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TRIMETHYLSILYL ENOL ETHERS FROM BICYCLIC KETONES AND DIMETHYLAMINOTRIMETHYLSILANE(I)[1]

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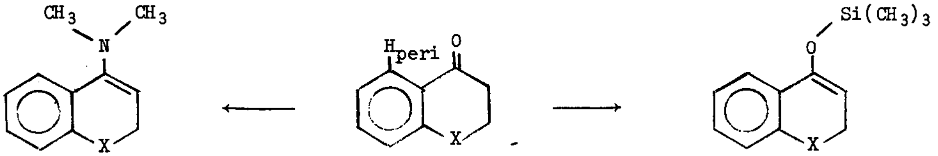
Since 1971 we have sought enamines of benzo[f]chroman-4-one and, later (1972), of chroman-4-one(II), despite publication (2a) and discussion (2b) regarding the failure (2c) to obtain the pyrrolidine enamine of II by classical means (3). When a new procedure appeared (4), we tried to prepare V from II with I, but the outcome was different from the successful synthesis of enamines of monocyclic ketones (4,5).

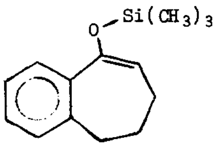
Reaction of I and II (4) (96°/96 hrs) gave a 35% yield of a product: ms m/e 220 (M^+), lacking the nmr absorption expected at δ 2.5 ($N-CH_3$) for V, known for VII (6). We assigned VIII



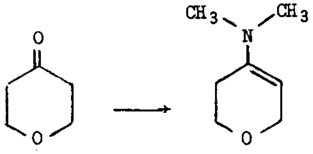
V X = -O-
VI X = -S-
VII X = $-CH_2-$

II X = -O-
III X = -S-
IV X = $-CH_2-$

VIII X = -O-
IX X = -S-
X X = $-CH_2-$



XI



XII XIII

TABLE

Product	Bp°(mm)	% Yield (hrs)[a]	ν(C=C–O–)(cm^{-1})	$\delta^{\text{vinyl H}}_{\text{triplet}}$(J)[b]
VIII	95-8(0.8)	70 (72)	1638	4.80(3.5)
IX	115-8(0.75)	92 (18)	1632	5.12(5.1)
X[c]	90-5(1.5)	81 (122)	1633	5.04(4.0)
XI	91-4(0.6)	66 (90)	1628	5.35(6.5)
XIII	64-5(8)	75 (2)	1649[d]	4.30(4.0)

[a] Conditions: room temperature for the hours indicated, with catalyst *p*-toluenesulfonic acid (5); all compounds exhibited a molecular ion (M^+) in their mass spectra and gave satisfactory elemental analyses. [b] VIII-XI exhibited δ(Si-CH_3) 0.15-0.31; XIII δ(N-CH_3) 2.55. [c] Cited (no properties or spectra) in G. M. Rubottom and M. I. Lopez, *J. Org. Chem.*, **38**, 2097 (1973). [d] C=C–N$<$.

as the structure of the product. When the generality of this reaction was examined using the more recent conditions (5), all of the bicyclic ketones gave the corresponding silyl enol ethers (VIII-XI) (TABLE). Only the monocyclic, 4-oxa analog (XII) of cyclohexanone gave an enamine (XIII).

Enamines of IV are formed sluggishly (7) and its pyrrolidine enamine is alkylated in low yield (7a) due to steric hinderance at the carbonyl from the peri-H (e.g. 8-H in IV). In this study the peri-H presumably hinders one step of enamine formation between the nitrogen of I and the carbonyl carbon (7b), allowing electrophilic attack by the silicon of I on the oxygen (8) to give the enol ether. A similar change in reaction course with changing steric hinderance has been observed in the reaction of ketones with dialkylaminostannanes (9).

References

1. Some Reactions of Enamines. Part IV. Part III: L. H. Hellberg, C. C. Adams, R. J. Milligan and R. N. Wilke, *Org. Preps. and Procedures Int.*, **3**, 77 (1971).
2. (a) F. M. Dean and K. B. Hindley, *Tet. Letts.*, 1445 (1972); (b) Personal Correspondence, F. M. Dean, June-July, 1972; (c) We also failed to obtain this enamine (3), even with acid catalyst (3a) and gentle dehydration (3c).
3. (a) F. W. Heyl and M. E. Herr, *J. Amer. Chem. Soc.*, **75**, 1918 (1953); (b) W. A. White and H. Weingarten, *J. Org. Chem.*, **32**, 213 (1967); (c) K. C. Brannock, R. D. Burpitt, V. W. Goodlett and J. G. Thweatt, *J. Org. Chem.*, **28**, 1464 (1963).
4. T. G. Selin, U. S. Patent 3,621,060; *Chem. Absts.* 76:45258a (1972).
5. R. Comi, R. W. Franck, M. Reitano, and S. M. Weinreb, *Tet. Letts.*, 3107 (1973).
6. B. Cox, M. S. Thesis, San Diego State University, 1973.
7. (a) L. H. Hellberg, R. J. Milligan and R. N. Wilke, *J. Chem. Soc.*, *C*, 35 (1970); (b) F. A. van der Vlugt, J. W. Verhoeven and U. K. Pandit, *Rec. Trav. Chim. Pays-Bas*, **89**, 1258 (1970).
8. While the enol seems the more reasonable reactant, the influence of the enol-keto equilibrium on the course of reaction is unclear, especially with acid catalyst present.
9. J.-C. Pommier and A. Roubineau, *J. Organometallic Chem.*, **50**, 101 (1973).