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Reaction of Organoaluminium Reagents with Cyclopropylmethyl Acetates and 2-Vinylcyclopropane-1,1-dicarboxylate Esters

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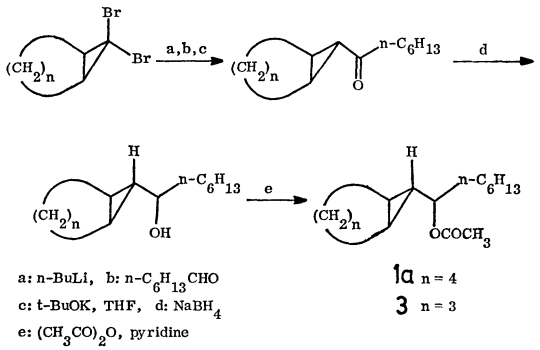
Ring-opening alkylation of cyclopropylmethyl acetates was studied. The acetoxyl group of 7-(1-acetoxyheptyl)norcarane is substituted by the alkyl group upon treatment with trialkylaluminium, but alkylation of *trans*-1-(1-acetoxyethyl)-2-phenylcyclopropane with trialkylaluminium gives rise to *trans*-5-phenyl-2-alkenes. The reaction of (1*S*,2*S*)-2-phenylcyclopropylmethyl acetate with trimethylaluminium resulted in the complete loss of optical activity to give racemic 4-phenyl-1-pentene. Alkylation of *trans*-1-(1-acetoxy-3-phenylpropyl)-2-vinylcyclopropane with trialkylaluminium proceeds under regioselective ring-opening to give 3-alkylated *trans*-8-phenyl-1,5-octadiene (selectivity 73—83%). The regio- and stereochemistry of homoconjugate addition to activated vinylcyclopropanes having a doubly carbonyl substituted ring carbon was studied. Trialkylaluminium on addition to diethyl 2-vinylcyclopropane-1,1-dicarboxylate in a 1,5-manner afford diethyl (2-alkyl-3-butenyl)-propanedioate (over 96% selectivity). In contrast, the reaction of this cyclopropane with tetraalkylaluminiumlithium takes place in a 1,7-manner to give diethyl (*trans*-4-alkyl-2-butenyl)propanedioate with 88—92% selectivity. Clean regiocontrol of the reaction is observed in the methylation of ethyl *exo*-6-(*trans*-1-propenyl)-2-oxobicyclo[3.1.0]hexane-1-carboxylate with trimethylaluminium or tetramethylaluminiumlithium. Alkylation with trimethylaluminium proceeds with 86% inversion of the configuration at C(6) of the substrate, affording (2*R**,3*R**)-2-ethoxycarbonyl-3-[(*S**)-*trans*-1-methyl-2-butenyl]cyclopentanone which is transformed into neonepetalactone.

Reagents of main group elements have furnished manifold synthetic methodologies.[1] The reaction of organolithium and -magnesium compounds provides a basic C–C bond forming process. The organometallics of electron-deficient elements such as boron and aluminium have intrinsic Lewis acidity and thus show to some extent Lewis acid catalysis. Examples are found in oxirane-allyl alcohol rearrangement, cyclization of neryl phosphate and alkylation of geranyl phosphate with the aid of organoaluminium reagents.[2] We have studied the reaction of organoaluminium reagents with cyclopropanes and found that (a) cyclopropylmethyl acetates undergo alkylation with or without ring-opening depending on the substituent on the cyclopropane ring and (b) regiochemistry in the homoconjugate addition of an alkyl group to 2-vinylcyclopropane-1,1-dicarboxylate esters is controlled by means of appropriate organoaluminium reagents.

Alkylation of Cyclopropylmethyl Acetates. The transformation of cyclopropylmethyl alcohols into (*E*)-homoallyl bromides is important for the stereoselective synthesis of olefins.[3,6] Strong Lewis acid such as hydrobromic acid or zinc bromide (plus phosphorus tribromide) is essential for the generation of homoallyl cations which react with bromide anion. The resulting homoallyl bromides should be treated with organometallics for the sake of carbon skeleton extention. We have found trialkylaluminium reagents can produce homoallylic cations in the presence of carbanionic species, attaining the C–C bond formation in a single step.

The cyclopropylmethyl esters **1a**, **1b**, and **3** were prepared starting with 7,7-dibromonorcarane (Scheme 1).[7] 7,7-Dibromonorcarane was treated with butyllithium at −95 °C, the lithium carbenoid generated being allowed to react with heptanal. The adduct was then treated with potassium *t*-butoxide to give *exo*-7-heptanoylnorcarane which was subsequently reduced with sodium borohydride to an alcohol, the acetylation and benzoylation of which gave **1a** and

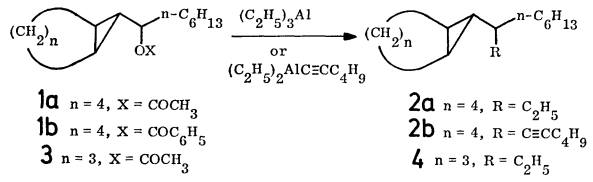


Scheme 1.

1b, respectively. **3** was prepared from 6,6-dibromobicyclo[3.1.0]hexane in a similar way.

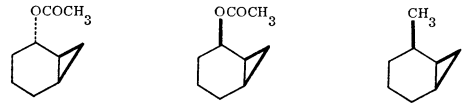
When the acetate **1a** was treated with 2.8 mol of triethylaluminium at room temperature, the acetoxyl group was substituted by ethyl group without ring-opening, giving **2a** in 91% yield.[8] The reaction took place likewise in benzene (98% yield) or hexane (93%) and even in dichloromethane at −78 °C (93%).

The benzoate **1b** was also converted into **2a** in 68% yield. Alkylation of **3** was somewhat less effective to give **4** in 57% yield. A mixed aluminium reagent $Et_2AlC{\equiv}CC_4H_9$, prepared by treatment of diethylaluminium chloride with an equimolar amount of 1-lithio-1-hexyne, afforded **2b** only upon reaction with **1a** (56% yield). Thus, ethynyl group is more reactive than the ethyl group.[9]



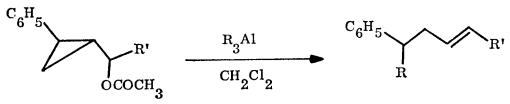
The reaction can be explained in terms of cyclopropylmethyl cation intermediates, since both *exo*- and

endo-2-acetoxynorcarane (**5a** and **5b** respectively) give *endo*-2-methylnorcarane **6** almost exclusively.[10]



5a **5b** **6**

In contrast to the alkylation of **1a**, **1b**, **3**, or **5a,b**, the phenyl substituted cyclopropylmethyl acetates underwent alkylation under ring-opening. The cyclopropylmethyl acetate **7** was prepared by the reaction of *trans*-2-phenylcyclopropanecarbaldehyde with methylmagnesium iodide followed by acetylation. When **7** (45:55 diastereomeric mixture) was treated with 3 mol of trimethylaluminium, *trans*-5-phenyl-2-hexene (**8a**) was produced in 86% yield. The newly produced C=C bond was found to be *trans* (over 97% purity). By a similar reaction **8a** (>94% *trans*) and **8c** (>96% *trans*) were produced as the sole products from **7** upon treatment with triethylaluminium and triisobutylaluminium, respectively. For the sake of stereochemical confirmation, both diastereomers of **7** were isolated and subjected to the alkylation with triethylaluminium. The sole product was found to be **8b** resulting from each diastereomer (75, 63% yield respectively). Similarly both the diastereomers of the *cis* isomer of **7** gave **8b** (53% and 67% yields from each diastereomer). The reaction was entirely independent of the stereochemistry of the starting material. The primary acetate **9a** was less reactive than the secondary one, **7**, giving **10a** in 59% yield.

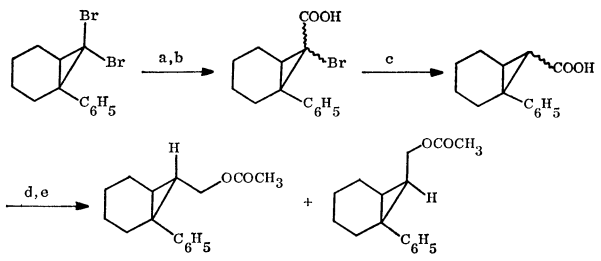


7 R' = CH_3
9a R' = H
9b R' = H (1S, 2S)

8a R' = CH_3, R = CH_3
8b R' = CH_3, R = C_2H_5
8c R' = CH_3, R = i-C_4H_9
10a R' = H, R = C_2H_5
10b R' = H, R = CH_3

In order to study the stereochemical aspect of alkylation, we prepared (1*S*,2*S*)-2-phenylcyclopropylmethyl acetate **9b** (optical purity >98%) by lithium aluminium hydride reduction of (1*S*,2*S*)-2-phenylcyclopropanecarboxylic acid followed by acetylation with acetic anhydride and pyridine. When **9b** was treated with trimethylaluminium, 4-phenyl-1-pentene (**10b**) having no optical activity was obtained. Since the carboxylic acid derived from **10b** by potassium permanganate-sodium periodate oxidation also showed no optical rotation, we can conclude that alkylation proceeds through a planar cationic intermediate.

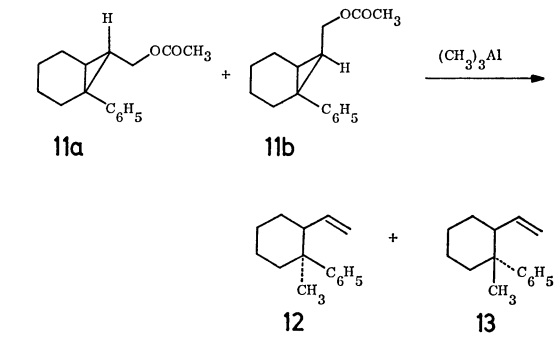
Alkylation of 7-acetoxymethyl-1-phenylnorcarane **11a,b** showed a similar stereochemical feature. The starting materials were prepared by bromine-lithium exchange of 7,7-dibromonorcarane with butyllithium, carbonation with carbon dioxide gas, lithium aluminium hydride reduction, and the final acetylation (Scheme 2). First, a 1:3 mixture of **11a** and **11b** thus prepared was treated with trimethylaluminium in dichloromethane to produce an inseparable mixture (35:65) of **12** and **13**. The stereochemical assignment is based on the observation that isomer **13** should give a methyl singlet signal at higher field due to the shielding effect of C=C bond.[11] When the stereoisomer of the starting acetate was separated and subjected to the alkylation reaction with trimethylaluminium, the same mixture was obtained. Thus, the aluminium-mediated alkylation proceeds through a common intermediate irrespective of the stereochemistry of the starting material.



11a **11b**

a: n-BuLi, b: CO_2, c: 2 n-BuLi, -78°C, d: $LiAlH_4$, e: $(CH_3CO)_2O$, pyridine

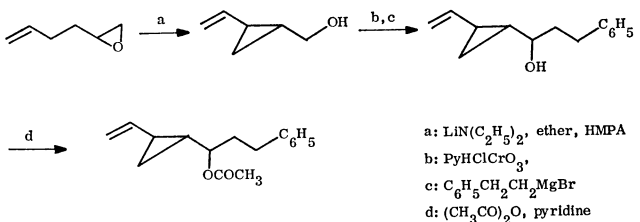
Scheme 2.



11a **11b**

12 **13**

Since a vinyl group also stabilizes a carbocation, we prepared the model compound **14** (Scheme 3).



14

a: $LiN(C_2H_5)_2$, ether, HMPA
b: $PyHClCrO_3$,
c: $C_6H_5CH_2CH_2MgBr$
d: $(CH_3CO)_2O$, pyridine

Scheme 3.

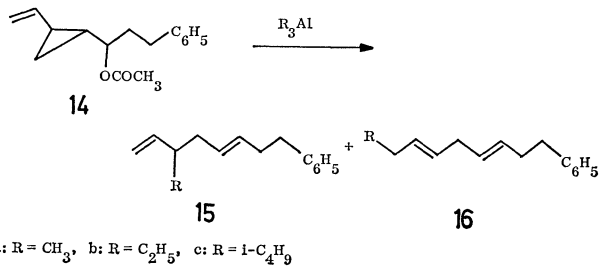
2-Vinylcyclopropylmethanol was obtained by the reaction of 1,5-hexadiene monoepoxide with lithium diethylamide in ether-hexamethylphosphoric triamide.[12] Subsequent oxidation with pyridinium chlorochromate and Grignard reaction with 2-phenylethylmagnesium bromide gave an alcohol the acetylation of which gave **14** as a 55:45 diastereomeric mixture (two epimers at the acetoxyl group-bearing carbon). Both diastereomers were isolated and subjected to alkylation with trimethylaluminium at 0 °C. Isomers as well as their mixture gave almost the same mixture of **15a** and **16a** (Table 1, run 11). Methylation takes place predominantly at the cyclopropane carbon rather than the terminal methylene carbon, the newly pro-

Table 1. Reaction of cyclopropane derivatives with organoaluminum reagents

Run	Substrate (mg, mmol)	Aluminium reagent (mmol)	Solvent[a] (ml)	Temp °C	Time h	Products (mg, %yield, ratio)
1	**1a** (250, 1.0)	Et_3Al[b] (2.8)	D (3)	r.t.	2	**2a** (200, 91)
2	**1b** (310, 1.0)	Et_3Al[b] (2.8)	D (5)	r.t.	2	**2a** (151, 68)
3	**1a** (250, 1.0)	$Et_2AlC{\equiv}CC_4H_9$[c] (5.0)	C (5)	0	2	**2b** (151, 56)
4	**3** (25, 0.10)	Et_3Al[b] (0.74)	D (3)	r.t.	2.5	**4** (12, 57)
5	**9a** (190, 1.0)	Et_3Al[d] (3.0)	D (2)	r.t.	2	**10a**[e] (94, 59)
6	**9b** (480, 2.5)	Me_3Al[d] (10)	D (7)	r.t.	12	**10b**[f] (148, 40)
7	**7**[g] (38, 0.19)	Et_3Al[d] (0.47)	D (5)	r.t.	1	**8b**[h] (24, 75)
8	**7**[i] (101, 0.51)	Me_3Al[d] (1.25)	D (5)	0	2	**8a** (71, 86)
9	**7**[i] (103, 0.50)	*i*-Bu_3Al[j] (1.52)	D (2)	r.t.	3	**8c**[k] (76, 75)
10	**11a,b**[l] (39, 0.16)	Me_3Al[d] (0.40)	D (5)	0	1.5	**12**+**13** (29, 91, 35:65)[m]
11	**14**[n] (115, 0.47)	Me_3Al[d] (1.18)	D (8)	0 r.t.	0.5 0.6	**15a**+**16a** (78, 81, 83:17)[o]
12	**14** (133, 0.54)	Et_3Al[d] (1.35)	D (8)	0	1.5	**15b**+**16b** (94, 80, 83:17)
13	**14** (116, 0.48)	*i*-Bu_3Al[j] (1.22)	D (8)	0	4.5	**15c**+**16c** (64, 56, 73:27)
14	**17** (40, 0.19)	Me_3Al[d,p] (0.56)	B (8)	0	0.1	**18a**+**19a** (38, 88 (94)[q], 96:4)[r]
15	**17** (50, 0.24)	Me_4AlLi (0.71)	E (7)	0	0.5	**18a**+**19a** (42, 78 (90)[q], 8:92)
16	**17** (50, 0.24)	Et_3Al[p] (0.62)	B (7)	0	0.5	**18b**+**19b** (44, 76, 98:2)
17	**17** (51, 0.24)	Et_4AlLi (0.71)	E (2)	0	0.5	**18b**+**19b** (39, 68, 12:88)
18	**17** (50, 0.24)	$Et_2AlC{\equiv}CC_6H_5$[s] (0.71)	D (6)	0	0.8	**18c** (52, 70)
19	**20** (730, 3.5)	Me_3Al (10.6)	D (12)	−20	0.5	**21**+**22** (680, 87, 86:14)[t]
20	**20** (47, 0.23)	Me_4AlLi (0.68)	E (3.5)	0	1	**23** (36, 71)
21	**29** (48, 0.23)	Me_3Al (0.69)	D (1.8)	0	0.2	**30** (42, 81)[u]
22	**29** (35, 0.17)	Me_4AlLi (0.50)	E (6)	0	0.3	**31** (30, 80)

a) D: dichloromethane, C: dichloroethane, B: benzene, E: ether. b) A hexane solution (1.84 M) used. c) Prepared from 1-hexyne (0.45 g, 5.5 mmol), butyllithium (5.0 mmol), and diethylaluminium chloride (5.0 mmol) in hexane. d) A hexane solution (1.0 M) used. e) A by-product, *trans*-2-phenylcyclopropylmethanol (43 mg, 25%), also formed. f) α_D^{18} −0.002 to −0.005° in 5 ml of $CHCl_3$, 5 cm cell. g) One diastereomer used. The same product was invariably produced from the other diastereomer of **7** and the two diastereomers derived from the *cis*-**7**. In another experiment with the diastereomeric mixture of **7**, **8b** was produced in 89% yield. h) GLC analysis (Apiezon L, 5%, on Chromosorb WAW DMCS, KOH 1%, 2 m, 110 °C) revealed over 94% purity. i) Diastereomeric mixture of **7** used. j) A hexane solution of reagent (0.76 M) used. k) GLC analysis of the crude product showed the presence of a trace amount of 5-phenyl-2-pentene. l) A 24:76 mixture of **11a** and **11b** used. With the stereochemically pure starting material of **11a** and **11b**, the following results were obtained: yield of **12** and **13**, **12** to **13** ratio; 75%, 38:62; 86%, 36:64 respectively. m) GLC assay (PEG 20 M, 20%, on Celite 545, 2 m, 142 °C) showed the R_t of **12**, 15.8 min and the R_t of **13**, 16.8 min. n) A diastereomeric mixture (55:45) used. Both diastereomers of **14** gave nearly identical results, or the total yield of 59% or 63%, and the ratio of **15a** to **16a**, 83:17, or 83:16. When $NiCl_2(PPh_3)_2$ (10 mol% or 100 mol% was added, the total yield and the ratio of **15a** to **16a** changed to 79%, 69:31 for one isomer and 63%, 52:48 for the other. o) GLC analysis (PEG 20 M, 5% on Cellite 545, 1.5 m, 160 °C). p) The substrate **17** added to the trialkylaluminium reagent solution. q) GLC yield. r) The following results were obtained under different conditions: solvent, temperature, total yield of **18a** and **19a** (ratio); benzene, r.t., 74% (92:8); dichloromethane, 0 °C, 62% (86:14). In dichloromethane a dimeric by-product (24%) was also produced. In ether or THF at 0 °C or r.t. no trace of the product was formed, **17** being recovered unchanged. s) Reagent prepared from butyllithium (0.71 mmol), phenylacetylane (0.71 mmol) and diethylaluminium chloride (0.71 mmol) in hexane at 0 °C. t) Under other conditions, the following results were obtained: solvent, temperature, total yield of **21** and **22** (ratio); dichloromethane, 0 °C, 55% (79:21); hexane, 0 °C, 66% (86:14), toluene, 0 °C, 63% (85:15). In ether or THF no trace of the product was produced. u) GLC (PEG 20 M, 5%, on Celite 545, 1.5 m, 143 °C) showed 87% purity, the major product assumed to be **30**, the minor one being its epimer.

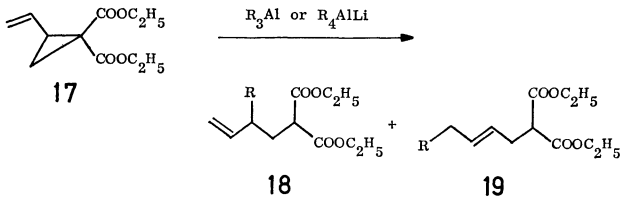
duced C=C bond being deduced to be *trans* (see Experimental). The regioselective alkylation takes place also with triethyl- and triisobutylaluminum. An attempt to change the regioselectivity by adding transition metal complexes failed except $NiCl_2(PPh_3)_2$ which accelerated the formation of **16a**.



a: R = CH_3, b: R = C_2H_5, c: R = i-C_4H_9

Regio- and Stereochemistry of Homoconjugate Addition to Activated Vinylcyclopropanes. Introduction of an alkyl group into 2-vinylcyclopropane-1,1-dicarboxylate esters or related compounds would control the regioselectivity, *i.e.* 1,5- or 1,7-homoconjugate addition.[13] Dialkylcopperlithium[14] would be a suitable reagent for 1,7-alkyl addition. However, none is known for 1,5-alkyl introduction. We have found that trialkylaluminium performs 1,5-homoconjugate addition and tetraalkylaluminiumlithium prepared from equimolar amounts of trialkylaluminium and alkyllithium effects 1,7-homoconjugate addition.

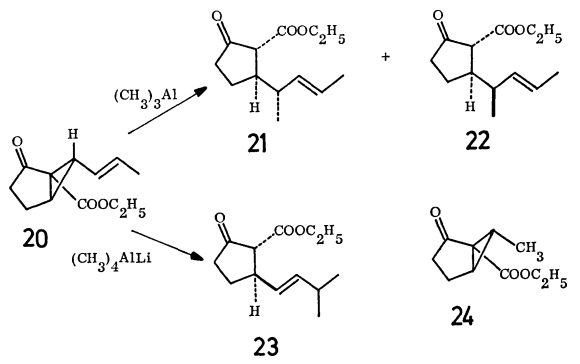
The vinylcyclopropane **17** was allowed to react with 3 mol of trimethylaluminium. The reaction took place immediately and ended usually in 10 min at 0 °C. Quenching with aq satd. sodium citrate solution, followed by work-up and isolation, gave a 96:4 mixture of **18a** and **19a**[14a] (Table 1, run 14). Among the solvents tested benzene gave best results as regards yield and selectivity. In dichloromethane a dimeric by-product was obtained. In a coordinating solvent such as ether the starting material was recovered unchanged. In order to accelerate the conversion of **17** into the products, use of 2.5 to 3 mol of trialkylaluminium is preferable, with less than 2 mol the reaction being extremely slow. Regioselectivity with triethylaluminium was almost perfect to give **18b** exclusively. Using the reagent of $Et_2AlC{\equiv}CPh$, **18c** only was produced. Thus, ethynyl carbon reacts in preference to ethyl group.[9]



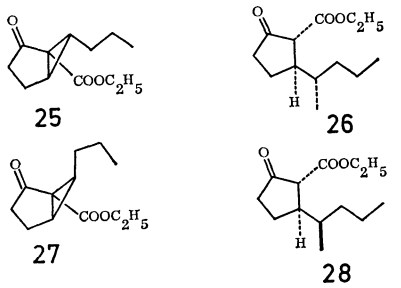
a: R = CH_3, b: R = C_2H_5, c: R = $C{\equiv}CC_6H_5$

The regioselectivity was reversed when tetramethylaluminiumlithium was used, the **18a**/**19a** ratio being 8:92 comparable to the cuprate reaction.[14] In a similar way tetraethylaluminiumlithium gave mainly **19b**. In these alanate reactions ether solvent was found to give the highest regioselectivity. Dilution with hexane gives rise to a decrease in the formation of 1,7-adduct **19**.

The regio-control of the homoconjugate addition was also attained in the reaction of a bicyclic β-keto ester **20** prepared according to the procedure shown in Scheme 4. With trimethylaluminium, **20** gave 1,5-homoconjugate adducts **21** and **22** as the sole products (Table 1, run 19). The reaction carried out in dichloromethane at −20 °C gave the adduct with the best yield. The product ratio **21**:**22** was almost independent of solvent except ether or tetrahydrofuran (THF) in which no reaction took place. The amount of trimethylaluminium necessary for alkylation was found to be more than 2 mol, 2.5 mol being usually employed.

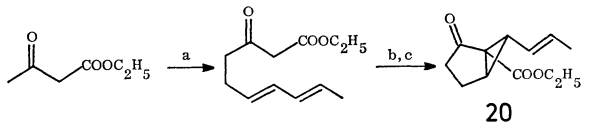


The stereochemistry of the products was determined by hydrogenating **21** and **22** and by comparing the spectral properties of the dihydro derivatives **26** and **28**, respectively. Each authentic sample was obtained by the reaction of **25** or **27** with dimethylcopperlithium.[15] We conclude that the 1,5-homoconjugate addition proceeds with *ca.* 86% inversion of the configuration at the cyclopropane carbon. This is in sharp contrast to the alkylation of **9** or **11a**,**b** in which complete loss of stereochemical integrity took place.



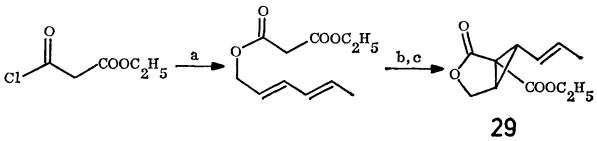
For successful homoconjugate addition, two necessary factors are (a) two activating carbonyl groups since ethyl chrysanthemate does not undergo conjugate addition, and (b) a vinyl group on the cyclopropane ring since compound **24** was recovered unchanged. Prolonged reaction of **24** with trimethylaluminium gave rise only to 1,2-methyl addition to the ketonic carbonyl.[16]

A similar regio- and stereochemical control was realized with **29** prepared according to Scheme 5. Using trimethylaluminium we obtained a 1,5-adduct of over 87% purity in 81% yield. We may assume



a: NaH, n-BuLi, $ClCH_2CH{=}CHCH{=}CHCH_3$, b: p-$CH_3C_6H_4SO_2N_3$, $(C_2H_5)_3N$
c: $Cu(acac)_2$, $C_6H_5CH_3$ reflux

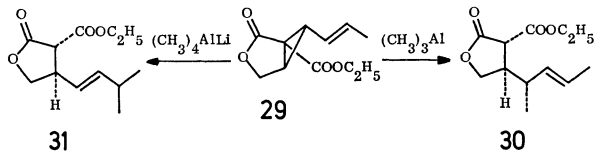
Scheme 4.



a: $HOCH_2CH{=}CHCH{=}CHCH_3$, pyridine, b: p-$CH_3C_6H_4SO_2N_3$, $(C_2H_5)_3N$
c: $Cu(acac)_2$, $C_6H_5CH_3$ reflux

Scheme 5.

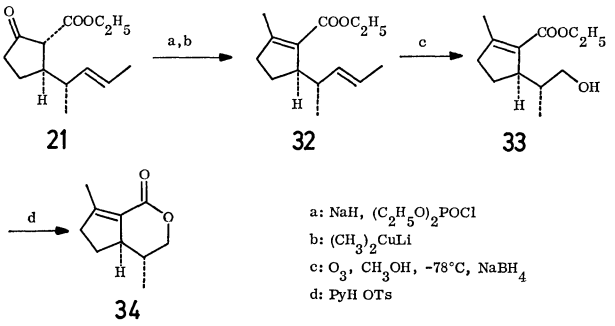
the reaction proceeded mainly with inversion in analogy to the case of **20**. The present major product would have the structure shown in the formula **30**. In contrast, the reaction of **29** with tetramethylaluminiumlithium gave **31** only in 80% yield.



31 29 30

Thus we control the stereochemistry of the α-carbon of a side chain (*e.g. cf.* structure **21**). This is particularly useful for the synthesis of neonepetalactone,[17] and should be extended to the preparation of such terpenes having the same structural unit as chrysomelidial[18] and juvabione.[19]

The synthesis of neonepetalactone **34** (Scheme 6) was carried out as follows. The β-keto ester **21** was freed from its epimer **22** by preparative TLC and converted into an enol phosphate which was then allowed to react with dimethylcopperlithium to give **32**. The two C=C bonds in **32** may be differentially cleaved. Ozonolysis of **32** at −78 °C followed by reductive work-up gave a hydroxy ester **33** whose lactonization gave neonepetalactone **32** exhibiting consistent spectral properties.[17]



Scheme 6.

Experimental

Temperatures are uncorrected. Distillation of small amount of samples (less than 1 g) was carried out with Kugelrohr. ^{1}H-NMR spectra (tetramethylsilane as an internal standard) were taken on a Varian EM 390 spectrometer or JEOL PMX-60 spectrometer, chemical shifts being given in ppm unit. IR spectra were obtained on a Shimadzu IR-27G spectrometer, MS on a Hitachi RMU-6L spectrometer. Trialkylaluminium (Nippon Alkyl Aluminium Co., Ethyl Corp., or Alfa Division of Ventron Corp., a neat liquid) was diluted with specified solvents. All the reactions with organometallics were carried out under an argon atmosphere. Preparative TLC plates (20 cm×20 cm) were prepared by use of Merck Kiesel-gel PF_{254}. Column chromatography was carried out with silica gel at atmosphereic pressure (Wacogel C-100) or under pressure of 4—6×10^5 N/m^2 (Wacogel C-300).

Synthesis of exo-*7-(1-Acetoxyheptyl)norcarane (**1a**) and* exo-*7-(1-Benzoyloxyheptyl)norcarane (**1b**).* Butyllithium (1.80 M hexane solution, 19.0 ml, 34 mmol) was added to a THF (50 ml) solution of 7,7-dibromonorcarane (7.2 g, 28 mmol) at −95 °C over a period of 7 min. After stirring for 10 min heptanal (4.6 ml, 34 mmol) was added at −95 °C and the reaction mixture was stirred at −95 °C for 30 min, at −78 °C for 1 h, then at room temperature for 15 min. Work-up gave a crude β-bromo alcohol which was dissolved in THF (20 ml) and the mixture was stirred overnight with potassium *t*-butoxide (4.0 g, 35 mmol). Work-up followed by column chromatography (hexane–ether 10:1) gave *exo*-7-heptanoylnorcarane (4.7 g, 73% yield), which was dissovled in ethanol (10 ml) and treated under a nitrogen atmosphere at 0 °C with sodium borohydride (0.43 g, 11.2 mmol). Work-up and column chromatography (hexane–ether 10:1) gave *exo*-7-(1-hydroxyheptyl)norcarane (3.7 g, 57% yield from 7,7-dibromonorcarane), bp 83—85 °C (bath temp)/1 Torr; IR (neat): 3350, 1065, 1024 cm^{-1}; MS: *m/e* 192 (M$^+$−18). Found: C, 80.10; H, 12.58%. Calcd for $C_{14}H_{24}O$: C, 79.93; H, 12.46%.

The alcohol (0.22 g, 1.10 mmol) was mixed with pyridine (1 ml), and acetic anhydride (0.8 ml), and allowed to react at room temperature overnight. All the volatile material was then evaporated under reduced pressure and the residue was purified with short silica-gel column to give **1a** (0.26 g, 96% yield), bp 98—100 °C (bath temp)/1 Torr. ^{1}H-NMR (CCl_4): δ 1.4—2.1 (m+s (δ 1.92), 27H), 4.12 (dt, J=8, 5 Hz, 1H); IR (neat): 2940, 2870, 1730, 1450, 1365, 1235, 1020 cm^{-1}; MS: *m/e* (rel intensity) 210 (M$^+$−CH_2CO, 7), 192 (15), 135 (18), 125 (32), 121 (34), 79 (43), 67 (44), 43 (100). Found: C, 76.36; H, 11.38%. Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18%.

The benzoate (**1b**) (1.22 g, 96% yield) was obtained by treating the alcohol (0.85 g, 4.0 mmol) with benzoyl chloride (0.49 ml, 4.2 mmol) and pyridine (2 ml) in dichloromethane (3 ml) at 0 °C for 1 h. Work-up and column chromatography (hexane–ether 10:1) gave **1b** as a colorless viscous oil, bp 165—170 °C (bath temp)/1 Torr. ^{1}H-NMR (CCl_4): δ 0.5—2.1 (m, 24H), 4.2—4.7 (m, 1H, CHOBz), 7.1—7.5 (m, 3H), 7.7—8.1 (m, 2H); IR (neat): 1715, 1605, 1587, 1110, 1025, 718 cm^{-1}; MS: *m/e* (rel intensity) 192 (M$^+$−C_6H_5COOH, 25), 135 (20), 122 (22), 105 (100), 94 (33), 79 (47), 77 (45), 41 (32). Found: C, 80.46; H, 9.74%. Calcd for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62%.

Preparation of exo-*7-(1-Ethylheptyl)norcarane (**2a**). A Typical Procedure for the Reaction with Trialkylaluminium.* A hexane solution of triethylaluminium (1.84 M, 1.5 ml, 2.8 mmol) was added to a dichloromethane (3 ml) solution of **1a** (0.25 g, 1.0 mmol) at room temperature. The reaction mixture was stirred for 2 h and then quenched with satd. aq sodium sulfate solution (few drops). This was stirred vigorously, diluted with dichloromethane and filtered through a short column of anhydrous sodium sulfate. Concentration followed by column chromatography gave **2a** (0.20 g, 91% yield), bp 160—168 °C/16 Torr; ^{1}H-NMR (CCl_4): δ 0.0—2.1 (m); IR (neat): 3020, 1370, 1070, 968 cm^{-1}; MS: *m/e* (rel intensity) 222 (M$^+$, 10), 193 (12), 137 (24), 110 (53), 95 (82), 81 (91), 70 (98), 68 (100), 55 (85), 40 (86). Found: C, 86.37; H, 13.62%. Calcd for $C_{16}H_{30}$: C, 86.40; H, 13.60%.

Reaction with Diethyl(1-Alkynyl)aluminium. Butyllithium (1 mol) hexane solution was added to 1-alkyne (slightly more than 1 mol) at 0 °C. After 10 min diethylaluminium chloride (1 mol) hexane solution was added, stirring being carried out for 15 min at 0 °C. The reaction mixture was concentrated *in vacuo* below room temperature. The residue was dissolved in a specified solvent, and a substrate was added.

Tetraalkylaluminiumlithium. This reagent was prepared by mixing equimolar amounts of trialkylaluminium (hexane solution) and alkyllithium (ether solution) at 0 °C for 20 min. Substrate dissolved in ether was added to the solution.

exo-*7-(1-Hexyl-2-heptynyl)norcarane* (**2b**): Bp 135—139 °C (bath temp)/2 Torr; ^{1}H-NMR (CCl_4): δ 0.2—2.3 (m); IR (neat): 2950, 2880, 1450 cm^{-1}; MS: *m/e* (rel intensity) 274 (M^+, 1.4), 217 (23), 189 (32), 147 (32), 133 (46), 107 (54), 91 (79), 79 (79), 43 (60), 41 (100). Found: C, 87.54; H, 12.76%. Calcd for $C_{20}H_{34}$: C, 87.51; H, 12.49%.

Synthesis of exo-*6-(1-Acetoxyheptyl)bicyclo[3.1.0]hexane* (**3**). The procedure for the synthesis of **1a** was applied to the one of *exo*-6-heptanoylbicyclo[3.1.0]hexane, bp 80—83 °C (bath temp)/0.04 Torr. Found: C, 80.51; H, 11.73%. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41%.

Sodium borohydride reduction of this ketone followed by acetylation gave **3** quantitatively. Bp 87—91 °C (bath temp)/0.04 Torr; ^{1}H-NMR (CCl_4): δ 0.5—2.5 (m+S (δ 1.92), 25H), 3.9—4.3 (m, 1H); IR (neat): 3030, 1728, 1235, 1018 cm^{-1}; MS: *m/e* (rel intensity) 196 (M^+-CH_2CO, 4), 178 (9), 135 (9), 121 (20), 111 (22), 93 (33), 79 (42), 67 (38), 55 (24), 43 (100). Found: C, 75.63; H, 11.29%. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00%.

exo-*6-(1-Ethylheptyl)bicyclo[3.1.0]hexane* (**4**): ^{1}H-NMR (CCl_4): δ 0.1—1.9 (m); MS: *m/e* (rel intensity) 208 (M^+, 3), 189 (4), 140 (10), 123 (14), 111 (22), 95 (33), 81 (54), 70 (100), 55 (65), 41 (81). Due to the lack of sample confirmation of the structure was not carried out.

Preparation of (1S,2S)-2-Phenylcyclopropylmethyl Acetate (**9b**). Optical resolution of *trans*-2-phenylcyclopropanecarboxylic acid with quinine[20] gave a sample of $[\alpha]_D^{16}$ +375° (*c* 2.3, $CHCl_3$), estimated to be 98% optically pure based on the reported value $[\alpha]_D^{14}$ +381° ($CHCl_3$),[20] $[\alpha]_D^{20}$ +376° ($CHCl_3$).[21] The carboxylic acid was reduced with lithium aluminium hydride and acetylated with acetic anhydride to give **9b**, $[\alpha]_D^{19}$ +87.6° (*c* 2.0, $CHCl_3$) quantitatively. Bp 75—79 °C (bath temp)/0.03 Torr; ^{1}H-NMR (CCl_4): δ 1.0—2.0 (m, 4H), 2.04 (s, 3H), 4.04 (d, J=6.4 Hz, 2H), 7.0—7.4 (m, 5H); IR (neat): 3035, 1743, 1608, 1500, 1237, 1030, 757, 698 cm^{-1}; MS: *m/e* (rel intensity) 190 (M^+, 10), 149 (15), 130 (100), 115 (48). Found: C, 75.87; H, 7.42%. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%.

trans-*1-(1-Acetoxyethyl)-2-phenylcyclopropane* (**7**). Methylmagnesium iodide (0.88 M ethereal solution, 0.99 ml, 0.87 mmol) was added to *trans*-2-phenylcyclopropanecarbaldehyde[22] (84 mg, 0.58 mmol) dissolved in ether (5 ml) at 0 °C, and the reaction mixture was stirred for 3 h, quenched with aq satd. ammonium chloride solution (10 ml) and extracted with dichloromethane. The combined dried organic phase was concentrated and the residue chromatographed with preparative TLC (dichloromethane) to give two diastereomers of *trans*-1-(1-hydroxyethyl)-2-phenylcyclopropane (R_f 0.4, 30 mg; R_f 0.3, 36 mg, 75% total yield). The more polar diastereomer gave ^{1}H-NMR (CCl_4): δ 0.7—1.4 (m, 3H), 1.26 (d, J=6.2 Hz, 3H), 1.5—2.0 (m, 1H), 2.08 (s, 1H), 3.1—3.7 (m, 1H), 6.7—7.4 (m, 5H). The less polar alcohol was acetylated with acetic anhydride (0.2 ml) and pyridine (0.2 ml) (r.t., 5 h) to give one diastereomer of **7** (38 mg, 95% yield). ^{1}H-NMR (CCl_4): δ 0.7—1.5 (m+d (δ 1.31, J=6.4 Hz, 6H), 1.8—2.2 (m+s (δ 1.97), 4H), 4.50 (quintet, J=6.4 Hz, 1H), 6.8—7.3 (m, 5H); IR (neat): 1735, 1605, 1503, 1372, 1242 cm^{-1}. The more polar alcohol was acetylated to give the other diastereomer of **7** (38 mg, 79% yield), bp 84—87 °C (bath temp)/0.05 Torr. ^{1}H-NMR (CCl_4): δ 0.8—1.6 (m+d(δ 1.33, J=6.4 Hz), 6H), 1.6—2.1 (m+s(δ 1.99), 4H), 4.99 (quintet, J=6.4 Hz, 1H), 6.8—7.3 (m, 5H); IR (neat): 1737, 1610, 1507, 1377, 1245 cm^{-1}; MS: *m/e* 204 (M^+). Found: C, 76.41; H, 8.01%. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90%.

Physical properties of the *cis* isomers of **7** (prepared from *cis*-2-phenylcyclopropanecarboxylic acid): bp 102—104 °C (bath temp)/0.09 Torr. Found: C, 76.71; H, 8.00%. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90%.

Each diastereomer was separated at the stage of alcohol (dichloromethane, R_f 0.6 and 0.4). The acetate of the less polar alcohol showed following spectra. ^{1}H-NMR (CCl_4): δ 0.7—1.6 (m+d (δ 1.23, J=6.2 Hz), 6H), 1.67 (s, 3H), 1.9—2.5 (m, 1H), 3.6—4.2 (m, 1H), 7.16 (s, 5H). IR (neat): 1733, 1605, 1503, 1370, 1245 cm^{-1}. The acetate of the more polar alcohol exhibited ^{1}H-NMR (CCl_4): δ 0.8—1.1 (m+d (δ 0.98, J=6.2 Hz), 6H), 1.9—2.4 (m+s (δ 1.92), 4H), 4.1—4.5 (m, 1H), 7.15 (s, 5H); IR (neat): 1730, 1605, 1503, 1370, 1245 cm^{-1}; MS: *m/e* (rel intensity) 204 (M^+, 4), 149 (34), 129 (100), 107 (70).

trans-*5-Phenyl-2-hexane* (**8a**): Bp 68—75 °C (bath temp)/1 Torr; ^{1}H-NMR (CCl_4): δ 1.22 (d, J=6.9 Hz, 1H), 1.60 (d, J=3.9 Hz, 3H), 2.1—2.4 (m, 2H), 2.67 (sextet, J=6.9 Hz, 1H), 5.2—5.4 (m, 2H), 7.0—7.3 (m, 5H); IR (neat): 3045, 1610, 1502, 968, 760, 704 cm^{-1}; MS: *m/e* (rel intensity) 160 (M^+, 6), 144 (2), 105 (100), 91 (5), 79 (5), 77 (5). Found: C, 90.17; H, 10.30%. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06%.

trans-*5-Phenyl-2-heptene* (**8b**): Bp 81—88 °C (bath temp)/1 Torr; ^{1}H-NMR (CCl_4): δ 0.77 (t, J=7.5 Hz, 3H), 1.3—2.1 (m+d (δ 1.56, J=4 Hz), 5H), 2.1—2.7 (m, 3H), 5.2—5.5 (m, 2H), 6.9—7.3 (m, 5H); IR (neat): 3030, 1604, 1497, 966, 756, 698 cm^{-1}; MS: *m/e* (rel intensity) 174 (M^+, 3), 145 (1), 119 (56), 91 (100), 77 (5). Found: C, 89.58; H, 10.53%. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41%.

trans-*7-Methyl-5-phenyl-2-octene* (**8c**): Bp 89—96 °C (bath temp)/1 Torr; ^{1}H-NMR (CCl_4): δ 0.7—1.0 (m, 6H), 1.1—1.7 (m+d (δ 1.52, J=4 Hz), 5H), 2.1—2.4 (m, 2H), 2.5—2.8 (m, 1H), 5.2—5.5 (m, 2H), 6.9—7.3 (m, 5H); IR (neat): 3040, 1606, 1500, 1468, 1456, 968, 760, 701 cm^{-1}; MS: *m/e* (rel intensity) 202 (M^+, 1), 147 (27), 105 (28), 91 (100), 77 (4). Found: C, 89.28; H, 10.81%. Calcd for $C_{15}H_{22}$: C, 89.04; H, 10.96%.

Preparation of endo- *and* exo-*7-Acetoxymethyl-1-phenylnorcarane* (**11a** *and* **11b**). Bromoform (0.36 ml, 4.1 mmol) was added to a mixture of 1-phenylcyclohexane (0.55 g, 3.5 mmol), potassium *t*-butoxide (4.3 mmol), and hexane (5 ml) at ice–salt temperature over a period of 30 min. After the addition was completed, the reaction mixture was warmed to room temperature, stirred for 1.5 h, then poured into water (20 ml). Extraction with dichloromethane (10 ml× 3 times) followed by the usual work-up and column chromatography gave 7,7-dibromo-1-phenylnorcarane (0.67 g, 58% yield; 79% yield based on the consumed olefin) as a viscous oil, bp 98—100 °C (bath temp)/0.03 Torr. ^{1}H-NMR (CCl_4): δ 1.2—1.7 (m, 5H), 1.9—2.5 (m, 4H), 7.24 (s, 5H); IR (neat): 3035, 1603, 1496, 1449, 753, 747, 697 cm^{-1}; MS: *m/e* (rel intensity) 264 (1.2), 262 (2.2), 260 (1.2), 251 (24), 249 (24), 169 (100), 141 (80), 126 (52), 115 (53), 91 (68). Found: C, 47.46; H, 4.20%. Calcd for $C_{13}H_{14}Br_2$: C, 47.31; H, 4.28%.

To a THF (10 ml) solution of the dibromonorcarane (0.33 g, 1.0 mmol) was added butyllithium (1.60 M hexane solution, 0.69 ml, 1.1 mmol) at −95 °C over a period of 5 min and the reaction mixture stirred for 20 min. Dry carbon dioxide gas was bubbled at −95 °C for 25 min into the reaction mixture which was then warmed to room temperature and acidified with dil hydrochloric acid. Work-up gave a crude bromo carboxylic acid (0.30 g, quantitative yield). ^{1}H-NMR ($CDCl_3$): δ 1.1—2.5 (m, 9H), 7.3—7.7 (m, 5H), 9.3—10.1 (br s, 1H); IR (neat): 3400, 2500, 1737, 1704, 1603, 1496, 1266, 760, 698 cm^{-1}; MS: *m/e* (rel intensity) 256 (1), 214 (77), 187 (28), 169 (79), 142 (83), 141

(77), 129 (60), 115 (70), 91 (100).

The bromocarboxylic acid (0.83 g, 2.8 mmol) was dissolved in THF (10 ml) and to this solution was added butyllithium (1.53 M hexane solution, 3.8 ml, 5.9 mmol) at −78 °C over a period of 8 min. The reaction mixture was stirred for 25 min, then treated with ethanol (1 ml) and warmed to room temperature. Acidification with dil hydrochloric acid followed by the work-up gave a crude carboxylic acid (0.50 g). Preparative TLC (hexane–ethyl acetate 2:1 double development) of the crude product (0.10 g) gave *endo*-carboxylic acid (R_f 0.6—0.7, 72 mg) and its *exo* isomer (R_f 0.5—0.6, 25 mg) in 80% total yield.

The *endo* isomer, 1-phenylnorcarane-*endo*-7-carboxylic acid (colorless prisms, mp 75—76 °C (hexane)), gave ^{1}H-NMR ($CDCl_3$): δ 1.1—2.4 (m, 10H), 7.41 (br s, 5H), 8.6—9.5 (m, 1H); IR (neat): 3400—2500, 3040, 1698, 1604, 760, 700 cm^{-1}; MS: *m/e* (rel intensity) 217 (4), 216 (M^+, 36), 198 (14), 171 (80), 129 (83), 115 (57), 91 (100). Found: C, 77.78; H, 7.44%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

The *exo* isomer, 1-phenylnorcarane-*exo*-7-carboxylic acid (colorless prisms, mp 139—140 °C (benzene)); ^{1}H-NMR ($CDCl_3$): δ 1.1—2.4 (m, 10H), 7.35 (br s, 5H), 8.0—9.0 (m, 1H); IR ($CHCl_3$): 3450—2500, 3060, 1693, 1604, 694 cm^{-1}; MS: *m/e* (rel intensity) 217 (M^+ +1, 7), 216 (M^+, 36), 198 (14), 171 (80), 129 (83), 115 (57), 91 (100). Found: C, 78.00; H, 7.37%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

The *exo* carboxylic acid (23 mg, 0.11 mmol) was reduced with lithium aluminium hydride (8.0 mg, 0.22 mmol) in ether (1 ml) to give *exo*-7-hydroxymethyl-1-phenylnorcarane, bp 93—98 °C (bath temp)/0.03 Torr; ^{1}H-NMR (CCl_4): δ 1.0—2.3 (m, 11H), 3.12 (dd, J=6.6, 3.0 Hz, 2H), 7.2 (br s, 5H); IR (neat): 3320, 2930, 1603, 1497, 1447, 1018, 759, 700 cm^{-1}; MS: *m/e* (rel intensity) 202 (M^+, 4), 184 (40), 171 (69), 141 (57), 129 (82), 115 (65), 91 (100). Found: C, 83.25; H, 9.20%. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97%.

The alcohol was acetylated with acetic anhydride (0.2 ml) and pyridine (0.2 ml) (r.t., 13 h) to give **11a** (27 mg, 97% yield for 2 steps). bp 108—110 °C (bath temp)/0.04 Torr; ^{1}H-NMR (CCl_4): δ 1.0—2.3 (m+s (δ 1.94), 13H), 3.56 (d, J=6.6 Hz, 2H), 7.17 (s, 5H); IR (neat): 3035, 1738, 1603, 1252, 1028, 960, 701 cm^{-1}; MS: *m/e* (rel intensity) 244 (M^+, 2), 184 (85), 141 (100), 129 (49), 115 (41), 91 (78). Found: C, 78.72; H, 8.24%. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25%.

The *endo* acetate **11b** was prepared similarly. *endo*-7-Hydroxymethyl-1-phenylnorcarane: bp 114—116 °C (bath temp)/0.06 Torr; ^{1}H-NMR (CCl_4): δ 1.1—2.3 (m, 11H), 3.8 (d, J=6.9 Hz, 2H), 6.9—7.3 (m, 5H); IR (neat): 3350, 3030, 1603, 1494, 1449, 1018, 749, 700 cm^{-1}; MS: *m/e* (rel intensity) 203 (0.8), 202 (M^+, 4), 184 (37), 171 (77), 141 (51), 129 (83), 91 (100). Found: C, 82.91; H, 8.93%. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97%.

Acetylation of the alcohol gave **11b**, bp 90—93 °C (bath temp)/0.04 Torr; ^{1}H-NMR (CCl_4): δ 1.2—2.1 (m+s (δ 2.06), 13H), 4.27 (d, J=5.4 Hz, 2H), 7.16 (br s, 5H); IR (neat): 3035, 1739, 1604, 1494, 1242, 1028, 759, 700 cm^{-1}; MS: *m/e* (rel intensity) 244 (M^+, 1), 184 (82), 141 (100), 91 (82). Found: C, 78.89; H, 8.47%. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25%.

1-Methyl-1-phenyl-2-vinylcyclohexane. This was obtained as a *ca.* 2:3 mixture of **12** and **13**: bp 117—123 °C (bath temp)/5 Torr; ^{1}H-NMR (CCl_4): δ 1.21 (s, 1.05 H, CH_3 for **12**), 1.32 (s, 1.95 H, CH_3 for **13**), 1.7—2.3 (m, 8H), 2.3—2.7 (m, 1H), 4.6—5.0 (m, 2H), 5.2—6.0 (m, 1H), 7.0—7.5 (m, 5H); IR (neat): 3070, 3040, 1638, 1602, 1497, 990, 908, 762, 697 cm^{-1}; MS: *m/e* (rel intensity) 200 (M^+, 29), 184 (45), 131 (56), 118 (100), 105 (64), 91 (45). Found: C, 89.67; H, 10.08%. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06%.

Synthesis of trans-*1-(1-Acetoxy-3-phenylpropyl)-2-vinylcyclopropane (**14**).* The major isomer of 2-vinylcyclopropylmethanol[12] (93:7 isomeric mixture based on GLC (PEG 20 M, 5%, on Celite 545, 1.5 m, 72 °C)) was assigned to be *trans* on the basis of ^{13}C-NMR (CCl_4): chemical shift (δ from TMS) (intensity), 112.25 (100) and 115.36 (8), 140.76 (64) and 136.72 (5), 66.00 (100) and 62.88 (7). Pyridinium chlorochromate (0.63 g) oxidation (0 °C, 16 h) of this alcohol (0.100 g, 2.0 mmol) followed by the reaction (0 °C, 2.5 h) with 2-phenylethylmagnesium bromide (2.4 mmol) and preparative TLC (hexane–ether 5:1) gave two diastereomers of (1*R**,2*S**)-1-(1-hydroxy-3-phenylpropyl)-2-vinylcyclopropane (R_f 0.3, 136 mg; R_f 0.2, 131 mg) totally in 65% yield. The less polar alcohol showed ^{1}H-NMR (CCl_4): δ 0.5—0.7 (m, 2H), 0.8—1.1 (m, 1H), 1.2—1.5 (m, 1H), 1.7—2.1 (m, 3H), 2.72 (dt, J=8.7, 3.0 Hz, 2H), 3.00 (q, J=6.6 Hz, 1H), 4.7—5.6 (m, 3H), 7.13 (s, 5H). The more polar alcohol gave ^{1}H-NMR (CCl_4) spectrum: δ 0.4—1.0 (m, 3H), 1.1—1.4 (m, 1H), 1.7—2.0 (m, 3H), 2.70 (dt, J=8.1. 2.6 Hz, 2H), 2.98 (q, J=6.6 Hz, 1H), 4.7—5.6 (m, 3H), 7.14 (s, 5H).

Acetylation of the less polar alcohol gave one diastereomer of **14**, ^{1}H-NMR (CCl_4): δ 0.5—1.7 (m, 3H), 1.8—2.1 (m+s (δ 1.95), 5H), 2.4—2.7 (m, 2H), 4.2—4.5 (m, 1H), 4.7—5.6 (m, 3H), 7.0—7.3 (m, 5H). The more polar alcohol afforded the other diastereomer of **14**, ^{1}H-NMR (CCl_4): δ 0.4—1.4 (m, 3H), 1.8—2.1 (m+s (δ 1.95), 5H), 2.5—2.7 (m, 2H), 4.2—4.5 (m, 1H), 4.8—5.6 (m, 3H), 7.0—7.3 (m, 5H). Physical properties of the diastereomeric mixture of **17** were as follows: bp 124—127 °C (bath tem)/0.1 Torr; IR (neat): 3080, 3040, 1730, 1638, 1605, 1497, 1240, 1020, 700 cm^{-1}; MS: *m/e* (rel intensity) 224 (M^+, 4), 184 (11), 160 (8), 130 (52), 117 (34), 104 (35), 91 (100), 77 (25), 65 (20). Found: C, 78.44; H, 8.41%. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25%.

*(E)-3-Methyl-8-phenyl-1,5-octadiene (**15a**) and (E,E)-1-Phenyl-3,6-nonadiene (**16a**).* The reaction product formed an 83:17 mixture of **15a** and **16a**, bp 83—93 °C (bath temp)/1 Torr; ^{1}H-NMR (CCl_4): δ 0.93 (d, J=6.6 Hz, 3H), 1.8—2.4 (m, 5H), 2.5—2.8 (m, 2H), 4.7—5.1 (m, 2H), 5.3—5.9 (m, 3H), 7.0—7.3 (m, 5H). Preparative GLC separation (PEG 20 M, 30%, on celite 545, 3 m, 180 °C) gave pure components. The product **15a** showed practically the same ^{1}H-NMR spectrum and IR (994, 969, 910 cm^{-1}) as those of the mixture. MS: *m/e* 200 (M^+). Found: C, 89.86; H, 10.30%. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06%. The geometry of the newly produced carbon-carbon double bond was inferred to be *trans* based on the IR absorptions at 969 cm^{-1}. The other product **16a** was characterized spectrometrically. MS: *m/e* 200 (M^+); IR (neat): 969 cm^{-1}; ^{1}H-NMR: (CCl_4): δ 0.97 (t, 3H), 1.7—2.5 (m, 6H), 2.5—2.8 (m, 2H), 5.2—5.6 (m, 4H), 7.10 (s, 5H). The IR absorption at 969 cm^{-1} was almost twice as intense as that of **16a** (based on the intensity of the phenyl absorptions), no absorptions near 800—750 cm^{-1} being detected. Consequently both of the C=C bonds in **16a** were assigned to be *trans*.

*(E)-3-Ethyl-8-phenyl-1,5-octadiene (**15b**) and (E,E)-1-Phenyl-3,6-decadiene (**16b**).* The reaction product formed an 83:17 mixture of **15b** and **16b**, bp 105—110 °C (bath temp)/1 Torr. Found: C, 89.49; H, 10.40%. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.35%. Each product was separated by

preparative GLC. The product **15b** showed IR (neat): 995, 970, 910, 745, 700 cm^{-1}; ^1H-NMR (CCl_4): δ 0.80 (t, J=7 Hz, 3H), 1.0—1.5 (m, 2H), 1.5—2.1 (m, 3H), 2.1—2.4 (m, 2H), 2.5—2.7 (distorted t, 2H), 4.7—5.0 (m, 2H), 5.2—5.7 (m, 3H), 7.0—7.3 (m, 5H); MS: *m/e* 214 (M^+). The isomer **16b** exhibited ^1H-NMR (CCl_4): δ 0.90 (t, J=6 Hz, 3H), 1.1—1.7 (m, 2H), 1.7—2.1 (m, 2H), 2.1—2.5 (m, 2H), 2.5—2.8 (m, 4H), 5.2—5.6 (m, 4H), 7.0—7.3 (m, 5H).

*(E)-3-Isobutyl-8-phenyl-1,5-octadiene (**15c**) and (E,E)-10-Methyl-1-phenyl-3,6-undecadiene (**16c**)*: Bp 89—93 °C (bath temp)/0.05 Torr; IR (neat): 3030, 1641, 1607, 1497, 994, 966, 909, 745, 700 cm^{-1}. Found: C, 89.16; H, 11.03%. Calcd for $C_{18}H_{26}$: C, 89.19; H, 10.81%. Preparative GLC separation gave pure **15c**: ^1H-NMR (CCl_4): δ 0.80 (d, J=6 Hz, 3H), 0.83 (d, J=6 Hz, 3H), 1.0—1.4 (m, 2H), 1.4—1.7 (m, 1H), 1.7—2.4 (m, 5H), 2.5—2.8 (m, 2H), 4.7—5.0 (m, 2H), 5.2—5.6 (m, 3H), 7.0—7.3 (m, 5H).

*Diethyl (2-Methyl-3-butenyl)propanedioate (**18a**)*: Bp 75—77 °C (bath temp)/0.05 Torr; ^1H-NMR (CCl_4): δ 1.04 (d, J=6.6 Hz, 3H), 1.29 (t, J=6.9 Hz, 6H), 1.7—1.9 (m, 2H), 1.9—2.2 (m, 1H), 3.21 (dd, J=8.4, 2.4 Hz, 1H), 4.10 and 4.12 (2q, J=6.9 Hz each, 4H), 4.8—5.1 (m, 2H), 5.4—5.8 (m, 1H); IR (neat): 3090, 1756, 1737, 1645, 1373, 1270, 1240, 1180, 1150, 1031, 998, 917 cm^{-1}; MS: *m/e* (rel intensity) 228 (M^+, 2), 183 (11), 160 (100), 137 (55), 109 (59), 81 (58), 68 (55). Found: C, 63.29; H, 8.95%. Calcd for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83%.

Spectral data of **19a**[14a] are as follows. ^1H-NMR (CCl_4): δ 0.95 (t, J=7.8 Hz, 3H), 1.27 (t, J=6.9 Hz, 6H), 1.8—2.2 (m, 2H), 2.43 (dd, J=7.5, 6.3 Hz, 2H), 3.19 (t, J=7.5 Hz, 1H), 4.12 (q, J=6.9 Hz, 4H), 5.1—5.6 (m, 2H); IR (neat): 1755, 1739, 1372, 1152, 1024, 969 cm^{-1}; MS: *m/e* 228 (M^+).

*Diethyl(2-Ethyl-3-butenyl)propanedioate (**18b**)*: Bp 123—126 °C (bath temp)/0.2 Torr. ^1H-NMR (CCl_4): δ 0.87 (t, J=7.8 Hz, 3H), 1.29 (t, J=6.9 Hz, 6H), 1.2—2.2 (m, 5H), 3.1—3.4 (m, 1H), 4.11 and 4.13 (2q, J=6.9 Hz each, 4H), 4.9—5.1 (m, 2H), 5.2—5.7 (m, 1H); IR (neat): 3080, 1752, 1736, 1645, 1252, 1225, 1178, 1145, 1031, 998, 917 cm^{-1}; MS: *m/e* (rel intensity) 242 (M^+, 1), 213 (2), 197 (15), 160 (100), 151 (38), 132 (48), 123 (48), 95 (55), 67 (57). Found: C, 64.26; H, 9.30%. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15%.

Alternative Synthesis of Diethyl trans-*2-Hexenylpropanedioate (**19b**)*. Diethylcopperlithium (0.71 mmol) was allowed to react with **17** (50 mg, 0.24 mmol) in ether (2 ml) at −23 °C. Work-up and preparative TLC (hexane–ethyl acetate 5:1, R_f 0.4—0.5) gave a mixture (5:95 by GLC) of **18b** and **19b** (40 mg, 70% yield), bp 114—116 °C (bath temp)/0.1 Torr; ^1H-NMR (CCl_4): δ 0.87 (t, J=7.8 Hz, 3H), 1.2—1.5 (m+t (δ 1.29, J=6.9 Hz), 8H), 1.8—2.1 (m, 2H), 2.4—2.6 (distorted t, 2H), 3.21 (t, J=7.8 Hz, 1H), 4.13 (q, J=6.9 Hz, 4H), 5.3—5.5 (m, 2H); IR (neat); 1753, 1738, 1230, 1174, 1150, 1034, 969 cm^{-1}; MS: *m/e* (rel intensity) 242 (M^+, 7), 197 (11), 160 (75), 125 (100), 95 (69), 67 (55). Found: C, 64.37; H. 9.30%. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15%.

*Diethyl [2-(Phenylethynyl)-3-butenyl]propanedioate (**18c**)*. Bp 163—167 °C (bath temp)/0.15 Torr; ^1H-NMR (CCl_4): δ 1.28 (t, J=6.9 Hz, 6H), 1.9—2.3 (m, 2H), 4.2—4.5 (m, 1H), 4.51 (dd, J=8.4, 2.1 Hz, 1H), 4.13 and 4.16 (2q, J=6.9 Hz each, 4H), 5.1—5.5 (m, 2H), 5.6—6.0 (m, 1H), 7.2—7.5 (m, 5H); IR (neat): 2220, 1734, 1643, 1602, 1494, 1260, 1230, 1178, 1156, 1030, 990, 925, 759, 693 cm^{-1}; MS: *m/e* (rel intensity) 314 (M^+, 6), 285 (1), 241 (10), 240 (11), 213 (11), 211 (11), 195 (34), 167 (39), 154 (100), 141 (32), 115 (69). Found: C, 72.35; H, 7.10%. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05%.

*Synthesis of Ethyl 2-Oxo-*exo*-6-(*trans*-1-propenyl)bicyclo[3.1.0]hexane-1-carboxylate (**20**)*. Ethyl (*E,E*)-3-oxo-6,8-decadienoate (1.32 g, 6.3 mmol)[23] was treated with *p*-toluenesulfonyl azide (TsN_3) (1.26 g, 6.4 mmol) and triethylamine (0.88 ml, 6.4 mmol) in acetonitrile (25 ml) (r.t., 7 h). Work-up gave the α-diazo β-keto ester (IR: 2140, 1723, 1662 cm^{-1}). The diazo compound was dissolved in benzene (27 ml) and heated to reflux in the presence of copper(II) acetylacetonate (0.18 g) for 7 h. Work-up followed by column chromatography (hexane–ethyl acetate 10:1 to 5:1) gave **20** (1.13 g, 86% yield); bp 132—134 °C (bath temp)/0.09 Torr; ^1H-NMR (CCl_4): δ 1.29 (t, J=6.9 Hz, 3H, $COOCH_2C\underline{H}_3$), 1.70 (dd, J=6.3, 1.8 Hz, 3H, $=CH-C\underline{H}_3$), 1.9—2.3 (m, 5H), 2.4—2.5 (m, 1H), 4.14 (q, J=6.9 Hz, 2H, $COOC\underline{H}_2CH_3$); IR (neat): 3000, 1750, 1730, 1374, 1296, 1184, 1033, 967 cm^{-1}; MS: *m/e* (rel intensity) 208 (M^+, 22), 179 (27), 162 (68), 151 (40), 91 (73), 79 (100). Found: C, 69.32; H, 7.80%. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74%.

(2R,3R*)-2-Ethoxycarbonyl-3-[(S*)-*trans*-1-methyl-2-butenyl]cyclopentanone (**21**) and Its Epimer (**22**)*: Bp 70—78 °C (bath temp)/0.15 Torr; ^1H-NMR (CCl_4): δ 1.03 and 0.98 (d, J=7.2 Hz, totally 3H, $CH-C\underline{H}_3$), 1.29 (t, J=6.9 Hz, 3H, $COOCH_2CH_3$), 1.60 (d, J=5.4 Hz, 3H, $=CHC\underline{H}_3$), 1.8—2.6 (m, 6H), 2.71 and 2.76 (d, J=10.8 Hz, totally 1H), 4.08 and 4.10 (2q, J=6.9 Hz, totally 2H, $OC\underline{H}_2CH_3$), 5.0—5.4 (m, 2H); IR (neat): 3060, 1760, 1726, 1460, 1370, 1276, 1180, 970 cm^{-1}; MS: *m/e* (rel intensity) 224 (M^+, 2), 206 (9), 178 (18), 155 (42), 109 (55), 95 (36), 83 (40), 69 (100). Found: C, 69.34; H, 9.10%. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99%.

(2R,3R*)-2-Ethoxycarbonyl-3-(*trans*-3-methyl-1-butenyl)cyclopentanone (**23**)*: Bp 109—112 °C (bath temp)/0.03 Torr; ^1H-NMR (CCl_4): δ 0.99 (d, J=7.2 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.27 (t, J=6.9 Hz, 3H, $OCH_2C\underline{H}_3$), 1.5—1.8 (m, 1H), 1.9—2.5 (m, 5H), 2.75 (d, J=11.1 Hz, 1H), 4.14 (q, J=6.9 Hz, 2H, $OC\underline{H}_2CH_3$), 5.1—5.5 (m, 2H); IR (neat): 1753, 1726, 1630, 1370, 967 cm^{-1}; MS: *m/e* (rel intensity) 224 (M^+, 1), 223 (1), 205 (1), 152 (30), 109 (24), 96 (56), 81 (71), 69 (100), 55 (55). Found: C, 69.67; H, 9.17%. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99%.

Synthesis of Ethyl exo-*6-Propyl-2-oxobicyclo[3.1.0]hexane-*1*-carboxylate (**25**)*. Ethyl acetoacetate (0.39 g, 3.0 mmol) dissolved in THF (5 ml) was added to sodium hydride (50% in oil, 0.16 g, 3.3 mmol) suspended in THF (10 ml) at 0 °C. After 15 min butyllithium hexane solution (1.70 M, 1.88 ml, 3.2 mmol) was added and the reaction mixture was stirred for 15 min at 0 °C. *Trans*-1-bromo-2-hexene (0.60 g, 3.7 mmol) dissolved in THF (4 ml) was then added and the reaction mixture was stirred for 50 min. Column chromatography (ethyl acetate–hexane 1:10) gave ethyl 3-oxo-trans-6-decenoate (0.34 g, 53% yield). IR (neat): 1750, 1723, 970 cm^{-1}; ^1H-NMR (CCl_4): δ 0.88 (t, J=6.9 Hz, 3H), 1.2—1.7 (m+t (δ 1.28 J=6.9 Hz, 5H), 1.8—2.6 (m, 6H), 3.28 (s, 2H), 4.16 (q, J=6.9 Hz, 2H), 5.3—5.5 (m, 2H).

The compound (0.34 g, 1.6 mmol) was converted into the diazo compound with TsN_3 (0.31 g, 1.6 mmol) and triethylamine (0.24 ml, 1.75 mmol) in acetonitrile (10 ml) (r.t., 15 h). The diazo compound was then heated in benzene (10 ml) with $Cu(acac)_2$ (49 mg) at reflux for 2.5 h. Concentration and column chromatography gave **25** (0.25 g, 74% yield), bp 124—127 °C (bath temp)/0.07 Torr; ^1H-NMR (CCl_4): δ 0.94 (t, J=6.3 Hz, 3H), 1.1—2.5 (m+t (δ 1.31, J=6.9 Hz), 13H), 4.16 (q, J=6.9 Hz, 2H); IR (neat): 3060, 1738, 1183, 1037 cm^{-1}. Found: C, 68.36; H, 8.69%. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63%.

*Reaction of **25** with Dimethylcopperlithium.* Compound **25** (27 mg, 0.13 mmol) was allowed to react at 0 °C for 30 min with dimethylcopperlithium generated from CuI (122 mg, 0.64 mmol), methyllithium (1.41 M ethereal solution, 0.64 ml, 1.28 mmol) and ether (3 ml). Preparative TLC (hexane–ethyl acetate 5:1, R_f 0.4—0.5) gave (2*R**,3*R**)-2-ethoxycarbonyl-3-[(*S**)-1-methylbutyl]cyclopentanone (**26**) (23 mg, 83% yield), bp 98—103 °C (bath temp)/1 Torr; ^{1}H-NMR (CCl_4): δ 0.75—1.8 (m+d (δ 0.91, J=7.2 Hz) +t (δ 1.28, J=6.9 Hz), totally 14H), 1.8—2.6 (m, 5H), 2.75 (d, J=11.1 Hz, 1H), 4.13 (q, J=6.9 Hz, 2H); IR (neat): 1757, 1726, 1184, 1116, 1024 cm^{-1}; MS: *m/e* (rel intensity) 226 (M^+, 3), 208 (3), 181 (6), 180 (6), 155 (19), 109 (44), 83 (100), 55 (96). Found: C, 69.14; H, 9.88%. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80%.

(2R,3R*)-2-Ethoxycarbonyl-3-[(R*)-1-methylbutyl]cyclopentanone (**28**).* This compound was prepared similarly starting with *cis*-1-bromo-2-hexene and characterized spectrometrically. ^{1}H-NMR (CCl_4): δ 0.8—2.5 (m+d (δ 0.89, J=6.3 Hz) +t (δ 1.30, J=6.9 Hz), totally 19H), 2.75 (d, J=11.1 Hz, 1H), 4.15 (q, J=6.9 Hz, 2H); IR (neat): 1757, 1727, 1249, 1180, 1113 cm^{-1}; MS: *m/e* (rel intensity) 226 (M^+, 5), 208 (3), 181 (14), 155 (41), 137 (40), 109 (100), 83 (45), 55 (70).

*Hydrogenation of a Mixture of **21** and **22**.* A mixture of **21** and **22** (56 mg, 0.25 mmol) dissolved in ethanol (5 ml) was stirred in the presence of 10% palladium on charcoal (*ca.* 10 mg) under a hydrogen atmosphere for 2 h. Removal of the catalyst by filtration, concentration, and preparative TLC (hexane–ethyl acetate 5:1, R_f 0.5) gave a mixture of dihydro derivatives of **26** and **28** (49 mg, 87% yield). The ^{1}H-NMR (CCl_4) was practically the same as that of the authentic specimen of **26** except for two doublets at δ 0.89 (attributable to that of **28**) and δ 0.91 (identical with the doublet of **26**). MS: *m/e* 226 (M^+).

Synthesis of Ethyl exo*-6-Methyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (**24**).* This compound was prepared from ethyl *trans*-3-oxo-6-octenoate[24] (0.62 g, 3.4 mmol) *via* diazotization (TsN_3 0.66 g, 3.4 mmol), Et_3N (0.47 ml, 3.4 mmol, CH_3CN (18 ml), r.t., 3 h) and decomposition ($Cu(acac)_2$ (34 mg), toluene (7 ml), reflux, 3 h) in 84% yield. Bp 99—103 °C/0.06 Torr; ^{1}H-NMR (CCl_4): δ 1.22 (d, J=6.3 Hz, 3H), 1.31 (t, J=6.9 Hz, 3H), 1.62 (dq, J=4.0, 6.3 Hz, 1H), 1.8—2.5 (m, 5H), 4.15 (q, J=6.9 Hz, 2H); IR (neat): 1732, 1193, 1034 cm^{-1}; MS: *m/e* (rel intensity) 182 (M^+, 28), 155 (42), 137 (92), 112 (89), 67 (100). Found: C, 65.72; H, 7.87%. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74%.

*Reaction of **24** with Trimethylaluminium.* A hexane solution of trimethylaluminium (1.0 M, 0.32 ml, 0.32 mmol) was added to a hexane (4 ml) solution of **24** (23 mg, 0.13 mmol) at 0 °C and the mixture was stirred for 1.5 h. Preparative TLC (hexane–ethyl acetate 2:1, double development, R_f 0.5—0.6) gave ethyl 2-hydroxy-2-*exo*-6-dimethylbicyclo[3.1.0]-hexane-1-carboxylate (18 mg, 72% yield), bp 88—90 °C (bath temp)/1 Torr; ^{1}H-NMR (CCl_4): δ 1.03 (d, J=5.9 Hz, 3H), 1.1—1.9 (m+t (δ 1.28, J=6.9 Hz) +s (δ 1.30), 12H), 2.2 (br s, 1H), 4.15 (q, J=6.9 Hz, 2H); IR (neat): 3500, 1714, 1117, 1050, 1010, 948 cm^{-1}; MS: *m/e* (rel intensity) 198 (M^+, 19), 183 (33), 137 (100), 124 (58). Found: C, 66.41; H, 9.14%. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15%.

Synthesis of Ethyl exo*-6-(*trans*-1-Propenyl)-3-oxa-2-oxo-bicyclo-[3.1.0]hexane-1-carboxylate (**29**).* Ethoxycarbonylacetyl chloride (1.82 g, 12.1 mmol) dissolved in ether (15 ml) was added at 0 °C to a mixture of (2*E*,4*E*)-2,4-hexadien-1-ol (0.99 g, 10.1 mmol) and pyridine (0.98 ml, 12.1 mmol) and the reaction mixture was stirred for 1.5 h. Work-up followed by column chromatography (hexane–ethyl acetate 10:1) gave ethyl (2*E*,4*E*)-2,4-hexadienyl propanedioate (1.96 g, 92% yield).

The mixed malonate (1.96 g, 9.3 mmol) was converted (Et_3N (1.42 ml), TsN_3 (1.82 g), CH_3CN (15 ml), r.t., 22 h) into the corresponding diazo compound which decomposed ($Cu(acac)_2$ (0.13 g), toluene (20 ml), reflux, 7 h). Work-up and column chromatography gave **29** (0.57 g, 63% yield), bp 154—157 °C (bath temp)/0.1 Torr; ^{1}H-NMR (CCl_4): δ 1.35 (t, J=6.9 Hz, 3H), 1.77 (dd, J=6.6, 2.1 Hz 3H) 2.21 (dd, J=8.7, 5.1 Hz, 1H), 2.61 (t, J=4.6 Hz, 1H), 4.1—4.4 (m+q (δ 4.23, J=6.9 Hz), 4H), 5.31 (dd, J=9.0, 15.6 Hz, 1H), 5.80 (dq, J=6.6, 15.6 Hz, 1H); IR (neat): 1785, 1723, 1184, 1051, 962 cm^{-1}; MS: *m/e* (rel intensity) 210 (M^+, 5), 164 (34), 137 (86), 93 (100), 79 (95). Found: C, 62.83; H. 6.67%. Calcd for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71%.

(3R,4R*)-3-(Ethoxycarbonyl-4-[(S*)-*trans*-1-methyl-2-butenyl]oxolan-2-one (**30**):* Bp 150—152 °C (bath temp)/0.09 Torr; ^{1}H-NMR (CCl_4): δ 1.00 (d, J=6.3 Hz, 3H), 1.30 (t, J=6.6 Hz, 3H), 1.63 (d, J=6.0 Hz, 3H), 1.9—2.4 (m, 1H), 2.6—3.1 (m, 1H), 3.13 (d, J=9.3 Hz, 1H), 3.87 (t, J=8.4 Hz, 1H), 4.1—4.6 (m+q (δ 4.18, J=6.6 Hz), 3H), 5.0—5.8 (m, 2H); IR (neat): 1782, 1736, 1146, 1017, 973 cm^{-1}; MS: *m/e* (rel intensity) 226 (M^+, 2), 181 (8), 180 (8), 157 (17), 107 (21), 69 (100). Found: C, 63.41; H, 8.13%. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02%.

*3-Ethoxycarbonyl-4-(*trans*-3-methyl-1-butenyl)oxolan-2-one (**31**):* Bp 134—136 °C (bath temp)/0.1 Torr; ^{1}H-NMR (CCl_4): δ 1.01 (d, J=6.6 Hz, 3H), 1.31 (t, J=6.5 Hz, 3H), 2.24 (heptet, J=6.4 Hz, 1H), 3.20 (d, J=9.6 Hz, 1H), 3.2—3.7 (m, 1H), 3.89 (t, J=8.4 Hz, 1H), 4.1—4.5 (m, 1H), 4.23 (q, J=6.5 Hz, 2H), 5.28 (dd, J=15.8, 7.1 Hz, 1H), 5.65 (dd, J=15.8, 6.4 Hz, 1H); IR (neat): 1787, 1738, 1150, 1020, 973 cm^{-1}; MS: *m/e* (rel intensity) 226 (M^+, 5), 182 (22), 139 (56), 107 (89), 95 (100), 81 (77), 79 (79). Found: C, 63.45; H, 7.86%. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02%.

*Transformation of **21** into **32**.* The β-keto ester **21** (142 mg, 0.63 mmol) dissolved in THF (5 ml) was added at 0 °C to sodium hydride (50% in oil, 33 mg, 0.70 mmol) suspended in THF (2 ml) and the reaction mixture was stirred for 15 min. Diethyl phosphorochloridate (101 μl, 0.70 mmol) was added and the mixture was stirred for 30 min. Work-up and preparative TLC (hexane–ethyl acetate 10:1, R_f 0.6—0.7) gave ethyl (5*R**)-2-methyl-5-[(*S**)-*trans*-1-methyl-2-butenyl]cyclopentene-1-carboxylate (**32**) (96 mg, 69% yield), bp 107—110 °C (bath temp)/0.08 Torr; ^{1}H-NMR (CCl_4): δ 0.81 (d, J=7.8 Hz, 3H), 1.30 (t, J=6.9 Hz, 3H), 1.6—2.0 (m+d (δ 1.65, J=3.9 Hz), 5H), 2.04 (br s, 3H), 2.2—2.8 (m, 3H), 2.8—3.2 (m, 1H), 4.12 (q, J=6.9 Hz, 2H), 5.2—5.4 (m, 2H); IR (neat): 1714, 1648, 1632, 1098, 970 cm^{-1}; MS: *m/e* (rel intensity) 222 (M^+, 6), 179 (14), 177 (15), 153 (70), 107 (74), 69 (100). Found: C, 75.42; H, 10.04%. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97%.

*Transformation of **32** into Neonepetalactone (**34**).* Ozone was bubbled into a methanol (1 ml) solution of **32** (40 mg, 0.18 mmol) at −78 °C under monitoring by TLC. When all the starting material was consumed, sodium borohydride (*ca.* 20 mg) was added to the reaction mixture, which was then allowed to react at room temperature. After most of the methanol was removed *in vacuo*, the residue was treated with brine and extracted with dichloromethane. Concentration of the extract followed by preparative TLC (hexane–ethyl acetate 2:1, R_f 0.3) gave an alcohol **33** (8 mg, 21%

yield). ^{1}H-NMR (CCl_4): δ 0.80 (d, J=6.3 Hz, 3H), 1.33 (t, J=6.9 Hz, 3H), 1.5—2.2 (m+br s (δ 2.09), 7H), 2.2—2.6 (m, 2H), 2.9—3.3 (m, 1H), 3.36 (d, J=6.0 Hz, 2H), 4.17 (q, J=6.9 Hz, 2H); IR (neat): 3450, 1705, 1108, 1054 cm^{-1}; MS: *m/e* (rel intensity) 212 (M^+, 2), 194 (4), 166 (30), 107 (44), 79 (100).

The alcohol (8 mg) was mixed with pyridinium *p*-toluenesulfonate (3 mg) in dichloromethane (1 ml) and the mixture heated to reflux for 7 h. Concentration and preparative TLC (hexane–ethyl acetate 2:1, R_f 0.7) gave neonepetalactone (**34**) (2 mg, 35% yield) having spectra consistent with the recorded ones. ^{1}H-NMR (CCl_4): δ 0.96 (d, J=6.9 Hz, 3H), 1.2—1.8 (m, 4H), 2.9 (br s, 3H), 2.3—2.7 (m, 2H), 3.78 (dd, J=12.4, 10.7 Hz, 1H), 4.17 (dd, J=4.7, 10.7 Hz, 1H); IR (CCl_4): 1722, 1645, 1244, 1197, 1105, 1056 cm^{-1}; MS: *m/e* (rel intensity) 166 (M^+, 46), 151 (16), 124 (61), 79 (100).

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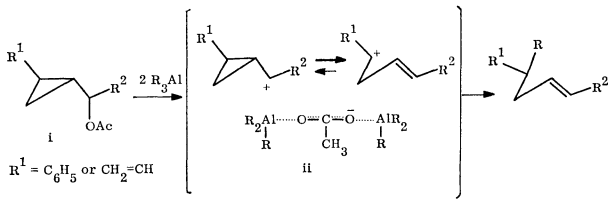
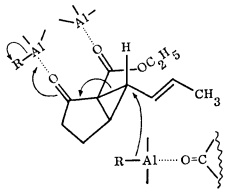


16) The reaction of **7**, **9**, **11a,b**, and **14** with trialkylaluminium can be understood in terms of the tight ion pairs shown in the bracket below. Trialkylaluminum dimer interacts with the leaving acetoxyl group of i to form fairly less nucleophilic complex ii whose R group on aluminium atom is in turn activated to some extent to attack an electron-deficient center. The cyclopropylmethyl cation generated undergoes rearrangement to the homoallyl cation stabilized by a phenyl or vinyl group. Thus, the overall reaction is reminiscent of an S_N1 type reaction[10] which proceeds in the absence of a polarizing solvent.

In contrast, the homoconjugate 1,5-addition to activated vinylcyclopropanes is explained by an S_N2-like mechanism illustrated in iii. Use of more than two mol of trialkylalu-



minium reagent as well as the presence of two activating carbonyls and a vinyl group in the substrate is essential for the reaction. Trialkylaluminium acid should possibly coordinate both of the carbonyls. The cyclopropane C–C bond is thus loosened and cleaved by the attack of an alkyl anion liberated from the third molecule of trialkylaluminium possibly coordinated on another substrate molecule.

The 1,7-homoconjugate addition may be explained by an electron-transfer mechanism as discussed in the conjugate addition of lithium organocuprate.[25]

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