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[14] *J. Levisalles & P. Garanger,* C.r. hebd. Séances Acad. Sci. *242,* 1336 (1956).
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[16] *P. Tóth, E. Kugler & E. sz. Kováts,* Helv. *42,* 2519 (1959).

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207. Stereospecific Olefin Synthesis *via* Lithium Vinylcuprates

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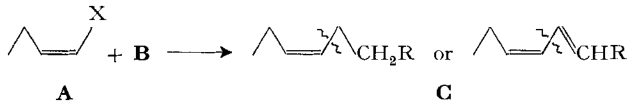
Dedicated to Dr. *Roger Firmenich* on the occasion of his 65th birthday

(14. V. 71)

Summary. The conjugate addition of *cis-* or *trans-*1-alkenyl-cuprolithium complexes $(R—CH{=}CH—)_2CuLi \cdot X_n$[1]) to α,β-unsaturated carbonyl compounds was found to occur with high retention of double bond geometry, affording isomerically pure *cis-* or *trans-*γ,δ-ethylenic carbonyl compounds. The same 1-alkenylcuprates also react stereospecifically with alkyl halides to give isomerically pure *cis-* or *trans-*olefins.

Introduction. – The wide occurrence of natural products containing oxygen and having *cis* or *trans* double bonds, and their application *e.g.* in perfumes or flavours[2]), encouraged us to elaborate a new general procedure for stereospecific olefin synthesis[3]).

Scheme 1



The present approach is characterized as follows (see Scheme 1): 1. C–Cσ bond formation between a vinyl unit **A** (a nucleophile) with a unit **B** (an electrophile) to give an olefin type **C**; 2. Stereospecificity of the bond formation.

An efficient method for C–C bond formation between unlike groups utilizes *organocuprate reagents*[4]) which undergo conjugate addition to α,β-unsaturated carbonyl compounds [5], and react easily with alkyl halides [1] [6].

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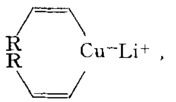
[1]) R = alkyl, X = ligands such as ether, tetrahydrofuran, $(CH_3O)_3P$ and $(n\text{-}Bu)_3P$. Physical studies to determine the structure of these copper reagents are in progress, see footnote [20]) of reference [1].

[2]) For a recent review see [2].

[3]) For a recent review on olefin synthesis see [3].

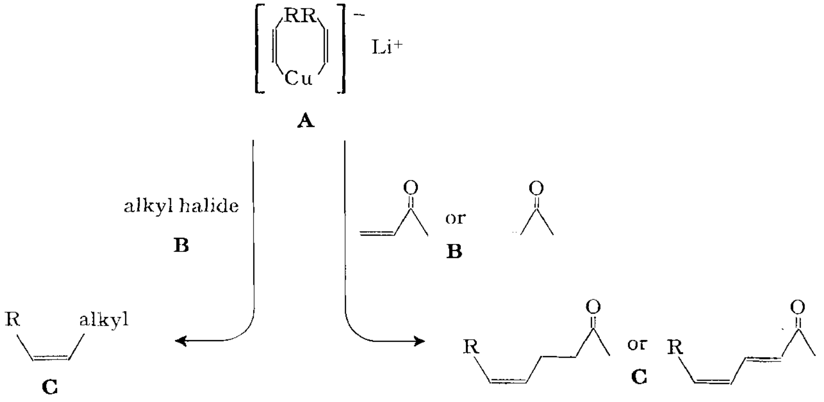
[4]) For reactions with 'ate' complexes of *d*-metals other than Cu^I see [4].

Intrigued by the cuprate method, we chose as nucleophilic vinyl unit **A**, a lithium vinylcuprate with the stoichiometric formula



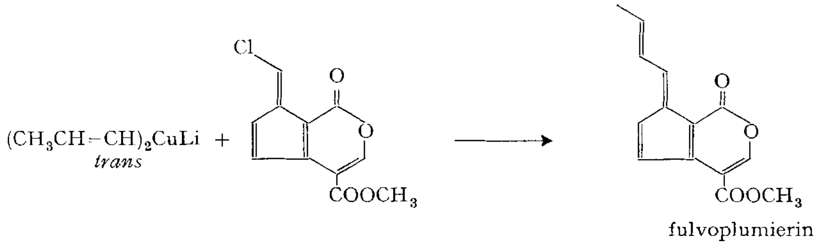
and as corresponding electrophile **B**, either an α,β-unsaturated carbonyl compound or an alkyl halide (see Scheme 2).

Scheme 2



The stereochemistry of reaction **A** → **C** was not clear at the beginning of the present investigation. Among the few known examples of the reaction outlined in Scheme 2 [1] [8] [9] only one, the formation of fulvoplumierin (*Büchi* & *Carlson* [8], see Scheme 3), poses the question of whether or not the double bond geometry of the cuprate **A** is preserved in the product **C**. Fulvoplumierin, however, is fully conjugated with the more stable *trans* configuration and could not be used to clarify this point. Lacking any conclusive experimental proof, *Büchi* & *Carlson* quite reasonably supposed that these reactions are stereospecific.

Scheme 3

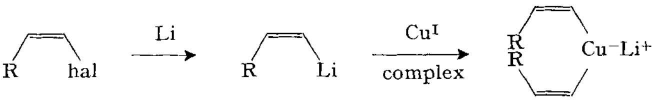


[8]

We have now thoroughly investigated the stereochemistry of the lithium vinylcuprate reaction with α,β-unsaturated carbonyl compounds and with alkyl halides and have found that double bond geometry is preserved. This result is consistent with the stereochemical features of *SE* type reactions, *i.e.* retention of configuration at the substrate atom.

Results and Discussion. – The isomerically pure *cis*- and *trans*-1-alkenylcuprates (C_3 to C_7) have been prepared following *Whitesides et al.* [7a]: transformation of pure *cis*- or *trans*-propenyl bromide to *cis*- or *trans*-propenyllithium and subsequent *trans*-metalation by means of a soluble copper(I) complex (see Scheme 4).

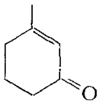
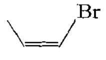
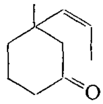
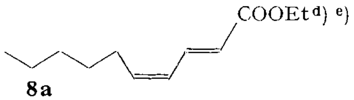
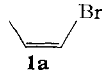
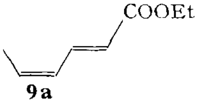
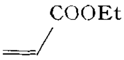
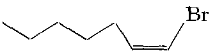
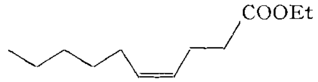
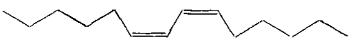
Scheme 4



It has long been known that 1-alkenyllithiums are formed from 1-alkenyl halides with retention of configuration [10], and *Whitesides et al.* [7] have recently shown that *trans*-metalation of 1-alkenyllithiums to form 1-alkenylate complexes also proceeds with retention of double bond geometry.

The di-1-alkenylcuprate complexes were allowed to react with a series of α,β-unsaturated carbonyl compounds (*e.g.* 3-methyl-2-cyclohexen-1-one (**4**), ethyl propio-

Table I. *Lithium vinylcuprate addition to α,β-unsaturated carbonyl compounds*
Reaction of cuprates obtained from 1-alkenyllithiums and cuprous iodide

α,β-unsaturated carbonyl compound	1-alkenyl bromide[c]	steric purity	product	steric purity	yield
 **4**	 **1a**	100%	 **7a**	100%	87% [a]
HC≡C—COOEt **5**	 **3a**	98%	 **8a**	95%	90% [a]
HC≡C—COOEt **5**	 **1a**	98%	 **9a**	95%	77% [a]
 **6**	 **3a**	98%	 **10a**	100%	8,4% [a]
			 **11**		76% [b]

) Based on α,β-unsaturated carbonyl compound.

) Based on 1-alkenyl bromide.

) *cis*-1-Alkenyl bromides were prepared according to [11].

) Isolated from *Bartlett* pear, see [12] [13]; first synthesis by *Crombie* [14].

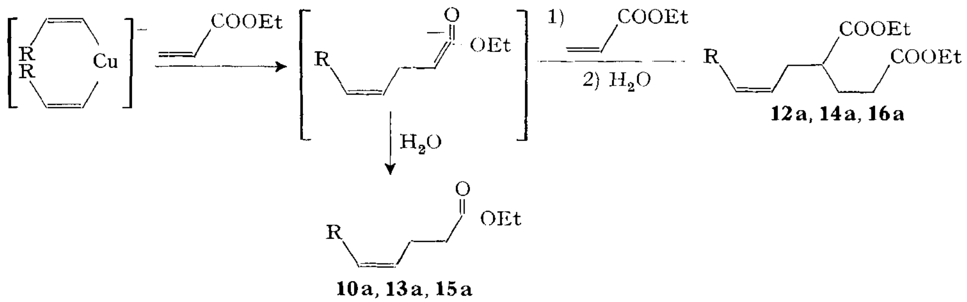
) We are much indebted to Dr. *M. Winter, Firmenich & Cie*, Geneva, for a sample of ethyl *trans*-2-*cis*-4-decadienoate (**8a**) and its *trans*-4-isomer **8b**, and for their spectra.

late (**5**), ethyl acrylate (**6**)) and with octyl iodide (**17**). The olefinic reaction products were analyzed by gas liquid partition chromatography (glpc.) and the usual spectroscopic methods (for results see Tables I–IV).

1. Lithium vinylcuprate addition to α, β-unsaturated carbonyl compounds. – a) *Reaction of cuprates obtained from 1-alkenyllithiums and cuprous iodide (Table I).* There is a distinct difference in reactivity between 3-methyl-2-cyclohexen-1-one (**4**), ethyl propiolate (**5**), both with high reactivity, and ethyl acrylate (**6**), with very low reactivity. Regardless of this difference there is a *retention of* cis *double bond geometry higher than 97%*[5] *in all cases.*

b) *Reaction of cuprates obtained from 1-alkenyllithiums and bis-(trimethoxyphosphine)-copper(I) iodide* [5] *(Table II).* The results in Table II by comparison with those in Table I clearly demonstrate that the choice of the reactive cuprate may play a decisive role; *e.g.* the cuprate complexed by trimethoxyphosphine adds to ethyl acrylate (**6**) to give 38% yield of addition product **10a** (Table II) whereas the uncomplexed cuprate gives only 8.5% yield of addition product **10a** (Table I). Unfortunately cuprate addition to ethyl acrylate (**6**) not only forms the expected γ,δ-ethylenic esters **10a**, **13a** or **15a** but also by-products, substituted glutaric esters **12a**, **14a** or **16a**.

Scheme 5



R = C_5H_{11}, for **10a**, **12a**; C_3H_7 for **13a**, **14a**; CH_3 for **15a**, **16a**

Formation of a glutaric ester can be explained by assuming that the carbanion intermediate formed initially adds to a second ethyl acrylate entity before the latter reacts with the cuprate complex (Scheme 5). In all cases investigated, only ethyl acrylate (**6**) showed this side reaction; ethyl propiolate (**5**) and 3-methyl-2-cyclohexen-1-one (**4**) do not form similar by-products. Regardless of these side reactions retention of double bond geometry during addition reaction *via* cuprates complexed by trimethoxyphosphine is nearly 100%[5] for the *cis* isomer and 93%[5] for the *trans* isomers.

The reactivity of *cis*-1-alkenylcuprates compared with the reactivity of *trans*-1-alkenylcuprates is also important. The deep red *cis*-1-propenyl-trimethoxyphosphine-cuprate reacts faster giving a higher yield and less polymers than the ink-blue *trans*-1-propenyl-trimethoxyphosphinecuprate (see Table III).

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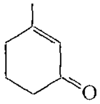
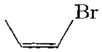
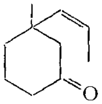
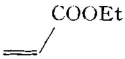
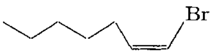
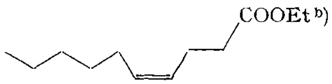
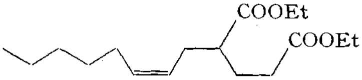
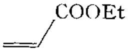
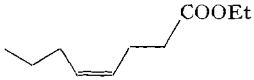
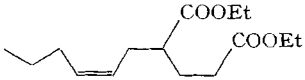
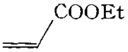
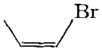
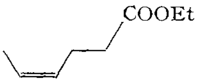
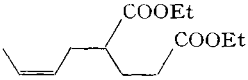
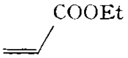
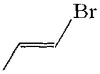
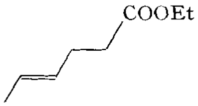
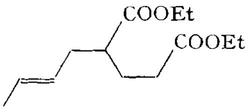
[5] Retention of double bond geometry has been calculated as follows:

$$\text{retention (\%)} = \frac{\text{isomeric purity of reaction product (\%)}}{\text{isomeric purity of starting bromide (\%)}} \cdot 100.$$

Table II. *Lithium vinylcuprate addition to α,β-unsaturated carbonyl compounds*

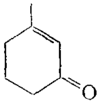
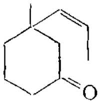
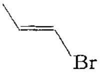
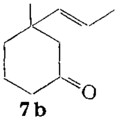
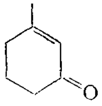
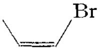
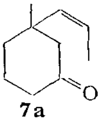
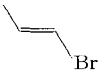
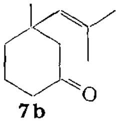
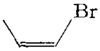
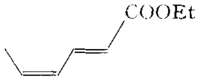
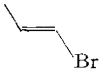
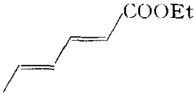
Reaction of cuprates obtained from 1-alkenyllithiums and bis-(trimethoxyphosphine)-copper(I) iodide [5]

α,β-unsaturated carbonyl compound	1-alkenyl bromide	steric purity	product	steric purity	yield[a]
 **4**	 **1a**	90%	 **7a**	94%	73%
 **6**	 **3a**	98%	 **10a**	100%	38%
			 **12a**	–	16%
 **6**	 **2a**	98%	 **13a**	100%	27%
			 **14a**	–	31%
 **6**	 **1a**	85%	 **15a**	100%	15.5%
			 **16a**	100%	21.2%
 **6**	 **1b**	91%	 **15b**	85%	3.4%
			 **16b**	85%	7.1%

) Based on unsaturated carbonyl compound.

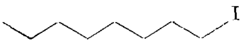
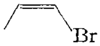
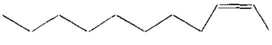
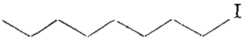
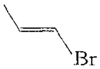
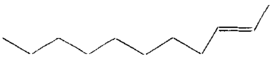
) Isolated from *Bartlett* pear, see [12].

Table III. *Reaction between mixtures of* cis- *and* trans-*1-alkenyl-lithiumcuprates and α,β-unsaturated carbonyl compounds*

α,β-unsaturated carbonyl compound	1-alkenyl bromide, *cis-trans* distribution		product, *cis-trans* distribution		yield of isomeric mixture[a])	type of cuprate
 **4**	 **1a**	64%	 **7a**	72%	66%	phosphorus-free
	+					
	 **1b**	36%	 **7b**	28%		
 **4**	 **1a**	25%	 **7a**	53%	79%	$(CH_3O)_3P$ complexed
	+					
	 **1b**	75%	 **7b**	47%		
HC≡C—COOEt **5**	 **1a**	65%	 **9a**	65%	71.5%	phosphorus-free
	+					
	 **1b**	35%	 **9b**	35%		

[a]) Based on α,β-unsaturated carbonyl compound.

Table IV. *Reaction of lithium vinylcuprates with alkyl halides*

halide	1-alkenyl bromide	steric purity	product	steric purity	yield of *cis-trans* mixture[a])	type of cuprate
 **17**	 **1a**	99% *cis*	 **18a**	97% *cis*	66%	(CH$_3$O)P complexed
 **17**	 **1b**	88% *trans*	 **18b**	77% *trans*	73%	(CH$_3$O)P complexed

[a]) Based on alkyl halide.

c) *Reaction between mixtures of* cis- *and* trans-*1-alkenyllithiumcuprates and α,β-unsaturated carbonyl compounds (Table III).* When an isomeric mixture of *cis*- and *trans*-1-alkenylcuprate (four-fold excess) was allowed to react with 3-methyl-2-cyclo-hexen-1-one (**4**) the *cis/trans* ratio of the reaction product was higher than the *cis/trans* ratio of the starting 1-alkenyl halide, *i.e.* formation of a *cis*-γ,δ-ethylenic carbonyl compound was favoured. As previously mentioned, experiments with pure *cis*- and pure *trans*-propenyl bromide clearly demonstrate that both isomers undergo stereospecific reaction. The preferential formation of the *cis*-ethylenic carbonyl compound **7a** is therefore determined by the reaction rate, and is not the result of isomerization during the reaction sequence.

2. Reaction of lithium vinylcuprates with alkyl halides (Table IV). – *Cis*- and *trans*-1-propenylcuprates react with 1-octyl iodide (**17**) stereospecifically to give *cis*- or *trans*-2-undecene (**18a**, **18b**, resp.). The slight difference in stereospecificity between the *cis*- and *trans*-isomers might be explained as in section 1c.

Experimental Part

All reactions were carried out in an atmosphere of argon. The ratio of *cis*- and *trans*-isomers was determined by gas liquid partition chromatography (glpc.) on a *Perkin-Elmer* 226 instrument using an UCON metal capillary column (length 200 ft, diam. 0.02 in). For column chromatography, silica gel *Merck* (0.05–0.2 mm) was used. Ultraviolet (UV.) spectra were measured in ethanol on an *Optica* CF4 instrument. Infrared (IR.) spectra were recorded in CCl_4 (unless otherwise stated) on a *Perkin-Elmer* 125 spectrometer. Nuclear magnetic resonance (NMR.) spectra were obtained with a *Varian* A-60 spectrometer, and peak positions are given in ppm downfield from tetramethylsilane as an internal standard, in CCl_4 solution. Mass spectra were measured on an *Atlas* CH-4 mass spectrometer using an inlet temperature of about 150° and an electron energy of 70 eV. For bulb distillation a *Büchi* apparatus with external temperature reading was used.

cis-*1-Alkenyl bromides* (**1a**, **2a**, **3a**) were prepared according to method given in [11]; yields 30–35%, of which 98% *cis*. The bromides were stored at –20° to prevent *cis/trans* isomerization.

*3-(*cis*-1′-Propenyl)-3-methyl-1-cyclohexanone* (**7a**) *and 3-(*trans*-1′-propenyl)-3-methyl-1-cyclohexanone* (**7b**). – A) A solution of 5.32 g (44 mmol) of *cis*-1-propenylbromide (**1a**) (100% *cis*) in 30 ml of anhydrous ether was added to 0.615 g (88 mmol) of finely cut lithium (containing 1.5% of Na) in 30 ml of ether at –10°. The resulting organolithium solution was added dropwise, at –40°, to a stirred suspension of 4.18 g (22 mmol) of dried Cu_2I_2 powder in 10 ml of anhydrous ether yielding a red suspension to which 0.82 g (7.5 mmol) of 3-methyl-2-cyclohexenone (**4**) in 5 ml of dry ether was added at –40° over 5 min. Stirring was continued for 2 h while the temperature was allowed to rise to that of the room. The reaction mixture was poured into a saturated NH_4Cl solution, filtered through celite and extracted with ether. The etheral extract was washed (saturated NaCl solution), dried ($MgSO_4$), concentrated, and distilled, giving 1.1 g (87%) of exclusively *cis*-isomer **7a**, b.p. 90°/11 Torr (bulb distillation).

B) Using the conditions and quantities as described in A) a mixture of 64% *cis*- and 36% *trans*-propenyl bromide yielded 0.83 g (66%) of ketone, b.p. 90°/11 Torr (bulb distillation), containing 72% *cis*-isomer **7a** and 28% *trans*-isomer **7b**.

C) The organolithium solution obtained from 5.32 g (44 mmol) of *cis*-1-propenyl bromide (**1a**) (90% *cis*) as above was added dropwise to a stirred suspension of 10 g of $[(CH_3O)_3P]_2CuI$ [5] in 20 ml of ether at –20 to –30°. The rate of addition was such that a deep red solution was obtained. After all the copper(I) complex had dissolved, 0.82 g (7.5 mmol) of 3-methyl-2-cyclohexenone (**4**) in 5 ml of ether was added dropwise with stirring which was continued for one hour while the temperature rose to 0°. The reaction mixture was poured into 100 ml of saturated aqueous NH_4Cl solution and filtered through celite. The organic layer was separated, the aqueous layer extracted twice with ether, and the combined organic solutions were washed (satured NH_4Cl and NaCl), dried ($MgSO_4$), and concentrated. The oily crystalline residue was taken up in 100 ml of hexane, kept overnight at 0°, and filtered through celite. Chromatography of the concentrated filtrate on 50 g of silica gel gave by elution with hexane some nonpolar impurities with a little starting material; subsequent elution with hexane-ether (95:5) and distillation gave 0.83 g (73%) of product, b.p. 92°/11 Torr (bulb distillation), containing 94% of *cis*-isomer **7a**.

D) Using the conditions and quantities as described in C) a mixture of 75% *trans*- and 25% *cis*-propenyl bromide gave 0.9 g (79%) of ketone, b.p. 90°/11 Torr (bulb distillation), containing 53% cis-*isomer* **7a** and 47% trans-*isomer* **7b**.

7a. NMR. spectrum: 1.17 (3H, *s*, CH_3); 1.7 (3H, *d*, J = 5 Hz, $C{=}C{-}CH_3$); 5.23 (2H, *m*, CH=CH *cis*) ppm. IR. spectrum (neat): bands at 3010 (CH=CH), 1705 (C=O), 710 (CH=CH *cis*) cm^{-1}. Mass spectrum *m/e* (rel. intensity): 152 (27), 137 (64), 123 (34), 109 (79), 95 (95), 81 (50), 67 (97), 55 (100), 42 (89), 27 (36).

$C_{10}H_{16}O$ Calc. C 78.89 H 10.59% Found C 78.61 H 10.67%

7b. NMR. spectrum: 1.01 (3H, *s*, CH_3); 1.6–1.75 (3H, *m*, $C{=}C{-}CH_3$); 5.26 (2H, *m*, HC=CH *trans*) ppm. IR. spectrum (neat): bands at 3030 (CH=CH), 1705 (C=O), 970 (CH=CH *trans*) cm^{-1}. Mass spectrum: 152 (41), 137 (63), 123 (44), 109 (77), 95 (100), 82 (55), 67 (90), 55 (87), 42 (80), 27 (32).

Ethyl trans-*2*-cis-*4-decadienoate* (**8a**)[6]) *and ethyl* trans-*2*-trans-*4-decadienoate* (**8b**)[6]). 1-Heptenyl (prepared at –10° from 11.15 g (63 mmol) of *cis*-1-heptenyl bromide (**3a**) (98% *cis*) and 0.88 g (126 mmol) of lithium (1.5% Na) dissolved in 60 ml of ether was added dropwise to a stirred suspension of powdered Cu_2I_2 (6.4 g; 32 mmol) in 80 ml of ether at –10°. To this cold, brown red reaction mixture at –10°, a solution of 3.14 g (32 mmol) of ethyl propiolate (**5**)[7]) in 20 ml of ether was added over 5 min with stirring. After stirring an additional 10 min the mixture was poured into a mixture of ice and 2 N HCl, the precipitate was removed by filtration, the organic layer of the filtrate separated, and the aqueous layer extracted twice with ether. The combined etheral solutions were washed successively with aqueous $Na_2S_2O_3$ and saturated aqueous $NaHCO_3$. After the ethereal solution had been dried ($MgSO_4$) and concentrated, glpc. showed 95% of *ethyl* trans-*2*-cis-*4-decadienoate* (**8a**) and 5% of *ethyl* trans-*2*-trans-*4-decadienoate* (**8b**). Distillation of the crude material afforded a colorless oil (5.7 g; 90%) with a typical pear flavor: b.p. 70–72°/0.05 Torr; **8a** content: 95%.

8a. NMR. spectrum[8]): 0.92 (3H, *t*, J = 5 Hz, CH_3); 1.27 (3H, *t*, J = 7 Hz, CH_3); 2.0–2.5 (2H, *m*, $C{=}C{-}CH_2$); 4.15 (2H, *q*, J = 7 Hz, $O{-}CH_2$); 5.8 (1H, *d*, J = 15 Hz, $C{=}CH_a$); 5.5–6.3 (2H, *m*, $C{=}CH_b$, $C{=}CH_c$); 7,55 (1H, *d* of *d*, J = 15 Hz, J' = 11 Hz, $C{=}CH_d$) ppm. IR. spectrum: bands at 3020 (C=CH), 1715, 1710 (C=O), 1635, 1600 (C=C–C=C), 990 (CH=CH *trans*) cm^{-1}. Mass spectrum: 196 (36), 167 (3), 151 (40), 139 (3), 125 (77), 108 (22), 97 (71), 81 (100), 67 (83), 55 (44), 41 (60), 29 (97). UV. (95% EtOH): λ_{max} 265 nm (ε = 24,800).

$C_{12}H_{20}O_2$ Calc. C 73.34 H 10.27% Found C 73.14 H 10.22%

8b. NMR. spectrum[8]): 0.89 (3H, *t*, J = 5 Hz, CH_3), 1.25 (3H, *t*, J = 7 Hz, CH_3), 1.9–2.3 (2H, *m*, $C{=}C{-}CH_2$), 4.15 (2H, *q*, J = 7 Hz, $O{-}CH_2$), 5.72 (1H, *d*, J = 15 Hz, $C{=}CH_a$), 6.0–6.25 (2H, *m*, $C{=}CH_b$, $C{=}CH_c$), 6.9–7.5 (1H, *m*, $C{=}CH_d$) ppm. IR. spectrum: 3020 (C=CH), 1715, 1705 (C=O), 1640, 1615 (C=C–C=C), 995 (CH=CH *trans*) cm^{-1}. Mass spectrum: 196 (44), 167 (2), 151 (41), 139 (3), 125 (100), 111 (13), 97 (77), 81 (87), 67 (67), 55 (41), 41 (55), 29 (92). UV. λ_{max} (95% EtOH): 262 nm (ε = 24,660).

Ethyl trans-*2*-cis-*4-hexadienoate* (**9a**) *and ethyl* trans-*2*-trans-*4-hexadienoate* (**9b**). – A) Using the conditions described for compound **8a**, 0.88 g (126 mmol) of lithium (1.5% Na), 7.6 g (63 mmol) of *cis*-1-propenyl bromide (**1a**) (98% *cis*), 6.4 g (32 mmol) of Cu_2I_2 and 3.14 g (32 mmol) of ethyl propiolate (**5**) gave 3.47 g (77%) of a mixture of 95% *ethyl* trans-*2*-cis-*4-hexadienoate* (**9a**) and 5% *ethyl* trans-*2*-trans-*4-hexadienoate* (**9b**), b.p. 69°/11 Torr.

B) Using a mixture of 65% *cis*- and 35% *trans*-propenyl bromide (**1a** and **1b** resp.) instead of pure *cis*-1-propenyl bromide (**1a**), 3.2 g (71.5%) of a mixture of 65% **9a** and 35% **9b**, b.p. 68–70°/11 Torr, were obtained.

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[6]) Isolated from *Bartlett* pear [12] [13], first synthesis [14].

[7]) From *Th. Schuchart*, Munich.

[8]) Designation of olefinic protons: $CH_3(CH_2)_4CH_c{=}CH_b{-}CH_d{=}CH_a{-}COOEt$.

9a. NMR. spectrum 9): 1.27 (3H, *t*, $J = 7$ Hz, CH_3); 1.89 (3H, *d*, $J = 6$ Hz, $C{=}C{-}CH_3$); 4.18 (2H, *q*, $J = 7$ Hz, $O{-}CH_2$); 5.84 (1H, *d*, $J = 15$ Hz, $C{=}CH_a$), 5.6–6.4 (2H, *m*, $C{=}CH_b$, $C{=}CH_c$); 7.62 (1H, *d*, of *d*, $J = 15$ Hz, $J' = 11$ Hz, $C{=}CH_d$) ppm. IR. spectrum: bands at 3030 (C=CH), 1715, 1705 (C=O), 1635, 1605 (C=C—C=C), 990 (CH=CH *trans*) cm^{-1}. Mass spectrum: 140 (50), 125 (34), 112 (12), 97 (81), 95 (100), 83 (5), 67 (99), 55 (10), 41 (60), 29 (28). UV. (95% EtOH): λ_{max} 265 nm ($\varepsilon = 24{,}260$). $C_8H_{12}O_2$ Calc. C 68.54 H 8.63% Found C 68.34 H 8.77%

9b. NMR. spectrum 9): 1.25 (3H, *t*, $J = 7$ Hz, CH_3); 1.86 (3H, *d*, $J = 5$ Hz, $C{=}C{-}CH_3$); 4.16 (2H, *q*, $J = 7$ Hz, $O{-}CH_2$); 5.75 (1H, *d* of *d*, $J = 15$ Hz, $J' = 1$ Hz, $C{=}CH_a$); 6.0–6.3 (2H, *m*, $C{=}CH_b$, $C{=}CH_c$); 7.0–7.5 (1H, *m*, $C{=}CH_d$) ppm. IR. spectrum: bands at 3020 (C=CH), 1720, 1705 (C=O), 1640, 1615 (C=C—C=C), 995 (CH=CH *trans*) cm^{-1}. Mass spectrum: 140 (36), 125 (26), 112 (8), 97 (75), 95 (100), 83 (8), 67 (99), 55 (12), 41 (58), 29 (46). UV. (95% EtOH): λ_{max} 260 nm ($\varepsilon = 27{,}960$).

Ethyl cis-*4-decenoate* (**10a**) 10). – A) Using the conditions described for compound **8a**, 0.88 g (126 mmol) of lithium (1.5% Na), 11.15 (63 mmol) of *cis*-1-heptenyl bromide (**3a**) (98% *cis*), 6.4 g (32 mmol) of Cu_2I_2 and 3.2 g (32 mmol) of ethyl acrylate (**6**) gave 5.28 g of an oil b.p. 90–100°/11 Torr containing *ethyl* cis-*4-decenoate* (**10a**) (8.4% based on ethyl acrylate) and *6,8-tetradecadiene* (**11**) (78% based on alkenyl bromide **3a**).

B) A solution of 5.6 g (32 mmol) of *cis*-1-heptenyl bromide (**3a**) (98% *cis*) in 8 ml of anhydrous ether was added to 0.44 g (63 mmol) of finely cut lithium (1.5% of Na) in 8 ml of ether at −10°. The resulting organolithium solution was added dropwise to a cooled (−25° to −30°), stirred suspension of 7.03 g (16 mmol) of $[(CH_3O)_3P]_2CuI$ [5] in 50 ml of dry ether. The rate of addition was so chosen that a deep red solution was obtained. After all the copper(I) complex had dissolved, the orange red solution was cooled to −30° to −40°, and a solution of 1.6 g (16 mmol) of freshly distilled ethyl acrylate (**6**) in 100 ml of dry ether was added over 30 min with stirring (slightly exothermic reaction). After stirring for an additional 40 min at −30° to −40° the mixture was poured into an excess of saturated aqueous ammonium chloride, the organic layer separated, and the aqueous layer extracted twice with ether. The combined etheral solutions were washed (satured NH_4Cl and NaCl), dried ($MgSO_4$) and concentrated. Filtration of the oily crystalline residue through a column of 50 g of silica gel, in hexane-ether 4:1, afforded a colorless oil. This oil was chromatographed on 50 g of silica gel. Elution with hexane-ether 95:5 gave 1.2 g (38%) of *ethyl* cis-*4-decenoate* (**10a**), b.p. 130°/12 Torr (bulb distillation), 100% *cis*. Subsequent elution with hexane-ether 90:10 gave 750 mg (16%) of *diethyl α-*(cis-*2-octenyl) glutarate* (**12a**), b.p. 150°/0.1 Torr (bulb distillation).

10a. NMR. spectrum: 0.88 (3H, '*t*', CH_3); 1.22 (3H, *t*, $J = 7$ Hz, CH_3); 1.8–2.4 (6H, $2C{=}C{-}CH_2$, $CH_2C{=}O$); 4.02 (2H, *q*, $J = 7$ Hz, $O{-}CH_2$); 5.28 (2H, *m*, CH=CH *cis*) ppm. IR. spectrum (neat): bands at 1735 (C=O), 725 (CH=CH *cis*) cm^{-1}. Mass spectrum: 198 (9), 169 (<1), 152 (46), 135 (20), 123 (15), 110 (93), 96 (51), 88 (100), 84 (53), 69 (91), 55 (93), 41 (90), 29 (95).

$C_{12}H_{22}O_2$ Calc. C 72.68 H 11.18% Found C 72.46 H 11.36%

11. NMR. spectrum: 0.89 (6H, '*t*', $2CH_3$); 1.8–2.3 (4H, $2C{=}C{-}CH_2$); 4.9–6.5 (4H, 2CH=CH) ppm. Mass spectrum: 194 (25), 165 (<1), 151 (<1), 137 (6), 124 (8), 109 (10), 95 (43), 81 (61), 67 (100), 54 (31), 41 (36), 29 (19).

12a. NMR. spectrum: 0.88 (3H, '*t*', CH_3); 1.21 (6H, *t*, $J = 7$ Hz, CH_3); 1.7–2.4 (7H, $2C{=}C{-}CH_2$, $CH_2C{=}O$, $CH{-}C{=}O$); 4.04 (4H, *q*, $J = 7$ Hz, $2O{-}CH_2$); 5.30 (2H, *m*, CH=CH *cis*) ppm. IR. spectrum: bands at 3010 (C=CH), 1735 (C=O) cm^{-1}. Mass spectrum: 298 (5), 253 (68), 224 (100), 179 (58), 150 (60), 136 (77), 114 (48), 95 (40), 79 (63), 67 (59), 55 (82), 41 (76), 29 (91).

$C_{17}H_{30}O_4$ Calc. C 68.42 H 10.13% Found C 68.64 H 9.84%

Ethyl cis-*4-octenoate* (**13a**). Using the conditions described for the ethyl decenoate **10a**, method B, 0.88 g (126 mmol) of lithium (1.5% Na), 9.5 g (63 mmol) of *cis*-1-pentenyl bromide (**2a**) (98% *cis*), 14.06 g (32 mmol) of $[(CH_3O)_3P]_2CuI$ [5] and 3.2 g (32 mmol) of ethyl acrylate (**6**) gave 1.47 g (27%) of cis-*4-octenoate* **13a**, b.p. 105°/11 Torr (bulb distillation), 100% *cis*, and 2.7 g (31%) of *diethyl α-*(cis-*2-hexen-1-yl*)*-glutarate* (**14a**), b.p. 105–120°/0.01 Torr (bulb distillation), 100% *cis*.

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9) Designation of olefinic protons: $CH_3CH_c{=}CH_b{-}CH_d{=}CH_a{-}COOEt$.

10) Isolated from *Bartlett* pear, see [12].

13a. NMR. spectrum: 0.90 (3H, *t*, J = 6 Hz, CH_3); 1.22 (6H, *t*, J = 7 Hz, CH_3); 1.8–2.4 (6H, 2C=C—CH_2, CH_2—C=O); 4.03 (2H, *q*, J = 7 Hz, O—CH_2); 5.2–5.4 (2H, *m*, CH=CH) ppm. IR. spectrum: bands at 3010 (C=CH), 1735 (C=O) cm^{-1}. Mass spectrum: 170 (9), 141 (3), 124 (41), 113 (3), 96 (46), 88 (66), 82 (69), 67 (45), 55 (100), 41 (64), 29 (69).

$C_{10}H_{18}O_2$ Calc. C 70.54 H 10.66% Found C 70.81 H 10.82%

14a. NMR. spectrum: 0.89 (3H, *t*, J = 6 Hz, CH_3); 1.20 (6H, *t*, J = 7 Hz, 2CH_3); 1.7–2.5 (7H, 2C=C—CH_2, CH_2—C=O, CH—C=O); 4.06 (4H, *q*, J = 7 Hz, 2O—CH_2); 5.2–5.5 (2H, *m*, CH=CH) ppm. IR. spectrum: bands at 3010 (C=CH), 1730 (C=O) cm^{-1}. Mass spectrum: 270 (0), 225 (4), 196 (6), 151 (3), 139 (4), 122 (5), 113 (83), 95 (13), 81 (14), 71 (100), 57 (33), 43 (60), 29 (23).

$C_{15}H_{26}O_4$ Calc. C 66.63 H 9.69% Found C 66.7 H 9.78%

Ethyl cis-*4-hexenoate* (**15a**) *and ethyl* trans-*4-hexenoate* (**15b**). – A) Using the conditions described for the ethyl decenoate **10a**, method B) 0.44 g (63 mmol) of lithium (1.5% Na), 3.87 g (32 mmol) of *cis*-propenyl bromide (**1a**) (85% *cis*, 15% *trans*), 7.03 g (16 mmol) of $[(CH_3O)_3P]_2CuI$ [5] and 1.6 g (16 mmol) of ethyl acrylate (**6**) gave 0.3 g (15.5%) of cis-*4-hexenoate* **15a**, b.p. 54–55°/11 Torr (bulb distillation), 100% *cis*, and 0.86 g (21%) of *diethyl* α-(cis-*2-buten-1-yl*)-*glutarate* (**16a**), b.p. 83–85°/0.05 Torr (bulb distillation), 100% *cis*.

B) Using the same conditions and quantities as in experiment A) *trans*-propenyl bromide **1b** (91% *trans*, 9% *cis*) gave a dark blue cuprate, which by reaction with ethyl acrylate (**6**) afforded 76 mg (3.4%) of trans-*4-hexenoate* **15b**, b.p. 100°/85 Torr (bulb distillation), 85% *trans*, and 275 mg (7%) of *diethyl* α-(trans-*2-buten-1-yl*)-*glutarate* (**16b**), b.p. 95–100°/0.05 Torr (bulb distillation), 85% *trans*. The remainder was a polymerized product.

15a. NMR. spectrum: 1.22 (3H, *t*, J = 7 Hz, CH_3); 1.61 (3H, *d*, J = 5 Hz, C=C—CH_2); 2.25 (4H, C=C—CH_2, CH_2—C=O); 4.04 (2H, *q*, J = 7 Hz, O—CH_2); 5.33 (2H, *m*, CH=CH) ppm. IR. spectrum (neat): bands at 3010 (C=CH), 1730 (C=O), 700 (CH=CH *cis*) cm^{-1}. Mass spectrum: 142 (46), 113 (7), 97 (43), 88 (42), 71 (67), 69 (98), 68 (100), 60 (48), 55 (84), 41 (86), 29 (76).

$C_8H_{14}O_2$ Calc. C 67.57 H 9.93% Found C 67.33 H 10.03%

15b. NMR. spectrum: 1.19 (3H, *t*, J = 7 Hz, CH_3); 1.5–1.7 (3H, *m*, C=C—CH_3); 2.25 (4H, C=C—CH_2, CH_2—C=O); 4.04 (2H, *q*, J = 7 Hz, O—CH_2); 5.3–5.5 (2H, *m*, CH=CH *trans*) ppm. IR. spectrum (neat): 3020 (C=CH), 1730 (C=O), 960 (CH=CH *trans*) cm^{-1}. Mass spectrum: 142 (44), 113 (5), 106 (1), 97 (45), 88 (40), 71 (66), 69 (97), 68 (100), 60 (42), 55 (96), 41 (99), 29 (90).

$C_8H_{14}O_2$ Calc. C 67.57 H 9.93% Found C 67.76 H 10.12%

16a. NMR. spectrum: 1.22 (6H, *t*, J = 7 Hz, 2CH_3); 1.6 (3H, *d*, J = 5 Hz, C=C—CH_3); 1.7–2.4 (5H, C=C—CH_2, CH_2—C=O, CH—C=O); 4.04 (4H, *q*, J = 7 Hz, 2O—CH_2); 5.2–5.5 (2H, *m*, CH=CH *cis*) ppm. IR. spectrum: bands at 3010 (C=CH), 1730 (C=O) cm^{-1}. Mass spectrum: 242 (<1), 197 (45), 168 (68), 151 (16), 123 (42), 94 (100), 81 (50), 67 (15), 55 (42), 41 (18), 29 (49).

$C_{13}H_{22}O_4$ Calc. C 64.44 H 9.15% Found C 64.21 H 9.23%

16b. NMR. spectrum: 1.18 (6H, *t*, J = 7 Hz, 2CH_3); 1.5–1.7 (3H, *m*, C=C—CH_3); 2.0–2.5 (5H, C=C—CH_2, CH_2—C=O, CH—C=O); 4.04 (4H, *q*, J = 7 Hz, 2O—CH_2); 5.2–5.5 (2H, *m*, CH=CH) ppm. IR. spectrum: bands at 3020 (C=CH), 1730 (C=O), 965 (CH=CH *trans*) cm^{-1}. Mass spectrum: 242 (<1), 197 (34), 168 (61), 151 (34), 141 (3), 123 (41), 114 (7), 94 (100), 81 (56), 67 (15), 55 (50), 41 (20), 29 (58).

$C_{13}H_{22}O_4$ Calc. C 64.44 H 9.15% Found C 64.55 H 9.15%

cis-*2-Undecene* (**18a**) *and* trans-*2-undecene* (**18b**). – A) A solution of 2.42 g of *cis*-1-propenyl bromide (**1a**) (99% *cis*) in 6 ml of anhydrous ether was added to 0.28 g (40 mmol) of finely cut lithium (1.5% Na) in 6 ml of ether at −10°. The resulting organolithium solution was added dropwise to a stirred suspension of 4.38 g (10 mmol) of $[(CH_3O)_3P]_2CuI$ [5] in 15 ml of dry ether at −25° to −30°; the rate of addition was such as to obtain a deep red solution. After all of the copper(I) complex had dissolved, 1.2 g (5 mmol) of 1-octyl iodide (**17**) in 2 ml of dry ether was added during 5 min at −30°, the reaction mixture was stirred an additional 15 min at −30°, and was then left during 90 min to reach room temperature. The mixture was poured into an excess of saturated aqueous ammonium chloride, filtered through celite, extracted with ether, and the ethereal extract was washed (saturated NH_4Cl and NaCl), dried ($MgSO_4$) and concentrated. Filtration of the oily crystalline residue through a column of 40 g of silica gel, with hexane as a solvent, afforded 0.5 g (66%) of cis-*2-undecene* (**18a**), b.p. 90–100°/11 Torr (bulb distillation), 97% *cis.*

B) Using the conditions and quantities described in experiment A) *trans*-propenyl bromide (**1b**) (88% *trans*, 12% *cis*) gave a dark blue cuprate which with 1-octyl iodide (**17**) afforded 0.55 g (73%) of trans-*2-undecene* (**18b**), b.p. 90°/11 Torr (bulb distillation), 77% *trans.*

18a. NMR. spectrum: 0.9 (3H, CH_3), 1.55 (3H, *d*, $J = 5$ Hz, $C{=}C{-}CH_3$), 5.1–5.5 (2H, *m*, CH=CH) ppm. IR. spectrum (neat): 3010 (C=CH), 1650 (C=C), 695 (CH=CH) *cis* cm^{-1}. Mass spectrum: 154 (26), 126 (2), 111 (8), 97 (20), 83 (34), 69 (73), 55 (100), 43 (80), 41 (81), 29 (48).

$C_{11}H_{22}$ Calc. C 85.63 H 14.37% Found C 85.63 H 14.67%

18b. NMR. spectrum: 0.9 (3H, CH_3), 1.6 (3H, *m*, $C{=}C{-}CH_3$); 5.17–5.5 (2H, *m*, CH=CH *trans*) ppm. IR. spectrum (neat): 3020 (C=CH), 1655 (C=C), 965 (CH=CH *trans*) cm^{-1}. Mass spectrum: 154 (27), 126 (2), 111 (8), 97 (21), 83 (33), 69 (70), 55 (100), 43 (76), 41 (77), 29 (44).

$C_{11}H_{22}$ Calc. C 85.63 H 14.37% Found C 85.67 H 14.31%

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