with $PhI(OAc)_2$–MeOH at −23 °C yielded the methyl 2-alkynoates (**2a**—**d**) in high yield (Scheme

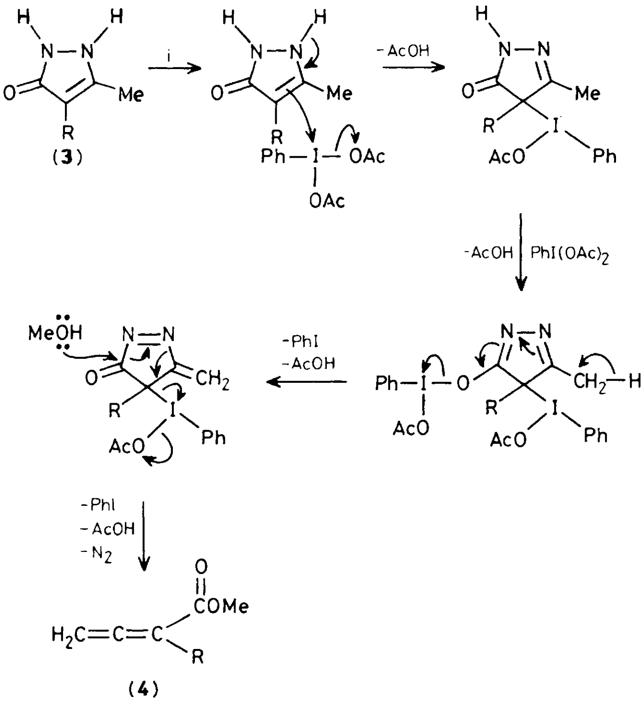


a; R = Me
b; R = Et
c; R = Ph
d; R = p-ClC_6H_4

Scheme 1. *Reagents:* $PhI(OAc)_2$ (0.02 mol)–MeOH (dropwise over 45 min), −23 °C, then stirred 1 h.

1).† Similar oxidation of (**3a**—**c**) (Scheme 2) yielded the 2,3-allenic methyl esters (**4a**—**c**),[5]† again in a manner analogous to that of $Tl(NO_3)_3$ reported by Taylor *et al.*[5]

A reasonable pathway for these transformations is shown in Schemes 1 and 2. The steps are (a) hyperiodination at C-4 to form an intermediate ylide. This type of ylide system is known for pyrazole.[6] (b) Ligand transfer to a second molecule of $PhI(OAc)_2$ followed by reductive elimination and fragmentative loss of molecular dinitrogen to yield the acetylenic ester (**2**). In the 5-substituted systems an ylide cannot be formed but two sequential additions of $PhI(OAc)_2$ with reductive elimination lead to the allenic ester (**4**) (Scheme 2).



a; R = Me
b; R = Et
c; R = CH_2Ph

Scheme 2. *Reagents:* as Scheme 1.

This method of hypervalent iodine oxidation of pyrazol-3(2*H*)-ones is advantageous because the inconvenient toxicity of thallium reagents is avoided.

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† To a methanolic solution (100 ml) of 5-substituted and 5-methyl-4-substituted pyrazol-2(3*H*)-one (0.01 mol) cooled to −23 °C, a methanolic solution (150 ml) of (diacetoxyiodo)benzene (0.02 mol) was added dropwise during 45 min. The mixture was stirred for an additional 1 h. The solvent was reduced to one third volume and the resulting solution was neutralized with saturated aqueous sodium hydrogen carbonate and extracted with dichloromethane. (**2a**) (60%), purified by column chromatography (hexane–ether), b.p. 80—83 °C at 85 mmHg (lit.[7] b.p. 80—82 °C at 85 mmHg); (**2b**) (63%), purified by column chromatography; (**2c**) (59%), b.p. 95—96 °C at 1 mmHg (lit.[8] b.p. 128 °C at 4 mmHg); (**2d**) (61%), m.p. 90—91 °C (lit.[8] m.p. 90—94 °C); (**4a**) (59%), b.p. 50—52 °C at 10 mmHg (lit.[5] b.p. 50—52 °C at 10 mmHg); (**4b**) (64%), b.p. 60—62 °C at 11 mmHg (lit.[6] b.p. 60—62 °C at 11 mmHg); (**4c**) (66%), b.p. 114—115 °C at 0.04 mmHg, (**4c**) gave satisfactory analysis (C and H).

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