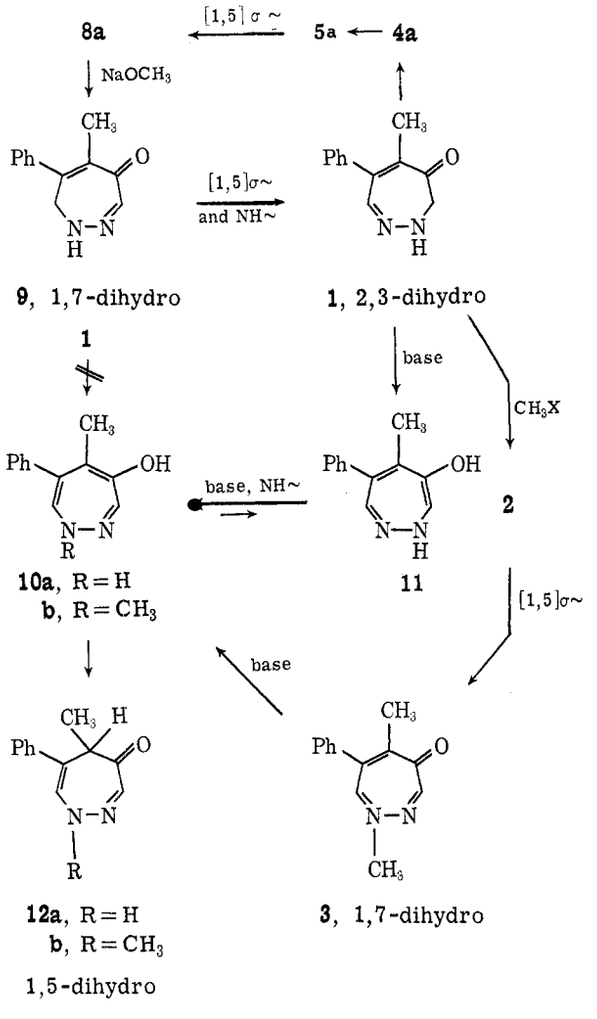
cm^{-1}) and its further transformations. Base-catalyzed methanolysis of **8a** at 25° gave the deacetylated 1,7-dihydrodiazepinone **9** (Scheme II) ($\nu_{C=O}^{Chf}$ 1605

SCHEME II



cm^{-1}) as very pale yellow crystals, mp 119–121°, then 148–150°. The double melting point reflects conversion to the 2,3-dihydrodiazepinone **1** (mp 152°). This isomerization occurred rapidly at 20° in stronger base and obeyed clean first-order kinetics on heating at 80° in neutral solution ($k_1^{CDCl_3}$ 2 × 10^{-5} sec^{-1}; k^{CD_3OD} 9 × 10^{-5} sec^{-1}). No deuterium incorporation occurred at C-3 in CD_3OD. The transformation **9** → **1** thus involves a 1,5-sigmatropic shift of hydrogen from C-7 to C-3, in the reverse direction to that of the 2,3-dihydrobetaines **2** and **5**.[8] The faster rate in CD_3OD, in contrast to the rearrangement of **2** to **3** which is slightly faster in $CHCl_3$ than in CH_3OH,[7] is consistent with the fact that proton transfer, in addition to sigmatropic hydrogen migration, is required in the reaction **9** → **1**.

Tautomeric Relationships in the 1,2-Dihydrodiazepin-4-one System.—The NH 1,7-dihydro compound **9** is the third of three possible unsubstituted tautomers in this series; all have been isolated in crystalline form. The NH 1,5-dihydrodiazepinone **12a** is obtained from the 2,3-dihydro isomer by base-catalyzed equilibration *via* the enols **10a** and **11** and is the more stable of the two ketones.[9] Furthermore, the 1-methyl-1,7-diazepinone **3** is converted completely to the 1-methyl derivative **12b** by base *via* the enol **10b**.[9] It is remarkable, therefore, that isomerization of **9**, even in the presence of base, gives exclusively the 2,3-dihydro tautomer and none of the more stable **12a**.

This combination of interconversions by sigmatropic rearrangements and enolizations establish the stability order 1,7 < 2,3 < 1,5 in this multitautomer system. The 1,7-dihydro system is accessible only when this stability sequence is reversed by the formation of 1-substituted 2,3-dihydrobetaines; it can be predicted that a 2-substituted 1,7-dihydrobetaine would undergo extremely rapid rearrangement to a 2-substituted 2,3-dihydro derivative.

(8) The same process was observed previously in the base-catalyzed conversion of the 7-methoxy-1-benzoyl-1,7-dihydrodiazepinone to the 7-methoxy-2,3-dihydrodiazepinone, but was not recognized as such, and was represented as a series of prototropic rearrangements: R. L. Wineholt, E. Wyss, and J. A. Moore, *J. Org. Chem.*, **31**, 48 (1966).

(9) M. G. Pleiss and J. A. Moore, *J. Amer. Chem. Soc.*, **90**, 1369 (1968).

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Thallium in Organic Synthesis. XXXVI. A New Synthesis of Allenic Esters†

Summary: α-Alkyl-β-keto esters can be converted in a single step into allenic esters by initial reaction with hydrazine (giving the 5-pyrazolones *in situ*) followed by oxidation by thallium(III) nitrate.

Sir: There has been much recent interest in the synthesis[1] and reactions[2] of allenic acids and esters. Available synthetic methods include addition of Wittig reagents to ketenes[3] or acid chlorides,[4] reaction of propargyl alcohols with nickel carbonyl,[5] and basic isomerization of acetylenes.[6] We now report a simple synthesis of allenic esters from α-alkyl-β-keto esters.

Our recently reported new synthesis of α,β-acetylenic esters[7] by thallium(III) nitrate (TTN)[8] oxidation of 3-substituted 5-pyrazolones (**2**, R_3 = H) involves, in a formal sense, the dehydration of a β-keto ester. We have now found that α-alkyl-β-keto esters (**1**) are converted under the same conditions to allenic esters (**6**). Thus, the β-keto ester is first converted to a 3,4-disub-

† Part XXXV: A. McKillop, J. D. Hunt, and E. C. Taylor, *J. Org. Chem.*, in press.

(1) S. C. Sandler and W. Karo, "Organic Functional Group Preparations," Vol. 2, Academic Press, New York, N. Y., 1971.

(2) M. Caserio in "Selective Organic Transformations," Vol. 1, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N. Y., 1970, p 239.

(3) W. S. Wadsworth and W. D. Emmons, *J. Amer. Chem. Soc.*, **83**, 1733 (1966).

(4) (a) H. J. Bestmann, G. Graf, H. Hartung, S. Kalewa, and E. Vilsmaier, *Chem. Ber.*, **103**, 2794 (1970); (b) H. J. Bestmann and H. Hartung, *ibid.*, **99**, 1198 (1966).

(5) E. R. H. Jones, G. H. Whitham, and M. C. Whiting, *J. Chem. Soc.*, 4628 (1957).

(6) G. Eglington, E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, *ibid.*, 3197 (1954).

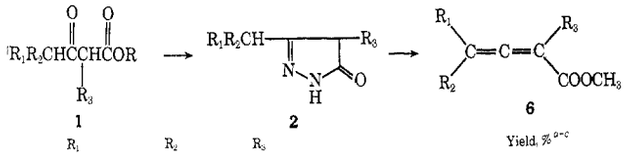
(7) E. C. Taylor, R. L. Robey, and A. McKillop, *Angew. Chem., Int. Ed. Engl.* **11**, 48 (1972).

(8) A. McKillop, J. D. Hunt, E. C. Taylor, and F. Kienzle, *Tetrahedron Lett.*, 5275 (1970).

stituted 5-pyrazolone (**2**, R_3 = alkyl) by addition of 1 equiv of hydrazine, and then a solution of 2 equiv of TTN in methanol is added to a suspension or solution of the pyrazolone in methanol. The reaction mixture is stirred at room temperature for 30 min and the precipitated thallium(I) nitrate removed by filtration. The filtrate is poured into water, which is extracted with chloroform, and the extracts are dried (Na_2SO_4) and filtered through a short column of Florisil. Evaporation of the solvent followed by distillation gives the pure allenic ester. Representative conversions are given in Table I.

TABLE I

SYNTHESIS OF ALLENIC ESTERS FROM β-KETO ESTERS WITH TTN/CH_3OH

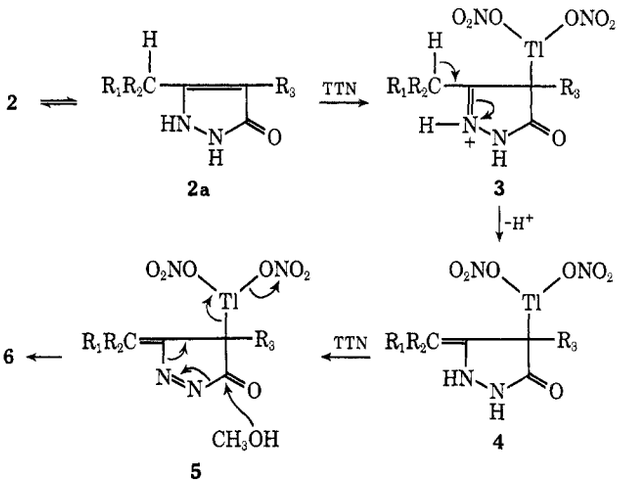


R_1	R_2	R_3	Yield, %[b,c]
H	H	CH_3	50
H	H	CH_2CH_3	48
H	H	$CH(CH_3)_2$	54
H	H	$(CH_2)_4CH_3$	70
CH_2CH_3	H	CH_3	55
CH_2CH_3	H	CH_2CH_3	61

[a] Based upon the intermediate 5-pyrazolone. [b] Yield after distillation. [c] Identity of products established *via* spectral and analytical data.

This reaction, like that of β-keto esters to α,β-acetylenic esters,[7] formally represents the dehydration of the precursor α-substituted β-keto ester. In fact, isolation of the intermediate 5-pyrazolone is unnecessary, and allenic esters can be formed in a single operation by initial addition of hydrazine to a methanol solution of the α-substituted β-keto ester followed by addition of TTN in methanol. In this manner, ethyl 2-isopropylacetoacetate was converted to 3-carbomethoxy-4-methyl-1,2-pentadiene [**6**, $R_1 = R_2 = H$; $R_3 = CH(CH_3)_2$] in 63% yield.

The conversion of 5-pyrazolones to allenic esters can be explained by electrophilic thallation of the enamine (3-pyrazolin-5-one) tautomer[9] (**2a**) of the 5-pyrazolone (**2**), followed by proton loss to give the alkylidene pyrazolidone (**4**). Subsequent oxidation to **5** and solvolysis by methanol would give the observed allenic ester (**6**).[10]



The ready availability of monoalkylated β-keto esters[13] and their facile (and usually quantitative) conversion to 5-pyrazolones[14] make this route to allenes particularly appealing. Further work in this area is in progress.

(9) A. R. Katritzky and J. M. Lagowski, *Advan. Heterocycl. Chem.*, **2**, 28 (1963).

(10) Although 5-pyrazolones have been mercurated in the 4 position[11] and oxidized to diazacyclopentadienones by lead tetraacetate,[12] no conversions analogous to those reported here are known.

(11) (a) W. Schrauth and H. Bauerschmidt, *Ber.*, **47**, 2736 (1914); (b) R. H. Kent and J.-P. Anselme, *Can. J. Chem.*, **46**, 2322 (1968).

(12) B. T. Gillis and R. Weinkam, *J. Org. Chem.*, **32**, 3321 (1967).

(13) E. C. Taylor, G. H. Hawks, and A. McKillop, *J. Amer. Chem. Soc.*, **90**, 2421 (1968).

(14) R. H. Wiley and P. Wiley, "Pyrazolones, Pyrazolidones, and Derivatives," Vol. 20 in the series "The Chemistry of Heterocyclic Compounds," A. Weissberger, Ed., Interscience, New York, N. Y., 1964.

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