Carbon-Carbon Bond Formation by the Use of Chloroiodomethane as a C_1 Unit. II.[1] The Preparation and Synthetic Application of 1-Chloro-3-iodoheptane[2]

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Terminal alkenes, R-CH=CH_2 (R=Et, *n*-Pr, *n*-Bu, *n*-Hex), were readily transformed into 1-chloro-3-iodoalkanes by the AIBN-induced free radical addition of chloroiodomethane. Thus, 1-chloro-3-iodoheptane was obtained from 1-hexene in an 88% yield; this in turn was allowed to react with dialkyl malonates in the presence of alkoxides in alcohols to give dialkyl 2-butylcyclobutane-1,1-dicarboxylates and dialkyl (*E*)-3-octene-1,1-dicarboxylates (**7**), either of which could be obtained preferentially by the choice of the experimental parameters. The olefinic product, **7**, was further utilized for the synthesis of (*E*)-5-decenyl acetate and/or 1,4-nonanolide.

The free radical-induced addition of polyhalogenated methanes to alkenes to give 1:1 products (Kharasch reaction) has been well known.[3] This reaction had, however, been practically restricted to those halides which contained no less than three halogen atoms unless they had other activating substituents, such as –CO– and –CN.[3a] In fact, only a few successful Kharasch reactions had been documented for dihalomethanes[4,5] before Walton *et al.* recently reported the peroxide- or photochemically initiated addition of chloroiodomethane and diiodomethane to ethylene and several fluoroalkenes from the mechanistic point of view.[6] Several other papers have claimed the formation of cyclopropanes *via* the reaction of diiodomethane with alkenes under the free radical reaction conditions.[7]

As part of a program directed toward a study of carbon–carbon bond formation by the use of chloroiodomethane as a C_1 unit,[1] we wish to report here a facile synthesis of 1-chloro-3-iodoalkanes (**1**) *via* the 2,2′-azobisisobutyronitrile (AIBN)-initiated addition of CH_2ClI to terminal alkenes. Also to be described is the utilization of 1-chloro-3-iodoheptane (**1c**) as an intermediate for several synthetic transformations, including a synthesis of (*E*)-5-decenyl acetate (**15**), a kind of insect pheromone.

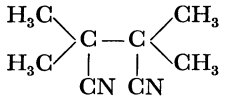
Results and Discussion

AIBN-initiated Addition of Chloroiodomethane to Terminal Alkenes. A mixture of CH_2ClI and AIBN in 1-alkene was stirred and heated at 80 °C for 6 h in a stainless steel autoclave. Employing *ca.* a 1/10 molar amount of AIBN to CH_2ClI, almost all of the halide was consumed to give 1-chloro-3-iodoalkanes in *ca.* 80—90% yields (Eq. 1 and Table 1).

Part of the AIBN was consumed in the formation of tetramethylsuccinonitrile **2**. Thus, when the molar ratio of AIBN to CH_2ClI was 1/20 or 1/100, the yield of 1-chloro-3-iodoheptane **1c** from 1-hexene was reduced to 38% or 17% respectively, leaving unchanged CH_2ClI, while appreciable amounts of the adduct (**1c**) were also obtained (6.2% yield) in the absence of the initiator.

$$R\text{-}CH{=}CH_2 + CH_2ClI \xrightarrow{AIBN} R\text{-}\underset{I}{CH}\text{-}CH_2\text{-}\underset{Cl}{CH_2} \quad (1)$$

1



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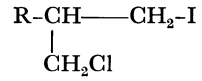

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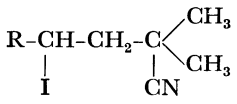

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The structure of the 1:1 adduct **1** was confirmed on the basis of its NMR spectra, which showed two hydrogens of $-CH_2Cl$ comprised of four lines of a double doublet centered at *ca.* δ 3.6 (A_2 portion of an A_2MM' system, $J_{AM}\approx5.5$ Hz, $J_{AM'}\approx6.5$ Hz) and one hydrogen of –CHI– at δ 4.5—4.0 as a mulitplet. The dehydroiodination reaction of the 1:1 adduct by potassium hydroxide in aq methyl alcohol also supported the 1-chloro-3-iodoalkane structure; **1d** gave (*E*)-1-methoxy-2-nonene (**5a**) and (*E*)-1-chloro-3-nonene (**6a**) as the major products. Small amounts of a substance

Table 1. AIBN-induced addition of CH_2ClI to R-CH=CH_2[a]

	R-CH=CH_2 R	R-CH(I)-CH_2-CH_2(Cl) (1) Yield[b]/%	Bp °C/mmHg	Found (Calcd)% C	H
a	Et	81 (54)	74—76/9.5	25.91 (25.83)	4.26 (4.34)
b	*n*-Pr	76 (48)	88—90/8	29.47 (29.23)	4.80 (4.91)
c	*n*-Bu	88 (81)	96—97/7	32.59 (32.27)	5.57 (5.42)[c]
d	*n*-Hex	80 (67)	112—115/2	37.75 (37.46)	6.13 (6.29)

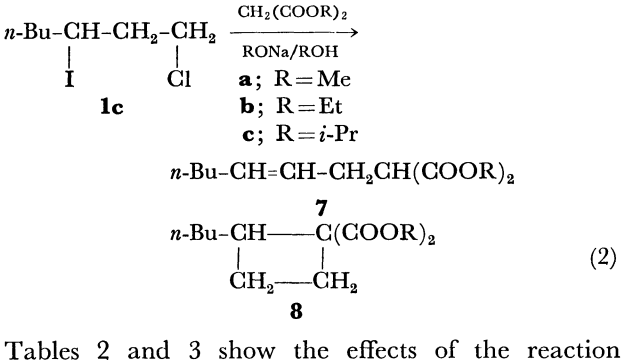
a) R-CH=CH_2, 15—20 ml; CH_2ClI, 3.0 ml (43 mmol); AIBN (mol)/CH_2ClI (mol)=1/10; 80 °C, 6 h. b) GLC yield based on CH_2ClI. Figures in parentheses show isolated yields. c) Halogen, 61.84%. Calcd for $C_7H_{14}ClI$: Cl, 13.61; I, 48.71%.

having a slightly longer GLC retention time than **1** were also detected (less than 4% of **1**). The substance was not isolated, but it seemed to have a branched chain structure, **3**, as was indicated by the reaction products from the dehydroiodination with potassium hydroxide in aq methyl alcohol (see Experimental). The isolation of the iodo nitrile **4** suggests that the initiation step of the radical chain involves mainly the attack of the isobutyronitrile radical from AIBN on the terminal carbon atom of the 1-alkenes.

Kaplan obtained cyclopropanes *via* a radical-induced methylene transfer from CH_2I_2 to alkenes using quite large amounts of peroxide initiators (more initiators than CH_2I_2 or alkenes).[7c] On the other hand, the AIBN-initiated addition of CH_2I_2 to 1-hexene gave 1,3-diiodoheptane in a 62% isolated yield under the reaction conditions of this work, while CH_2Br_2 was recovered unchanged.

An attempted addition to styrene resulted in the formation of a polymeric product, leaving CH_2ClI intact. Though little effort was made to optimize the reaction, extension to internal alkenes, including 2-heptenes, (*E*)-2-butene, (*E*)-stilbene, and cyclohexene, was not practical, either; large amounts of **2** were formed, and more than 80% of the CH_2ClI was recovered in these cases.

*Reaction of 1-Chloro-3-iodoheptane (**1c**) with Dialkyl Malonates/Alkoxides in Alcohols.* The treatment of **1c** with dimethyl malonate in the presence of sodium methoxide in methyl alcohol gave several products, as evidenced by GLC; among them we obtained dimethyl (*E*)-3-octene-1,1-dicarboxylate, **7a**, and dimethyl 2-butylcyclobutane-1,1-dicarboxylate, **8a**, as the major products in yields of 71% and 6.5% respectively (Eq. 2). Among other by-products were also identified (*E*)-1-methoxy-2-heptene, **5b**, and (*E*)-1-chloro-3-heptene, **6b**.



(2)

Tables 2 and 3 show the effects of the reaction variables on the relative yield of the olefinic products, **7**, to the ring-closure products, **8**. By the use of potassium *t*-butoxide or sodium isopropoxide, **1c** was preferentially transformed into the cyclobutanes, **8**, while dehydroiodination preceded when sodium methoxide or ethoxide was utilized, especially in lower concentrations. These results may be explained in terms of the base strength and steric bulkiness of the alkoxides used; these are both in the order of $MeO^- < EtO^- < i\text{-}PrO^- < t\text{-}BuO^-$. The E2-type dehydroiodination to **7** becomes unfavored as the base becomes bulkier, while the concentration of the malonate carbanion will increase with the basicity of the alkoxide. These

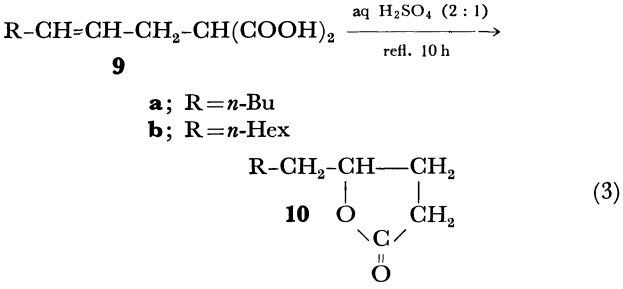
Table 2. Reaction of **1c** with $CH_2(COOR)_2$/RONa[a]

	$CH_2(COOR)_2$ R	Solvent ROH(50 ml)	Yield/% **7**+**8**	**7**/**8** Ratio
a	Me	MeOH	78	92/8
b	Et	EtOH	75	59/41
c	*i*-Pr	*i*-PrOH	57	11/89

a) **1c**, 19 mmol; $CH_2(COOR)_2$, 45 mmol; RONa, 44 mmol; Reflux, 3 h.

factors facilitate nucleophilic displacement at the iodine-bearing carbon atom in **1c** by the malonate anion. Subsequent intramolecular S_N2 attack on the terminal chlorine-carrying carbon atom leads to ring closure. On the other hand, where the carbanion concentration is not so much prevailing with the less strong bases of smaller bulk, dehydroiodination by alkoxides preceds to give allylic chloride, which is then displaced in a nucleophilic manner by the malonate anion to give **7**.

Synthesis of γ-Butyrolactones. The hydrolysis of **7a** with potassium hydroxide in boiling aq methyl alcohol gave the free dicarboxylic acid, **9a**, a pure sample of which was obtained as white crystals after recrystalization from petrol. ether. Heating at reflux in aq H_2SO_4 (2:1) changed **9a** into 1,4-nonanolide, **10a**; this is the so-called "coconut aldehyde," one of the most important lactones in perfumes and flavors, having a delicately fruity and coconutty odor of an excellent tenacity.[8] Starting from 1-octene, a similar treatment of **9b** gave 1,4-undecanolide, **10b**, the so-called "peach aldehyde," which has high quality, peach-like taste.



(3)

Utilization of the trans-*1,2-Disubstituted Olefinic Structure of **7** as a Synthetic Intermediate.* *trans*-1,2-Disubstituted olefinic bonds are common functional groups which are found in many synthetically useful intermediates and naturally occurring compounds.[9] Although the dehydroiodination-alkylation of **1c** with malonate/alkoxide should give rise several possible products in respect to stereo- and regiochemistry, the preferential formation of the *trans*-1,2-disubstituted alkene, **7a**, in a reasonable yield seemed to have some synthetic utility.

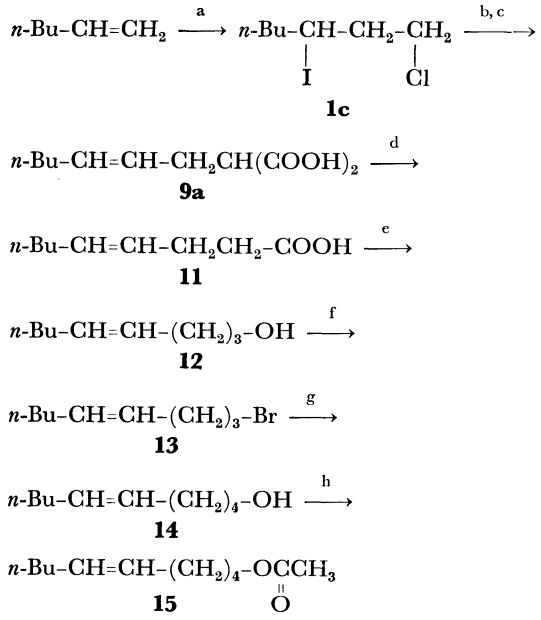
The thermolysis of **9a** at *ca.* 150 °C caused its decarboxylation to (*E*)-4-nonenoic acid, **11**.[10] The series of well-established transformations shown in Scheme 1 converted **11** to (*E*)-5-decen-1-ol, **14**, and its acetate, **15**, both of which are constituents of the sex pheromone for the male peach twig borer moth, *Anarsia lineatella Zeller*.[11] Another synthesis of **15** has been briefly reported, without any detailed physical or spectral data.[11] A synthesis of the (*Z*)-counterpart of **15** has appeared recently; (*Z*)-**15** is a sex attractant for the

Table 3. Reaction of **1c** with $CH_2(COOEt)_2$/EtONa

1c (mmol)	$CH_2(COOEt)_2$ (mmol)	EtONa (mmol)	EtOH (ml)	Reaction conditions[a]	**7b**/**8b** Ratio
19	45	44	50	A, reflux, 3 h	59/41
5.1	9.6	11	30	A, reflux, 3 h	82/18
4.3	9.2	23	30	B, reflux, 3 h	65/35
9.7	19	40	30	B, reflux, 3 h	20/80
5.8	11	13	30	A, ambient, 24 h	91/9
		t-BuOK	*t*-BuOH		
4.0	9.2	39	30	A, reflux, 3 h	1/99

a) A, **1c** was added drop by drop; B, EtONa was added drop by drop.

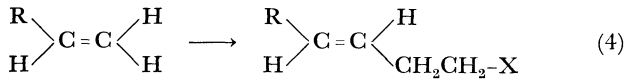
male turnip moth *Agrotis segetum*.[12]



a; CH_2ClI, AIBN. b; $CH_2(COOCH_3)_2$/MeONa/MeOH. c; KOH/aq MeOH. d; 150 °C. e; $LiAlH_4/Et_2O$. f; Ph_3PBr_2/CH_3CN. g; Mg, CH_2O/Et_2O. h; CH_3COCl/Pyridine/PhH.

Scheme 1.

In conclusion, the net effect of the above transformations can be visualized as the displacement of the terminal *trans*-hydrogen atom with an alkyl moiety of more than two methylene units (Eq. 4).



(4)

Experimental

The IR spectra were obtained using a Shimadzu IR 430 grating spectrophotometer. The NMR spectra were recorded on a Hitachi R-24A spectrometer (60 MHz), using carbon tetrachloride as the solvent (1—5% solution) unless otherwise noted. The absorption peaks were recorded in ppm units downfield from hexamethyldisiloxane as an internal standard. The analytical GLC was conducted on a Shimadzu GC 3AF and Hitachi 163 gas chromatograph equipped with flame-ionization detectors; a 300×0.3 cm stainless steel column packed with Silicone DC 550 (20%), Apiezon Grease L (20%), Silicone DC 410 (20%), or FFAP (10%) on Diasolid M (60—80 mesh), or a 20-m glass capillary column (0.25 mm i.d.) coated with silicone oil (OV-1 column), was used. The GLC yields of the reaction products were determined on the basis of the molar response, as determined from standard solutions of the products and appropriate internal standards. Preparative GLC separations were achieved with a Shimadzu GC 2C gas chromatograph using the appropriate column from among those noted above.

Materials. The chloroiodomethane was obtained by the procedure described before;[13] it was stored over a few tin pellets in the dark. The alkenes were distilled from sodium wire before use. The AIBN (dec 102 °C) and (*E*)-stilbene were used without further purification. The commercial dialkyl malonates were dried over $MgSO_4$ and distilled under reduced pressure. The solvents were purified as usual before use.

Addition of Chloroiodomethane to 1-Alkenes by Means of AIBN. A dry, 100-ml-inner-volume stainless steel autoclave equipped with a magnetic stirrer and a thermometer was charged with 4 mmol of AIBN, evacuated, and refilled with nitrogen. Then, 15—20 ml of 1-alkene and 3.0 ml (7.6 g, 43 mmol) of CH_2ClI were added by means of hypodermic syringe through a three-way cock under nitrogen. (1-Butene was distilled from a pressure bottle into the reaction vessel containing AIBN and CH_2ClI.) The mixture was stirred and heated in the course of 0.5 h to 80 ± 5 °C in an oil bath; that temperature was then maintained for 6 h. At the end of the reaction, the vessel was cooled in a water bath. The mixture was then subjected to distillation; after the excess alkene and tetramethylsuccinonitrile (**2**) had been removed *in vacuo*, the residue was fractionated through a short, packed column to give the corresponding 1-chloro-3-iodoalkane, **1**. Table 1 lists the results.

Diiodomethane was used in place of chloroiodomethane to give 1,3-diiodoheptane from 1-hexene: bp 105—107 °C/3.8 mmHg; yield, 62%. Found: C, 24.08; H, 3.91%. Calcd for $C_7H_{14}I_2$: C, 23.88; H, 4.01; I, 72.11%. NMR: δ 0.6—1.1 (3H, H_3C-), 1.1—2.0 (6H, H_3C-(CH_2)$_3$-), 2.0—2.5 (2H, -CH_2-CH_2I), 3.1—3.5 (2H, -CH_2I), 3.8—4.4 (1H, -CHI-).

Tetramethylsuccinontirile (2): An analytical sample was purified by sublimation: mp, 166—168 °C (lit,[14] 170.5—171.5 °C). The IR spectrum of the sample was superimposable upon that of the authentic one[14]; (KBr), 2220 cm^{-1} (νC≡N). NMR: δ 1.6 ($4\times H_3C$-).

2-Methyl-2-cyano-4-iodoheptane (4a): After 1-chloro-3-iodohexane had been recovered from the reaction mixture of 1-pentene, the distillation of the residue afforded a 0.6-g sample of **4a** boiling at 85—90 °C/1.5 mmHg. NMR: δ 0.7—1.1 (3H, H_3C-CH_2-), 1.3 and 1.4 (3H (s) and 3H (s), -C(CN)(CH_3)$_2$), 1.3—2.0 (4H, H_3C-(CH_2)$_2$-), 2.25 (2H, d, $J=6.4$ Hz, -CH_2-C(CN)(CH_3)$_2$), 3.9—4.4 (1H,

–CHI–). IR (neat): 2250 cm^{-1} (νC≡N).

A substantial rotational barrier, as judged by the PCK molecular model, may cause a magnetic non-equivalence between the two methyl groups of –C(CN)$(CH_3)_2$. The chemical shift of the C_3 methylene protons was assigned as above, because the irradiation of the sample at the –CHI– proton caused a collapse of the δ 2.25 doublet to a sharp singlet.

The **4a** was further transformed to (*E*)-2,2-dimethyl-3-heptenoic acid by heating at reflux for 5 h with KOH in ethylene glycol. NMR: δ 0.6—1.0 (3H, H_3C–CH_2–), 1.2 (6H, s, –C(COOH)$(CH_3)_2$), 1.1—1.7 (2H, H_3C–CH_2–), 1.7—2.4 (2H, –CH_2–CH=CH–), 5.3—5.6 (2H, –CH=CH–), 11.5 (1H, s, –COOH). IR (neat): 1700 (νC=O), 980 cm^{-1} (δ =CH_{trans}).

*Reaction of 1-Chloro-3-iodononane (**1d**) with Potassium Hydroxide in Aq Methyl Alcohol.* A heterogeneous mixture of **1d** (5.2 g) in a KOH (4 g) solution in MeOH (15 ml)–H_2O (4 ml) was stirred and then heated at reflux for 3 h. The cooled mixture was diluted with water and extracted with portions of ether. The ether extracts were then combined, washed successively with 2 M HCl and water, and dried over $MgSO_4$. The GLC analysis of the solution showed the presence of seven peaks (Apiezon Grease L column) (the following information is the compound, the percent of peak area on GLC, and the relative retention time); 1,3-nonadiene, 2.0%, 0.50; 3-methoxy-1-nonene, 0.4%, 0.72; 2-(methoxymethyl)-1-octene, 3.3%, 0.86; (*E*)-1-methoxy-3-nonene, 1.4%, 0.95; (*E*)-1-methoxy-2-nonene. 82.1%, 1.00; (*E*)-1-chloro-3-nonene, 10%, 1.15; unidentified, 0.8%, 1.33.

After the solvents had been removed by distillation, the residue was subjected to preparative GLC. A pure sample of (*E*)-1-methoxy-3-nonene was not isolated, but it was inferred from the fact that the treatment of (*E*)-1-chloro-3-nonene with KOH in aq MeOH increased the GLC peaks of the retention times of 0.50 (*i.e.*, 1,3-nonadiene) and of 0.95.

1,3-Nonadiene: NMR: δ 0.6—1.1 (3H, H_3C–), 1.1—1.7 (6H, H_3C–$(CH_2)_3$–), 1.7—2.4 (2H, –CH_2–CH=CH–), 4.6—6.8 (5H, –CH=CH–CH=CH_2). IR (neat): 1650 and 1605 (νC=C_{diene}), 1000 and 900 cm^{-1} (δ =CH_{vinyl}).

3-Methoxy-1-nonene: NMR: δ 0.6—1.0 (3H, H_3C–CH_2–), 1.0—1.8 (10H, –$(CH_2)_5$–), 3.0—3.5 (1H, –CH(OCH_3)–), 3.1 (3H, s, H_3CO–), 4.7—5.9 (3H, –CH=CH_2). IR (neat): 1640 (νC=C), 995 and 915 cm^{-1} (δ =CH_{vinyl}).

2-(Methoxymethyl)-1-octene: NMR: δ 0.7—1.1 (3H, H_3C–), 1.1—1.6 (8H, H_3C–$(CH_2)_4$–), 1.6—2.2 (2H, –CH_2–CH_2–CH=), 3.2 (3H, s, H_3CO–), 3.6—3.7 (2H, –CH_2–OCH_3), 4.6—4.9 (2H, >C=CH_2). IR (neat): 1650 (νC=C), 900 cm^{-1} (δ =$CH_{terminal\ methylene}$).

(E)-1-Methoxy-2-nonene: NMR: δ 0.7—1.1 (3H, H_3C–), 1.1—1.7 (8H, H_3C–$(CH_2)_4$–), 1.7—2.3 (2H, –CH_2–CH_2–CH=), 3.2 (3H, s, H_3CO–), 3.6—3.8 (2H, H_3CO–CH_2–), 5.3—5.7 (2H, –CH=CH–). IR (neat): 1670 (νC=C), 970 cm^{-1} (δ =CH_{trans}). Found: C, 76.61; H, 13.19%. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90%. The assignment of the *E* structure was based on the strong IR absorption at 970 cm^{-1}.

(E)-1-Chloro-3-nonene: NMR: δ 0.7—1.1 (3H, H_3C–), 1.1—1.7 (6H, H_3C–$(CH_2)_3$–), 1.7—2.2 (2H, –CH_2–CH_2–CH=), 2.2—2.7 (2H, –CH_2–CH_2Cl), 3.4 (2H, t, J=6.8 Hz, –CH_2Cl), 5.2—5.6 (2H, –CH=CH–). IR (neat): 970 cm^{-1} (δ =CH_{trans}).

Treatment of 1-Chloro-3-iodoheptane with Dimethyl Malonate/Sodium Methoxide in Methyl Alcohol. To a 200-ml, round-bottomed flask equipped with a condenser topped with a nitrogen inlet, a pressure-equalized dropping funnel, a thermometer, and a magnetic stirrer were added, under a nitrogen atmosphere, 50 ml of methyl alcohol and 1.0 g (43.5 mg-atom) of sodium metal. After the dissolution of the sodium, a 6.0 g (45 mmol) portion of dimethyl malonate was added. The mixture was heated to gentle reflux, and then a 5.0-g (19 mmol) portion of 1-chloro-3-iodoheptane **1c** was added dropwise. Stirring was continued for 3 h under gentle reflux. At the end of the reaction, the mixture was cooled, diluted with 30 ml of water, and extracted rapidly with portions of ether. The ether extracts were combined, washed successively with aq NH_4Cl and water, and dried over $MgSO_4$. An aliquot of the solution was used for the quantitative determination of the dimethyl (*E*)-3-octene-1,1-dicarboxylate, **7a**, and the dimethyl 2-butylcyclobutane-1,1-dicarboxylate, **8a**, by GLC. After the solvents and small amounts of the fore-run had been removed *in vacuo*, the residue was fractionated through a short, packed column. The yield of **7a** boiling at 100—104 °C/2 mmHg was 2.22 g, including small amounts of **8a** and trace amounts of an unidentified product; the retention time on GLC was in the order of **8a**, the unidentified, and **7a** (FFAP column). Pure sample of **7a** and **8a** were collected by preparative GLC.

The recovered solvent and the fore-run portion was concentrated to *ca.* a 1-ml volume, from which were detected and collected by preparative GLC 1-methoxy-2-heptene (**5b**) and 1-chloro-3-heptene (**6b**) among several other unidentified products.

*Dimethyl 2-Butylcyclobutane-1,1-dicarboxylate (**8a**)*: NMR: δ 0.6—1.0 (3H, H_3C–CH_2–), 1.0—1.5 (6H, H_3C–$(CH_2)_3$–), 1.5—2.1 (4H, ring–$(CH_2)_2$–), 2.1—2.6 (1H, –CH–), 3.6 (6H, 2×H_3CO–). IR (neat): 1730 cm^{-1} (νC=O).

*Dimethyl (E)-3-Octene-1,1-dicarboxylate (**7a**)*: Bp, 117 °C/2 mmHg; n_D^{15}, 1.4453. NMR: δ 0.6—1.0 (3H, H_3C–), 1.0—1.5 (4H, H_3C–$(CH_2)_2$–), 1.6—2.1 (2H, –CH_2–CH_2–CH=), 2.2—2.6 (2H, =CH–CH_2–CH–), 3.0—3.4 (1H, –CH–), 3.6 (6H, s, 2×H_3CO–), 5.0—5.5 (2H, –CH=CH–). IR (neat); 1740 (νC=O), 970 cm^{-1} (δ =CH_{trans}). Found: C, 63.01; H, 8.75%. Calcd for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83%.

*(E)-3-Octene-1,1-dicarboxylic Acid (**9a**)*: The diester **7a** was hydrolyzed by refluxing it in aq MeOH in the presence of KOH. Mp, 65.5 °C (petr. ether) (lit,[10] 60—63 °C). Found: C, 60.28; H, 8.23%. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05%. NMR ($CDCl_3$): δ 0.6—1.0 (3H, H_3C–), 1.0—1.5 (4H, H_3C–$(CH_2)_2$–), 1.7—2.2 (2H, –CH_2–CH_2–CH=), 2.3—2.8 (2H, =CH–CH_2–CH<), 3.4 (1H, t-like, –CH<), 5.1—5.7 (2H, –CH=CH–), 11.8 (2H, s, 2×–COOH). IR (KBr): 1710 (δC=O), 965 cm^{-1} (δ =CH_{trans}).

*1-Methoxy-2-heptene (**5b**)*: NMR: δ 0.6—1.1 (3H, H_3C–), 1.1—1.7 (4H, H_3C–$(CH_2)_2$–), 1.7—2.4 (2H, –CH_2–CH_2–CH=), 3.2 (3H, s, H_3CO–), 3.6—4.0 (2H, H_3CO–CH_2–), 5.2—5.7 (2H, –CH=CH–). IR (neat): 1670 (νC=C), 970 cm^{-1} (δ =CH_{trans}).

*1-Chloro-3-heptene (**6b**)*: NMR: δ 0.7—1.1 (3H, H_3C–), 1.1—1.7 (2H, H_3C–CH_2–), 1.7—2.2 (2H, Et–CH_2–), 2.2—2.7 (2H, $ClCH_2$–CH_2–), 3.4 (2H, t, J=6.5 Hz, $ClCH_2$–), 5.1—5.6 (2H, –CH=CH–). IR (neat): 975 cm^{-1} (δ =CH_{trans}).

Similar treatment of **1c** with diethyl and diisopropyl malonate gave the corresponding alkene **7** and cyclobutane **8** (see Table 2); all the compounds exhibited satisfactory IR and NMR spectra.

*Diethyl (E)-3-Octene-1,1-dicarboxylate (**7b**)*: Bp, 117—120 °C/2 mmHg; n_D^{17}, 1.4405 (lit,[10] n_D^{25}, 1.4410). Found: C, 65.75; H, 9.62%. Calcd for $C_{14}H_{24}O_4$: C, 65.60: H, 9.44%.

*Diethyl 2-Butylcyclobutane-1,1-diacrboxylate (**8b**)*: Bp, 98—100 °C/2 mmHg; n_D^{17}, 1.4403. Found: C, 65.89; H, 9.52%. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44%.

*Diisopropyl 2-Butylcyclobutane-1,1-dicarboxylate (**8c**)*: Bp, 115—117 °C/2 mmHg; n_D^{15}, 1.4390. Found: C, 67.90; H, 9.59%. Calcd for $C_{16}H_{28}O_4$: C, 67.60; H, 9.89%.

*Reaction of (E)-3-Octene-1,1-dicarboxylic Acid (**9a**). (E)-4-Nonenoic Acid (**11**)*: A sample of the dicarboxylic acid **9a** (37.7 g, 0.19 mol) was heated to 150—160 °C. After gas evolution had ceased, the mixture was analyzed by GLC to show that it consisted of *ca.* 95% of (*E*)-4-nonenoic acid (**11**) and *ca.* 5% of 1,4-nonanolide (**10a**) (*vide infra*). The mixture was dissolved in 2 M Na_2CO_3 and extracted with portions of ether to remove the **10a**. The aqueous phase was acidified with 2 M HCl; the regenerated free acid was extracted with ether. The ether extracts were combined, washed with water, and dried over $MgSO_4$. Distillation gave (*E*)-4-nonenoic acid boiling at 98—102 °C/2.5—3 mmHg (lit,[10] bp, 112—113 °C/5 mmHg); 18.7 g (yield, 64%). NMR: δ 0.6—1.1 (3H, H_3C–), 1.1—1.6 (4H, H_3C–$(CH_2)_2$–), 1.6—2.1 (2H, *n*-Pr–CH_2–), 2.1—2.6 (4H, –$(CH_2)_2$–CO–), 5.1—5.5 (2H, –CH=CH–), 11.9 (1H, –COOH). IR (neat): 1710 (νC=O), 965 cm^{-1} (δ =CH_{trans}).

*1,4-Nonanolide (**10a**)*: The dicarboxylic acid **9a** (0.83 g) was refluxed in H_2O (40 ml)–H_2SO_4 (20 ml) for 10 h. After steam distillation, the distillate was worked up as usual. Bp, 105—107 °C/2 mmHg; 0.65 g; n_D^{13}, 1.4473 (lit,[15] n_D^{20}, 1.4462). Found: C, 69.15; H, 9.94%. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.33%. NMR: δ 3.9—4.6 (1H, –CH–). IR (neat): 1770 cm^{-1} (νC=O).

*1,4-Undecanolide (**10b**)*: The method described above was applied to 1-chloro-3-iodononane (**1d**) to give **10b**. Bp, 132—135 °C/2 mmHg; n_D^{13}, 1.4512 (lit,[16] n_D^{20}, 1.4512). Found: C, 71.85; H, 11.33%. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94%. NMR: δ 3.9—4.6 (1H, –CH–). IR (neat): 1770 cm^{-1} (νC=O).

*Synthesis of (E)-5-Decenyl Acetate (**15**)*. To a stirred suspension of $LiAlH_4$ (0.6 g) in 300 ml of ether, we added a solution of (*E*)-4-nonenoic acid (**11**) (18.7 g, 0.12 mol) in ether (250 ml) over a 40-min period. The mixture was heated at reflux for another 3 h and then treated as usual. The subsequent evaporation of solvents left a 12.6 g sample of (*E*)-4-nonen-1-ol (**12**), the purity of which was *ca.* 97% as judged by GLC. NMR: δ 0.6—1.1 (3H, H_3C–), 1.1—1.7 (6H, 3×–CH_2–), 1.7—2.3 (4H, –CH_2–CH=CH–CH_2–), 2.5—2.8 (1H, –OH), 3.5 (2H, t, J=6.5 Hz, –CH_2–OH), 5.1—5.5 (2H, –CH=CH–). IR (neat): 970 cm^{-1} (δ =CH_{trans}).

Into an ice-chilled solution of triphenylphosphine (36 g) in 200 ml of acetonitrile was dropped 21.9 g of bromine (0.14 mol) to give triphenylphosphine dibromide, to which was then added the alcohol **12** (12.6 g). After the mixture had been stirred and heated at reflux for 1 h, the acetonitrile was evaporated *in vacuo*. The crude product (*E*)-1-bromo-4-nonene (**13**) was collected as a portion boiling at 50—55 °C/2—3 mmHg (*ca.* 85% yield); it was then filtered through a silica-gel column to give 5.03 g of a pure sample. NMR: δ 0.6—1.0 (3H, H_3C–), 1.0—1.5 (4H, –$(CH_2)_2$–CH_3), 1.5—2.5 (6H, 3×–CH_2–), 3.2 (2H, t, J=6.4 Hz, –CH_2Br), 5.1—5.5 (2H, –CH=CH–). IR (neat): 965 cm^{-1} (δ =CH_{trans}).

The bromide **13** (5.0 g) was treated with 1.5 g of magnesium turnings (62 mg-atom) in 80 ml of ether, to which was passed formaldehyde gas (prepared from 5 g of paraformaldehyde). A conventional work-up gave a 3.0-g portion distilling out at 78—84 °C/2—3 mmHg, which was finally purified by preparative GLC (FFAP column) to give **14** with a purity of 98% plus, as judged by the OV-1 capillary column GLC. Bp, 95—96 °C/2 mmHg; n_D^{15}, 1.4513. Found: C, 77.03; H, 12.66%. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90%. NMR: δ 0.6—1.0 (3H, H_3C–), 1.0—1.6 (8H, 4×–CH_2–), 1.5—1.7 (1H, –OH), 1.7—2.2 (4H, 2×–CH_2–), 3.3—3.6 (2H, t-like, –CH_2–OH), 5.1—5.3 (2H, –CH=CH–). IR (neat): 965 cm^{-1} (δ =CH_{trans}).

The treatment of the alcohol **14** with an excess amount of acetyl chloride in pyridine-benzene gave (*E*)-5-decenyl acetate, **15**: bp, 110—115 °C/16—17 mmHg; n_D^{19}, 1.4393. Found: C, 73.00; H, 11.22%. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18%. NMR: δ 0.6—1.0 (3H, H_3C–CH_2–), 1.0—1.6 (8H, 4×–CH_2–), 1.6—2.2 (7H, –OH+3×–CH_2–), 3.9 (2H, t, J=6.6 Hz, –CH_2–O–), 5.1—5.4 (2H, –CH=CH–). IR (neat): 1745 (νC=O), 970 cm^{-1} (δ =CH_{trans}).

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