indicates that reactions similar to the first step of the stepwise process in Scheme II compete effectively with the cyclodimerization process (which is occurring simultaneously).

In order to test the viability of the second step of the two-step mechanism in Scheme II, ditropyl (**11**)[17] was subjected to lithium–ammonia reduction at −33° which, by analogy with the similar reduction of cycloheptatriene,[18] is expected to produce the proposed intermediate **12** (Scheme II). In fact, partial reduction of **11** for 5 min at −33° gave a product mixture consisting of *ca.* 40% dimer **4**,[19] *ca.* 50% unchanged **11**, and *ca.* 10% **5**.

In summary, we suggest that the available data are best accommodated by a rapid stepwise cycloaddition of the cycloheptatrienyl anion (**1**) and cycloheptatriene (**2**) (Scheme II) and that the high stereoselectivity of this reaction is best explained on the basis of steric effects in the second step of this process. The latter point is supported by an examination of molecular models. Furthermore, since this is the first time in which the feasibility of the second step of a possible two-step ionic cycloaddition has been tested, our results provide a caveat regarding the common conclusion that stereoselectivity in ionic cycloadditions implies concertedness.

Acknowledgment. We thank the National Science Foundation for support of this work.

(17) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **79**, 352 (1957).

(18) A. P. ter Borg and A. F. Bickel, *Recl. Trav. Chim. Pays-Bas*, **80**, 1229 (1961).

(19) This conversion could, in principle, occur *via* an initial cleavage of **12** to **1** and **2**, but this is expected to be highly unfavorable on thermodynamic grounds.

(20) Gillette Research Foundation Fellow, 1972–1973.

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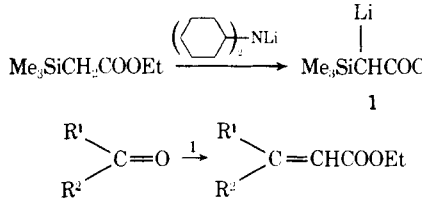
A New Synthesis of α,β-Unsaturated Carboxylic Esters

Sir:

This communication describes a new synthetic method which allows the conversion of carbonyl compounds to α,β-unsaturated carboxylic esters in high yields. The method was designed on the assumption that the well-known affinity of the suitably substituted silyl group to an alkoxide ion[1] should result in transformation of ethyl lithiotrimethylsilylacetate (**1**) as shown below.



(1) (a) D. J. Peterson, *J. Org. Chem.*, **33**, 780 (1968); (b) T. H. Chan, E. Chang, and E. Vinokur, *Tetrahedron Lett.*, 1137 (1970); (c) F. A. Carey and A. S. Court, *J. Org. Chem.*, **37**, 939, 1926 (1972); (d) D. Seebach, B-Th. Gröbel, A. K. Beck, M. Braun, and K.-H. Geiss, *Angew. Chem. Int. Ed. Engl.*, **11**, 443 (1972); (e) C. Trindle, J-T. Hwang, and F. A. Carey, *J. Org. Chem.*, **38**, 2664 (1973); (f) F. A. Carey and O. Hernandez, *ibid.*, **38**, 2670 (1973); (g) H. Sakurai, K. Nishiwaki, and M. Kira, *Tetrahedron Lett.*, 4193 (1973); (h) see, also, D. J. Peterson, *Organometal. Chem. Rev., Sect. A*, **7**, 295 (1972).

Ethyl trimethylsilylacetate was known to be condensed with aromatic aldehydes under rather drastic conditions in the presence of basic catalyst to yield β-trimethylsiloxycarboxylates.[2] The mechanism proposed earlier[2] to involve ethyl sodiotrimethylsilylacetate was questioned and the intermediacy of ethyl sodioacetate was shown to be more probable ($Me_3SiCH_2COOEt + B^- \rightarrow {}^-CH_2COOEt + Me_3SiB$).[3] The formation of the lithium enolate **1** was realized by treatment of ethyl trimethylsilylacetate[4] with lithium dicyclohexylamide[5,6] in dry tetrahydrofuran at −78° for 10 min. Quenching with water followed by analysis by glpc revealed >95% recovery of the starting ester. The formation of the anion **1** was further verified by reaction with carbonyl compounds to yield the bis-homologated carboxylic esters in the yields indicated: benzaldehyde → ethyl cinnamate (84%, E/Z = 3:1); nonanal → ethyl 2-undecenoate (81%, E/Z = 1:1); cyclohexanone → ethyl cyclohexylideneacetate (95%); cyclododecanone → ethyl cyclododecylideneacetate (94%); cyclopentanone → ethyl cyclopentylideneacetate (81%); chalcone → ethyl 2,4-diphenylbutadiene-1-carboxylate (86%, E/Z = 7:3).

The best current method for the above transformations involves a direct analog of the Emmons–Wadsworth–Horner method,[7] which generally works fairly well. Although often an excellent procedure, the aforementioned results revealed several situations where our new, milder method would be preferred. Readily enolizable ketone may be inert to the phosphonate carbanion.[8] Proton transfer reactions may occur faster than carbonyl addition with the risk of enolate condensation reactions. Such behavior is especially characteristic of cyclopentanone in the Wittig-type reaction,[8a,c] whereas we obtain exclusively ethyl cyclopentylideneacetate in good yield.[9] Chalcone is known to react with the phosphonate anion to give either/both a Michael or a Wittig–Horner product in low yields,[7f] whereas the lithium enolate **1** gave only the 1,2-addition product.

The reaction of cyclododecanone to ethyl cyclododecylideneacetate is typical. A solution of dicyclohexylamine (3.65 g, 20 mmol) in dry tetrahydrofuran (100 ml) was treated with *n*-butyllithium (13.5 ml of a

(2) L. Birkofer and A. Ritter, *Chem. Ber.*, **95**, 971 (1962).

(3) C. Eaborn and R. W. Bott in "Organometallic Compounds of the Group IV Elements," Vol. 1, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1968, p 1; L. Birkofer and A. Ritter, *Angew. Chem.*, **77**, 414 (1965).

(4) This colorless liquid was easily prepared on a 0.1–0.3 *M* scale from ethyl bromoacetate by the method of Fessenden [*J. Org. Chem.*, **32**, 3535 (1967)] in 70–80% yield after distillation, bp 85° (68 mm).

(5) R. A. Olofson and C. M. Dougherty, *J. Amer. Chem. Soc.*, **95**, 582 (1973).

(6) Preparation and reactions of ethyl lithioacetate: M. W. Rathke, *J. Amer. Chem. Soc.*, **92**, 3222 (1970); M. W. Rathke and A. Lindert, *ibid.*, **93**, 2318 (1971); M. W. Rathke and J. Deitch, *Tetrahedron Lett.*, 2953 (1971).

(7) (a) W. S. Wadsworth, Jr., and W. D. Emmons, *J. Amer. Chem. Soc.*, **83**, 1733 (1961); (b) H. Takahashi, K. Fujiwara, and M. Ohta, *Bull. Chem. Soc. Jap.*, **35**, 1498 (1962); (c) A. K. Bose and R. T. Dahill, Jr., *Tetrahedron Lett.*, 959 (1963); *J. Org. Chem.*, **30**, 505 (1965); (d) J. Wolinsky and K. L. Erickson, *ibid.*, **30**, 2208 (1965); (e) W. S. Wadsworth, Jr., and W. D. Emmons, *Org. Syn.*, **45**, 441 (1965); (f) E. D. Bergmann and A. Solomonovici, *Tetrahedron*, **27**, 2675 (1971).

(8) (a) E. J. Corey and J. I. Shulman, *J. Org. Chem.*, **35**, 777 (1970); (b) R. L. Sowerby and R. M. Coates, *J. Amer. Chem. Soc.*, **94**, 4758 (1972), and references cited therein; (c) see, also, D. R. Coulson, *Tetrahedron Lett.*, 3323 (1964).

(9) The reaction should be quenched at −25° in this case; the usual reaction conditions gave a mixture of α,β- and β,γ-unsaturated ester in 9:1 ratio (by nmr assay).

1.50 *M* hexane solution, 20 mmol) at −78°. After 15 min, ethyl trimethylsilylacetate (3.20 g, 20 mmol)[4] was added dropwise over a 10-min period and the mixture was stirred for 10 min at the same low temperature. Cyclododecanone (1.82 g, 10 mmol) in tetrahydrofuran (20 ml) was added dropwise and the resulting pale yellow solution was stirred at −78° for 1 hr, −25° for 1 hr, and 25° for 1 hr. Extractive work-up followed by chromatography (silica gel, 100 g, using hexane as eluent) gave the desired ester as a colorless semisolid (2.36 g, 94%).[10]

Acknowledgment. We are indebted to Dr. Keiji Yamamoto for stimulating discussions.

(10) Bp 155° (bath temp, 2 mm); ir (neat) 1720 (conjugated ester), 1644 (C=C), 1150 cm^{-1}; nmr (CCl_4, TMS) δ 1.24 (t, J = 7 Hz, $-CH_3$), 2.21 (br t, J = 7 Hz, $-CH_2C=$), 2.71 (br t, J = 7 Hz, $-CH_2C=$), 4.06 (q, J = 7 Hz, CH_2CH_3), 5.63 (br s, olefinic proton); mass m/e 252 (M^+), 128 (base peak); homogeneous by tlc. *Anal.* Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18. Found: C, 75.89; H, 11.11.

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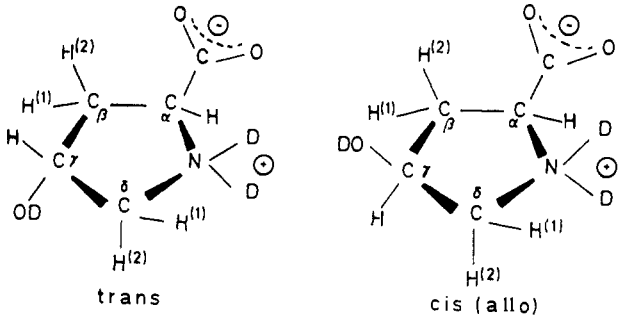
Anisotropy Effects of the Carboxylic Group in the Proton Magnetic Resonance Spectra of L-Hydroxyproline

Sir:

In the course of a systematic investigation of proline compounds by proton magnetic resonance (pmr),[1,2] we have paid special attention to the anisotropy effect of the carboxylic plane on the chemical shift of the ring protons. The comparison between the chemical shift titration curves corresponding to each proton provides a qualitative location of the carboxylic group, *i.e.*, gives a rough value of the torsion angle around the C^{α}–C^{O} axis (ψ angle in the peptides).

Abraham and Thomas[3] have analyzed the pmr spectra of *allo*- and *trans*-L-hydroxyproline in strong



acid, neutral, and strong alkaline solutions and deduced the conformation of the molecular ions in these solutions from the observed coupling constants. If we plot their chemical shift data against the pH and examine them in the light of our recent results on proline[2] and *trans*-hydroxyproline[1] some interesting conclusions about the carboxyl position in the trans and allo compounds can be reached.

The trend of the curves is the one expected from the titration of the neighboring carboxyl and amino

(1) L. Pogliani and M. Ellenberger, *Spectrosc. Lett.*, **6**, 261 (1973).
(2) M. Ellenberger, L. Pogliani, K. Häuser, and J. Valat, *Chem. Phys. Lett.*, in press.
(3) R. J. Abraham and W. A. Thomas, *J. Chem. Soc.*, 3739 (1964).

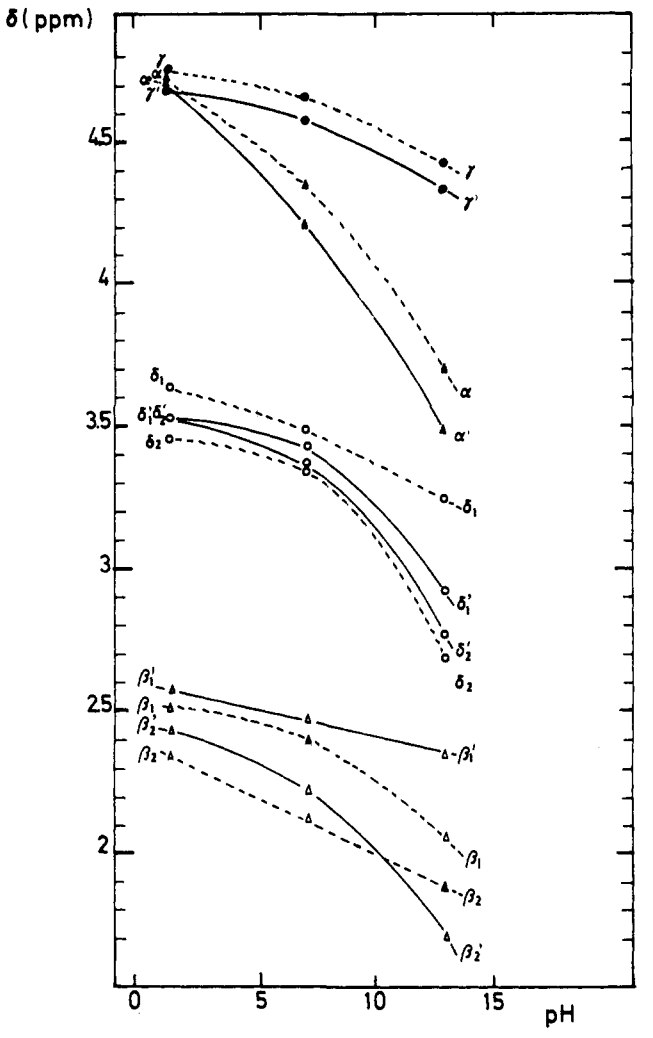


Figure 1. Chemical shift *vs.* pH of the protons of hydroxyproline cis (allo) and trans in aqueous solution, data from ref 3. Chemical shifts are given in ppm. Internal reference in DSS: (—) allo compound, (- - - -) trans compound.

functional groups (the hydroxyl titration which occurs at higher pH has not been considered here), but, since the pK's for both functions are the same within 0.1 pH unit in the trans and allo isomer, the difference between the curves belonging to the same proton in both species and their relative position reflects mainly structural features (Figure 1). Roughly, a high field shift denotes a position above the COO^- π plane and a low field shift denotes a location in this plane.[4]

The curves have to be discussed by keeping in mind the conformation of both species as given by Abraham and Thomas.[3] These conformations are briefly summarized here. The *trans*-L-hydroxyproline (THP) is in an exo envelope conformation in acid and neutral solution. In alkaline solution a rapid interconversion occurs between the isomers corresponding to the two positions of the nitrogen lone pair, one of which allows an intramolecular hydrogen bonding.

The *allo*-L-hydroxyproline (AHP) is in an endo envelope conformation in acid and neutral solution. In alkaline solution two rapidly exchanging half-chair conformations are mixed to this envelope, an intramolecular hydrogen bond occurring also between the

(4) L. M. Jackman and S. Sternhell, "Applications of NMR Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, 1969, p 88.