G. K.; Holton, J.; Hunter, W. E.; Lappert, M. F.; Pierce, R. *J. Am. Chem. Soc.* **1977**, *99*, 6645-6651.

(10) The photolyses of $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ and of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ in the presence of hydrogen have been briefly described by others: Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6733-6735. Huffman, J. C.; Stone, J. G.; Krusell, W. C.; Caulton, K. G. *Ibid.* **1977**, *99*, 5829-5831.

(11) In all photochemical reactions involving **1** in heptane solution either alone or in the presence of phosphines, a yellow precipitate is also invariably formed. An IR spectrum (Nujol) of this product exhibits characteristic cyclopentadienyl bands as well as a strong absorption at 2055 cm^{-1}. The ^{1}H NMR spectrum (C_6D_6) of the yellow solid contains a single broad resonance centered at ca. τ 3.8 and is reminiscent of the spectrum of photochemically generated black titanocene.[12] The product, which may possibly be an oligomeric hafnocene carbonyl, is under further investigation.

(12) Rausch, M. D.; Boon, W. H.; Alt, H. G. *J. Organomet. Chem.* **1977**, *141*, 299-312.

(13) Clark, R. J.; Busch, M. A. *Acc. Chem. Res.* **1973**, *6*, 246-252.

(14) Alt. H.; Rausch, M. D. *J. Am. Chem. Soc.* **1974**, *96*, 5936-5937.

(15) All of the above reactions involving **1** have also been successfully completed for $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$: Sikora, D. J.; Rausch, M. D., unpublished studies.

David J. Sikora, Marvin D. Rausch*
Department of Chemistry, University of Massachusetts
Amherst, Massachusetts 01003

Robin D. Rogers, Jerry L. Atwood*
Department of Chemistry, University of Alabama
University, Alabama 35486

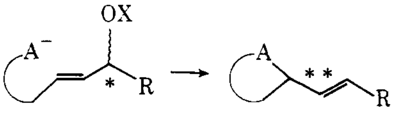
Received April 22, 1979

Concerted Intramolecular Displacement with Rearrangement in Allylic Systems. Displacement of an Allylic Ester with a Carbanion

Sir:

The formation of a ring by intramolecular displacement with rearrangement of an allylic departing group,[1] as shown in **1** → **2**, could be a valuable reaction:[2] if the displacement is stereospecific it will result in predictable transfer of chirality from the secondary alcohol center in **1** (easily obtainable from any readily available chiral ethynyl carbinol)[3] to a carbon atom of the newly formed ring.

Our initial investigation[1] of such an intramolecular internal $S_{N'}$ reaction (for which we suggest the symbol $S_{CN'}$[4]) represented by **1** → **2** showed that, when A is sulfur, reaction results



1 2

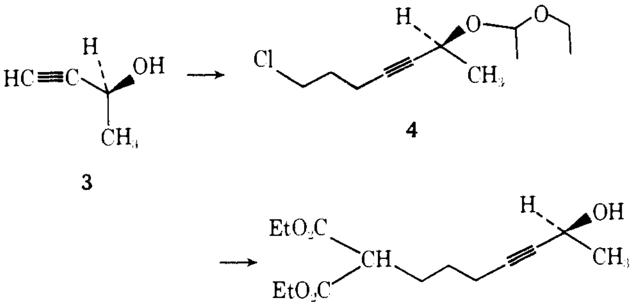
in a transfer of chirality (* → **) which corresponds to very largely anti relationship of A⁻ and X in the transition state for the cyclization (to a tetrahydrothiophene).

This result was surprising because it is in contrast to the clean syn relationship reported for the only previous cyclization of this type.[2a,5] In that instance, the departing oxygen function was part of an epoxide rather than, in our case, of an ester group; and the displacing group A was carbon rather than sulfur.

The difference in stereochemical course might be the result, inter alia, of different geometry relating entering and departing groups (metal chelation with epoxide?); or it might be due to some peculiarity of the sulfide ion (one-electron transfer?) involved in the cyclization in which A is sulfur.

In order to examine the latter possibility, as well as to establish the usefulness of the chiral synthesis shown in **1** → **2**, we have now examined the situation in which A in structure **1** above is carbon rather than sulfur and now demonstrate that anti relationship between entering and departing group is observed here also, resulting now in the formation of a cyclopentane ring.

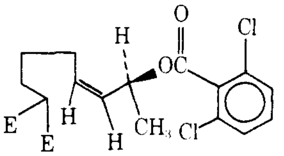
The required material for the cyclization studies was prepared starting with partially resolved (*S*)-(−)-1-butyn-3-ol[6] (**3**), $[\alpha]^{22}_{D}$ − 26.7° (*c* 3.3, dioxane), which had 49.7% enantiomeric excess.[7] Protection of the secondary hydroxyl group (ethyl vinyl ether, trace of $POCl_3$, 0-10 °C, 2 h), followed by alkylation with 1-bromo-3-chloropropane (1.5 equiv of $LiNH_2$-liquid NH_3, −33 °C, 8 h), gave the 1-ethoxyethyl ether of 7-chloro-3-heptyn-2-ol (**4**), bp 91-92 °C (0.35 mm).



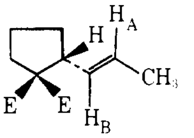
3 4 5

Alkylation in the presence of sodium iodide (~0.3 equiv) with sodium diethylmalonate (~2 equiv of 1:3 DMF-EtOH, 105 °C, 12 h), followed by removal of the protecting group (~3:1:1 AcOH-THF-H_2O, 35 °C, 6 h), gave the ethynylcarbinol **5** which had $[\alpha]^{22}_{D}$ − 7.8 ° (*c* 1.95, benzene), after purification by MPLC on silica gel (30:70 ethyl acetate-hexane).[8] Selective hydrogenation (5% Pd/$BaSO_4$, CH_3OH, trace of quinoline) to the cis olefinic carbinol and esterification with 2,6-dichlorobenzoyl chloride[9] (1.5 equiv of pyridine, 105 °C, 2 h) gave ester **6**, *m/e* 445 (M + 1)$^+$, $[\alpha]^{22}_{D}$ +28.6° (*c* 2.1, benzene), after purification by silica gel chromatography (1:4 ethyl acetate-petroleum ether).

Cyclization of (*S*)-(+)-**6** was best achieved with sodium hydride (2 equiv in 2.6:1 THF-DMF, 55-60 °C, 9 h) which gave, after chromatography on silica gel (5:95 ethyl acetate-benzene), a 70-80% yield of diethyl 2-*trans*-1-propenylcyclopentane 1,1-dicarboxylate (**7**). The structure of **7**-$[\alpha]^{22}_{D}$ +29.6° (*c* 2.1, benzene), was supported by the ^{1}H and ^{13}C NMR data and, as indicated on the formula, it is particularly important for the further analysis that the double bond in **7** is clearly trans.

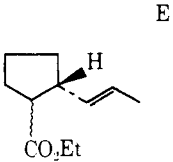


6

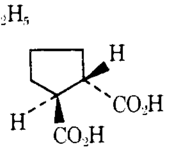


7 (J_{AB} = 15 Hz)

E = $CO_2C_2H_5$



8



9

Absolute Configuration of 7. The appreciable rotation of the cyclization product **7** suggests strongly that the reaction must be concerted with considerable bias, whether in favor of syn or anti displacement. This was confirmed by studying the ^{1}H NMR spectrum of **7** in presence of the optically active shift reagent tris[(3-heptafluorobutyryl)-camphorato-*d*]europium(III).[10] The proton labeled H_A in **7** gave separate doublets (irradiation of methyl) for the two antipodes in the ratio ~72:28. Since the ratio of the two antipodes of the starting

0002-7863/79/1501-5081$01.00/0

alcohol **3** was (vide supra) ~75:25, the reaction is clearly highly stereoselective.

Monodecarbethoxylation of **7** with lithium chloride in aqueous Me_2SO[11] gave the mixture of esters **8**, $[\alpha]^{22}_{D}$ +9.5° (*c* 1.6, benzene). This gave a single peak on 5% FFAP at 140 °C, but was (^{13}C NMR) a trans-cis mixture, as expected. Oxidation of the mixture of stereoisomers with ruthenium oxide-sodium periodate in aqueous acetone[12] to the half ethyl ester of cyclopentane-1,2-dicarboxylic acid, $[\alpha]^{22}_{D}$ +21.2° (*c* 2.1, benzene), and hydrolysis (0.9 M potassium hydroxide in 1:1 THF-EtOH at room temperature) gave the desired cyclopentane-1,2-dicarboxylic acid **9**. The identity of the product thus obtained, a cis-trans mixture of cyclopentane-1,2-dicarboxylic acids, was established by comparison (as the dimethyl esters) with authentic racemic material.[13] The absolute configuration of the trans diacid **9** in the mixture could easily be established, since the cis isomer does not contribute to the rotation. The mixture of acids had $[\alpha]^{22}_{D}$ +17.2° (*c* 1.2, H_2O). This establishes the presence of an excess of the (1*S*,2*S*)-(+) trans isomer of the absolute stereochemistry shown in **9** since the (1*R*,2*R*)-(−) diacid antipode of **9** has been correlated with the (1*S*,2*S*)-(−) isomer of 1,2-cyclopentanediacetic acid.[14,15]

We conclude that the internal displacement with rearrangement ($S_{cN'}$) of a reactive ester of an allyl alcohol takes place anti to the departing carboxylate function when the displacing (cyclizing) group is a carbanion. This is the same stereochemistry which we had previously established for displacement by sulfide ion.[1] The apparent agreement with some recent theoretical proposals[16] is probably illusory because (a) some intermolecular displacements also involving negatively charged displacing groups have been shown to involve syn displacement;[17] (b) at least one intramolecular displacement, involving an allylic epoxide, seems to take place syn.[2a]

It is indeed likely that the nature of the counterion, of the departing group and of the medium will all be involved. It does however appear possible, in many cases, to delineate those systems which may be expected to lead to predictable chirality transfer. We intend to pursue this goal.

Acknowledgment. We thank the National Science Foundation for partial support of this work and also NATO and the French CNRS for Fellowship support to A.R.S.

References and Notes

(1) Stork, G.; Kreft, A. F. *J. Am. Chem. Soc.* **1977,** *99*, 3851–3853.

(2) Cf.: (a) Martel, J.; Blade-Font, A.; Marle, C.; Vivat, M.; Toromanoff, E.; Buendia, *J. Bull. Soc. Chim. Fr.* **1978,** *II*, 131–139. Buendia, J.; Vivat, M.; Toromanoff, E; Martel, J. *Ibid.* **1978,** *II*, 140–143. (b) See also: Chiche, L.; Coste, J.; Christol, H.; Plenat, F. *Tetrahedron Lett.* **1978,** 3251–3254. Uebel. J. J.; Milaszewski, R. F.; Art, R. E. *J. Org. Chem.* **1977,** *42*, 585–591.

(3) This would be especially attractive since (a) ethynylcarbinols are easily obtained in high optical purity by reduction of ethynyl ketones with chiral hydride reagents (Brinkmeyer, R. S.; Kapoor, V. M. *J. Am. Chem. Soc.* **1977,** *99*, 8339–8341). (b) A given chiral ethynylcarbinol can lead to either absolute configuration in the ring compound **2**, depending on whether the ethynylcarbinol is reduced to a *cis*- or to a *trans*-vinylcarbinol before cyclization.

(4) It is unsatisfactory to refer to an internal $S_{N'}$ reaction as "internal S_N2'" since it cannot be second order. We suggest the symbol $S_{cN'}$, the c signifying that the reaction involves cyclization.

(5) *Inter*molecular S_N2' reactions often take place by syn displacement. See: Stork, G.; Kreft, A. F. *J. Am. Chem. Soc.*, **1977,** *99*, 3850–3851. Magid, R. M.; Fruchey, O. S. *Ibid.* **1977,** *99*, 8368–8370. Dobbie, A. A.; Overton, K. H. *J. Chem. Soc., Chem. Commun.* **1977,** 722–723. Oritani, T.; Overton, K. H. *Ibid.* **1978,** 454–455. Toromanoff, E. *Tetrahedron*, **1978,** *34*, 1665–1673. Also see ref 17.

(6) Weidmann, R.; Schoofs, A. R.; Horeau, A. *Bull. Soc. Chim. Fr.* **1976,** 645–648. Olsson, L. I.; Claesson, A. *Acta Chem. Scand., Ser. B* **1977,** *31*, 614–618.

(7) Determined by the method of Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969,** *34*, 2543–2549.

(8) All new compounds gave satisfactory infrared, as well as proton and carbon NMR spectra and chemical Ionization mass spectra. Optical rotations were measured on a Perkin-Elmer Model 141 polarimeter.

(9) Stork, G.; White, W. N. *J. Am. Chem. Soc.* **1956,** *78*, 4609–4619.

(10) Fraser, R. R.; Petit, M. A.; Saunders, J. K. *Chem. Commun.* **1971,** 1450–1451.

(11) Krapcho, A. P.; Weimaster, J. F.; Eldridge, J. M.; Jahngen, E. G. E., Jr.; Lovey, A. J.; Stephens, W. P. *J. Org. Chem.* **1978,** *43*, 138–147.

(12) Pelletier, S. W.; Iyer, K. N.; Chang, C. W. J. *J. Org. Chem.* **1970,** *35*, 3535–3538.

(13) The trans isomer has the shorter retention time on 5% FFAP at ~150 °C.

(14) Inouye, Y.; Sawada, S.; Ohno, M.; Walborsky, H. M. *Tetrahedron* **1967,** *23*, 3237–3243.

(15) Bourn, P. M.; Klyne, W. *J. Chem. Soc.* **1960,** 2044–2046.

(16) Yates, R. L.; Epiotis, N. D.; Bernardi, F. *J. Am. Chem. Soc.* **1975,** *97*, 6615–6621.

(17) Klrmse, W.; Scheidt, F.; Vater, H.-J., *J. Am. Chem. Soc.* **1978,** *100*, 3945–3946.

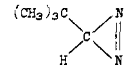
Gilbert Stork,* Alain R. Schoofs
Department of Chemistry, Columbia University
New York, New York 10027

Received April 4, 1979

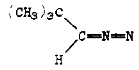
Roles of Multiplicity and Electronic Excitation on Intramolecular Reactions of Alkylcarbenes in Condensed Phase

Sir:

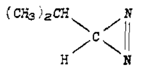
Little information exists as to the roles of multiplicity and electronic excitation in intramolecular reactions of alkylcarbenes in condensed phase. Such intermediates generated thermally have been presumed to rearrange and insert by singlet mechanisms.[1] Triplet alkylcarbenes have had little study but are theorized to resist rearrangement and concerted carbon–hydrogen insertion because the conversions into triplet products are unfavorable energetically.[2-4] Recently, thermal, photolytic, and photosensitized decompositions of 1-diazo-2-methyl-2-phenylpropane to 1-methyl-1-phenylcyclopropane, 2-methyl-1-phenylpropene, 2-methyl-3-phenylpropene, *cis*- and *trans*-2-phenyl-2-butenes, and 2-phenyl-1-butene have been interpreted to involve varying mixed singlet and triplet carbenic processes.[5] It is also not clear whether triplet alkylcarbenes undergo intramolecular carbon–hydrogen insertion by abstraction, spin inversion, and recombination.[6] Important further theory is that the more indiscriminate intramolecular gas-phase insertion and rearrangement reactions upon photolysis than by thermolysis of alkyldiazirines have been attributed to vibrationally excited carbenes (hot radicals) as generated photochemically.[7] A study is now reported of carbenic decomposition of 3-*tert*-butyldiazirine (**1**),[8a] 1-diazo-2,2-dimethylpropane (**2**),[8b] and 3-isopropyldiazirine (**3**)[8a] by various methods in condensed phase. Particular emphasis has been directed to the intramolecular triplet processes from **1–3**.



1



2



3

Decompositions of **1–3** by thermal and photochemical methods occur efficiently by carbenic routes in environments which minimize cationic processes.[9] Thermolysis of **1** and **2** in decalin or cumene (Table I) at 130–180 °C in the presence of sodium hydride thus gives 1,1-dimethylcyclopropane (**4**, 87–91%) and 2-methyl-2-butene (**5**, 9–12%) in the indicated proportions. The 2-methyl-1-butene (**6**, 3.2%) from **2** is an initial contaminant of the diazo compound and is also formed by cationic decomposition of **2** upon warming. The similarities in the ratios of **4** and **5** from thermolyses of **1**[10] and **2** imply that common reaction intermediates are involved.

Irradiation (Table I) of **1**[11] at 25 and −80 °C in solvents containing tetramethylguanidine or sodium hydride yields **4** (45–46%) and **5** (54–55%). Similarly, photolyses (phot) of **2** in tetrahydrofuran at 25 and −80 °C give **4** (46.5 and 51.9%)

0002-7863/79/1501-5082$01.00/0