mixture of butenes was injected into (1) a 0.30 *M* solution of silver nitrate in DMSO; (2) a mixture of silver iodide and silver nitrate in DMSO which resulted from the reaction of 0.22 *M* 2-butyl iodide with 0.30 *M* silver nitrate in DMSO; (3) a 0.11 *M* solution of silver nitrate in *tert*-butyl alcohol; and (4) a mixture of silver iodide and silver nitrate in *tert*-butyl alcohol which resulted from the reaction of 0.10 *M* 2-butyl iodide with 0.11 *M* silver nitrate in *tert*-butyl alcohol. The results which follow (Table V) demonstrate the stability of olefinic products to the reaction conditions.

Reaction of 2-Butyl Bromide with Silver Nitrate in *tert*-Butyl Alcohol in the Presence of Silver Bromide.—To 5 ml of a 0.11 *N* solution of silver nitrate in *tert*-butyl alcohol in the reaction apparatus was injected 0.2 ml of 0.5 *N* solution of HBr in slightly aqueous *tert*-butyl alcohol. Into the resulting milky white suspension was immediately injected 0.08 g of 2-butyl bromide. The reaction was then carried out in the customary fashion.

It was subsequently demonstrated that reaction of 2-butyl bromide with HBr in *tert*-butyl alcohol produced negligible yields of butenes under the reaction conditions.

Registry No.—$AgNO_3$, 7761-88-8; 2-BuI, 513-48-4; 2-BuBr, 78-76-2; $AgClO_4$, 7783-93-9; AgOAc, 563-63-3; $Hg(NO_3)_2$, 10045-94-0; AgI, 77883-96-2; AgBr, 7785-23-1; $HgBr_2$, 7789-47-1.

Reactions of π-Allylic Nickel(II) Bromide with Organic Halides. A Novel Synthesis of Monoterpenoid Compounds[1]

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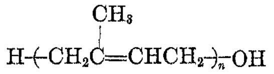
A novel synthesis of monoterpenoid compounds from isoprene as a major starting material is described. Reaction of isoprene with *N*-bromosuccinimide in ethanol or glacial acetic acid gives 1-bromo-4-ethoxy-2-methyl-2-butene and 4-acetoxy-1-bromo-2-methyl-2-butene, respectively. The two allylic bromides react in benzene with 1,1-dimethyl-π-allylnickel bromide prepared by reacting prenyl bromide with excess nickel carbonyl to give geranyl ethyl ether and geranyl acetate, respectively. Under similar condition, ethyl γ-bromosenecioate and 1,1-dimethyl-π-allylnickel bromide give ethyl geranate in a moderate yield.

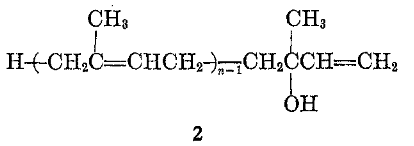
The synthesis of polyprenyl alcohols **1** and **2**, which are not only naturally occurring terpenes but also serve as important materials for synthesis, is achieved by a five-carbon (isoprene skeleton) homologation involving successive two- and three-carbon elongation reactions.[2] This method suffers from low over-all yields in the synthesis of higher analogs of **1** and **2**.

Previously we have reported[3] that such a C-5 homologation can be achieved in one step by using an organophosphorus compound, 4-pentyn-1-ylidenetriphenylphosphorane. This reacted with a isoprenoid ketone to afford its higher analogs *via* the intermediate γ,δ-unsaturated acetylene. In the present paper we describe another method for the desired chain extension, using π-allylnickel complexes.



$$H\!\left(CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CHCH_2\right)_{\!n}OH$$

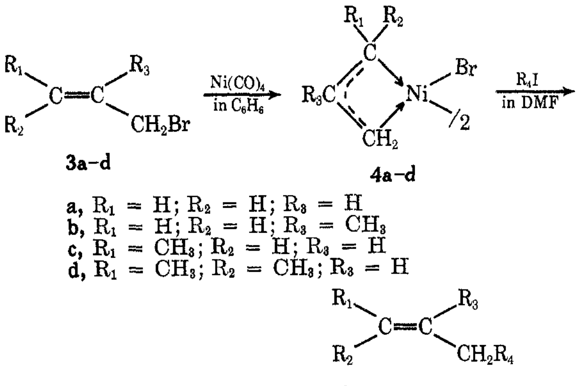
1



$$H\!\left(CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CHCH_2\right)_{\!n-1}CH_2\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}CH{=}CH_2$$

2

During the last decade, organo-transition metal compounds have been shown to be interesting and useful substances in synthetic chemistry. For instance, an efficient and useful method for the attachment of an allylic group **3** to an alkyl, vinyl, or aryl unit by means of π-allylnickel reagents has recently been described by Corey and Semmelhack.[4] However, because these π-allylnickel halides **4**, which can be obtained expeditiously by the reaction of allylic halides **3** with nickel carbonyl in benzene are somewhat unstable and air-sensitive, the purification of these π-allylic complexes must be conducted below room temperature with rigorous exclusion of oxygen. In a preliminary experiment we found that this troublesome purification can be omitted without any noticeable diminution of yields to give **5a–d** (See Experimental Section).



3a–d

4a–d

a, R_1 = H; R_2 = H; R_3 = H
b, R_1 = H; R_2 = H; R_3 = CH_3
c, R_1 = CH_3; R_2 = H; R_3 = H
d, R_1 = CH_3; R_2 = CH_3; R_3 = H

5a–d, $R_4 = C_6H_5$
e, $R_1 = R_2 = R_3 = H$; $R_4 = (CH_3)_2CHCH_2CH_2$

We intended at first to generate the π-allylnickel complex from an allylic halide possessing a functionalized carbon substituent which can be elaborated to an allylic halide function. Thus, ethyl *trans*-γ-bromocrotonate (**6a**) was heated with nickel carbonyl in benzene, the progress of the reaction being evidenced by evolution of carbon monoxide and the appearance

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[1] A portion of this paper was presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April 1970.

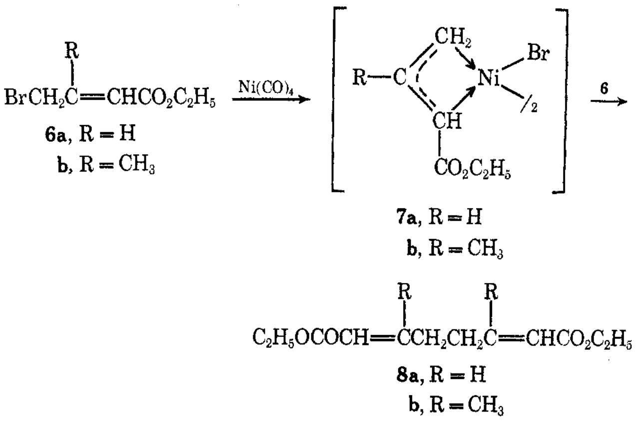
[2] (a) W. Kimel and A. C. Cope, *J. Amer. Chem. Soc.*, **65**, 1992 (1943); (b) O. Isler and K. Doebel, *Helv. Chim. Acta*, **37**, 225 (1954); (c) G. Saucy and R. Marbet, *ibid.*, **50**, 2091 (1967).

[3] K. Sato, S. Inoue, and S. Ota, *J. Org. Chem.*, **35**, 565 (1970).

[4] (a) E. J. Corey and M. F. Semmelhack, *J. Amer. Chem. Soc.*, **89**, 2755 (1967); (b) E. J. Corey and E. K. Wat, *ibid.*, **89**, 2757 (1967); (c) E. J. Corey and E. Hamanaka, *ibid.*, **89**, 2758 (1967).

of characteristic red color. However, treatment of the mixture with iodobenzene in *N*,*N*-dimethylformamide (DMF) resulted in the isolation of the self-condensation product of **6a**, diethyl 2,6-octadiene-1,8-dioate (**8a**) as a mixture of trans,trans and trans,cis isomers, but no cross-coupled product, ethyl γ-phenylcrotonate. Iodobenzene was recovered almost quantitatively.

To determine the manner in which the dimerization product **8a** was formed, the reaction mixture was quenched with hydrogen bromide before being treated with iodobenzene. By this operation **8a** was also obtained. This indicates that the rate of the coupling reaction of **6a** with the π complex **7a** formed by the initial interaction of **6a** and nickel carbonyl is very rapid even in nonpolar solvent such as benzene, in which coupling of π-allylnickel bromide with allyl bromide proceeds to only a slight degree (*vide supra*), although the corresponding methyl ester of **6a** has been reported[5] to undergo dimerization in ethyl ether, acetone, or methyl acetate in the presence of nickel carbonyl.



$BrCH_2C(R)=CHCO_2C_2H_5 \xrightarrow{Ni(CO)_4}$

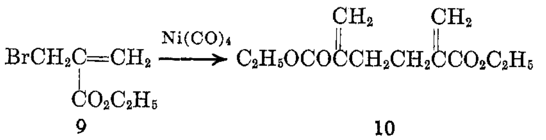
6a, R = H
b, R = CH_3

7a, R = H
b, R = CH_3

$C_2H_5OCOCH=C(R)CH_2CH_2C(R)=CHCO_2C_2H_5$

8a, R = H
b, R = CH_3

A similar result was obtained with ethyl γ-bromosenecioate (**6b**). Because these results might reflect an activating effect of the ethoxycarbonyl group on the allylic bromide function of 4-bromo-2-butenoate esters **6a** and **6b**, it became of interest to study ethyl α-bromomethylacrylate (**9**), a positional isomer of **6a**. When **9** was reacted with nickel carbonyl in benzene at 50°, the dimer of **9**, diethyl 2,5-dimethylene-1,6-hexanedioate, was obtained in 70% yield.[6]

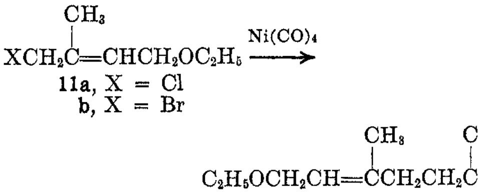


$$BrCH_2C(CO_2C_2H_5)=CH_2 \xrightarrow{Ni(CO)_4} C_2H_5OCOC(=CH_2)CH_2CH_2C(=CH_2)CO_2C_2H_5$$

9 **10**

We were thus unable to isolate ethoxycarbonyl-substituted π-allylnickel bromides irrespective of the position of substitution. Hence, we considered the use of another series of allylic halides, *i.e.* allyl halides substituted with a protected hydroxymethyl radical. Thus, *trans*-1-chloro-4-ethoxy-2-methyl-2-butene[7] (**11a**) was heated with nickel carbonyl in benzene at 50°; the mixture gradually exhibited a pink coloration, indicating very slow reaction of the substrate with nickel carbonyl. Heating for 3 hr, followed by the usual work-up resulted in almost quantitative recovery of the starting chloride **11a**.

On the other hand the bromo analog of **11a**, *trans*-1-bromo-4-ethoxy-2-methyl-2-butene (**11b**) reacted with nickel carbonyl in benzene at 50° with evolution of carbon monoxide, but the corresponding π complex could not be isolated and the self-coupled dimer, 1,8-diethoxy-3,6-dimethyl-2,6-octadiene (**12**) was obtained instead in 72% yield as a mixture of trans,trans and trans,cis isomers.

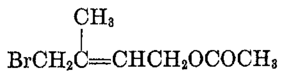


$$XCH_2C(CH_3)=CHCH_2OC_2H_5 \xrightarrow{Ni(CO)_4}$$

11a, X = Cl
b, X = Br

$$C_2H_5OCH_2CH=C(CH_3)CH_2CH_2C(CH_3)=CHCH_2OC_2H_5$$

12



$$BrCH_2C(CH_3)=CHCH_2OCOCH_3$$

13

In contrast to **11a** and **11b**, *trans*-4-acetoxy-1-bromo-2-methyl-2-butene (**13**) was found to react clearly with nickel carbonyl under similar condition. However, neither the starting bromide **13** nor the self-coupled dimer was obtained from the reaction mixture. It seems most probable that isoprene was generated in this reaction by analogy to what was observed in the use of 1-acetoxy-4-chloro-2-butene.[8]

The results described so far led to the conclusion that allylic bromides **6a**, **6b**, **9**, and **11b** are so reactive that they react easily with the π complexes generated by the reaction of the bromide itself with nickel carbonyl to afford self-coupled dimers. These results suggested in turn that these reactive bromides would readily react with a simple π-allylnickel bromide under the present reaction conditions.

Thus, the investigation was extended to the reactions of the π-allylnickel complexes **4** with allylic bromides **6b**, **9**, etc. As expected, dropwise addition of ethyl γ-bromosenecioate (**6b**) to the solution of 1,1-dimethyl-π-allylnickel bromide (**4d**) in benzene at 50° resulted in the formation of ethyl 3,7-dimethyl-2,6-octadienoate (ethyl geranate) (**14**) in 40% yield. Surprisingly, however, similar reaction of ethyl α-bromomethylacrylate (**9**) with **4d** in benzene at 50° for 3 hr afforded 70% ethyl 2,5-dimethylene-1,6-hexanedioate (**10**), which had previously been obtained by the direct reaction of **9** with nickel carbonyl. On the other hand, the reaction of **11b** and **13** with **4d** gave geranyl ethyl ether (**15**) and geranyl acetate (**16**), respectively, in moderate yields.

The distinct course of the reaction of **9** with **4d** can be interpreted as follows: the cross-coupling reaction of **9** and **4d** to give ethyl 2-methylene-6-methyl-5-heptenoate is slower than the ligand-exchange reaction[9]

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[5] G. P. Chiusoli and G. Cometti, *Chim. Ind.* (*Milan*), **45**, 401 (1963).

[6] E. J. Corey and M. F. Semmelhack [*Tetrahedron Lett.*, 6237 (1966)] reported that the corresponding π-allylic complex of **9** was obtained by the reaction of bis(1,5-cyclooctadiene)nickel or nickel carbonyl with **9** in benzene, but the experimental detail was not described.

[7] W. Oroshnik and R. A. Mallory, *J. Amer. Chem. Soc.*, **72**, 4608 (1950).

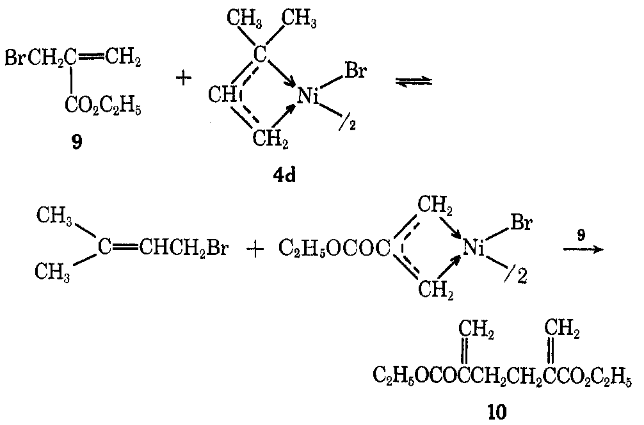
[8] J. B. Mettalia and E. H. Specht, *J. Org. Chem.*, **32**, 3941 (1967).

[9] E. J. Corey, *et al.* [*J. Amer. Chem. Soc.*, **90**, 2417 (1968)], reported the occurrence of rapid exchange reactions according to the equation (A = allyl)

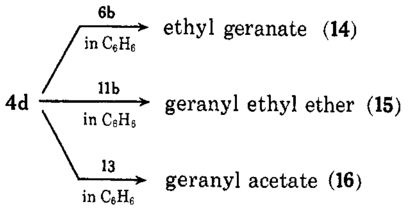
$$(\pi\text{-}A^1NiBr)_2 + 2A^2Br \rightleftharpoons (\pi\text{-}A^2NiBr)_2 + 2A^1Br$$

under several solvent systems including tetraglyme, DMF, and toluene. The present observation is an another example of rapid exchange reaction occurring in hydrocarbon solvent.

between **9** and **4d** which generates prenyl bromide (**3d**) and 2-carbethoxy-π-allylnickel bromide. The latter compound then reacts rapidly with **9** to afford **10**.



All the other reactions afforded mainly cross-coupling products. The formation of dimers **8b** and **12** was minimal indicating that the exchange reactions[9] occur only to a very small extent, if at all.



It is evident that the present reaction provides a highly convenient procedure for achieving a C-4 or C-5 homologation. At the same time extension of this reaction provides a facile route for the synthesis of polyprenyl alcohols **1** and other acyclic terpenes using isoprene as the sole starting material. The realization of this synthesis as well as the examination of the stereochemical course of the reaction including π-allylic nickel complex is in progress in these laboratories.

Experimental Section

General.—Boiling points are uncorrected. Infrared spectra were recorded with a Hitachi Model EPI-S2 spectrophotometer. Nmr spectra were obtained on a JEOL Model C-60 spectrometer in carbon tetrachloride solution with tetramethylsilane as an internal reference. Gas chromatography was carried out on a Shimadzu GC-4A gas chromatograph using a 3-mm, 300-cm column of 25% silicone DC-200 or 3-mm, 190-cm of 15% Carbowax 20M on Celite 545 with He as the carrier gas.

Allyl bromide,[10] methallyl bromide,[11] crotyl bromide,[12] prenyl bromide,[13] isoamyl iodide,[14] ethyl γ-bromocrotonate,[15] ethyl γ-bromosenecioate,[15] ethyl α-bromomethylacrylate,[16] and 4-acetoxy-1-chloro-2-methyl-2-butene[7,17] were prepared by the methods described in the literature. The other chemicals were commercially available and purified by usual procedures before use. All reactions of π-allylnickel complexes were carried out in a nitrogen atmosphere.

Allylbenzene (5a). The Typical Procedure of the Reaction of Iodobenzene with Simple π-Allylic Nickel Bromide.—Allyl bromide (6.8 g, 50 mmol) and nickel carbonyl (14.5 g, 85 mmol) in benzene (85 ml) were heated with stirring at 50° for 3 hr. Benzene and any remaining nickel carbonyl were removed under reduced pressure at room temperature and the residue was dissolved in DMF (40 ml) with cooling in an ice-water bath. To this solution was added iodobenzene (8.6 g, 42 mmol) in DMF (40 ml) at 22° over 1 hr. Stirring was continued further for 2 hr. The mixture was then poured into ice-water, acidified by hydrochloric acid, and extracted with petroleum ether (bp 40–60°). The organic layer was washed with saturated brine and dried with magnesium sulfate. Distillation gave allylbenzene (**5a**) (4.1 g, 82%): bp 74–77° (46 mm), $n^{20}\text{D}$ 1.5103 (lit.[18] bp 158–159°, $n^{20}\text{D}$ 1.5104).

A similar procedure afforded methallylbenzene [**5b**, 81%, bp 77–78° (32 mm), $n^{20}\text{D}$ 1.5094], crotylbenzene [**5c**, 75%, bp 72–76° (23 mm), $n^{20}\text{D}$ 1.5221],[19] and prenylbenzene [**5d**, 75%, bp 74–77° (8 mm), $n^{20}\text{D}$ 1.5165] by using methallyl bromide, crotyl bromide, and prenyl bromide, respectively, instead of allyl bromide.

6-Methyl-1-heptene (5e).—Allyl bromide (4.5 g, 37 mmol) and nickel carbonyl (8.5 g, 50 mmol) were allowed to react by the procedure described above. Solvent was removed under reduced pressure, DMF (30 ml) was added in return, and isoamyl iodide (5.3 g, 27 mmol) in DMF (30 ml) solution was added at 22°, and the mixture was allowed to react for 19 hr. Distillation gave 6-methyl-1-heptene (0.9 g, 30%): bp 110–113.5° (676 mm), $n^{20}\text{D}$ 1.4052 (lit.[20] bp 113.2°, $n^{20}\text{D}$ 1.4068).

This compound was identified by comparison of ir, nmr, and vpc retention time with those of an authentic sample obtained from allyl magnesium chloride and isoamyl chloride in tetrahydrofuran.[20]

Diethyl 2,6-Octadiene-1,8-dioate (8a).—Ethyl *trans*-γ-bromocrotonate (5.8 g, 30 mmol) in benzene (32 ml) was added dropwise to a solution of nickel carbonyl (8.5 g, 50 mmol) in benzene (48 ml) at 50° during 1.5 hr, and the mixture was stirred at 50° for 1.5 hr. The solvent was evaporated under reduced pressure (10–20 mm); the residue was dissolved in 25 ml of DMF. To this solution was added iodobenzene (51g, 25 mmol) over 1 hr. The mixture was stirred at 22° for 3 hr, poured into ice-water, acidified with diluted hydrochloric acid, and extracted with petroleum ether (bp 35–50°). The organic layer was washed with aqueous sodium bicarbonate, dried over magnesium sulfate, and distilled, giving iodobenzene (4.4 g, 86% recovery) and 3.0 g (76%) of diethyl 2,6-octadiene-1,8-dioate: bp 115–118° (0.45 mm); $n^{20}\text{D}$ 1.4725 [lit.[21] bp 97–99° (0.3 mm); $n^{20}\text{D}$ 1.4606]; ir (neat) 1715, 1650, 1265, 1175, 975 cm^{-1}; nmr δ 1.26 (t, CH_3, 6 H, J = 7 Hz), 2.37 and 2.80 (each dt, CH_2CH_2, total 4 H), 4.11 (q, OCH_2, 2 H, J = 7 Hz), 5.72 and 5.75 (each d, C=CHCOO, total 2 H), 6.18 and 6.88 (each dt, CH_2CH=C, total 2 H).

Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.54; H, 8.25.

Vpc analysis of the product on a 15% Carbowax 20M on Celite 545 column (1.9 m) at 225° showed two peaks (4.7 and 6.4 min) in the ratio of 65:35. The relative integrals at δ 2.37, 6.88 (dt, J = 7 and 17 Hz), and 5.75 (d, J = 17 Hz) (*trans*-CH_2CH=CH-COO) and 2.80, 6.18 (each dt, J = 7 and 12 Hz), and 5.72 (d, J = 12 Hz) (*cis*-CH_2CH=CHCOO) were measured and the product ratio was determined as *trans,trans*-**8a** (35%) and *trans,cis*-**8a** (65%).

Diethyl 3,6-Dimethylocta-2,6-diene-1,8-dioate (8b).—A solution of ethyl γ-bromosenecioate (mixture of stereoisomers, 6.2 g 30 mmol), and nickel carbonyl (8.5 g, 50 mmol) in benzene (85 ml) was stirred at 50° for 2 hr, and then, after remaining nickel carbonyl was removed under reduced pressure, acidified with 0.8 *N* HBr–benzene solution, washed with water, dried, and distilled to give diethyl 3,6-dimethylocta-2,6-diene-1,8-dioate (2.1 g, 73%): bp 119° (0.45 mm); $n^{20}\text{D}$ 1.4810 [lit.[22] bp 105–106° (0.1

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[10] O. Kamm and C. M. Marvel, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 27.

[11] (a) P. Teuscher, *J. Amer. Chem. Soc.*, **72**, 4316 (1950). (b) B. K. Merejkowsky, *Bull. Soc. Chim. Fr.*, **37**, 711 (1925).

[12] W. G. Young and J. F. Lane, *J. Amer. Chem. Soc.*, **59**, 2054 (1937).

[13] J. Tanaka, T. Katagiri and S. Yamada, *Nippon Kagaku Zasshi*, **87**, 877 (1966).

[14] H. S. King, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 399.

[15] A. Akiyoshi and K. Ueno, *Nippon Kagaku Zasshi*, **73**, 126 (1952).

[16] A. F. Ferris, *J. Org. Chem.*, **20**, 780 (1955).

[17] A. A. Petrov and T. A. Zyryanow, *Zh. Obshch. Khim.*, **26**, 2189 (1956).

[18] W. H. Urry and M. S. Kharasch, *J. Amer. Chem. Soc.*, **66**, 1438 (1944).

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[20] A. L. Henne, H. Chanan, and A. Jurk, *J. Amer. Chem. Soc.*, **63**, 3474 (1941).

[21] G. I. Bazilevskaya, D. V. Gura, M. S. Bainova, K. M. Dyumaev, I. K. Sarycheva, and N. A. Preobrazhenskii, *Zh. Obshch. Khim.*, **28**, 1097 (1958).

[22] J. P. Petrovich, J. D. Anderson, and M. M. Baizer, *J. Org. Chem.*, **31**, 3897 (1966).

mm); n^{20}D 1.4762]; ir (neat) 1715, 1220, 1155, 860 cm^{-1}; nmr δ 1.24 (t, CH_3, 6 H, J = 7 Hz), 1.89 (s, *trans*-CH_3, 3 H), 2.17 (s, *cis*-CH_3, 3 H), ~2.07–2.37 and ~2.59–2.90 (m, CH_2CH_2, 4 H), 4.06 (q, OCH_2, 4 H, J = 7 Hz), 5.62 (s, =CH, 2 H).

Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 66.24; H, 8.87.

The product showed only one peak on vpc, using a 3 mm × 190 cm column of Carbowax 20M, and was shown to be *trans,cis*-**8b** by analysis by nmr spectra.

Diethyl 2,5-Dimethylene-1,6-hexanedioate (10).—Ethyl α-bromomethylacrylate (**9**) (5.2 g, 28 mmol) was treated with nickel carbonyl (6.67 g, 39 mmol) in benzene (81 ml) at 50° for 3 hr. The usual work-up described above afforded diethyl 2,5-dimethylene-1,6-hexanedioate (2.2 g, 70%): bp 134–138° (0.75 mm); n^{20}D 1.4527 [lit.[23] bp 81–82° (0.1 mm); $n^{25.5}$D 1.4470]; ir (neat) 1720, 1629, 1195, 1140, 940, 920 cm^{-1}; nmr δ 1.30 (t, CH_3, 6 H, J = 7.2 Hz), 2.42 (s, CH_2CH_2, 4 H), 4.15 (q, OCH_2, 4 H, J = 7.2 Hz), 5.48 and 6.08 (each s, =CH_2, 4 H).

Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.98; H, 8.09.

1-Bromo-4-ethoxy-2-methyl-2-butene (11b).—Isoprene (34 g, 0.5 mol) was dissolved in 200 ml of absolute ethanol at 10°, and *N*-bromosuccinimide (36 g, 0.2 mol) was added at 10° to react for 5 hr, then at 30° for 3 hr. Products were extracted with ether and dried with magnesium sulfate. Distillation gave 22 g (56%) of 4-bromo-3-ethoxy-3-methyl-1-butene, bp 63–64° (20 mm), n^{20}D 1.4720 [lit.[17] bp 60–62.2° (20 mm)], and 5 g (13%) of *trans*-1-bromo-4-ethoxy-2-methyl-2-butene, bp 62–63° (8 mm), n^{20}D 1.4852 (lit.[17] bp 100–104.5° (50 mm)]. The former product showed the following spectra: ir (neat) 1640, 1440, 1410, 1390, 1370, 1105, 1065, 995, 930 cm^{-1}; nmr δ 1.15 (t, CH_3, 3 H, J = 7 Hz), 1.38 (s, CH_3, 3 H), 3.32 (s, $BrCH_2$, 2 H), 3.39 (q, OCH_2, 2 H, J = 7 Hz), 5.19 and 5.27 (each d, =CH_2, total 2 H, J = 18 and 11 Hz, respectively), 5.90 (dd, CH=C, 1 H, J = 18 and 11 Hz).

Anal. Calcd for $C_7H_{13}BrO$: C, 43.54; H, 6.78. Found: C, 43.92; H, 6.88.

The latter (**11b**) had the following spectra: ir (neat) 1655, 1430, 1368, 1192, 1090, 1000, 970 cm^{-1}; nmr δ 1.17 (t, CH_3, 3 H, J = 7 Hz), 1.90 (s, CH_3, 3 H), 3.41 (q, OCH_2, 2 H, J = 7 Hz), 3.91 (s, $BrCH_2$, 2 H), 3.93 (d, OCH_2, 2 H, J = 10 Hz), 5.72 (t, CH=C, 1 H, J = 10 Hz).

Anal. Calcd for $C_7H_{13}BrO$: C, 43.54; H, 6.78. Found: C, 42.98; H, 6.23.

4-Acetoxy-1-bromo-2-methyl-2-butene (13).—Isoprene (34 g, 0.5 mol) was dissolved in 200 ml of glacial acetic acid at 10°, *N*-bromosuccinimide (36 g, 0.2 mol) was added, and the mixture was allowed to react for 8 hr. The reaction mixture was extracted with ether and dried with magnesium sulfate. Distillation gave 18.6 g (45%) of 3-acetoxy-4-bromo-3-methyl-1-butene, bp 41–43° (5 mm), n^{20}D 1.4942, and 6.5 g (16%) of 4-acetoxy-1-bromo-2-methyl-2-butene, bp 95–100° (6 mm), n^{20}D 1.4902 [lit.[17] bp 108° (12 mm), $n^{24.3}$D 1.4906]. The former ester showed the following spectra: ir (neat) 1735, 1640, 1445, 1410, 1250, 1170, 1020, 990, 930 cm^{-1}; nmr δ 1.61 (s, CH_3, 3 H), 2.01 (s, CH_3CO_2–, 3 H), 3.75 (s, $BrCH_2$, 2 H), 5.22 and 5.25 (each d, =CH_2, total 2 H, J = 10 and 17 Hz, respectively), 6.11 (dd, CH=C, 1 H, J = 10 and 17 Hz).

Anal. Calcd for $C_7H_{11}BrO_2$: C, 40.59; H, 5.37. Found: C, 40.35; H, 5.26.

The latter ester showed the following spectra: ir (neat) 1735, 1668, 1440, 1385, 1230, 1030, 964 cm^{-1}; nmr δ 1.88 (s, CH_3, 3 H), 2.02 (s, CH_3COO, 3 H), 3.95 (s, $BrCH_2$, 2 H), 4.58 (d, CH_2O, 2 H, J = 7 Hz), 5.73 (t, =CH, 1 H, J = 7 Hz).

Anal. Calcd for $C_7H_{11}BrO_2$: C, 40.59; H, 5.37. Found: C, 40.28; H, 5.21.

The latter compound **13** was also obtained by another method, starting from *trans*-1,4-dibromo-2-methyl-2-butene.[24] The mixture of *trans*-1,4-dibromo-2-methyl-2-butene (8.6 g, 33 mmol) and 3.2 g (33 mmol) of dry potassium acetate in 80 ml of *N,N*-dimethylformamide (DMF) was stirred at 0–1° for 18 hr, and the product was extracted with petroleum ether (bp 35–50°) and dried with magnesium sulfate. Distillation of the product gave only *trans*-4-acetoxy-1-bromo-2-methyl-2-butene (3.2 g, 46%), bp 73–74° (0.3 mm), n^{20}D 1.4896.

This compound was identified by comparison of ir, nmr, and retention time by vpc with those of an authentic sample obtained from the previous method.

1,8-Diethoxy-3,6-dimethyl-2,6-octadiene (12).—The method was the same as that described before. The mixture of 1-bromo-4-ethoxy-2-methyl-2-butene (4.8 g, 25 mmol) and nickel carbonyl (6.8 g, 40 mmol) in benzene (85 ml) was stirred at 50° for 3 hr, after substitution of solvent, 4.1 g (20 mmol) of iodobenzene in 30 ml of DMF, solution was added at 22°, and the mixture was allowed to react for 8 hr. A similar work-up as described before afforded 3.8 g (92% recovery) of iodobenzene, and 2.1 g (72%) of 1,8-diethoxy-3,6-dimethyl-2,6-octadiene: bp 64–65° (0.3 mm); n^{20}D 1.4631; ir (neat) 1660, 1440, 1338, 1100, 1030 cm^{-1}; nmr δ 1.17 (t, CH_3, 3 H, J = 7 Hz), 1.68 (s, CH_3, 6 H), ~2.05–2.57 (m, CH_2CH_2, 4 H), 3.40 (q, OCH_2, 4 H, J = 7 Hz), 3.92 (d CH_2O, 4 H, J = 11 Hz), 4.73 and 5.30 (each broad s, =CH, total 2 H).

Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58. Found: C, 73.88; H, 11.41.

Vpc analysis of the product on a 15% Carbowax 20M on Celite 545 column (1.9 m) at 170° showed two peaks (7.2 and 8.3 min) in the ratio of 60:40, respectively. The former peak (60%) was thought to be *trans,cis*-**12** and the latter (40%) to be *trans,trans*-**12**.

Ethyl 3,7-Dimethyl-2,6-octadienoate (14).—Prenyl bromide (5.4 g, 36 mmol) was allowed to react with nickel carbonyl (8.5 g, 50 mmol) in benzene (80 ml) at 50° for 2.5 hr. Excess nickel carbonyl was removed under reduced pressure, and 6.2 g (30 mmol) of ethyl γ-bromosenecioate in benzene (34 ml) was added at 50° during 1.5 hr. Reaction was continued for 3 hr more, and the reaction mixture was extracted with ether and dried with magnesium sulfate. Distillation gave ethyl 3,7-dimethyl-2,6-octadienoate (2.3 g, 40%): bp 102–104° (10 mm); n^{20}D 1.4716 [lit.[25] bp 112–114° (10 mm); n^{20}D 1.4667]; ir (neat) 1740, 1660' 1455, 1384, 1220, 1150, 1060, 1040, 850 cm^{-1}; nmr δ 1.25 (t, CH_3, 3 H, J = 7 Hz), 1.62, 1.69, and 1.88 (each s, CH_3, 9 H), ~2.02–2.37 and ~2.48–2.75 (m, CH_2CH_2, 4 H), 4.08 (q, OCH_2, 2 H, J = 7 Hz), 5.10 (broad s, =CH, 1 H), 5.58 (s, CH=, 1 H).

The product showed two peaks on vpc in the ratio of 70:30. The first (70%) peak was identified as ethyl *cis*-geranate and the latter as ethyl *trans*-geranate by comparison of nmr spectra and vpc retention time with those of the authentic samples prepared by oxidizing citral with silver oxide[25] to geranic acid followed by esterification.

Reaction of Ethyl α-Bromomethylacrylate with 4d.—To the solution of 1,1-dimethyl-π-allylnickel bromide [prepared from 7.5 g (50 mmol) of prenyl bromide and 12 g (70 mmol) of nickel carbonyl in 80 ml of benzene] was added 7.9 g (40 mmol) of ethyl α-bromomethyl acrylate in 30 ml of benzene at 50° over 30 min, and the mixture was stirred at 50° for 5 hr, cooled, poured into ice-water, extracted with ether, and dried. Distillation gave 3.1 g (70%) of diethyl 2,5-dimethylene-1,6-hexanedioate (**10**): bp 87–91° (0.7 mm); n^{20}D 1.4492 [lit.[23] bp 81–82° (0.1 mm); $n^{25.5}$D 1.4470].

This compound was identified by comparison of ir, nmr, and vpc retention time with those of an authentic sample obtained by reaction of ethyl α-bromomethylacrylate and nickel carbonyl as described before.

Geranyl Ethyl Ether (15).—To a solution of 1,1-dimethyl-π-allylnickel bromide (prepared from 7.5 g of prenyl bromide and 12 g of nickel carbonyl as described above) was added 5.8 g (30 mmol) of 1-bromo-4-ethoxy-2-methyl-2-butene in benzene (23 ml) solution at 50° over 1.5 hr, and the mixture was stirred at 50° for 5 hr. The usual work-up described above afforded 2.4 g (45%) of geranyl ethyl ether: bp 115–118° (20 mm); n^{20}D 1.4665 [lit.[26] bp 115° (19 mm); n^{20}D 1.4662].

This compound was identified as *trans*-geranyl ethyl ether, containing below 5% of cis form (neryl ethyl ether) by comparison of ir, nmr, and vpc retention time with those of an authentic sample obtained from the reaction of *trans*-geranyl bromide and sodium ethoxide in absolute ethanol at 35–40°.

Geranyl Acetate (16).—A solution of 1,1-dimethyl-π-allylnickel bromide prepared as described previously and 4-acetoxy-1-bromo-2-methyl-2-butene (6.2 g, 30 mmol) in benzene (100 ml) was stirred at 50° for 6 hr. After cooling, the solution was poured into ice-water and acidified with hydrochloric acid, and the aqueous phase was extracted with ether. The combined

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[23] C. S. Marvel and R. D. Vest, *J. Amer. Chem. Soc.*, **79**, 5771 (1957).

[24] (a) R. C. Krug and T. F. Yen, *J. Org. Chem.*, **21**, 1082 (1956). (b) V. L. Heasley, G. E. Heasley, S. K. Taylor, and C. L. Frye, *ibid.*, **35**, 2967 (1970).

[25] F. W. Semmler, *Ber.*, **23**, 2965, 3556 (1890).

[26] M. O. Forster and D. Cardwell, *J. Chem. Soc.*, **103**, 1338 (1913).

layer was washed with water and dried over magnesium sulfate. Removal of solvent and distillation of the product gave 3.5 g (60%) of geranyl acetate: bp 92–94° (3.5 mm); $n^{20}\text{D}$ 1.4645 (lit.[27] bp 242; $n^{20}\text{D}$ 1.4628). Vpc and nmr spectra analysis showed that the product was *trans*-geranyl acetate contaminated with a minor amount (below 5%) of the cis isomer (neryl acetate).

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[27] "The Merck Index," 8th ed, Merck & Co., Rahway, N. J., 1968, p 487.

Registry No.—**4a**, 12012-90-7; **4b**, 12145-58-3; **4c**, 32650-03-6; **4d**, 32650-02-5; *trans,trans*-**8a**, 32829-97-3; *trans,cis*-**8a**, 32829-98-4; *trans,cis*-**8b**, 32829-99-5; **10**, 32670-57-8; *cis*-**11b**, 32659-09-9; *trans*-**11b**, 32659-10-2; *trans,trans*-**12**, 32659-11-3; *trans,cis*-**12**, 32659-12-4; *cis*-**13**, 32659-13-5; *trans*-**13**, 32659-14-6; *cis*-**14**, 32659-20-4; *trans*-**14**, 32659-21-5.

Studies on Chrysanthemic Acid. VIII.[1] Syntheses of 1-Vinyl-2-isobutenyl- and 1,2-Diisobutenyl-3,3-dimethylcyclopropanes. Their Thermal Behavior in Comparison with *cis*-2,2-Dimethyl-3-isobutenylcyclopropyl Isocyanate and *cis*-2,2-Dimethyl-3-isobutenylcyclopropanecarboxaldehyde

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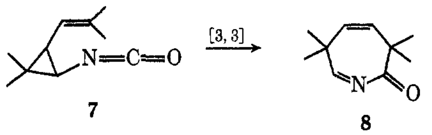
cis- (**9**) and *trans*-1-vinyl-2-isobutenyl- (**10**) and *cis*- (**11**), and *trans*-1,2-diisobutenyl-3,3-dimethylcyclopropanes (**12**) were prepared by the Wittig reaction of *cis*- (**13**) and *trans*-2-isobutenyl-3,3-dimethylcyclopropanecarboxaldehyde (**19**) with methylene- and isopropylidenetriphenylphosphoranes in 52–85% yields, respectively. Cis olefins **9** and **11** were both very stable at room temperature. However, heating the substances neat under nitrogen resulted exclusively in cis-trans isomerization but no Cope rearrangement; the ratio of **9** to **10** was 1:3 after 3 hr at 180° and that of **11** to **12** was 1:2.6 after 3 hr at 170°. From the first-order rate constants for the **11** → **12** isomerization, the kinetic parameters, E_a, log A, and $\Delta S^{\ddagger}$, were calculated as 33 kcal/mol, 12.4 sec^{-1}, and −3.8 eu (443°K), respectively. Similarly, from the rate constants for the Cope rearrangement of 2,2-dimethyl-3-isobutenylcyclopropyl isocyanate (**7**), E_a, log A, and $\Delta S^{\ddagger}$ were calculated as 23 kcal/mol, 7.06 sec^{-1}, and −29 eu (450°K), respectively. Thermal rearrangement of cis aldehyde **13** proceeded rapidly at 173° (the half-life = 14 min) affording exclusively 5-methyl-3-isopropyl-4-hexenal (**14**) by a homo[1,5]sigmatropic rearrangement. The characteristic thermal behavior of **7**, **9**, **11**, and **13** was explained in terms of the steric repulsion between the face to face methyl groups in the cis-like quasiboat transition state required for the Cope rearrangement, in comparison with the simple *cis*-divinylcyclopropane systems, **1**, **3**, and **5**.

It is well known that *cis*-divinylcyclopropane (**1**) cannot be isolated even at −45° because of its extremely facile Cope rearrangement to 1,4-cycloheptadiene (**2**).[2–4] Similar facile concerted bisallylic rearrangements have been recorded for the *cis*-vinylcyclopropyl isocyanate (**3**) → 3,6-dihydro-2*H*-azepin-2-one (**4**) system and the *cis*-vinylcyclopropanecarboxaldehyde (**5**) → 2,5-dihydrooxepin (**6**) system.[5–7] In a previous communication,[8] we reported that *cis*-2,2-dimethyl-3-isobutenylcyclopropyl (chrysanthemyl) isocyanate (**7**) was quite stable and that Cope rearrangement to **8** occurred only under drastic conditions at 144°. We now wish to report syntheses of *cis*- (**9**) and *trans*-1-vinyl-2-isobutenyl- (**10**) and *cis*- (**11**) and *trans*-1,2-diisobutenyl-3,3-dimethylcyclopropanes (**12**) and their thermal behavior in comparison with **7** and *cis*-2,2-dimethyl-3-isobutenylcyclopropanecarboxaldehyde (**13**).

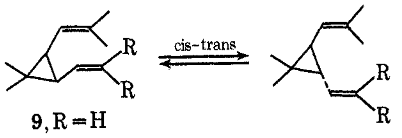
1, X = CH; Y = CH_2
3, X = N; Y = CO
5, X = CH; Y = O

2, X = CH; Y = CH_2
4, X = N; Y = CO
6, X = CH; Y = O



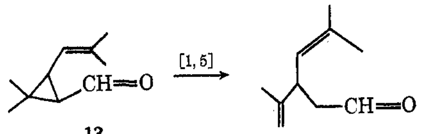
7

8



9, R = H
11, R = CH_3

10, R = H
12, R = CH_3



13

14

Results

cis-Chrysanthemyl alcohol (**15**) was converted to cis aldehyde **13** in 71% yield by oxidation with pyri-

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