corded on an AEI-MS-30. GLC analyses were accomplished with a Hewlett-Packard 5750 machine using a glass column ($^1/_4 \times 6$ ft) packed with 10% SE-30 on GAS-CHROM Q. The γ-iodo ketones were fully characterized by their spectral data. Subsequently, they were converted into the corresponding γ-keto sulfides by reaction with lithium thiophenoxide in THF for high-resolution mass spectroscopic analysis. In some cases, the γ-iodo ketones were also reduced to the corresponding ketones by using tri-*n*-butyltin hydride for comparison with authentic samples. This technique was also employed when isomeric mixtures of iodo ketones were obtained from the reaction of trimethylsilyl iodide with certain cyclopropyl ketones to facilitate analysis. These results were compared with those obtained by direct spectroscopic analysis of the γ-iodo ketone mixtures.

Materials. Methylcyclopropyl ketone and phenylcyclopropyl ketone, purchased from Aldrich Chemical Co., were dried over 4-Å molecular sieves and used without further purification. 1-Methylcyclopropyl phenyl ketone (**2**) was generated from the corresponding carboxylic acid by treatment with phenyllithium in ether. In a similar manner, **3** was produced from the carboxylic acid which was in turn available by the basic hydrolysis of the corresponding nitrile.[15] 3-Cyclopropylcyclohex-2-en-1-one (**4**) was formed by treatment of commercially available 3-ethoxycyclohex-2-en-1-one with cyclopropyllithium followed by hydrolysis with 5% hydrochloric acid in THF (25 °C). The bicyclic ketone **5** was generated by treatment of the respective acid with methyllithium in ether. The acid was produced by basic hydrolysis of the corresponding ethyl ester resulting from the decomposition of ethyl diazoacetate catalyzed by Cu_2I_2 in cyclohexene. The cyclopropyl ketones **6**–**8**, **10**, and **11** were produced from the corresponding enones by the method described by Vorbrüggen and co-workers.[16] Tricyclo[3.3.0.$0^{2,8}$]octan-3-one (**23**) was prepared as described by Monti and co-workers.[11d] In a similar fashion, the tricyclic ketone **9** was prepared from 3-(1-cyclohexenyl)-propionic acid.

General Procedure for the Ring Opening of Cyclopropyl Ketones with Iodotrimethylsilane. Ring opening of **2** is representative. To a solution of 160 mg (1 mmol) of **2** in 3 mL of carbon tetrachloride at −10 °C was added 0.155 mL (1.1 mmol) of iodotrimethylsilane. The solution was then stirred 1 h at −10 °C and 1 h at 25 °C. The solution was diluted with 50 mL of ether and washed with 25 mL of saturated Na_2SO_3 solution. The organic phase was removed and dried ($MgSO_4$). Solvent removal yielded 282 mg (98%) of the iodo ketone **13**. The following compounds were also obtained. **12a**: ^{1}H NMR δ (CCl_4) 3.12 (t, J = 7 Hz, 2 H), 2.49 (t, J = 7 Hz, 2 H), 1.82–2.17 (m with superimposed s, 5 H); IR (neat) 3000, 2980, 1715, 1425, 1370, 1220, 1180 and 790 cm^{-1}.[4i] **12b**: ^{1}H NMR δ (CCl_4) 7.76 (m, 2 H), 7.25 (m, 3 H), 3.20 (t, J = 7 Hz, 2 H), 2.97 (t, J = 7 Hz, 2 H), 2.12 (m, 2 H); IR (neat) 3060, 2960, 1685, 1600, 1580, 1450, 1225, 1215, 990, 750, 740, and 690 cm^{-1}.[4i] **13**: ^{1}H NMR δ (CCl_4) 7.83 (m, 2 H), 7.28 (m, 3 H), 3.6 (m, 1 H), 3.1 (m, 2 H), 1.6–2.5 (m, 2 H), 1.15 (d, J = 6 Hz, 6 H); IR (neat) 3080, 3060, 3020, 2960, 1680, 1595, 1580, 1450, 1255, 1220, 970, 705 cm^{-1}. **14**: ^{1}H NMR δ (CCl_4) 7.80 (m, 2 H), 7.32 (m, 3 H), 3.09 (m, 2 H), 1.88 (m with superimposed s, 8 H); IR (neat) 2975, 2930, 1715, 1460, 1390, 1100 cm^{-1}. **15**: ^{1}H NMR δ (CCl_4) 5.66 (br s, 1 H), 3.12 (*t*, J = 7 Hz, 2 H), 1.77–2.45 (m, 10 H); IR (neat) 3015, 2940, 1670, 1625, 1430, 1330, 1255, 1195, 890 cm^{-1}. **16**: ^{1}H NMR δ (CCl_4) 3.95 (ddd, J = 11, 11, 5 Hz, 1 H), 1.0–2.7 (m with s (2.05) superimposed, 14 H); IR (neat) 2940, 2860, 1715, 1450, 1360, 1170, 1145, 655 cm^{-1}. **17**: ^{1}H NMR δ (CCl_4) 3.09 (m, 2 H), 1.1–2.82 (m, 13 H); IR (neat) 2940, 2860, 1700, 1455, 1180 cm^{-1}. **18**: ^{1}H NMR δ (CCl_4) 3.2 (d, J = 6 Hz, 2 H), 1.4–2.6 (m, 7 H); IR (neat) 2960, 2900, 1740, 1400, 1180, 1160 cm^{-1}. **19**: ^{1}H NMR δ ($CDCl_3$) 3.2 (d, J = 4.5 Hz, 2 H), 1.2–2.7 (m, 9 H); IR (neat) 2940, 2860, 1710, 1450, 1430, 1295, 1225, 1175 cm^{-1}.[4i] **20**: ^{1}H NMR δ (CCl_4) δ 4.43 (m, 1 H), 1.22–2.3 (m with s (2.17) superimposed, 14 H); IR (neat) 2940, 2860, 1740, 1450, 1405, 1170 cm^{-1}.

Analysis of Iodo Ketone Mixtures Produced upon Ring Opening of Cyclopropyl Ketones. Iodo ketone mixtures produced from reaction of cyclopropyl ketones with Me_3SiI were analyzed by reduction of the mixtures with tributyltin hydride. The ketones obtained from reduction were then compared spectrally and chromatographically with authentic samples. Reduction of a mixture of **22a** and **22b** is representative. To a refluxing solution of 0.31 g (1.07 mmol) of tri-*n*-butyltin hydride in 5 mL of cyclohexane was added dropwise a solution containing 0.246 g (0.98 mmol) of a mixture of **22a** and **22b** and a few milligrams of azobis(isobutyronitrile) in 3 mL of cyclohexane. The solution then heated to reflux for 4 h. The solution was then diluted with 75 mL of ether, and the resulting organic phase was washed with 25 mL of 5% potassium fluoride solution, water, and saturated sodium chloride solution and then dried ($MgSO_4$). The residue obtained after solvent removal was chromatographed on 15 g of neutral alumina (activity II) with 5% ether in hexane to yield 120 mg of product. The ketone mixture was then compared spectrally and chromatographically with authentic material and shown to consist of 54% 3-methylcycloheptanone and 46% cyclooctane.

Registry No. **1a**, 765-43-5; **1b**, 3481-02-5; **2**, 26921-44-8; **3**, 5685-43-8; **4**, 34194-40-6; **5**, 13332-18-8; **6**, 5743-85-1; **7**, 4160-49-0; **8**, 5771-58-4; **9**, 13705-50-5; **10**, 2862-90-0; 11, 16335-43-6; **12a**, 3695-29-2; **12b**, 65488-05-3; **13**, 77070-49-6; **14**, 77070-50-9; **15**, 77070-51-0; *trans*-**16**, 19093-22-2; **17**, 77070-52-1; **18**, 71987-94-5; **19**, 72003-75-9; **20**, 77070-53-2; *trans*-**21a**, 71988-01-7; **21b**, 77070-54-3; **22a**, 71987-95-6; **22b**, 77070-55-4; **23**, 20826-85-1; **24**, 77070-56-5; **25**, 77070-57-6; trimethylsilyl iodide, 16029-98-4.

(15) Nelson, E. R.; Maienthal, M.; Lane, L. A.; Benderly, A. A. *J. Am. Chem. Soc.* **1957**, *79*, 3467.
(16) Mende, U.; Badüchel, B.; Skuballa W.; Vorbrüggen, H. *Tetrahedron Lett.* **1975**, 629.

Palladium-Catalyzed Reactions: Stereoselective Synthesis of Substituted Cyclopropanes Related to Chrysanthemic Acid. A Simple Route to *cis*-Chrysanthemonitrile

Jean Pierre Genet* and Frederique Piau

Laboratoire de Chimie Organique de Synthèse, Université Pierre et Marie Curie, Equipe de Recherche Associée au CNRS, 75005 Paris, France

Received July 16, 1980

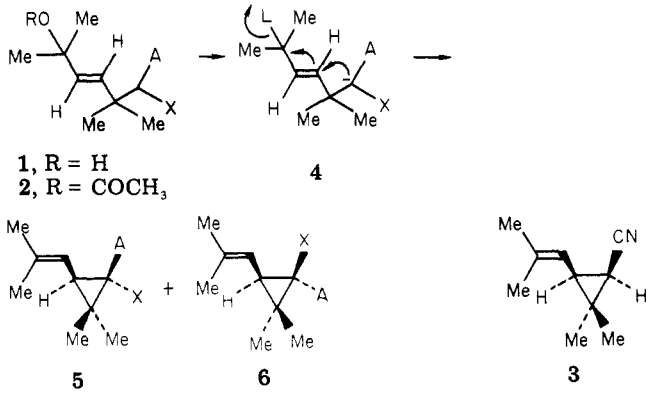
Considerable interest continues to be shown in functionalized cyclopropanes[1] because of their insecticidal properties. The cyclopropanecarboxylic acid with a cis vinylic side chain (as in several synthetic pyrethroids)[2] is a more potent insecticide than the corresponding trans compound. We report here a convenient and general approach for the synthesis of substituted functionalized cyclopropanes (e.g., **5** and **6**, Scheme I) in which C_1–C_3 bond formation occurs via an intramolecular $S_{N'}$ (via **4**) mechanism and its application to the preparation of *cis*-chrysanthemonitrile (**3**).[4]

The acyclic precursors **1** are available via organopalladium intermediates.[5] The reaction of the cis mon-

(1) Reviews: (a) Yanovskaya, L. A.; Dombrovskii, V. A. *Russ. Chem. Rev. (Engl. Transl.)* **1975**, *44*(2) 154; (b) "Methoden der Organischen Chemie (Houben-Weyl)"; Georg Thieme Verlag: Stuttgart, 1952; Band IV/3, p 94.
(2) Review: Synthetic Pyrethroid. A new class of insecticide. Eliott, M.; Janes, N. F. *Chem. Rev.* **1979**, 473.
(3) For a preliminary report of this work see: Genêt, J. P.; Piau, F.; Ficini, J. *Tetrahedron Lett.* **1980**, *21*, 3183.
(4) Julia, S.; Julia, M.; Linstrumelle, G. *Bull. Soc. Chim. Fr.* **1966**, 3499.
(5) Reviews: (a) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615; (b) Trost, B. M. *Pure Appl. Chem.* **1979**, *51*, 787; (c) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385; (d) "Organic Synthesis with Palladium Compounds"; Tsuji, J., Ed. Springer Verlag: West Berlin and Heidelberg, 1979; (e) Tsuji, J. *Pure Appl. Chem.* **1979**, *51*, 1235.

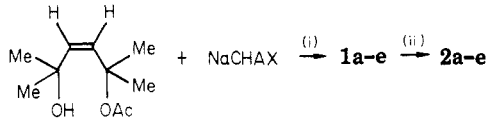
0022-3263/81/1946-2414$01.25/0

Scheme I



1, R = H
2, R = $COCH_3$

Scheme II[a]



[a] (i) THF or DME, $(PPh_3)_4Pd$ (5–10%), 15 h, 65 °C; (ii) Ac_2O, NEt_3 in CH_2Cl_2, DMAP (10–20%).

Table I. Preparation of the Alcohols 1 and Acetates 2

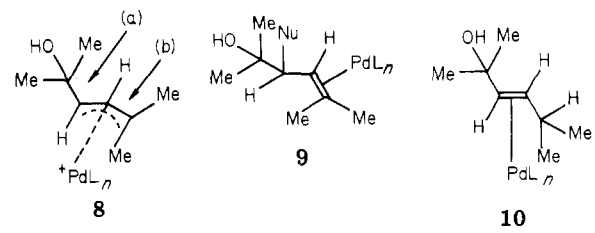
alcohols 1				acetates 2	
R = H	A	X	yield, %	R = $COCH_3$	yield, %
1a	CO_2-*t*-Bu	CO_2-*t*-Bu	85	2a	65
1b	CN	CN	85	2b	65
1c	CO_2Me	$SO_2C_6H_4$-*o*-*i*-Pr	60	2c	90
1d[6]	CN	CO_2Et	95	2d	85
1e	CN	SO_2Ph	90	2e	85

oacetate 7 with various stabilized carbanions (e.g., malonates and β-keto or β-cyano sulfones) and tetrakis(triphenylphosphine)palladium (5–10%) in tetrahydrofuran or dimethoxyethane for 15 h at 65 °C gives 1 in high yield (Table I). This reaction shows high *regio-* and *stereoselectivity*. The alkylation occurs at the more substituted carbon and gives compounds 1 with exclusive *E* double bond stereochemistry (Scheme II).

The high stereochemical control in the carbon–carbon bond formation may be accounted for by consideration of the stability of the two pathways for nucleophilic attack on the π-allylic, cationic, palladium intermediate 8[7] (Chart I).

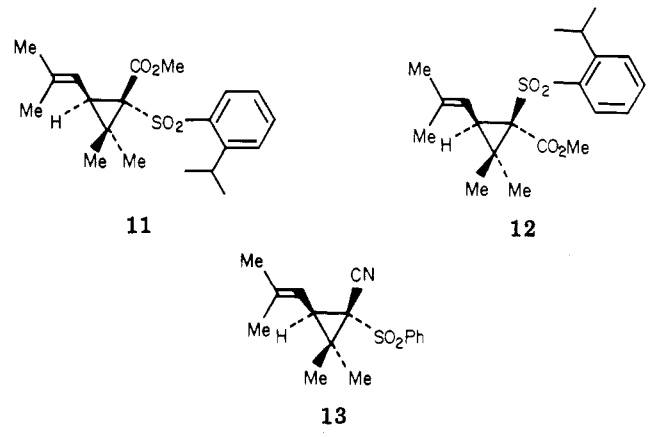
Normally, the alkylation of π-allylpalladium complexes occurs at the sterically more accessible, less substituted end of the π-allyl unit.[5a,8] Here the reaction occurs via pathway b in intermediate 8, namely, at the more substituted carbon. This unexpected result is quite noteworthy, and this high regioselectivity can be understood by the fact that alkylation via pathway a initially gives the π olefin complex 9, which is less stable than the complex 10 resulting from alkylation via pathway b. Also it appears that attack at the tertiary center (pathway b) is less

Chart I[a]



[a] Nu = CHAX.

Chart II



crowded than the neopentyl-type alkylation (attack via pathway a).

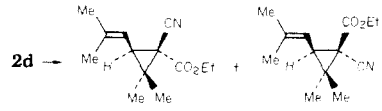
The cyclopropanation of the 6-hydroxyhept-4-enoic acid derivatives 1 via an intramolecular $S_{N'}$ reaction can give two stereoisomers (5 and 6, Scheme I). The stereoselectivity of the ring formation was studied and shows that there are two factors which control the stereochemistry, namely, whether the cyclization is catalyzed or not and the nature of the carbanionic unit.

We were unable to effect direct intramolecular cyclization with the allylic alcohols 1 with activation by palladium catalysts.[9] The best substrates in the cyclopropanation appear to be the corresponding allylic acetate 2 prepared by acetylation[10] (Ac_2O in CH_2Cl_2 with DMAP). The cyclization was performed by treating the acetates 2 with sodium hydride (1 equiv) in hot THF (60–65 °C). However, no cyclized product was detected with **2a** (X = A = CO_2-*t*-Bu) probably due to the lower acidity of this substrate. In contrast, the more acidic compounds such as **2b** (A = X = CN) gave smooth cyclization under these conditions and afforded 1,1-dicyano-2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropane in 75% yield. With **2c** the cyclization again occurs cleanly in an 80% yield, but an interesting stereoselectivity was observed; the *E* isomer 11 (Chart II) was obtained as the major product in a 3:1 ratio with the *Z* isomer 12. A completely stereocontrolled cyclization was observed with **2e**, giving in 80% yield a single product, 13, in which the nitrile and isobutenyl groups are cis.

The determination of the stereochemistry of 11 and 12 was based first on NMR data. The chemical shifts of the vinylic protons (δ 5.12 for 11, δ 5.60 for 12, and δ 4.9 for 13) supported this assignment.[3] The final proof of the

(6) Barreau, B.; Bost, H.; Julia, M.; Lallemand, J. Y. *Tetrahedron Lett.* **1975**, *40*, 1975.
(7) Trost, B. M.; Klun, T. P. *J. Am. Chem. Soc.* **1979**, *101*, 6756.
(8) For a discussion of regioselectivity of alkylation on π-allylpalladium complexes, see: Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietshe, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3420; Trost, B. M.; Verhoeven, T. R. *Ibid.* **1980**, *102*, 4730.
(9) For an intermolecular process using an allylic alcohol and a palladium catalyst, see: Atkins, K. E.; Walker, W. E.; Manyik, R. M. *Tetrahedron Lett.* **1970**, *43*, 3821.
(10) Steglisch, W.; Hofle, G. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 98. See also a review: Hofle, G.; Steglisch, W.; Vorbruggen, H. *Ibid.* **1978**, *17*, 569.

Table II. Stereoselectivity in Reaction of 2d



14 15

reaction conditions	14/15 ratio	yield, %
2.5 h, 65 °C	1:1	75
1.5 h, 65 °C, 5–10% $(PPh_3)_4Pd$	19:1	70

structure for the different stereoisomers was inferred from the rather difficult hydrolysis of the ester or nitrile moiety cis to the isobutenyl chain.[11] For example, compound **13** was completely unchanged upon treatment with NaOH for 24 h at 100 °C. Thus the cyano group must be cis to the alkyl chain in this molecule.

The stereochemical course of this reaction was also investigated for compound **2d**: without catalysis no stereoselectivity was observed, and a 1:1 mixture of *E* isomer **14** and *Z* isomer **15** was obtained. It is noteworthy that addition of catalytic quantities of palladium accelerates the reaction and causes a remarkable stereoselectivity. The two products are formed in 70% yield, with the *E* isomer **14** being favored over the *Z* isomer **15** by a ratio of 19:1 (Table II).

The completion of the synthesis of *cis*-chrysanthemonitrile[12] (**3**) was accomplished by simple desulfonylation[13] of **13** with 6% sodium amalgam at −35 °C for 1 h. This reaction gave retention of configuration at the C_1 carbon atom. To our knowledge, this is the first case in which retention of configuration in a cyclopropane system during desulfonylation has been observed, although this stereochemical course has been observed in olefinic systems.[14]

In conclusion, our results demonstrate a facile S_N' approach to a synthesis of substituted functionalized cyclopropanes from acyclic substrates such as **2**. The nature of the carbanionic unit as well as the nature of the cyclization (uncatalyzed or via π-allyl complex) both play crucial roles in determining the stereochemical preference. The overall approach seems very attractive, and we are investigating its application to other systems.

Experimental Section

Infrared spectra were determined on either a Perkin-Elmer 297 or 257 spectrophotometer; NMR spectra were obtained on either a Bruker WP-80 or a Varian Associates Model T-60 spectrometer. Chemicals shifts are given in parts per million relative to Me_4Si as an internal standard. Mass spectra were taken on an AEI MS-30 spectrometer at an ionizing voltage of 70 V. Elemental analyses were performed by the microanalytical service at the Université Pierre et Marie Curie. All the new compounds gave analyses within ±0.40% of theory.

All reactions were performed under an atmosphere of either argon or nitrogen. Chromatography employed Merck silica gel 60 F_{254}. Tetrahydrofuran (THF) and dimethoxyethane (DME) were freshly distilled from sodium benzophenone ketyl.

Tetrakis(triphenylphosphine)palladium was prepared according to the literature method.[15] Benzenesulfonylacetonitrile[16] was obtained by oxidation of phenylthioacetonitrile in methylene chloride with *m*-chloroperbenzoic acid. 2,5-Dimethyl-3-hexyne-2,5-diol was purchased from Fluka A.G. and 4-(dimethylamino)pyridine from Merck.

General Procedure for the Synthesis of 1. To a suspension of 60% sodium hydride (1.2 mmol) in 0.5 mL of dry THF was added 1.3 mmol of the appropriate malonyl-type compound in 1 mL of dry THF. After complete formation of the corresponding stabilized anion, 1 mmol of the *Z* monoacetate **7**[3] in 1 mL of DME and then 5–10% of tetrakis(triphenylphosphine)palladium were added. The reaction mixture was stirred at 65–70 °C for 15 h, 10 mL of 2% HCl solution was added, and the water layer was extracted with ether or methylene chloride (3 × 30 mL). The combined organic extracts were washed with water to neutral pH, dried ($MgSO_4$), and evaporated in vacuo. The crude material was distilled or chromatographed on silica gel (column or PLC). In each case, the purity was established by TLC on silica gel.

Di-*tert*-butyl (2*E*)-2-(4-Hydroxy-1,1,4-trimethylpent-2-enyl)propane-1,3-dioate (1a). From sodium *tert*-butyl malonate was obtained **1a** (0.290 g, 85% yield) after column chromatography with hexane–ether (3:1): IR (neat) 3400, 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.2 (s, 6 H), 1.27 (s, 6 H), 1.37 (s, 18 H), 3.05 (s, 1 H), 5.65 (d, *J* = 16 Hz, 1 H), 5.75 (d, *J* = 16 Hz, 1 H), 1.8 (OH). Anal. Calcd for $C_{19}H_{34}O_5$: C, 66.82; H, 10.01. Found: C, 66.55; H, 9.7.

(2*E*)-2-(4-Hydroxy-1,1,4-trimethylpent-2-enyl)propanedinitrile (1b). From sodiomalononitrile was obtained **1b** (0.170 g, 85% yield) after column chromatography with pentane–ether (1:1): IR (neat) 3400, 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.32 (s, 6 H), 1.35 (s, 3 H), 2 (OH), 3.50 (s, 1 H), 5.72 (d, *J* = 16 Hz, 1 H), 5.77 (d, *J* = 16 Hz, 1 H).

Methyl (*E*)-6-Hydroxy-2-[(*o*-isopropylphenyl)-sulfonyl]-3,3,6-trimethyl-4-heptenoate (1c). For methyl [(*o*-isopropylphenyl)sulfonyl]acetate: IR (film) 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.26 (d, *J* = 7 Hz, 6 H), 3.6 (s, 3 H), 3.66 (m, 1 H), 4.1 (s, 2 H), 7.4 (m, 3 H), 7.9 (d, *J* = 6 Hz, 1 H).

From sodium methyl [(*o*-isopropylphenyl)sulfonyl]acetate was obtained **1c** (0.230 g, 60% yield) after column chromatography with hexane–ether (1:2): IR ($CDCl_3$) 3400, 1730 cm^{-1}; NMR (CCl_4) δ 1.5–1.2 (18 H with d, *J* = 7 Hz, centered at 1.27, $(CH_3)_2CH$), 1.9 (s, 3 H), 3.3 (s, 3 H), 3.8 (s, 1 H, and m, $HC(CH_3)_2$), 5.7 (d, *J* = 16 Hz, 1 H), 5.9 (d, *J* = 16 Hz, 1 H), 7.4 (m, 2 H), 7.8 (m, 2 H).

Ethyl (*E*)-2-Cyano-6-hydroxy-3,3,6-trimethyl-4-heptenoate (1d).[6] From sodium ethyl cyanoacetate was obtained **1d** (0.225 g, 95% yield) after distillation: bp 142 °C (0.1 mm); IR (neat) 3400, 2240, 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.2–1.5 (m, 15 H), 1.8 (OH), 3.30 (s, 1 H), 4.26 (q, 2 H), 5.66 (s, 2 H). Anal. Calcd for $C_{13}H_{21}O_3N$: C, 65.24; H, 8.95; N, 5.86. Found: C, 65.42; H, 9.01; N, 6.05.

(*E*)-6-Hydroxy-2-(phenylsulfonyl)-3,3,6-trimethyl-4-heptenenitrile (1e). From sodio(phenylsulfonyl)acetonitrile was obtained **1e** (0.270 g, 90% yield) after column chromatography with hexane–ether (1:3): IR (CCl_4) 3500, 3400, 3060, 2240 cm^{-1}; ^1H NMR (CCl_4) δ 1.27 (s, 6 H), 1.42 (s, 6 H), 2.2 (OH), 3.87 (s, 1 H), 5.72 (d, *J* = 16 Hz, 1 H), 5.70 (d, *J* = 16 Hz, 1 H), 7.6 (m, 3 H), 7.9 (m, 2 H); ^{13}C NMR ($CDCl_3$) 25.8, 26.3, 29.7, 40.9, 67, 70.95, 113.8, 129.35, 192.5, 130.5, 135, 138.3, 138.4.

General Procedure for the Synthesis of the Acetates 2. To the appropriate allylic alcohol **1** (1 mmol) in solution with 0.2 mL (1.3 mmol) of triethylamine and 0.025 g (0.13 mmol) of DMAP at 0 °C was added 0.1 mL (1.15 mmol) of acetic anhydride in dichloromethane (0.7 mL). After 5 h at 0 °C and 2 h at 25 °C the resulting mixture was evaporated in vacuo, 20 mL of methylene chloride was added to the crude material, and the solution was washed with 2% HCl and then with water. The organic layer was dried ($MgSO_4$) and evaporated in vacuo to give the product after

(11) For a recent observation of this type in the chrysanthemic series, see: Lindsay, R. J.; Ferguson, I.; Costello, A. T.; Thomas, A. (Imperial Chemical Industries Ltd.) German Patent 2751610; British Appl. 76/48078; *Chem. Abstr.* **1978**, *89*, 108333.

(12) The hydrogenation of **3** on $Pd/CaCO_3$ gave *cis*-dihydrochrysanthemonitrile.[4] We express sincere thanks to Professor M. Julia and Dr. Linstrumelle for copies of NMR spectra of *cis*- and *trans*-dihydrochrysanthemonitrile.

(13) For reductive cleavage of the sulfonyl group, see: Field, L. *Synthesis* **1978**, 731; Magnus, P. D. *Tetrahedron* **1977**, *33*, 2037. Only the recent improved procedure (Trost, B. M.; Arndt, H. C.; Strege, P.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, *39*, 3477) with 6% Na/Hg/methanol and Na_2HPO_4 works cleanly in our case.

(14) (a) Pascali, V.; Umani-Ronchi, A. *J. Chem. Soc., Chem. Commun.* **1973**, 351. (b) Julia, M. "7th International Symposium on Organic Sulfur Chemistry"; Tišler, A., Ed.; Potorŏz, Yugoslavia, 1978; p 121.

(15) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

(16) Dijkstra, R.; Backer, M. J. *Recl. Trav. Chim. Pays-Bas* **1954**, *73*, 569.

column chromatography on silica gel (single spot on TLC).

Acetate (2a). From **1a** was obtained **2a**: 0.250 g (65% yield); IR (neat) 1735 cm^{-1}; NMR ($CDCl_3$) δ 1.2 (s, 6 H), 1.45 and 1.40 (s, 24 H), 1.95 (s, 3 H), 3.08 (s, 1 H), 5.67 (d, J = 16 Hz, 1 H), 5.9 (d, J = 16 Hz, 1 H).

Acetate (2b). From **1b** was obtained **2b** (0.160 g, 65% yield) after chromatography with ether–pentane (1:7): IR (neat) 2240, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.4 (s, 6 H), 2 (s, 3 H), 3.50 (s, 1 H), 5.61 (d, J = 16 Hz, 1 H), 5.94 (d, J = 16 Hz, 1 H).

Acetate (2c). From **1c** was obtained **2c** (0.380 g, 90% yield) after chromatography with ether–hexane (1:1): IR (neat) 1730 cm^{-1}; NMR (CCl_4) δ 1.2–1.5 (18 H, with d, J = 7 Hz, centered at 1.40, $(CH_3)_2CH$), 1.86 (s, 3 H), 3.23 (s, 3 H), 3.80 (s, 1 H, and m, 1 H), 5.73 (d, J = 16 Hz, 1 H), 5.78 (d, J = 16 Hz, 1 H), 7.4 (m, 3 H), 7.80 (br d, J = 8 Hz, 1 H).

Acetate (2d). From **1d** was obtained **2d** (0.240 g, 85% yield) after column chromatography with ether–hexane (1:1): IR (neat) 2240, 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.27 (s, 6 H), 1.3 (t, J = 7Hz, 3 H), 1.50 (s, 6 H), 1.96 (s, 3 H), 3.32 (s, 1 H), 4.20 (q, J = 7 Hz, 2 H), 5.67 (d, J = 16 Hz, 1 H), 5.75 (d, J = 16 Hz, 1 H). Anal. Calcd for $C_{15}H_{23}O_3N$: C, 64.0; H, 8.24; N, 4.98. Found: C, 63.77; H, 8.11; N, 5.14.

Acetate (2e). From **1e** was obtained **2e** (0.298 g, 85% yield) by column chromatography with ether–hexane (3:1): oil; TLC [silica gel, ether–hexane (3:1)] R_f 0.37; IR (neat) 3060, 2240, 1730, 1580 cm^{-1}; ^1H NMR (CCl_4) δ 1.45 (s, 6 H), 1.52 (s, 6 H), 1.97 (s, 3 H), 3.87 (s, 1 H), 5.85 (s, 2 H), 7.55 (m, 3 H), 7.95 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.16, 25.6, 26.2, 26.7, 26.9, 40.9, 66.9, 79.9 (quaternary carbon, >COAc), 113.7, 129.4, 129.5, 132.5, 134.9, 138.6, 169.8. Anal. Calcd for $C_{18}H_{23}O_4SN$: C, 61.86; H, 6.83; N, 4.01; S, 9.17. Found: C, 61.68; H, 7.02; N, 4.25; S, 9.05.

General Procedure for the Synthesis of the Substituted Cyclopropanes. The appropriate acetate **2** (1 mmol) in THF solution (3 mL) was added at room temperature to a suspension of 1.1 mmol of NaH in 0.5 mL of THF. The mixture was stirred at 65 °C and monitored by TLC on silica gel. The reaction was quenched with dilute HCl (2%). The aqueous layer was extracted with ether or methylene chloride. The organic extracts were washed with water, dried over $MgSO_4$, and evaporated in vacuo. The residue was purifed by recrystallization or chromatography.

1,1-Dicyano-2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropane (6, A = X = CN). From the sodio derivative of **2b** (1.5 h at 65 °C) after chromatography with ether–pentane (1:9) was obtained **6**: 0.130 g (75% yield); mp 94 °C; IR ($CDCl_3$) 2230 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (s, 3 H), 2 (s, 3 H), 1.83 (s, 3 H), 1.85 (br s, 3 H), 2.43 (d, J = 7 Hz, 1 H), 4.95 (br d, J = 7 Hz, 1 H); mass spectrum, m/e 174 (molecular ion). Anal. Calcd for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.10. Found: C, 75.7; H, 8.09; N, 16.32.

(*E*)- and (*Z*)-Methyl 2,2-Dimethyl-3-(2-methyl-1-propenyl)-1-[(*o*-isopropylphenyl)sulfonyl]carboxylates (11 and 12). From the sodio derivative of **2c** after 3 h at 65 °C was obtained a mixture of **11** and **12**: 0.320 g, (100% yield); TLC [silica gel ether–hexane (1:1)] R_f 0.35. For **11**: IR (Nujol) 1730 cm^{-1}; NMR ($CDCl_3$) δ 1–1.25 (m, 12 H), 1.5–1.8 (m, 6 H), 2.90 (d, J = 8 Hz, 1 H), 3.13 (s, 3 H), 3.5 (m, 1 H), 5.12 (d, J = 8 Hz, 1 H), 7.2 (m, 3 H), 7.73 (d, J = 8 Hz, 1 H). For **12**: NMR ($CDCl_3$) 1–1.25 (m, 12 H), 1.5–1.8 (m, 6 H), 2.73 (d, J = 8 Hz, 1 H), 3.13 (s, 3 H), 5.60 (d, J = 8 Hz), 7.2 (m, 3 H), 7.73 (d, J = 8 Hz, 1 H).

1-Cyano-2,2-dimethyl-3-(2-methylpropenyl)-1-(phenylsulfonyl)cyclopropane (13). From the sodio derivative of **2e** after 3 h at 65 °C and after recrystallization (hexane) was obtained **13**: mp 90 °C; 0.232 g (80% yield); IR ($CHCl_3$) 3060, 2230, 1580 cm^{-1}; NMR (CCl_4) δ 1.27 (s, 3 H), 1.60 (s, 3 H), 1.80 (s, 6 H), 2.85 (d, J = 8 Hz, 1 H), 4.89 (d, J = 8 Hz, 1 H), 7.6 (m, 3 H), 7.90 (m, 2 H); mass spectrum, m/e 289 (molecular ion). Anal. Calcd for $C_{16}H_{19}O_2SN$: C, 66.45; H, 6.62; N, 4.84; S, 11.08. Found: C, 66.65; H, 6.68; N, 4.9; S, 11.17.

(*E*)- and (*Z*)-Ethyl 1-Cyano-2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylates (14 and 15). (i) From the sodio derivative of **2d** after 2.5 h at 65 °C a 1:1 mixture of **14** and **15** was obtained after column chromatography on silica gel (eluting with pentane): 0.166 g (75% yield); TLC [silica gel, ether–pentane (1:1)] R_f 0.32.

(ii) From sodio derivative of **2d** (performed at 10 °C) and subsequent addition of 10% of tetrakis(triphenylphosphine)-palladium, with the reaction mixture being heated at 65 °C for 1.5 h, was obtained 0.150 g (70% yield, no optimization) of **14** as the major product (95%) with 5% of **15**.

For **14**: IR ($CDCl_3$) 2220, 1725 cm^{-1}; NMR ($CDCl_3$) δ 1.20–1.45 (m, 9 H, with 2 s at 1.34 and 1.36), 1.75 (s, 3 H), 1.80 (s, 3 H), 2.7 (d, J = 8 Hz, 1 H), 4.27 (q, J = 7 Hz, 2 H), 5.07 (br d, J = 7 Hz, 1 H).

For **15**: NMR ($CDCl_3$) δ 1.20–1.45 (m, 9 H, 2 s at 1.73 and 1.78), 2.45 (d, J = 8 Hz, 1 H), 4.18 (q, J = 7 Hz, 2 H), 5.28 (d, J = 8 Hz, 1 H).

Synthesis of *cis*-Chrysanthemonitrile (3).[4] A stirred mixture of –35 °C of 0.250 g (0.84 mmol) of **13** in dry methanol, 1.3 g of 6% Na/Hg, and 0.490 g of Na_2HPO_4 gave after a conventional workup 0.125 g (100% yield) of chrysanthemonitrile: bp 130–134 °C (15 mm); IR (neat) 2230 cm^{-1}; NMR ($CDCl_3$) δ 1.1–1.45 (7 H, with s at 1.25), 1.2–2 (7 H, with 2 br s at 1.75 and 1.82), 5.07 (d, J = 8 Hz, 1 H). Less than 10% of trans compound was detected: NMR δ 1.15 (s), 1.37 (s), 4.87 (d, J = 8 Hz); mass spectrum, m/e 149 (molecular ion).

Registry No. 1a, 77081-06-2; **1b**, 77081-07-3; **1c**, 77081-08-4; **1d**, 58773-90-3; **1e**, 77081-09-5; **2a**, 77081-10-8; **2b**, 77081-11-9; **2b** Na, 77081-12-0; **2c**, 77081-13-1; **2c** Na, 77081-14-2; **2d**, 77081-15-3; **2d** Na, 77081-16-4; **2e**, 77097-75-7; **2e** Na, 77097-76-8; **3**, 2198-88-1; **6**, 38111-13-6; **11**, 77081-17-5; **12**, 77081-18-6; **13**, 77081-19-7; **14**, 77081-20-0; **15**, 77081-21-1; sodium *tert*-butyl malonate, 55573-13-2; sodiomalononitrile, 20334-42-3; methyl [(*o*-isopropylphenyl)-sulfonyl]acetate, 77081-22-2; sodium methyl [(*o*-isopropylphenyl)-sulfonyl]acetate, 77081-23-3; sodium ethyl cyanoacetate, 18852-51-2; sodio(phenylsulfonyl)acetonitrile, 77081-24-4; **7**, 75646-37-6; tetrakis(triphenylphosphine)palladium, 14221-01-3.

Conversion of Lactones into Ethers

George A. Kraus,* Kevin A. Frazier, Bruce D. Roth, Michael J. Taschner, and Kent Neuenschwander

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received October 3, 1980

Although tetrahydrofurans and tetrahydropyrans are important structural subunits of many classes of natural products,[1] comparatively few general synthetic methods are known.[2] Since γ- and δ-lactones are readily available,[3] an efficient and versatile transformation to the ether would significantly extend current methodology. The conversion of a lactone to an ether has been accomplished by hydride reduction to a diol followed by cyclization by way of a monotosylate[4] or other activated ester.[5] Certain Lewis acid–hydride complexes have also been employed.[6] This strategy has seen limited use due to the restrictions on the functional groups which are compatible with the reaction conditions. A clever method utilizing trichlorosilane has been developed independently by Baldwin[7] and Tsurugi.[8] Although lactones can be reduced in the presence of esters, there are some limitations on the types of lactones with which this method can be used. We report a mild, con-

(1) Nakanishi, K. *Nat. Prod. Chem.* **1974**, *1,2*.
(2) Patai, S., Ed. "Chemistry of the Ether Linkage"; Wiley: New York, 1967: p 373–443.
(3) Kroper, H. "Methoden der Organischen Chemie (Houben-Weyl)"; Verlag Chemie: Weinheim/Bergstr., Germany, 1963; p 571.
(4) Picard, P.; Leclereq, D.; Moulines, J. *Tetrahedron Lett.* **1975**, 2731.
(5) VanTamelen, E. E.; Schnur, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 465.
(6) For ester reduction: Petit, G. R.; Piatak, D. M. *J. Org. Chem.* **1952**, *27*, 2127; *Ibid.* **1961**, *26*, 4553.
(7) Baldwin, S.; Hant, S. A. *J. Org. Chem.* **1975**, *40*, 3885.
(8) Tsurugi, J.; Nakao, R.; Fukumoto, T. *J. Am. Chem. Soc.* **1969**, *91*, 4587.

0022-3263/81/1946-2417$01.25/0