Similarly when the downfield quartet (δ 5.26) was irradiated, the downfield methyl resonance (δ 1.73) collapsed to a singlet.

Although little if any rearrangement of the syn component of the 1/2 allene mixture can be detected at GC oven and injector temperatures at 160 °C or below, substantial rearrangement occurs at higher temperatures. When 50 μL of a 31:69 1/2 mixture was injected (flow rate = 10 mL/min) at column/injector temperatures of 175/175 °C, 200/200 °C, 225/225 °C, and 225/300 °C, the percent of 1 that rearranged was 51.0, 76.8, 79.7, and 86.5%, respectively.[13] For the small 1-μL injection of the pure syn allene at 225/300 °C discussed above, the percent of rearrangement to 4 was determined to be 97.9% by HPLC analysis of collected material.

The diastereomeric trienes 4 obtained from the GC pyrolyses were usually contaminated with about 3–4% of 1-ethylindan.[14] In fact when a triene sample was reinjected on the GC at 225/300 °C, much of it rearranged further to 1-ethylindan as determined by both HPLC and NMR analysis.

Given the fact that anti allene 2 did not rearrange under conditions in which syn allene 1 readily affords a mixture of trienes (*E*)-4 and (*Z*)-4, the 1 → 4 rearrangement is likely a concerted one and the orbital symmetry rules[15] apply. The difference in the thermal stability of 1 and 2 is especially important when compared to the results[2b] with the vinyl systems **5a** and **5b** discussed above. Furthermore, Berson[16] has found that the vinyl hydrocarbon *syn*-7-ethenylnorbornene is stable at 250 °C and at 320 °C it decomposes without rearrangement. Thus the allenyl group likely affords an improved pathway for the Cope rearrangement relative to a vinyl group in the present case. Our current results support our earlier interpretation[1] that the 1 → (*E*)-4 + (*Z*)-4 rearrangement is likely facilitated through the intervention of a $[{}_{\sigma}2_s + {}_{\pi}2_s + ({}_{\pi}2_s + {}_{\pi}2_a)]$[1,17] augmented eight-electron Cope process. Racemic (*E*)-4 would result from the cleavage of the bridgehead C–C bond anti to the methyl group in racemic 1 (i.e., the 1,7-bond in (*S*)-1 or the 4,7-bond in (*R*)-1) whereas racemic (*Z*)-4 would result from cleavage of the C–C bond syn to the methyl group (i.e., the 1,7-bond in (*R*)-1 or the 4,7-bond in (*S*)-1).[18]

Work directed toward the synthesis and rearrangement of a 1-methyl-substituted analogue of 1 is in progress. The observed stereochemistry of such a rearrangement should provide more valuable information concerning the mechanism of these rearrangements.

Acknowledgment. Supported by a M. J. Murdock Charitable Trust Grant of Research Corporation, for which we are most grateful. We also thank Professor C. Klopfenstein of the University of Oregon for securing the 360-MHz ^{1}H NMR spectra for us.

Registry No. 1, 81141-97-1; 2, 81141-98-2; 3, 4830-99-3; (*E*)-4, 85371-48-8; (*Z*)-4, 85371-49-9.

(13) Percentages, corrected for a triene/syn allene response ratio of 0.91, determined by HPLC analysis.

(14) On occasion, considerably more 1-ethylindan relative to triene formed.

(15) Woodward, R. B.; Hoffman, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim/Bergstr., Germany, and Academic Press: New York, 1970.

(16) Berson, J. A., Yale University, personal communication, 1975.

(17) For a discussion of the possible use of an allene moiety as a ($_{\pi}2 + {}_{\pi}2$) component, see: Pasto, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 37–46, and references therein.

(18) It is perhaps noteworthy that no 1,3-sigmatropic shift of carbon is observed for 1 or 2, given that **5a** and **5b** both give a formal 1,3-shift product (2-methoxybicyclo[3.2.2]nona-2,6-diene),[2b] albeit likely through a diradical mechanism. Apparently an augmented six-electron concerted 1,3-sigmatropic rearrangement ($[{}_{\sigma}2_s + ({}_{\pi}2_s + {}_{\pi}2_s)]$) is not as plausible as the augmented Cope process, especially given the fact that 2, which is precluded from the concerted Cope process but not from the 1,3 process, does not rearrange at all under our established conditions.

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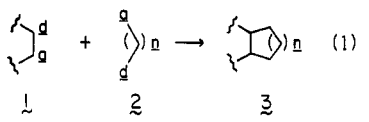
4-Chloro-2-lithio-1-butene, a Novel Donor–Acceptor Conjunctive Reagent

Summary: Transmetalation of 4-chloro-2-(trimethylstannyl)-1-butene (**10**) provides 4-chloro-2-lithio-1-butene (**11**), which reacts smoothly at −78 °C with aldehydes, ketones, and α,β-unsaturated *N,N',N'*-trimethylhydrazides to produce, after warming of the resultant intermediates in the presence of HMPA, the 3-methylenetetrahydrofuran derivatives **24–29** and the 3-methylenecyclopentanecarboxylic acid derivatives **36–38**, respectively.

Sir: Although conjunctive reagents that are equivalent to synthons possessing both a donor (d)[1] and an acceptor (a)[1] carbon atom (see **2** in eq 1) are known, they are, as yet,



(1)

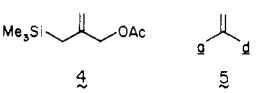
quite rare. This scarcity is particularly true for species in which the d and a centers are separated by one or more carbon atoms (n in **2** ≥ 1) and/or in which these centers are to be deployed "simultaneously" (or sequentially) in a "one-pot" process. Clearly such reagents are (would be) very useful in organic synthesis. For example, the (theoretical) combination of the reagent synthons **2** with substrate synthons **1** containing adjacent a and d sites (e.g., α,β-unsaturated carbonyl compounds) would provide the corresponding cyclic products **3** (eq 1).[2]

We report herein (a) the straightforward, efficient conversion of ethyl (*E*)-3-(trimethylstannyl)-2-butenoate (**6**)[3] into 4-chloro-2-(trimethylstannyl)-1-butene (**10**), (b) transmetalation of the latter substance to provide 4-chloro-2-lithio-1-butene (**11**), and (c) reaction of this novel, functionalized butenyllithium reagent with aldehydes, ketones, and α,β-unsaturated *N,N',N'*-trimethylhydrazides.

Conversion of compound **6**[3] into the corresponding enolate anion, followed by quenching of the latter species

(1) Seebach, D. *Angew, Chem., Int. Ed. Engl.* **1979**, *18*, 239.

(2) For recent, very interesting examples of such a process in which the conjunctive reagent **4** served as the formal equivalent of the a,d synthon **5**, see: Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1979**,

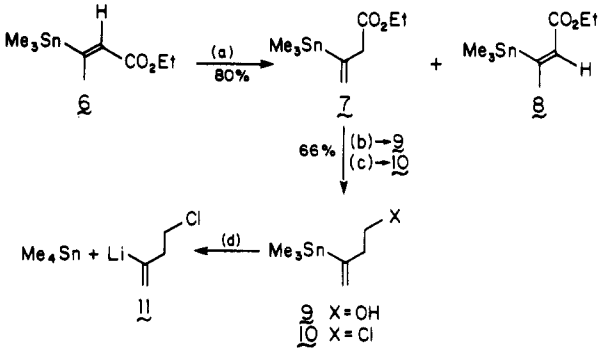


101, 6429, 6432; **1980**, *102*, 6359. For other pertinent reports, see: Hayakawa, Y.; Yokoyama, K.; Noyori, R. *Ibid.* **1978**, *100*, 1791. Semmelhack, M. F.; Yamashita, A.; Tomesch, J. C.; Hirotsu, K. *Ibid.* **1978**, *100*, 5565. Trost, B. M.; Vincent, J. E. *Ibid.* **1980**, *102*, 5681. Danheiser, R. L.; Carini, D. J.; Basak, A. *Ibid.* **1981**, *103*, 1604. Knapp, S.; O'Conner, U.; Mobilio, D. *Tetrahedron Lett.* **1980**, *21*, 4557. Klein, H.; Mayr, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1027. Magnus, P.; Quagllato, D. A. *Organometallics* **1982**, *1*, 1243. Bucheister, A.; Klemarczyk, P.; Rosenblum, M. *Ibid.* **1982**, *1*, 1679.

(3) Piers, E.; Morton, H. E. *J. Org. Chem.* **1980**, *45*, 4263. Piers, E.; Chong, J. M.; Morton, H. E. *Tetrahedron Lett.* **1981**, *22*, 4905.

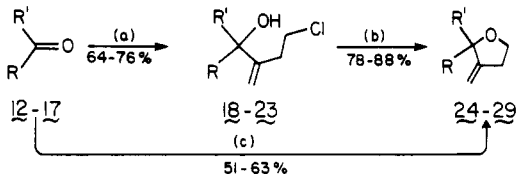
0022-3263/83/1948-1774$01.50/0

Scheme I[a]



[a] (a) i, 2.3 equiv of $LiN(i\text{-}Pr)_2$, THF, -78 °C, 30 min, 0 °C, 1 h; ii, recool to -78 °C; iii, inverse addition to cold (-95 °C) HOAc (2.5 equiv) in Et_2O. (b) $LiAlH_4$, Et_2O, -20 °C; H_2O. (c) $(C_6H_5)_3P$, CCl_4, Et_3N, reflux 18 h. (d) MeLi, THF, -78 °C, 10 min.

Scheme II[a]



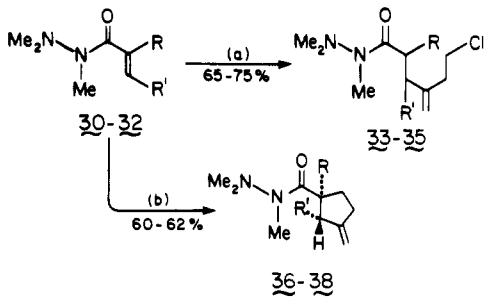
12, 18, 24 R = H, R' = C_6H_5
13, 19, 25 R = H, R' = (2-cyclopentenyl)methyl
14, 20, 26 R, R' = $(CH_2)_4$
15, 21, 27 R, R' = $(CH_2)_5$
16, 22, 28 R, R' = $(CH_2)_6$
17, 23, 29 R, R' = $(CH_2)_3CH{=}CH$

[a] (a) i, 0.83 equiv of 11, THF, -78 °C, 1.5-2 h; ii, NH_4Cl, H_2O, -78 °C. (b) 1.2 equiv of KH, THF, room temp, 2-3 h. (c) as in (a) i, then add 1.4 equiv of HMPA and warm to room temp, 2-3 h.

with acetic acid at low temperatures, afforded in good yield a mixture consisting very largely (94%) of the β,γ-unsaturated ester **7**,[4] accompanied by a small amount (6%) of the α,β-unsaturated ester **8**[3] (geometric isomer of the starting material **6**) (see Scheme I). These substances could be separated readily by subjection of the mixture to column chromatography on silica gel. Reduction of **7**, followed by treatment of the resultant alcohol **9** with $(C_6H_5)_3P$–CCl_4[6] in the presence of triethylamine, provided 4-chloro-2-(trimethylstannyl)-1-butene (**10**).

It was very gratifying to find that compound **10** underwent transmetalation cleanly and rapidly at -78 °C to produce a solution of the organolithium reagent **11**. When this solution was treated with a slight excess (1.2 equiv) of benzaldehyde and was subsequently quenched with saturated aqueous ammonium chloride at -78 °C, the chloro alcohol **18** could be isolated in 76% yield (see Scheme II).[7] Alternatively and importantly, when the cold solution derived from reaction of benzaldehyde with

Scheme III[a]



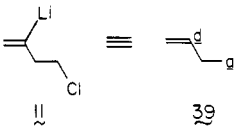
30, 33, 36 R = R' = H
31, 34, 37 R = Me, R' = H
32, 35, 38 R = H, R' = Me

[a] (a) i, 0.83 equiv of 11, THF, -78 °C, 1 h; ii, NH_4Cl, H_2O, -78 °C. (b) as in (a) i, then add 1.4 equiv of HMPA and warm to room temp, 2 h.

reagent **11** was treated with 1.4 equiv of HMPA and then was allowed to warm to room temperature, 2-phenyl-3-methylenetetrahydrofuran (**24**) was obtained directly in 63% yield. In very similar fashion, (2-cyclopentenyl)-acetaldehyde (**13**) and the cyclic ketones **14–17** could be converted into the chloro alcohols **19** (64%) and **20–23** (67%, 69%, 69%, 72%) or directly into the substituted 3-methylenetetrahydrofurans **25** (56%) and **26–29** (51%, 58%, 62%, 62%).[8]

When the butenyllithium reagent **11** was allowed to react with each of the α,β-unsaturated *N,N',N'*-trimethylhydrazides **30–32**,[9] the outcome of the process could again be controlled by regulating the temperature of the reaction mixture (see Scheme III). Thus, when the solution was quenched at -78 °C, the acyclic hydrazides **33–35** (65%, 75%, 65%, respectively)[7] were obtained. On the other hand, when each of the reaction mixtures was treated with 1.4 equiv of HMPA and then was allowed to warm to room temperature, the substituted 3-methylenecyclopentanecarboxylic acid derivatives **36–38** (60%, 62%, 60%) were produced. Product **38** consisted of a single diastereomer and, although the relative configuration of this substance was not established rigorously, it is reasonable to propose that the two substituents on the five-membered ring have a trans relationship.

It is evident from the preliminary results reported herein that the unusual organolithium reagent **11** is readily prepared and that it is a synthetically viable equivalent to the 1-butene d^2, a^4 synthon **39**. Clearly, many extensions to this work can be envisaged and we are actively pursuing some of these.



Acknowledgment. We are very grateful for financial support from the Natural Sciences and Engineering Research Council of Canada.

Registry No. **6**, 74854-51-6; **7**, 85370-31-6; **8**, 17421-42-0; **9**, 76077-30-0; **10**, 85370-32-7; **11**, 85370-33-8; **12**, 100-52-7; **13**, 19656-91-8; **14**, 120-92-3; **15**, 108-94-1; **16**, 502-42-1; **17**, 930-68-7; **18**, 85370-34-9; **19**, 85370-35-0; **20**, 85370-36-1; **21**, 85370-37-2; **22**,

(4) All compounds reported herein exhibited spectral data in full accord with structural assignments. In addition, new compounds gave satisfactory high-resolution mass spectrometric measurements. In accord with previous observations,[5] the trimethylstannyl compounds did not exhibit molecular ion peaks. In these cases, the high-resolution measurements were carried out on the $m/e = M^+ - 15$ fragments.

(5) Kuivila, H. G.; Tsai, K.-H.; Kingston, D. G. I. *J. Organomet. Chem.* **1970**, *23*, 129.

(6) Downie, I. M.; Holmes, J. B.; Lee, J. B. *Chem. Ind. (London)* **1966**, 900.

(7) The yields of the reactions summarized in Schemes I and II refer to distilled, purified products, were not optimized, and are based on the amount of compound **10** employed. In each case, 1.2 equiv of the substrate (compounds **12–17**, **30–32**) were added to a solution of reagent **11** prepared from 1 equiv of the trimethylstannyl derivative **10**.

(8) The chloro alcohols **18–23** could also be converted readily into the corresponding tetrahydrofurans **24–29** [step b, Scheme II]. For example, treatment of compounds **18**, **19**, **21**, and **22** with potassium hydride in THF afforded the cyclic ethers **24**, **25**, **27**, and **28** (yields 84%, 78%, 81%, and 88%, respectively).

(9) Knapp, S.; Calienni, J. *Synth. Commun.* **1980**, *10*, 837.

85370-38-3; **23**, 85370-39-4; **24**, 85370-40-7; **25**, 85370-41-8; **26**, 85370-42-9; **27**, 85370-43-0; **28**, 85370-44-1; **29**, 85370-45-2; **30**, 77144-30-0; **31**, 77144-38-8; **32**, 85370-46-3; **33**, 85370-47-4; **34**, 85370-48-5; **35**, 85370-49-6; **36**, 85370-50-9; **37**, 85370-51-0; **38**, 85370-52-1.

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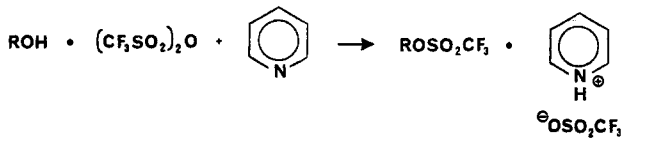
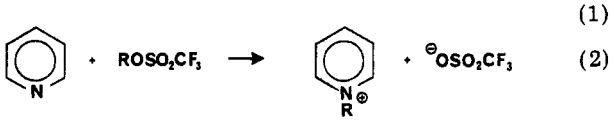
Reaction of 2,6-Dimethyl- and 2,4,6-Trimethylpyridine with Trifluoromethanesulfonic Anhydride

Summary: The reaction of trifluoromethanesulfonic anhydride with 2,6-dimethyl- and 2,4,6-trimethylpyridine produces compounds in which a methyl hydrogen is replaced by either a trifluoromethyl or a [(trifluoromethyl)sulfinyl]oxy group.

Sir: The most convenient and widely used method for preparation of esters of trifluoromethanesulfonic (triflic) acid consists of reacting the appropriate alcohol with triflic anhydride in the presence of pyridine.[1] Although pyridine is added primarily to neutralize the triflic acid formed (eq 1), its reaction with the triflate is sometimes the major pathway (eq 2).[2,3] One solution to this problem[3] is to



(1)

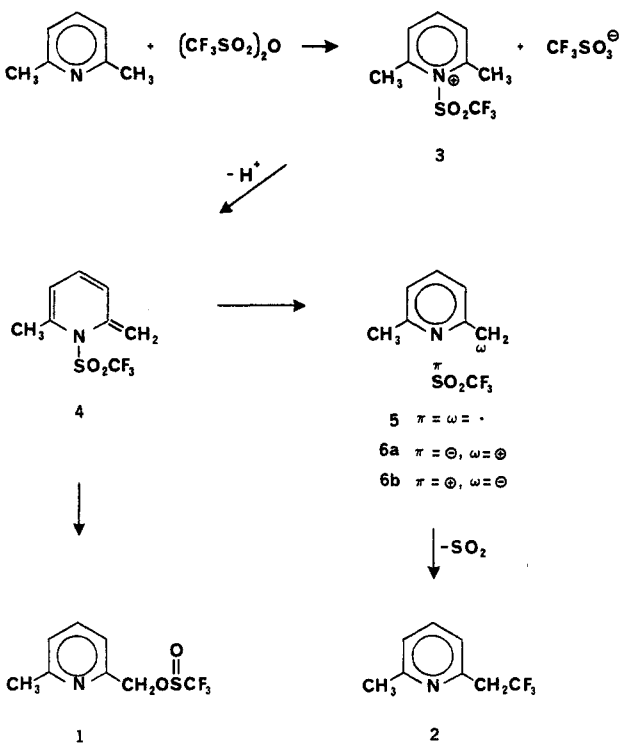


(2)

replace pyridine with one of its less nucleophilic derivatives (e.g., 2,6-dimethyl- or 2,4,6-trimethylpyridine). Although this substitution discourages displacement, new difficulties can arise. Methyl-substituted pyridines react with triflic anhydride to give products of unknown identity. These products are contained in reaction mixtures that are difficult to purify.[4] If the uncertainty about product structure could be eliminated from these reactions, the difficulty in using methyl-substituted pyridines might be overcome. With this thought in mind, we examined the reaction between triflic anhydride and 2,6-dimethylpyridine (2,6-lutidine) and found that two unusual products were formed.

Dropwise addition of triflic anhydride (3.0 mmol) to a solution of 2,6-lutidine (6.0 mmol) in carbon tetrachloride at room temperature results in an exothermic reaction that produces a dark red solution. Chromatography of the reaction mixture on silica gel removes the color and separates the mixture into three components, one of which is lutidine. The major product (48% yield, based on reacted lutidine) is 6-methyl-2-[[[(trifluoromethyl)sulfinyl]oxy]methyl]pyridine (1) and the minor product (17% yield) is 2-(2,2,2-trifluoroethyl)-6-methylpyridine (2).[5]

Scheme I



A proposed mechanism for the formation of these compounds (1 and 2) is shown in Scheme I; several observations are pertinent to this proposed process. First, pyridine derivatives are known[6] to react with triflic anhydride to form salts such as **3**. The positive charge on nitrogen in **3** should sufficiently enhance the acidity of the methyl hydrogens to permit deprotonation to give **4**.[7] The proposed rearrangement of **4** to the major product (1) can be either a concerted reaction or a stepwise process. If a nonconcerted reaction involving the radical pair **5** (Scheme I) were operative, CIDNP effects might be observable.[8] Although reaction was complete in a few seconds and measurement was made in less than 1 min, no polarized ^{1}H NMR signals were detectable. In order to gain more definitive information about the final step (**4** → 1) in this proposed mechanism (Scheme I), a second compound, 2,4,6-trimethylpyridine (*s*-collidine) was investigated.

If a mechanism similar to that shown in Scheme I is assumed for reaction between *s*-collidine and triflic anhydride, then any substitution on the 4-methyl group, must arise from a nonconcerted process. Triflic anhydride and *s*-collidine react readily to give 2-[[[(trifluoromethyl)-

(1) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85.
(2) Hall, L. D.; Miller, D. C. *Carbohydr. Res.* **1976**, *47*, 299.
(3) (a) Leroux, J.; Perlin, A. S. *Carbohydr. Res.* **1976**, *47*, C8. (b) Leroux, J.; Perlin, A. S. *Ibid.* **1978**, *67*, 163.
(4) Reference 1, p 107.

(5) Characterizing data for compound 1: bp 100–102 °C (2 torr); ^{1}H NMR ($CDCl_3$) δ 7.74–6.95 (m, H-3, H-4, H-5), 5.39, 5.12 (CH_2, J = 12.6 Hz), 2.52 (s, CH_3); ^{13}C NMR ($CDCl_3$) δ 158.75 (C_6), 153.19 (C_2), 137.40 (C_4), 123.46 (C_5), 123.10 (q, CF_3, $^1J_{CF}$ = 338 Hz), 119.23 (C_3), 70.36 (CH_2), 24.28 (CH_3) (off-resonance decoupling produced the expected multiplicity for each signal); mass spectrum (CI, methane), m/z (rel intensity) 240 (18), 170 (15), 106 (100). Compound 1 was homogenous by TLC and VPC but decomposed upon standing overnight as a neat liquid. Characterizing data for compound 2: ^{1}H NMR (CD_3COCD_3) δ 7.83–6.92 (m, H-3, H-4, H-5), 3.56 (q, CH_2, $^3J_{HF}$ = 10.6 Hz), 2.47 (s, CH_3); ^{13}C NMR (CD_3COCD_3) δ 158.67 (C_6), 150.12 (C_2), 136.96 (C_4), 125.00 (q, CF_3), 122.42, 121.48 (C_3, C_5), 42.94 (q, CH_2, $^2J_{CF}$ = 28.79 Hz), 23.79 (CH_3) (off-resonance decoupling produced the expected multiplicity for each signal); mass spectrum (CI, methane), m/z (rel intensity) 176 (45), 156 (100). Compound 2 also was homogenous by TLC and VPC. Anal. Calcd for $C_8H_8F_3N$: C, 54.86; H, 4.60; N, 8.00. Found: C, 54.64; H, 4.61; N, 7.89.
(6) Stang, P. J.; Treptow, W. *Synthesis* **1980**, 283.
(7) Phillips, A. P. *J. Org. Chem.* **1947**, *12*, 333.
(8) CIDNP effects clearly were observable in a reaction that involved radicals similar to **5**. Bleeker, P. I.; Engberts, J. B. F. N. *J. Org. Chem.* **1981**, *46*, 1012.

0022-3263/83/1948-1776$01.50/0