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Chemistry of Substituted [α-(Carboethoxy)vinyl]cuprates and Their Synthetic Application to Cyclopentenone Annulations

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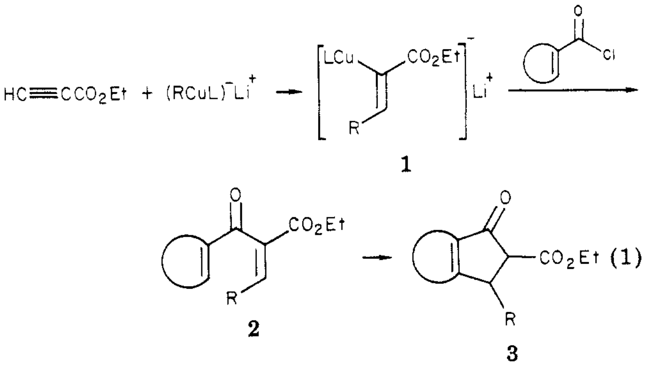
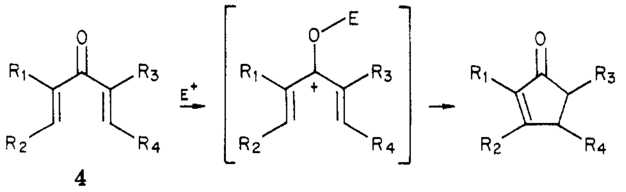
The conjugate addition of mixed alkyl cuprates to ethyl propiolate generates substituted [α-(carboethoxy)vinyl]cuprates that readily react with acid chlorides of α,β-unsaturated acids to produce α,α'-dienones. These unsaturated ketones bearing an α-carboethoxy group can serve as precursors to annulated cyclopentenones via a Nazarov-type cyclization. With this two-step sequence, it is possible to efficiently prepare substituted cyclopentenones fused to five-, six-, and seven-membered rings. As part of an effort to optimize yields in the Nazarov cyclizations, trimethylsilyl iodide was shown to be a new and effective reagent for this transformation.

In the past decade, the chemistry of functionalized vinyl organocopper reagents has grown steadily since their introduction in prostaglandin syntheses.[1] We have been concerned with the development of new functionalized vinylcuprates as synthons for the total synthesis of a variety of natural products. Since our initial report on the use of [α-(carbomethoxy)vinyl]cuprate for the construction of α-methylene-γ-butyrolactones,[2] we have been investigating the chemical reactivity of this parent system[3] as well as substituted analogues. In this paper we describe: (1) the conjugate addition of mixed alkyl cuprates to ethyl propiolate, (2) the trapping of the resultant substituted [α-(carboethoxy)vinyl]cuprates 1 with acid chlorides of cyclic α,β-unsaturated acids, and (3) the conversion of the resulting α,α'-dienones 2 into ring-fused cyclopentenones 3 via a Nazarov-type cyclization. A generalized scheme for this two-step sequence is shown in eq 1.



Cyclopentenone synthesis by an annulation process has great utility in natural product chemistry. Sesquiterpenes possessing the hydroazulene ring system as well as compounds containing a substituted pentalene moiety are prevalent in nature. Recent syntheses of pentalenolactone,[4] coriolin,[5] and hirsutene[6] exemplify the importance of methods to construct cyclopentenones that can serve as versatile intermediates in total syntheses. Thus, methodology that produces a functionalized cyclopentenone with regiochemical control is highly desirable.

The Nazarov reaction,[7] which proceeds through a pentadienyl cation that undergoes conrotatory electrocyclic ring closure,[8] provides an efficient route to cyclopentenones. The reaction is often limited by the available methods[9] to construct the precursor dienones 4, especially those that contain additional functionality. The recent modification of the original Nazarov conditions, from strong mineral acid to Lewis acid catalysis,[10] should allow for greater compatibility of different functional groups.



Variations in dienone structures become a major consideration for extension of the Nazarov reaction to more complicated systems. Organocuprate methodology can provide many highly functionalized and reactive vinyl species.[11] Formation of an adduct by the reaction of an unsaturated acid chloride and a vinyl cuprate readily produces a dienone suitable for cyclization. Therefore, the sequential application of vinylcuprate/Nazarov cyclization conditions has potential for the synthesis of highly substituted cyclopentenones.

In our laboratory we have been studying reactions of [α-(carboalkoxy)vinyl]cuprates[2,3] in order to apply these functionalized vinyl reagents to the cuprate/Nazarov annulation sequence. Since it had been established that an alkyl cuprate will form a 1:1 adduct with an α,β-unsaturated acid chloride without concomitant conjugate addition,[11a] it was anticipated that a carboalkoxy-substituted dienone would be readily available. Prior results in our laboratory revealed that the tertiary alcohol product formed by 1,2-carbonyl addition of 5[2] to 1-acetylcyclo-

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(1) For two comprehensive reviews on the synthesis of Prostaglandins, see: A. Mitra, "The Synthesis of Prostaglandins", Wiley, New York, 1977; R. F. Newton and S. M. Roberts, *Tetrahedron*, **36**, 2163 (1980).

(2) J. P. Marino and D. M. Floyd, *J. Am. Chem. Soc.*, **96**, 7138 (1974).

(3) (a) J. P. Marino and D. M. Floyd, *Tetrahedron Lett.*, 3897 (1975); (b) J. P. Marino and D. M. Floyd, *ibid.*, 675 (1979).

(4) (a) S. Danishefsky, M. Hirama, K. Gombatz, T. Harayama, E. Berman, and P. Schuda, *J. Am. Chem. Soc.*, **100**, 6536 (1978); (b) F. Plavac and C. H. Heathcock, *Tetrahedron Lett.*, 2115 (1979); (c) W. H. Parsons, R. H. Schlessinger, and M. L. Quesada, *J. Am. Chem. Soc.*, **102**, 889 (1980).

(5) S. Danishefsky, R. Zamboni, M. Kohn, and S. J. Etheredge, *J. Am. Chem. Soc.*, **102**, 2097 (1980).

(6) (a) K. Tatsuta, K. Akimoto, and M. Kinoshita, *J. Am. Chem. Soc.*, **101**, 6116 (1979); (b) Y. Ohfune, H. Shirahama, and T. Matsumoto, *Tetrahedron Lett.*, 2795 (1976); (c) S. Nozoe, J. Furukawa, U. Sankawa, and S. Shibata, *Tetrahedron Lett.*, 195 (1976); (d) A. E. Greene, *ibid.*, 3059 (1980); (e) T. Hudlicky, . M. Kutchan, S. R. Wilson, and D. T. Mao, *J. Am. Chem. Soc.*, **102**, 6351 (1980).

(7) I. N. Nazarov and I. I. Zaretskaya, *Zh. Obshch. Khim.*, **27**, 693 (1957).

(8) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim/Bergstr., Germany, 1971.

(9) (a) S. Hacini, R. Pardo, and M. Santelli, *Tetrahedron Lett.*, 4553 (1979); (b) F. Cooke, J. Schwindeman, and P. Magnus, *ibid.*, 1995 (1979); (c) W. E. Fristad, D. S. Dime, T. R. Bailey, and L. A. Paquette, *ibid.*, 1999 (1979); (d) L. A. Paquette, W. E. Fristad, D. S. Dime, and T. R. Bailey, *J. Org. Chem.*, **45**, 3017 (1980), and references therein.

(10) See ref 9b and T. Hiyama, M. Shinoda, and H. Nozaki, *Tetrahedron Lett.*, 771 (1978).

(11) (a) G. H. Posner, *Org. React.* **19**, 1 (1972); (b) *ibid.*, **22**, 253 (1975); (c) J. F. Normant, *Synthesis*, 63 (1972); (d) J. F. Normant in "New Applications of Organometallic Reagents in Organic Synthesis", D. Seyferth, Ed., Elsevier, Amsterdam, 1976, p 219.

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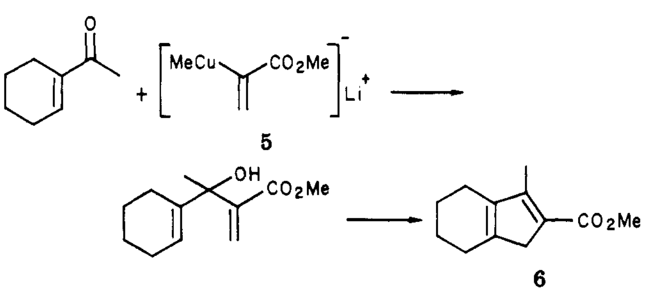
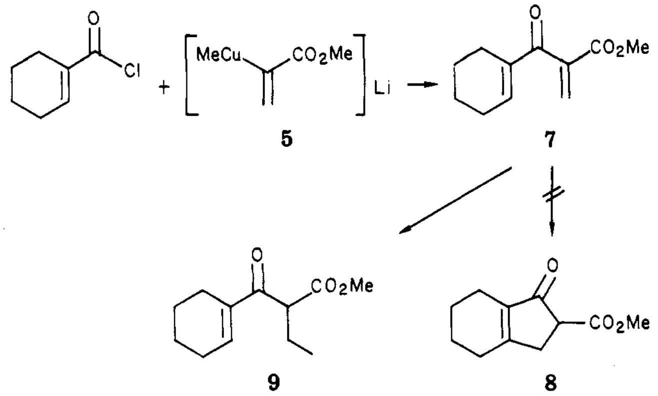
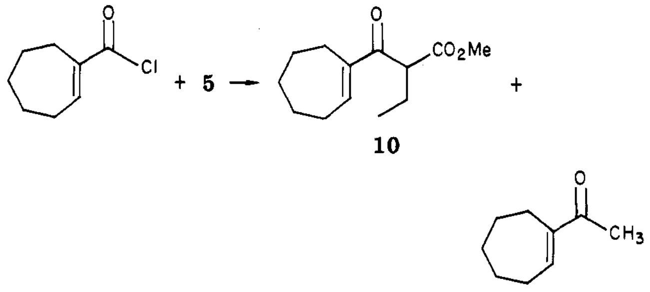
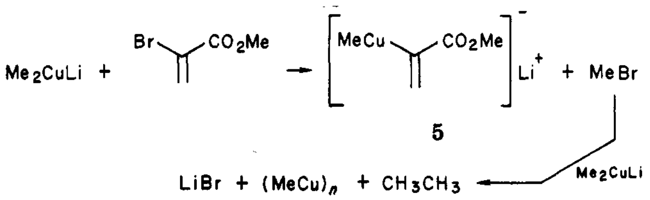
hexene was cyclized under acidic conditions to a cyclopentadienyl compound, 6.[12] The reaction is analogous to the classic Nazarov reaction in that a pentadienyl cation intermediate is presumably formed by protonation of the tertiary alcohol and elimination of water. The product diene 6 is then formed by electrocyclic ring closure and loss of a proton. Clearly, the electrocyclic ring closure was not hampered by the presence of the carbomethoxy group. With this result in mind, it was envisaged that adducts of [α-(carbomethoxy)vinyl]cuprates and cyclic α,β-unsaturated acid chlorides, such as 1-cyclohexene-1-carboxylic acid chloride,[13] could serve as general precursors to α′-(carbomethoxy)cyclopentenones, such as 8.





When 5 and the acid chloride were combined in a 1:1.1 molar ratio, the expected adduct 7 could not be isolated. Instead, the reactive dienone was found to undergo further reaction with methylcopper, generated in the reaction mixture, to produce 9 in 30% yield. The major product of the reaction was identified as 1-acetylcyclohexene (50% yield). Previous reactions[12] of 5 had also given alkyl rather than vinyl ligand transfer and therefore methyl transfer was not unexpected. In an analogous fashion, 10 was produced from 1-cycloheptene-1-carboxylic acid chloride[14] in 60% yield, with less than 20% 1-acetylcycloheptene isolated. Methylcopper is present in the reaction mixture as a byproduct produced during formation of the reagent, 5. Two equivalents of lithium dimethylcuprate are required to generate the vinyl species from methyl α-bromoacrylate. The first equivalent produces the vinylcuprate by metalation of the vinyl bromide, while the second equivalent is required to remove methyl bromide from the reaction mixture. This latter reaction produces ethane and methylcopper, observed as a bright-yellow precipitate in the red ethereal solution of the vinylcuprate.[12]

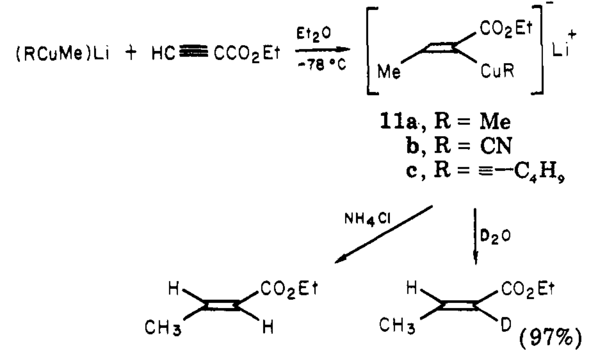




Because of the complexity of the vinyl bromide metalation process and the presence of additional reactive copper species in the reaction mixture, alternative methods for generating [α-(carbalkoxy)vinyl]cuprates were studied.

The early work of Corey[17a] and Siddall[17b] showed that conjugate additions of organocuprates to substituted acetylenic esters proceed regiospecifically and stereospecifically to generate cis 1,4 adducts. While these workers have trapped the intermediate [α-(carbalkoxy)vinyl]cuprate with deuterium, iodine, and methyl iodide, further trapping with other carbon electrophiles is lacking. Until very recently, there were no reports of conjugate additions to terminal acetylenic esters. Problems have been encountered in the copper-catalyzed additions of Grignard reagents to propiolates because of the basic nature of these reagents.[18] In 1980, Normant[19] reported the cis addition of vinylcuprates to ethyl propiolate, and subsequent quenching with a proton source yielded the trans unsaturated ester. In 1976, we reported the cis 1,4 addition of dicyclopropylcopper lithium to methyl propiolate.[20] In this paper, we report that homo- and heterocuprates do add in a controlled manner to ethyl propiolate to generate synthetically useful monosubstituted [α-(carboethoxy)vinyl]cuprates of known configuration. Furthermore, our study offers some additional insight into the structure of this class of α-functionalized vinylcuprates.

Additions of lithium dimethylcuprate, lithium cyanomethylcuprate as well as lithium hexynylmethylcuprate to ethyl propiolate generate a vinylcuprate 11. Quenching



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(12) D. M. Floyd, Ph.D. Thesis, University of Michigan, Ann Arbor, MI, 1976.

(13) Prepared from the acid by reaction with thionyl chloride in benzene.

(14) Prepared from cycloheptanone by cyanohydrin formation and elimination to the vinyl nitrile[15] (43% overall) and basic hydrolysis to the acid[16] (65%).

(15) S. J. Assony and N. Kharasch, *J. Am. Chem. Soc.*, **80**, 5978 (1958).

(16) K. C. Mathur and G. S. Saharia, *Indian J. Chem.*, **6**, 248 (1968).

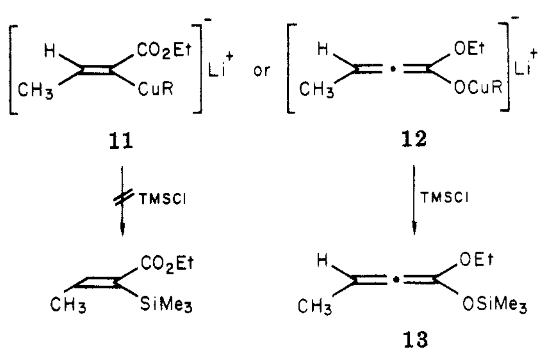
(17) (a) E. J. Corey and J. A. Katzenellenbogen, *J. Am. Chem. Soc.*, **91**, 1851 (1969); (b) J. B. Siddall, M. Biskup, and J. H. Fried, **91**, 1853 (1969).

(18) See ref 11a and 11c and references therein.

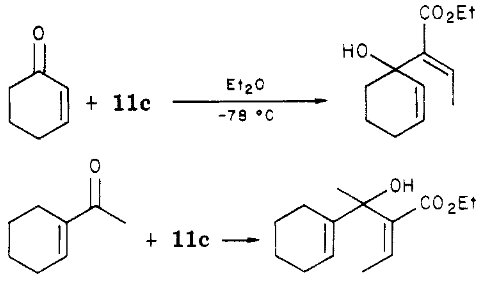
(19) A. Alexakis, G. Cahez, and J. F. Normant, *Tetrahedron*, **36**, 1961 (1980). See also ref 11d.

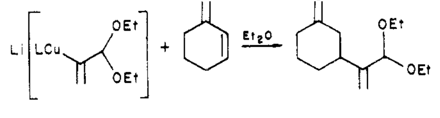
(20) J. P. Marino and L. J. Browne, *J. Org. Chem.*, 41, 3629 (1976).

11 with deuterium oxide produces isomerically pure (*E*)-ethyl 2-deuteriocrotonate. It is noteworthy that the reaction to form **11** is carried out with a 1:1 molar ratio of cuprate to acetylenic ester. The vinyl cuprate **11** is depicted by us[2] and others[17,19] as possessing a covalent copper to sp^2-carbon bond. However, based on our earlier work with **5** (i.e., 1,2 addition to ketones)[3] and the fact that intermediates such as **11a** also add 1,2 to ketones and enones,[21] we believe that an equally viable structure for **11** is a configurationally fixed copper allenoate **12**. Siddall[17b] proposed an intermediate of this type but was unable to trap the species. Klein and Levine[22] have presented experimental evidence for the presence of an allenoate structure by infrared data. Other workers[17a,23] in related additions have attributed isomeric mixtures of *E* and *Z* double bonds to isomerization of an enolic intermediate. We have now found that by quenching the reaction mixture with a solution of trimethylsilyl chloride, triethylamine, and HMPA (3:3:1), a silylated product, **13**, possessing an infrared absorption at 1950 cm^{-1}, was isolated. No vinylsilane was detected in the reaction mixture.



The second most compelling reason for considering an allenoate structure for these cuprates is that no conjugate addition to α,β-unsaturated ketones is observed. Like the parent [α-(carbomethoxy)vinyl]cuprate **5**,[2] substituted analogues **11** were found to add exclusively 1,2 to cyclohexenone and 1-acetylcyclohexene. These [α-(carbalkoxy)vinyl]cuprates **5** and **11** have the potential to form an allenoate structure and therefore exhibit reactivity more like enolates rather than vinylcuprates. If the ability to enolize is removed as in the case of (3,3-diethoxyisopropenyl)cuprate,[24] only 1,4-conjugate addition to enones is observed.





The reactivity of the [α-(carboethoxy)vinyl]cuprate **11**, generated from ethyl propiolate, is dependent on the secondary ligand. The cyanocuprate **11b** is unreactive toward cyclohexenone and cyclohexanone, while the hexynylcuprate **11c** does form 1,2 addition adducts in moderate yields (50–70%). This difference in reactivity is attributed to solubility problems encountered with the cyanocuprate. The reagent **11c** is formed in ether at −78 °C and exists as a bright orange/red fine dispersion, while **11b** forms a heavy red precipitate. Variation of solvent (ether vs. THF) as well as efforts to solubilize **11b** with complexing agents were unsuccessful in increasing its reactivity.

For simplicity and clarity of structure, the vinyl cuprates will be shown as **11** when their reactions with electrophiles occur at carbon. There have been very few reports[25] of acylations of substituted vinylcuprates, and no reports of reactions of substituted vinylcuprates with acid chlorides of α,β-unsaturated acids. We found that both the cyano (**11b**) and hexynyl (**11c**) vinylcuprates were reactive at low temperatures toward a series of unsaturated acid chlorides. Unlike the mixed methylvinylcuprate **5**, only the desired vinyl ligand was transferred, and no further reactions (1,2 or 1,4 additions) of the product α,α'-dienones were observed. In the case of the mixed methylcuprate **11a**, only a methyl ligand was transferred to the unsaturated acid chlorides. Reaction products and yields are summarized in Chart I.

The reactions in Chart I were carried out at low temperature (−78 °C) with a slight excess (10%) of acid chloride. The crude reaction mixtures contained high yields (75–95%) of adducts that required little purification. The stereochemistry of the methyl groups in the adducts **14**–**19** was assigned on the basis of literature[19] precedent and on the fact that ^{13}C NMR, ^{1}H NMR, and VPC analysis indicated single isomers. The absence of isomeric products for dienones **14**–**19** warrants some comment in reference to literature reports of temperature dependent stereochemical mixtures.[17a,b,23] All of the reported reactions led to mixtures of *E,Z* alkenes and involved additions to substituted acetylenic esters. In these cases, equilibrating reaction conditions do indeed yield the *E* isomer as the major product. Our study involves an unsubstituted propiolate ester in which the thermodynamic isomer is the same as the initially formed cis adduct, **11**.

The 1:1 stoichiometry for the reactions provides for complete utilization of the vinyl species, a situation which is contrasted with many cuprate reactions that require a large excess of the organometallic reagent. With the utilization of reagents **11b** and **11c**, the desired dienone systems for study in the Nazarov cyclization were readily available.

Nazarov cyclization reactions are "temperamental" in that a given set of reaction conditions will often not work as a general method in closely related systems.[26] Since the ester carbonyl group of dienones **14**–**19** should facilitate the formation of Lewis acid complexes, we speculated that the Nazarov cyclizations might occur under milder conditions than those reported for simple dienones.

Among the various reaction conditions investigated for the cyclization of dienone **18** to **22** were stannic chloride (1–3 equiv in CH_2Cl_2, 3–48 h), trifluoroacetic acid (2–3 equiv in CH_2Cl_2 or CCl_4, or neat at room temperature, 6–24

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(21) Preliminary work by D. M. Floyd[12] had generated the methyl ester analogue of **11a**.

(22) J. Klein and R. Levene, *J. Chem. Soc., Perkin Trans. 2*, 1971 (1973).

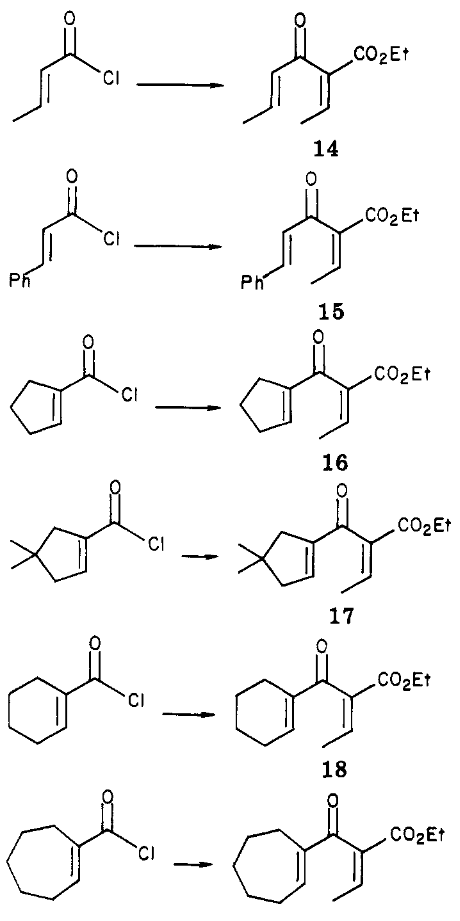
(23) E. Piers and H. E. Morton, *J. Org. Chem.*, **45**, 4263 (1980).

(24) (a) J. P. Marino and J. S. Farina, *Tetrahedron Lett.*, 3901 (1975); (b) P. A. Grieco, C. J. Wang, and G. Majetich, *J. Org. Chem.*, **41**, 726 (1976).

(25) A. Marfat, P. R. McQuirk, and P. Helquist, *Tetrahedron Lett.*, 1363 (1978).

(26) T. Hiyama, M. Shinoda, M. Tsukanaka, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **53**, 1010 (1980).

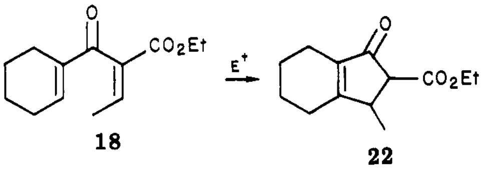
Chart I



	reagent	yield, %[a,b,c]
14	11b	75
15	11c	82
16	11c	87
17	11b 11c	75 80
18	11a 11b 11c	*d* 80 85
19	11b 11c	90 92

[a] Isolated; chromatographed on Florisil. [b] Single isomer by ^{1}H NMR, VPC analysis. [c] Yields based on ethyl propiolate. [d] Only 1-acetylcyclohexene is obtained (78%).

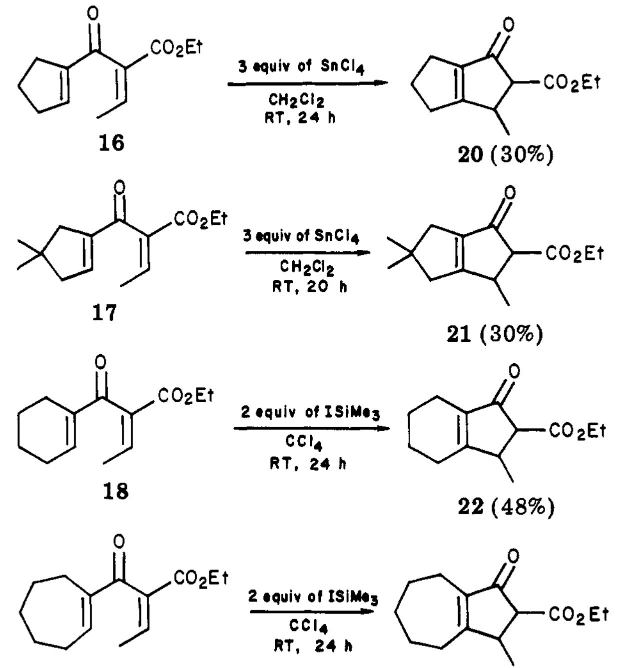
h), and boron trifluoride etherate (4 equiv in benzene at room temperature or reflux, 12 h). Titanium tetrachloride was not used as a catalyst because of its propensity to form chlorinated byproducts.[27] Yields for the conversion of **18** to **22** ranged from 10 to 20% under these conditions, and no starting dienone was recovered from the reaction mixture. Examination of the residues suggested that the major loss of dienone was due to polymerization. While the yields of **22** were not very satisfying, an effort was made to find a milder reagent for affecting a Nazarov cyclization.



18 **22**

Since a number of reactive trimethylsilyl compounds have been shown to add conjugately to enones,[28] we reasoned that trimethylsilyl iodide might form an intermediate enol ether iodide such as **24**. This very reactive dienyl iodide, **24**, would be expected to undergo facile ionization to the requisite pentadienyl cation, **25**, for the electrocyclic closure.

Scheme I

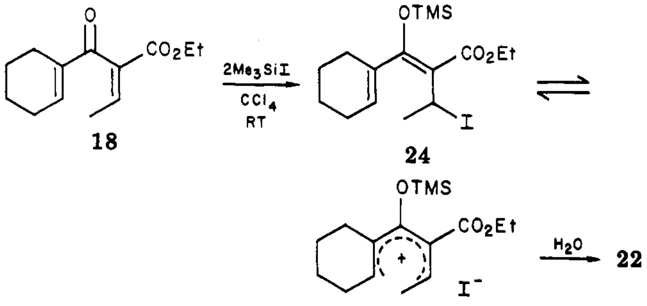


16 → **20** (30%)

17 → **21** (30%)

18 → **22** (48%)

19 → **23** (35%)



18 **24** **25**

Our predictions were borne out in that 2 equiv of trimethylsilyl iodide in carbon tetrachloride affected the Nazarov-type cyclization, and after an aqueous workup, a 48% yield of **22** was isolated. To our knowledge, this is the first example of a Nazarov cyclization being promoted by trimethylsilyl iodide.[29] The ease of workup for this type of reaction as compared to the Lewis acid catalyzed reactions also makes trimethylsilyl iodide a superior reagent. It also became apparent as we studied the cyclizations of **16**, **17**, and **19** that each ring system behaved differently with the aforementioned electrophilic reagent. Reactions of **16** and **17** with trimethylsilyl iodide produced annulated products **20** and **21** in less than 20% yield. In these ring-fused cyclopentenoid systems, tin tetrachloride proved to give the highest yields (30%). The optimum reaction conditions for each of the four dienones, **16**–**19**, are summarized in Scheme I.

The cyclization products were all obtained as single regioisomers. Usually a mixture of alkene isomers is obtained in the tin-catalyzed cyclization reactions.[9c,d] However, within the limits of ^{1}H and ^{13}C NMR no isomeric products were detected. While the yields of the cyclized products **20**–**23** are not very high, they are comparable to

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[27] Titanium tetrachloride has been found to be a poor choice in that 1,4-addition to the activated enone readily occurs; see ref 9d.

[28] (a) R. D. Miller and D. R. McKean, *Tetrahedron Lett.*, 2305 (1979); (b) R. D. Miller and D. R. McKean, *ibid.*, 2639 (1980); (c) A. Hosomi and H. Sakurai, *J. Am. Chem. Soc.*, **99**, 1673 (1977).

[29] Cyclization of **18** with 48% HBr led predominantly to product loss by polymerization; **22** obtained in less than 10%.

those reported for simple alkyl-substituted dienones.[9a,b,d,26] The efficiency with which the substituted dienones may be constructed using the [α-(carbalkoxy)vinyl]cuprates **11** should allow for ready access to numerous substituted annulated cyclopentenones. The presence of the α'-carbalkoxy group in the product cyclopentenones provides another synthetic handle for regiospecific carbanion reactions.

Experimental Section

General. Infrared spectra were obtained on a Perkin-Elmer 727B or 457 grating spectrophotometer. ^{1}H NMR spectra were obtained on a Varian T60A or JEOL-FX90Q spectrometer with tetramethylsilane as the standard. ^{13}C NMR spectra were obtained on a JEOL-FX90Q spectrometer with deuteriochloroform as the standard ($CDCl_3$, 77.00 ppm). Mass spectra were obtained on a Finnigan automated GC/MS-EICI system mass spectrometer at 70 eV. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI. Gas chromatographic separations were accomplished on a 1.5% OV-101 on Chrom GHP (100–120 mesh) column (unless otherwise noted) on a Varian 1400 instrument with a thermal conductivity detector. Column chromatography was carried out on EM Reagents silica gel 60 (230–400 mesh ASTM) or Fisher Scientific Co. Florisil (100–200 mesh). Preparative thin-layer chromatography was carried out on EM Reagents silica gel 60 F-254 precoated (2 mm) PLC plates. All chromatography solvents were distilled before use. Diethyl ether was freshly distilled from LAH (under N_2) and methylene chloride from P_2O_5. Hexyne and ethyl propiolate were purchased from Farchan and used without further purification. Technical grade cuprous cyanide was purchased from J. T. Baker. Ninety-eight percent cuprous iodide was purchased from Alfa and purified by the procedure of House.[30] Commercial methyllithium, low halide in ether, was obtained from Alfa and titrated[31] prior to use. All reactions were carried out in flame-dried glassware under an inert atmosphere of dry nitrogen. Nitrogen gas was purified by passage through a column of Ascarite and magnesium perchlorate.

Cuprate Preparation. Preparation of 5. A 5.71-g (0.03 mol) sample of ultrapure CuI was suspended in 100 mL of dry ether, and the flask was cooled to −30 °C. A 60.6-mL (0.06 mol) sample of a 0.99 M solution of methyllithium was added slowly. The resulting clear, slightly yellow solution was cooled to −78 °C (CO_2/acetone) and 2.47 g (0.015 mol) of freshly distilled[32] methyl 2-bromopropenoate[33] was added as a neat liquid. After the solution was stirred for 1 h at −78 °C, the heterogeneous red solution of the reagent was ready for use.

Preparation of 11a. Ultrapure CuI (0.78 g, 4.1 mmol) was suspended in 45 mL of dry ether, and the flask was cooled to −30 °C. A 5.8-mL (8 mmol) sample of a 1.38 M solution of methyllithium was added dropwise. The resulting clear-yellow solution was cooled to −78 °C. To the rapidly stirred solution of lithium dimethylcuprate was added 0.40 mL (4 mmol) of ethyl propiolate. The addition produced a deep orange-red heterogeneous solution. After the solution was stirred for 1 h at −78 °C, the reagent was ready for use.

Preparation of 11b. A 0.73-g (8.2 mmol) sample of CuCN was suspended in 45 mL of dry ether and cooled to −40 °C. A 5.8-mL (8 mmol) sample of a 1.38 M solution of methyllithium was added. The slightly yellow solution was stirred at −40 °C for 15 min and then cooled to −78 °C. After the solution was stirred for 30 min at −78 °C, 0.785 g (8 mmol) of ethyl propiolate was added to the solution of lithium cyanomethylcuprate. The addition immediately produced an orange slurry, which gradually darkened to a deep-red color with the formation of a red/black precipitate. After being stirred 1 h at −78 °C, the reagent was ready for use.

Preparation of 11c. A 0.48-mL (4.2 mmol) sample of hexyne was dissolved in 20 mL of dry ether and cooled to 0 °C (ice/water). A 2.53-mL (4 mmol) sample of a 1.58 M solution of methyllithium was added and the mixture stirred for 15 min. The white slurry of hexynyllithium was transferred to a second flask (via cannula) which contained 0.78 g (4.1 mmol) of ultrapure CuI suspended in 20 mL of ether at 0 °C. The bright-yellow slurry was stirred for 50 min at 0 °C and then cooled to −78 °C. A 2.53-mL (4 mmol) sample of a 1.58 M solution of methyllithium was added and the mixture stirred at −78 °C for 30 min. A 0.41-mL (4 mmol) sample of ethyl propiolate was added to the rapidly stirred lithium hexynylmethylcuprate, producing a bright orange/red heterogeneous mixture. The reagent was ready for use after being stirred 45–60 min at −78 °C.

Reactions of 5. 2-(Carbomethoxy)-3-(1-cyclohexen-1-yl)-1-buten-3-ol (90%).[12] 1-Acetyl-1-cyclohexene (0.25 g, 2 mmol) was added to **5** (3 mmol) and the mixture was stirred at −78 °C for 6 h. The reaction mixture was quenched by the addition of 10 mL of NH_4Cl (saturated aqueous) at −78 °C and allowed to warm to room temperature. The mixture was filtered through Celite, and the organic layer was washed with 20 mL of NH_4Cl (saturated aqueous) and 20 mL of brine and dried over $MgSO_4$. The solvent was removed in vacuo. The crude product was chromatographed on silica gel with 5:2 petroleum ether/ether as eluant: ^{1}H NMR ($CDCl_3$) δ 6.21 (s, 1 H), 5.78 (m, 2 H), 4.09 (br s, 1 H), 3.73 (s, 3 H), 2.10–1.75 (4 H), 1.78–1.30 (7 H, containing singlet at 1.48); IR (liquid film) cm^{-1} ν_{OH} 3475, ν_{CO} 1705, $\nu_{C=C}$ 1625; mass spectrum, *m/e* 210 (M$^+$), 133 (base), 192, 105, 91, and 97.

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.63; H, 8.64. Found: C, 68.52; H, 8.68.

Methyl 2-Ethyl-3-oxo-3-(1-cyclohexen-1-yl)propanoate (9; 30%). To **5** (7 mmol), 1.08 g (7.5 mmol) of 1-cyclohexene-1-carboxylic acid chloride[13] was added as a neat liquid. The solution was stirred for 4 h at −78 °C. The reaction mixture was quenched (at −78 °C) by the addition of 10 mL of NH_4Cl (saturated aqueous) and allowed to warm to room temperature. The mixture was filtered through Celite, and the organic phase was washed with 20 mL of brine and dried over $MgSO_4$. The solvent was removed in vacuo. The resulting crude product was chromatographed on silica gel with 5:1 petroleum ether/ether as eluant: ^{1}H NMR (CCl_4) δ 6.75 (m, 1 H), 3.82 (t, 1 H, J = 6 Hz), 3.52 (s, 3 H), 2.35–1.40 (10 H), 0.85 (t, 3 H); IR (liquid film) cm^{-1} $\nu_{C=O}$ 1740, 1640; mass spectrum, *m/e* 211.3 (M$^+$ +1), 109.3 (base), 81.3 53.2, 69.1, 95.2, 123.2, and 178.2.

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.63; H, 8.64. Found: C, 68.45; H, 8.41.

Methyl 2-Ethyl-3-oxo-3-(1-cyclohepten-1-yl)propanoate (10; 30%). To **5** (7 mmol), 1.19 g (7.5 mmol) of 1-cycloheptene-1-carboxylic acid chloride[14] was added as a neat liquid. The solution was left stirring at −78 °C for 4 h. The reaction mixture was quenched (at −78 °C) by the addition of 10 mL of NH_4Cl (saturated aqueous) and allowed to warm to room temperature. The mixture was filtered through Celite, and the organic phase was washed with 20 mL of brine and dried over $MgSO_4$. The solvent was removed in vacuo. The resulting crude product was chromatographed on silica gel with 5:1 petroleum ether/ether as eluant: ^{1}H NMR (CCl_4) δ 6.75 (t, 1 H), 3.70 (t, 1 H), 3.50 (s, 3 H), 2.50–1.20 (12 H), 0.88 (t, 3 H); IR (liquid film) cm^{-1} $\nu_{C=O}$ 1750, 1670, $\nu_{C=C}$ 1635; mass spectrum, *m/e* 224.3 (M$^+$), 123.3 (base), 95.3, 55.2, 67.2, 49.1, 84.2, and 192.3.

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.60; H, 9.00. Found: C, 69.67; H, 8.92.

Reactions of 11. Ethyl 2-Deuteriocrotonate (97%). A stirred suspension of **11b** (8 mmol) was quenched by the addition of 6 mL of D_2O at −78 °C and allowed to warm to room temperature. The mixture was filtered through Celite, and the organic phase was washed with 20 mL of NH_4Cl and 20 mL of brine and dried over $CaCl_2$. The solvent was removed by distillation. Product was obtained directly: ^{1}H NMR (CCl_4) δ 6.84 (m, 1 H), 4.12 (q, 2 H, J = 7 Hz), 1.92 (d, 3 H, J = 6 Hz), 1.12 (t, 3 H, J = 7 Hz).

1-Ethoxy-1-[(trimethylsilyl)oxy]-3-methylallene (13). A solution of **11a** (4 mmol) was prepared. A 0.695-mL (4 mmol) sample of pure HMPA was added at −78 °C followed by a mixture of 1.52 mL of trimethylsilyl chloride and 2 mL of triethylamine in 3 mL of ether. After being stirred 8 h, the yellow/brown

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(30) H. O. House, C. Y. Chu, J. M. Wilkins, and M. J. Umen, *J. Org. Chem.*, **40**, 1860 (1975).

(31) S. C. Watson and J. E. Eastham, *J. Organomet. Chem.*, **9**, 165 (1967).

(32) Methyl 2-bromopropenoate must be distilled (from hydroquinone under vacuum) immediately before addition.

(33) G. B. Payne and M. R. Johnson, *J. Org. Chem.*, **33**, 1285 (1968).

heterogeneous mixture was quenched by the addition of 10 mL of NH_4Cl (saturated aqueous), and the slurry was warmed to room temperature. The mixture was filtered through Celite, and the organic layer was washed with 20 mL of brine and dried over Na_2SO_4. The solvent was carefully removed by distillation at atmospheric pressure. The crude product showed IR (liquid film) cm^{-1} 1950 and 1725. (Ester carbonyl of ethyl crotonate was obtained by hydrolysis of the enol ether.)

Ethyl 2-Ethylidene-3-(1-cyclohexen-1-yl)-3-hydroxybutanoate (72%). A 0.26-mL (2 mmol) sample of 1-acetyl-1-cyclohexene was added to a solution of **11c** (4 mmol) at −78 °C. The mixture was stirred for 2 h at −78 °C and then warmed to −10 °C and then quenched by the addition of 10 mL of NH_4Cl (saturated aqueous). The slurry was filtered through Celite, and the organic phase was washed with 25 mL of NH_4Cl (saturated aqueous) and 25 mL of brine and dried over $MgSO_4$. Solvent was removed in vacuo. The crude product was chromatographed on silica gel with chloroform as eluant: ^1H NMR ($CDCl_3$) δ 6.02 (q, 1 H, J = 7 Hz), 5.70 (m, 1 H), 4.18 (q, 2 H, J = 7 Hz), 3.55 (br m, 1 H), 2.2–1.1 [15 H, containing 1.82 (d, J = 7 Hz), 1.42 (s), 1.25 (t, J = 7 Hz)]; IR (liquid film) cm^{-1} ν_{OH} 3460, $\nu_{C=O}$ 1720.

Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.54; H, 9.32. Found: C, 70.48; H, 9.25.

Cyclization Reactions. Cyclization of the 1,2 Adduct of 1-Acetylcyclohexene and 5. 2-(Carbomethoxy)-3-methyl-4,5,6,7-tetrahydro-1*H*-indene (6; 70%). A 286-mg (1.32 mmol) sample of the alcohol was dissolved in 3 mL of carbon tetrachloride, and 0.3 mL (4 mmol) of trifluoroacetic acid was added, resulting in a dark-purple solution. After being stirred 3 h at room temperature, the mixture was diluted with ether (30 mL) and washed with 2 × 10 mL of $NaHCO_3$. The organic phase was dried over $MgSO_4$, and the solvent was then removed in vacuo. Crude product was purified by preparative gas chromatography on a 5% SE-30 on Chromosorb W: ^1H NMR ($CDCl_3$) δ 3.80 (s, 3 H), 3.13 (m, 2 H), 2.28 (m, 7 H), 1.75 (m, 4 H); IR (liquid film) cm^{-1} $\nu_{C=O}$ 1690; mass spectrum, *m/e* 192 (M^+), 133 (base), 105, 91, 117, 161, and 77.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.75; H, 8.25.

General Reaction of 11b or 11c with Acid Chlorides. The acid chloride was added to the stirred cuprate reagent as a neat liquid in a 1.1:1 (acid chloride/cuprate) ratio. The mixture was stirred for 30 min at −78 °C and then allowed to warm to 0 °C. The reaction mixture was quenched at 0 °C by the addition of 10 mL of NH_4Cl (saturated aqueous). The mixture was filtered through Celite. The organic phase was washed with 10 mL of NH_4Cl (saturated aqueous), 20 mL of $NaHCO_3$, and 20 mL of brine and dried over $MgSO_4$. The solvent was removed in vacuo. The crude product was chromatographed on Florisil.[40]

Ethyl 2-Ethylidene-3-oxohex-4-enoate (14). From crotonoyl chloride: ^1H NMR (CCl_4) δ 6.9–6.2 (m, 2 H), 6.08 (m, 1 H), 5.75 (m, 1 H), 4.05 (q, 2 H, J = 7 Hz), 1.82 (br d, 6 H), 1.22 (t, 3 H); IR (CCl_4 solution) cm^{-1} $\nu_{C=O}$ 1735, 1710, $\nu_{C=C}$ 1660 (75%).

Ethyl 2-Ethylidene-3-oxo-5-phenylpent-4-enoate (15). From cinammoyl chloride: ^1H NMR ($CDCl_3$) δ 7.10 (br s, 5 H), 6.80–6.20 (m, 2 H), 5.65 (br s, 1 H), 4.15 (q, 2 H, J = 7 Hz), 1.85 (m, 3 H, J = 7 Hz), 1.20 (t, 3 H, J = 7 Hz); IR ($CDCl_3$ soln) cm^{-1} $\nu_{C=O}$ 1740, 1710, $\nu_{C=C}$ 1660 (82%).

Ethyl 2-Ethylidene-3-oxo-3-(1-cyclopenten-1-yl)propanoate (16). From 1-cyclopentene-1-carboxylic acid chloride:[34b] ^1H NMR (CCl_4) δ 6.80 (q, 1 H, J = 7 Hz), 6.48 (m, 1 H), 4.05 (q, 2 H, J = 7 Hz), 2.7–2.3 (m, 4 H), 2.2–1.6 (m, 4 H), 1.65 (d, 3 H, J = 7 Hz), 1.22 (t, 3 H, J = 7 Hz); IR (liquid film) cm^{-1} $\nu_{C=O}$ 1725, 1700, $\nu_{C=C}$ 1660, 1640; ^{13}C NMR ($CDCl_3$) δ 192.17, 164.38, 147.48, 145.91, 141.19, 135.56; all (s), off-resonance spectra (87%).

Ethyl 2-Ethylidene-3-oxo-3-(3,3-dimethyl-1-cyclopenten-1-yl)propanoate (17). From 3,3-dimethyl-1-cyclopentene-1-carboxylic acid chloride:[34a] ^1H NMR (CCl_4) δ 6.62 (q, 1 H, J = 7 Hz), 6.04 (br s, 1 H), 4.00 (q, 2 H, J = 7 Hz), 2.28 (br s, 4 H), 1.65 (d, 3 H, J = 7 Hz), 1.20 (t, 3 H, J = 7 Hz), 1.05 (s, 6 H); IR (CCl_4 soln) cm^{-1} $\nu_{C=O}$ 1730, 1705, $\nu_{C=C}$ 1660, 1640 (80%).

Ethyl 2-Ethylidene-3-oxo-3-(1-cyclohexen-1-yl)propanoate (18). From 1-cyclohexene-1-carboxylic acid chloride:[13] ^1H NMR (CCl_4) δ 6.61 (q, 1 H, J = 7 Hz), 6.30 (br s, 1 H), 4.00 (q, 2 H, J = 7 Hz), 2.3–1.95 (m, 4 H), 1.75–1.4 (7 H, containing a doublet (J = 7 Hz) at 1.62), 1.08 (t, 3 H, J = 7 Hz); IR (CCl_4 soln) cm^{-1} $\nu_{C=O}$ 1725, 1710, $\nu_{C=C}$ 1660, 1640 (85%).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.23; H, 8.18. Found: C, 70.20; H, 8.23.

Ethyl 2-Ethylidene-3-oxo-3-(1-cyclohepten-1-yl)propanoate (19). From 1-cycloheptene-1-carboxylic acid chloride:[14] ^1H NMR (CCl_4) δ 6.55 (m, 2 H), 3.95 (q, 2 H, J = 7 Hz), 2.5–2.0 (m, 4 H), 1.8–1.2 (6 H, containing a doublet (J = 7 Hz) at 1.62), 1.08 (t, 3 H, J = 7 Hz); IR (CCl_4 soln) cm^{-1} $\nu_{C=O}$ 1725, 1710, $\nu_{C=C}$ 1660, 1640 (95%).

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.14; H, 8.55. Found: C, 71.11; H, 8.51.

Nazarov Cyclization: General Conditions. Tin(IV)-Catalyzed Reaction. The dienone was dissolved in 10 mL of dry CH_2Cl_2 and tin(IV) chloride (anhydrous fuming reagent) was added as a CH_2Cl_2 solution. The solution was stirred at room temperature or refluxed. **Workup**: The reaction mixture was poured into 50 mL of HCl, the layers were carefully separated, and the organic phase was diluted to 75 mL with CH_2Cl_2. The CH_2Cl_2 solution was washed with 2 × 25 mL of $NaHCO_3$ and 2 × 25 mL of NaCl and dried over $MgSO_4$. The solvent was removed in vacuo and the crude product was purified by preparative thin-layer chromatography on silica gel.

Boron Trifluoride Etherate Catalyzed Reaction. The dienone was dissolved in 10 mL of dry benzene. $BF_3{\cdot}Et_2O$ was added, and the solution was stirred at room temperature or refluxed. **Workup**: The reaction mixture was poured into 30 mL of $NaHCO_3$, and the aqueous layer was extracted with 2 × 50 mL of ether. The combined ether extracts were washed with 20 mL of brine and dried over $MgSO_4$. The solvent was removed in vacuo, and the crude product was purified by preparative thin-layer chromatography on silica gel.

Trifluoroacetic Acid Catalyzed Reaction. The dienone was either dissolved in 10 mL of CCl_4 and trifluoroacetic acid was added or the dienone was dissolved in 3 mL of neat trifluoroacetic acid. The solution became dark purple within 1 h. **Workup**: The reaction mixture was diluted with ether to a volume of 25 mL. The ethereal solution was washed with $NaHCO_3$ (3 × 20 mL) or until gas evolution ceased and 20 mL of brine and dried over $MgSO_4$. The solvent was removed in vacuo, and the crude product was purified by preparative thin-layer chromatography on silica gel.

Iodotrimethylsilane[38] Catalyzed Reaction. The dienone was dissolved in dry carbon tetrachloride, and 2 equiv of iodotrimethylsilane[39] was added as the neat liquid. The solution was stirred at room temperature. **Workup**: The crude reaction mixture was concentrated (in vacuo) to a black oily residue, which was taken up in 50 mL of ether. The ether phase was washed with 20 mL of Na_2SO_3 and 20 mL of brine and dried over $MgSO_4$. The crude material was purified by preparative thin-layer chromatography on silica gel.

2-(Carboethoxy)-3-methyl-3,4,5,6-tetrahydro-2*H*-pentalen-1-one (20). From tin(IV) cyclization of **16**: ^1HNMR (CCl_4) δ 4.05 (q, 2 H, J = 7 Hz), 3.02 (br d, 2 H, J = 6 Hz), 2.60–2.30 (br s, 5 H), 1.80 (m, 1 H), 1.25 (t, 3 H, J = 7 Hz), 1.22 (d, 3 H, J = 6 Hz); IR (liquid film) cm^{-1} $\nu_{C=O}$ 1745, 1708, $\nu_{C=C}$ 1640, enol OH ν_{OH} 3400 (30%).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.20; H, 7.76. Found: C, 68.98; H, 7.70.

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(34) (a) 4,4-Dimethyl-1-cyclopentene-1-carboxylic acid chloride:[13] from 4,4-dimethylcyclopentene-1-carboxaldehyde[35] by oxidation to the acid with $AgNO_3$/NaOH. (b) 1-Cyclopentene-1-carboxylic acid chloride:[13] prepared from cyclopentanone by cyanohydrin formation,[36] hydrolysis to the vinylnitrile,[15] and basic hydrolysis to the acid.[37]

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(36) (a) R. F. Cox and R. T. Stormont, "Organic Syntheses", Collect. Vol. II, Wiley, New York, 1943, p 7; (b) S. M. McElvain and R. E. Starn, Jr., *J. Am. Chem. Soc.*, **77**, 4571 (1955).

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(39) The iodotrimethylsilane used in the cyclization reaction must be clear and colorless.

(40) Correct elemental analyses could not be obtained for compounds **14–17** because of their rapid decomposition during purification steps (PLC or VPC).

2-(Carboethoxy)-5,5-dimethyl-3-methyl-3,4,6-trihydro-2*H*-pentalen-1-one (21). From tin(IV) cyclization of **17**: ^{1}H NMR (CCl_4) δ 4.13 (q, 2 H, J = 7 Hz), 2.70–2.30 (m, 2 H), 2.03 (s, 2 H), 2.00–1.65 (m, 2 H), 1.27 (t, 3 H, J = 7 Hz), 1.20 (d, 3 H, J = 6 Hz), 1.15 (s, 3 H), 1.00 (s, 3 H); IR (CCl_4 soln) cm^{-1} $\nu_{C=O}$ 1730 (with shoulder at 1760), 1680, $\nu_{C=C}$ 1640, enol OH ν_{OH} 3200; ^{13}C NMR ($CDCl_3$) δ 171.42, 169.85, 121.64, 105.22, 60.48, 57.93, 53.22, 48.61, 40.54, 39.46, 28.79, 27.78, 20.71, 14.27; mass spectrum, *m/e* 236 (M^+), 57 (base), 180, 124, 71, 169, 83, 191, and 109 (30%).

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.14; H, 8.55. Found: C, 71.02; H, 8.52.

2-(Carboethoxy)-3-methyl-3,4,5,6,7-pentahydro-2*H*-inden-1-one (22). From iodotrimethylsilane cyclization of **18**: ^{1}H NMR (CCl_4) δ 4.10 (q, 2 H, J = 7 Hz), 3.20–2.80 (m, 2 H), 2.40–1.50 (two br m, 8 H), 1.27 (t, 3 H, J = 7 Hz), 1.20 (d, 3 H, J = 6 Hz); IR ($CDCl_3$ soln) cm^{-1} $\nu_{C=O}$ 1735, 1710, $\nu_{C=C}$ 1645, enol OH (weak) ν_{OH} 3400; ^{13}C NMR ($CDCl_3$) δ 200.46, 176.73, 169.53, 136.48, 61.29, 60.15, 40.97, 25.86, 21.96, 21.42, 20.06, 17.68, 14.16; mass spectrum, *m/e* 222 (M^+), 148 (base), 133, 79, 91, 105, 177, 121, and 55 (48%).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.23; H, 8.18. Found: C, 70.20; H, 8.16.

2-(Carboethoxy)-3-methyl-3,4,5,6,7,8-hexahydro-2*H*-azulen-1-one (23). From iodotrimethylsilane cyclization of **19**: ^{1}H NMR (CCl_4) δ 4.12 (q, 2 H, J = 7 Hz), 3.10–2.70 (m, 2 H), 2.55–2.10 (m, 4 H), 1.80–1.30 (m, 6 H), 1.27 (t, 3 H, J = 7 Hz), 1.20 (d, 3 H, J = 6 Hz); IR (liquid film) cm^{-1} $\nu_{C=O}$ 1740, 1710, $\nu_{C=C}$ 1650; ^{13}C NMR ($CDCl_3$) δ 200.40, 180.36, 169.31, 140.32, 61.28, 59.93, 41.62, 31.17, 30.95, 26.34, 26.14, 23.31, 18.05, 14.16; mass spectrum, *m/e* 236 (M^+), 162 (base), 91, 79, 54, 133, 190, 68, and 147 (35%).

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.14; H, 8.55. Found: C, 70.96; H, 8.49.

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Registry No. **5**, 71068-74-1; **6**, 78064-71-8; **9**, 78064-72-9; **10**, 78090-04-7; **11a**, 78063-95-3; **11b**, 78063-96-4; **11c**, 78063-97-5; **13**, 78064-73-0; **14**, 13176-53-9; **15**, 78064-74-1; **16**, 78064-75-2; **17**, 78064-76-3; **18**, 78064-77-4; **19**, 78064-78-5; **20**, 78064-79-6; **21**, 78064-80-9; **22**, 78064-81-0; **23**, 78064-82-1; crotonoyl chloride, 10487-71-5; cinnamoyl chloride, 102-92-1; 1-cyclopentene-1-carboxylic acid chloride, 59253-90-6; 3,3-dimethyl-1-cyclopentene-1-carboxylic acid chloride, 78064-83-2; 1-cyclohexene-1-carboxylic acid chloride, 36278-22-5; 1-cycloheptene-1-carboxylic acid chloride, 72233-47-7; methyl 2-bromopropenoate, 4519-46-4; ethyl propiolate, 623-47-2; 2-(carbomethoxy)-3-(cyclohexen-1-yl)-1-buten-3-ol, 58371-16-7; 1-acetyl-1-cyclohexene, 932-66-1; ethyl 2-deuteriocrotonate, 78064-84-3; ethyl 2-ethylidene-3-(1-cyclohexen-1-yl)-3-hydroxybutanoate, 78064-85-4.

Terpene Amine Synthesis via Palladium-Catalyzed Isoprene Telomerization with Ammonia

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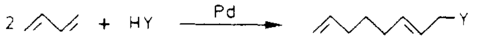
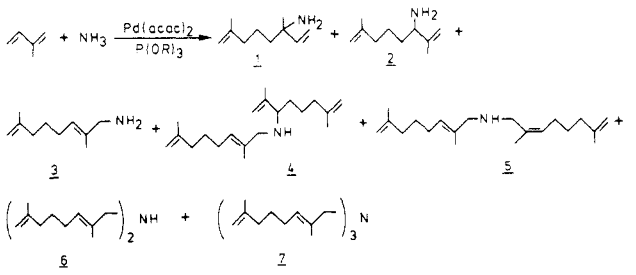
Isoprene and dry ammonia could be converted in a catalytic process in good yields into a mixture of primary, secondary, and tertiary terpene amines. Homogeneous catalysts formed from palladium acetylacetonate and tributyl phosphite showed the best activities and selectivities for the telomerization. Seven amines were isolated as the main products from the reaction mixture and were characterized by their spectral data. Tail-to-tail coupling of the isoprene units was predominant though under certain conditions α-linalylamine, which shows a head-to-tail structure, prevailed. The product distribution could be controlled by cocatalysts and reaction parameters. The formation of primary terpene amines was favored by short reaction times and high ammonia/isoprene ratios. The proper choice of solvents and especially ligands is shown to be essential, and a strong dependence on the catalyst concentration was observed. A mechanism involving bridged binuclear palladium complexes as the active species is discussed.

The telomerization of 1,3-dienes with nucleophiles catalyzed by homogeneous catalysts has been of considerable interest in the recent literature.[1,2] A variety of nucleophiles such as alcohols, amines, acids, and water undergo this reaction, affording predominantly 2,7-octadienyl derivatives.



Tsuji extended this reaction to ammonia by synthesizing tris(2,7-octadien-1-yl)amine.[3] We now report for the first time the telomerization of isoprene and ammonia to yield a spectrum of novel terpene amines. The dimerization of isoprene and the concomitant addition of ammonia represents a potential and facile route to aminated terpene products, useful as starting material for insecticides and fungicides. By considering tail-to-tail, tail-to-head, head-to-tail, and head-to-head dimerizations of the isoprene

Scheme I



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