Communications

See Editorial, *J. Org. Chem.*, **37**, No. 13, 4A (1972).

Heterocyclic Studies. 36. Acyldiazepinium Intermediates in Thermal Reactions of Diazabicyclo[3.2.0]heptenones†[1]

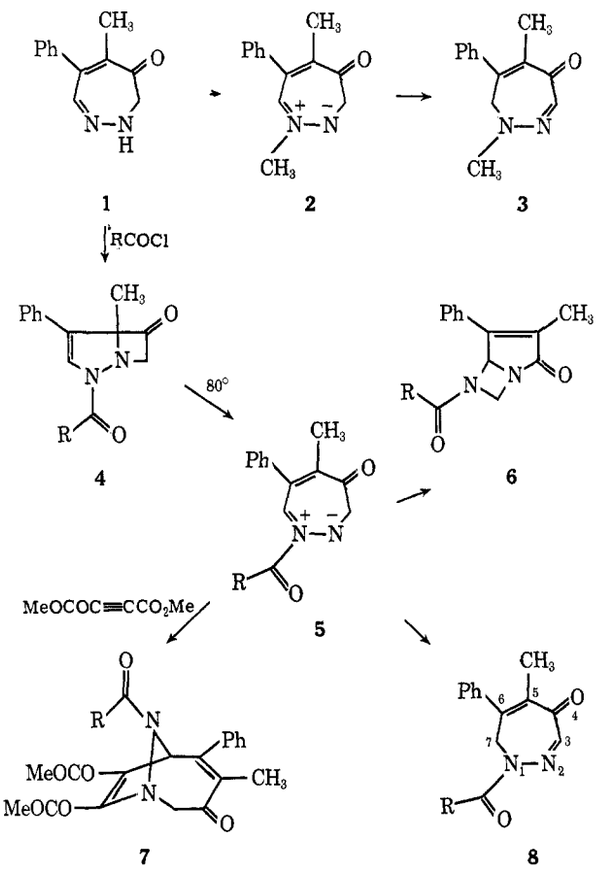
Summary: The bicyclic ketones **4** undergo thermal ring opening to acyldiazepinium betaines **5** which can be trapped by 1,3 cycloaddition; rearrangement of **5** gives the bicyclic lactams **6** and 1-acyl-1,7-dihydrodiazepinones **8**.

Sir: Methylation of the 2,3-dihydrodiazepinone **1** at N-1 gives the betaine **2**,[2] but the corresponding 1-acyl derivatives of **1** exist entirely as the 2-acyl-1,2-diazabicyclo[3.2.0] ketones **4**.[3] This difference in structure can be attributed to the poor stabilization of positive charge in the acyl betaine **5**, as compared to **2**. The facile formation of cycloaddition products from **2**[2] prompted us to examine whether acyl betaines could be produced from the acylbicyclic ketones and trapped at elevated temperatures. On heating **4a** or **4b** at 80° in excess dimethyl acetylenedicarboxylate, the crystalline adducts **7a** and **7b** were in fact obtained in yields of 55 and 30%, respectively (Scheme I). The spectra of these products were fully consistent with the bicyclo[4.2.1] structures and resembled those of the methyl betaine adduct,[2] although the methylene protons were nonequivalent in **7a** and **7b** [for **7a**, δ_A 5.20, δ_B 5.35 (J_{AB} = 4.2)].[4]

Thermal isomerization of the benzoyl ketone **4** in the absence of dipolarophile involves an unusual rearrangement leading in 75% yield to the bicyclic lactam **6b**.[5] The isolation of the acyl–azomethine imine adducts **7** indicates the accessibility of the acyl betaine at moderate temperature and strongly suggests that **5b**, rather than the intermediates previously postulated,[6] is the precursor of **6b**. This behavior, however, appeared to be in marked contrast to the thermal reaction of the methyl betaine **2**, which undergoes sigmatropic hydrogen migration to the 1-methyl-1,7-dihydrodiazepinone **3**.[7]

To examine this point, the acetyl bicyclic ketone **4a** was heated in benzene solution at 80°. The nmr spectrum of the resulting mixture showed peaks corresponding to the lactam **6a** and the acetyldihydrodiazepinone **8a**, in a ratio of 2 : 1, accounting for over 90% of the total integral. The two products were then isolated by crystallization, the less soluble yellow minor product **8a** crystallizing first. Structure **6a** is based on the very close correspondence of spectra with those of **6b** and the characteristic reaction of the methylene diamine ring of **6a** with acidic methanol to give the 5-acetamido-1-methoxymethylpyrrolone, analogous to the well-characterized methanolysis product of **6b**.[5]

SCHEME I



The contrasting results with the methyl and acyl betaines thus reflect merely a difference in product distribution. Reexamination of the reaction product from pyrolysis of **4b** by nmr, after removing a first crop of **6b**, showed a trace (maximum ~8%) of **8b**. The role of the substituent in the partition of the acyl betaines between products **6** and **8**, and the pathway from **5** to **6** are now being studied.

The 1-acetyl-1,7-dihydrodiazepinone structure **8a** follows from the close correspondence of properties with those of the 1-methyl derivative **3** (including the characteristic low ir C-4 carbonyl frequency, ν^{Chf} 1622

† Attention is called to the possibility of including supplementary data [*e.g.*, see footnote 4 of this communication and editorial, *J. Org. Chem.*, **37**, No. 13, 4A (1972)]: F. D. G.

(1) Supported by Grant GP-9322 from the National Science Foundation.

(2) O. S. Rothenberger, R. T. Taylor, D. L. Dalrymple, and J. A. Moore, *J. Org. Chem.*, **37**, 2540 (1972).

(3) J. A. Moore, F. J. Marascia, R. W. Medeiros, and R. L. Wineholt, *ibid.*, **31**, 34 (1966).

(4) Complete experimental details on all compounds described in this communication will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 16th Street, N.W., Washington, D. C. 20036, by referring to code number JOC-72-2796. Remit $3.00 for photocopy or $2.00 for microfiche.

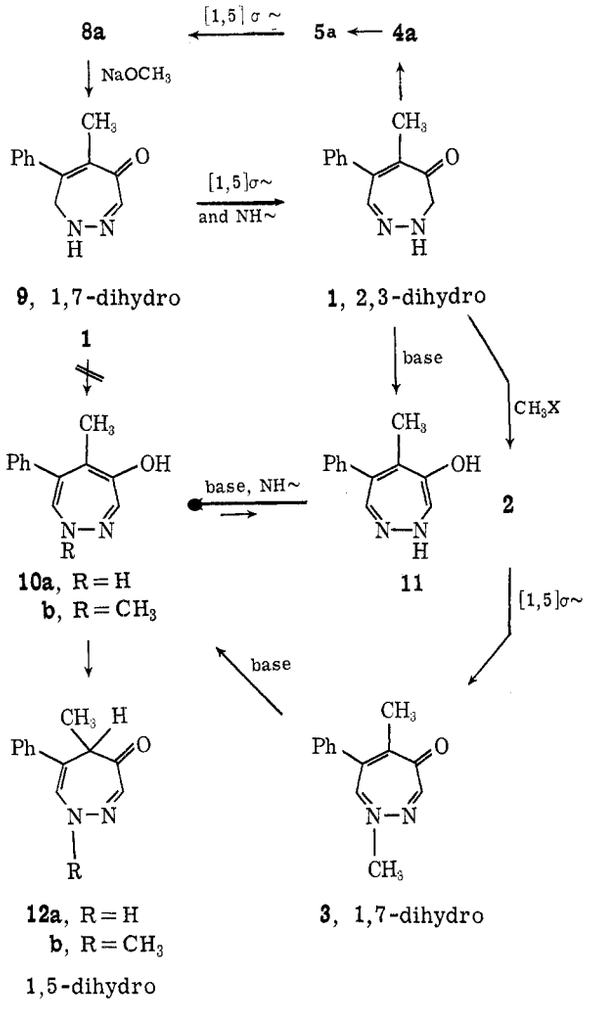
(5) J. M. Eby and J. A. Moore, *ibid.*, **32**, 1346 (1967).

(6) J. A. Moore, R. L. Wineholt, F. J. Marascia, R. W. Medeiros, and F. J. Creegan, *ibid.*, **32**, 1353 (1967).

(7) M. G. Pleiss and J. A. Moore, *J. Amer. Chem. Soc.*, **90**, 4738 (1968).

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.

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(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).

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