225. Preparation of Mikanecic Ester[1]) and its Precursor, 1,3-Butadiene-2-carboxylic Ester

by **L. K. Sydnes** and **L. Skattebøl**

Department of Chemistry, University of Oslo, Blindern, Norway

and **Christopher B. Chapleo[2]), David G. Leppard[3]), Karen L. Svanholt[4])** and **André S. Dreiding**

Organisch-Chemisches Institut der Universität Zürich, Rämistrasse 76, 8001 Zürich

(27. VIII. 75)

Zusammenfassung. Eine thermische (a) und eine reduktive (b) Methode zur Herstellung von Mikanez-Estern wird beschrieben. Bei der ersten gelang der Nachweis des monomeren Vorläufers, 1,3-Butadien-2-carboxylester.

(a) *trans/cis*-Gemische von Methyl resp. Äthyl 2-Brom-1-methylcyclopropancarboxylat (**14/15** resp. **16/17**), mit Tri-*n*-butylzinnhydrid aus den entsprechenden 2,2-Dibrom-1-methylcyclopropancarboxylaten **12** resp. **13** hergestellt, wurden bei 480°/1,7 Torr pyrolysiert. Die bei −78° daraus abgefangenen Kondensate bestanden aus den 1,3-Butadien-2-carboxylaten **5** und **6**, im Falle des Äthylesters **6** durch seine ^{1}H-NMR.-Signale charakterisiert und als Addukt (**19**) mit 4-Phenyl-1,2,4-triazolin-3,5-dion (**18**) abgefangen (55%). Beim Erwärmen der Kondensate dimerisierten die Dienester **5** resp. **6**, so dass sich Dimethyl resp. Diäthyl Mikanezat (**9** resp. **10**) isolieren liess (67 resp. 100%).

(b) Behandlung von Methyl 2(*E*)-2-Methyl-2-butenoat (**20**) mit 2 Äquivalenten N-Bromsuccinimid gab (25%) Methyl 2(*Z*)-4-Brom-2-brommethyl-2-butenoat (**21**). (Mit 3 Äquivalenten entstand ein Stereomerengemisch 2(*Z*)- und 2(*E*)-4,4-Dibrom-2-brommethyl-2-butenoat (**22** und **23**)). Reduktion des Dibromesters **21** mit Zink in Tetrahydrofuran, Methanol oder Eisessig ergab (50%) Dimethyl Mikanezat (**9**). Von einer Iodolaktonisierung der aus **9** durch Verseifung hergestellten Mikanezsäure (**8**) erhielt man 4-Iodo-7-oxo-1-vinyl-6-oxabicyclo[3.2.1]octan-4*endo*-carbonsäure (**24**), dessen Bildungsleichtigkeit und IR.-Bande bei 1780 cm eine unabhängige Bestätigung dafür liefert, dass Mikanezsäure (**8**) durch Kopf-zu-Kopf-*Diels-Alder*-Dimerisierung von 1,3-Butadien-2-carbonsäure (**4**) entsteht.

Aus Methyl (*E*)-2-Methyl-2-pentenoat (**25**) wurde auf gleiche Weise, d.h. über Dibromierung zu **27** und Reduktion mit Zink in Äther, Dimethyl 3,2'-Dimethylmikanezat (**29**) gewonnen. Die Multiplizität des ^{1}H-NMR.-Signals von H—C(3) in **29** bestätigt, wiederum unabhängig, dass die Dimerisierung des Dienesters (in diesem Fall **28**) in Kopf-zu-Kopf-*Diels-Alder*-Weise stattfindet.

1. Introduction. – Mikanecic acid, $C_{10}H_{12}O_4$, m.p. 239°, has an interesting history which is not well known. First isolated in 1901 [1] from alkali treatment of ethyl 2-methyl-3,3-di-(phenylsulfonyl)-butanoate [1], it has also been obtained from the pyrolysis of methyl 2-acetoxy-2-methyl-3-butenoate [2], from the nickel-carbonyl carbonylation of vinyl acetylene [3], from the thermal reaction of formaldehyde with

---

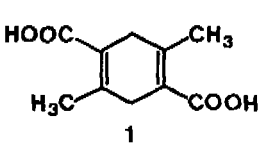
[1]) The systematic name of mikanecic acid is 4-vinyl-cyclohex-1-ene-1,4-dicarboxylic acid; it is used in the Experimental Part.

[2]) Post-doctoral fellow, University of Zürich 1972–1975.

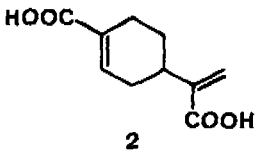
[3]) Royal Society Post-doctoral fellow 1972–1973. Present address: *Ciba-Geigy, Photochemie*, 1723 Marly, Switzerland.

[4]) University of Zürich, 1968–1971. Present address: Maglemosevej 43, 2900 Hellerup, Danmark.

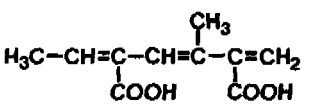
allyl-cyanide [4] and with crotonaldehyde [5], from the dimerization of cyanoprene [6] and from the alkaloids mikanoidine (hence the name) [7] [8] and sarracine [9]. Among the structures which have been proposed are **1** [1], **2** [3] and **3** [8].



1

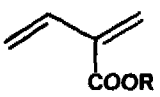


2

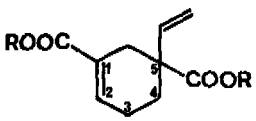


3

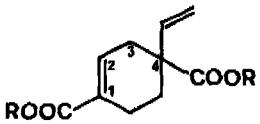
The derivation of mikanecic acid suggested it to be a dimer of 1,3-butadiene-2-carboxylic acid (**4** = isoprenoic acid) and degradation [3b] [4] [6] eventually estab-



4, 5, 6



7



8, 9, 10

4, 7, 8 : R = H; 5, 9 : R = CH_3; 6, 10 : R = C_2H_5

lished one of the two *Diels-Alder* dimerization structures, namely **8**, as first proposed by *Marvel* [6] and accepted by others [2] [3b] [9] [10]. Structure **8** represents a head-to-head isoprene assembly, whereas the alternative *Diels-Alder* dimer **7** would have been a head-to-tail assembly. The monomer, isoprenoic acid (**4**), and its esters have so far not been isolated.

The structure **8** of mikanecic acid as a 1,4,4-trisubstituted cyclohexene (rather than 1,5,5-substituted, **7**) is pertinent to the regiospecificity problem in the *Diels-Alder* reaction of substituted butadienes. This, along with experimental evidence in other cases [11], has led to the generalization that *Diels-Alder* reactions between 1- or 2-substituted butadienes and polar dienophiles usually produce 3,4- or 1,4- (rather than 3,5- or 1,5-) substituted cyclohexenes, respectively, and that this regiospecificity[5]) is independent of the electron-accepting or releasing nature of the butadiene substituent. The effect has also been theoretically rationalized [12] [13].

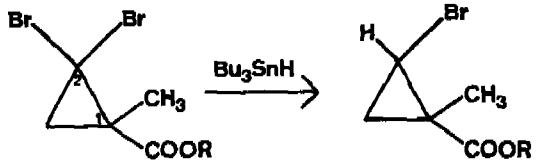
We had previously encountered the methyl ester of mikanecic acid (**9**) in our work on the NBS-bromination of 2-methyl-2-butenoic (tiglic and angelic) esters [14] as a

---

[5]) This regiospecificity problem is often referred to [13] as the '*ortho vs. meta*' or '*para vs. meta*' orientation problem in the *Diels-Alder* reaction of 1- or 2-substituted butadienes.

minor product[6]) of unexplained[7]) origin. This background [14] and our previous observations [15] on the ring opening of alkyl-dihalo-cyclopropanes lead us to new methods of preparation of esters of mikanecic acid as well as a dimethyl derivative and to the first direct observation as well as the capture of the precursor, 1,3-butadiene-2-carboxylic (isoprenoic) ester. Two methods will be reported here, a thermal and a reductive one.

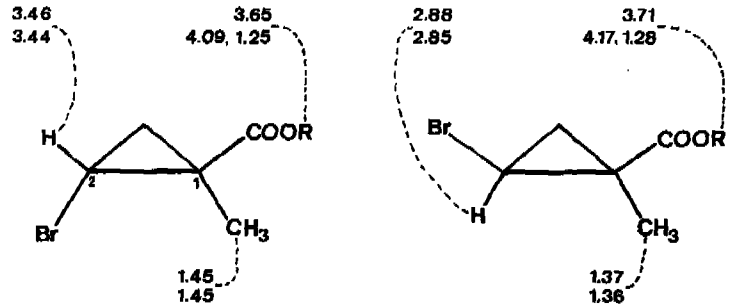
2. Thermal route: *via* methyl and ethyl 2-bromo-1-methylcyclopropanecarboxylates. – The previously known [16] methyl (**12**) and ethyl (**13**) 2,2-dibromo-1-methylcyclopropanecarboxylate were prepared by an improved [17] method (in the methyl ester case the corresponding 2,2-dibromo-1-methylcyclopropanecarboxylic acid (**11**) was also obtained) and reduced with tributyltin hydride [18]



11, 12, 13 **14, 15, 16, 17**

11 : R = H; 12, 14, 15 : R = CH_3; 13, 16, 17 : R = C_2H_5

to mixtures (6:4 and 7:3 respectively) of two stereoisomers (*trans* and *cis*) each of methyl (**14** and **15**) and ethyl (**16** and **17**) 2-bromo-1-methylcyclopropanecarboxylate. The two stereoisomers were not separated in both cases, but configurations could be assigned with the help of the separately visible signals in the ^{1}H-NMR.-spectra, on the assumption that vicinal protons or protons of a vicinal substituent *cis* to a bromine atom or to an alkoxycarbonyl group absorb at a lower field than the same *trans* to such groups, as follows:



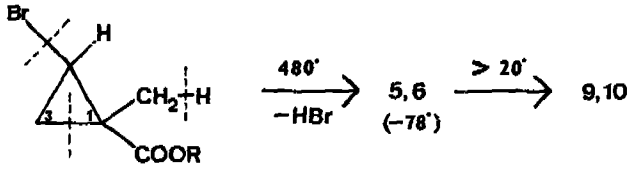
14, 16 : trans **15, 17 : cis**

upper figures : R = CH_3 (14, 15); lower figures : R = C_2H_5 (16, 17)

[6]) Not having realized at that time the history of the compound isolated, we had considered [14] the polarity controlled *Diels-Alder* structure **7**.

[7]) It was postulated [14] that the base treatment applied to the mixture of monobrominated methyl 2-methyl-2-butenoates was responsible for the appearance of **9** (*via* **8**). This has since been confirmed by Dr. *Ora Goldberg* in this laboratory, who obtained **8** from the action of potassium *t*-butoxide on pure ethyl 2-bromomethyl-2-butenoate. The details will be reported in another connection.

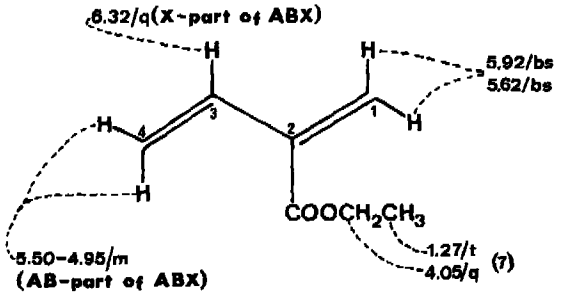
Both stereoisomer mixtures of the monobromo esters **14/15** and **16/17** respectively were pyrolyzed by passing them at 1.7 Torr through a pyrex tube at 480°. When the pyrolyzates, collected at −78°, were allowed to warm to room temperature 67% and 100% of dimethyl (**9**) and diethyl (**10**) esters of mikanecic acid, respectively, were isolated. This reaction probably proceeds by thermal elimination of hydrogen bromide under opening of the ring bond (C(1)–C(3)) vis à vis the bromine-carrying carbon atom to give the esters of 1,3-butadiene-2-carboxylic acid **5** and **6**, which then dimerise to the esters of mikanecic acid **9** and **10** respectively. The high yields of **9** and especially **10** indicate that both the *trans*- (**14/16**) and the *cis*-bromoesters (**15/17**)



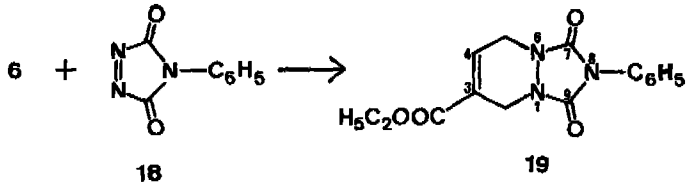
14/15, 16/17

undergo the thermal eliminative ring opening. The mechanism of the reaction is under investigation.

The dimerization occurs only on warming, for a solution of the cold pyrolyzate from the ethyl ester **16/17** in $CDCl_3$ showed ^{1}H-NMR.-signals attributable to ethyl 1,3-butadiene-2-carboxylate (**6**) as follows:

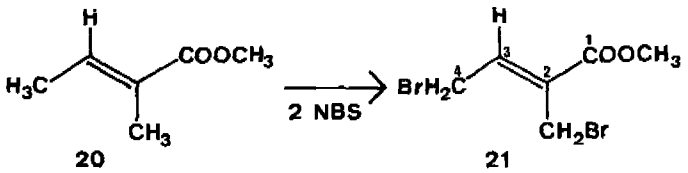


It was also possible to capture the diene ester **6** by allowing it to enter a *Diels-Alder* reaction with 4-phenyl-1,2,4-triazoline-3,5-dione (**18**) [19]. This cycloaddition evidently competes favorably with the above mentioned dimerization of **6**. The product (m.p. 139°, 55% yield) was shown to be a 1:1 adduct with structure **19** by the mass- (*m/e* 301/100%), the IR.- (bands at 1775, 1720, 1660 and 1595 cm^{-1}) and the ^{1}H-NMR.-spectra (multiplets at $\delta = 7.5$, 7.12 and 4.38 in the ratio of 5:1:4, along with the well known ethoxy signals). These results represent the first direct observation of an ester of isoprenoic acid.



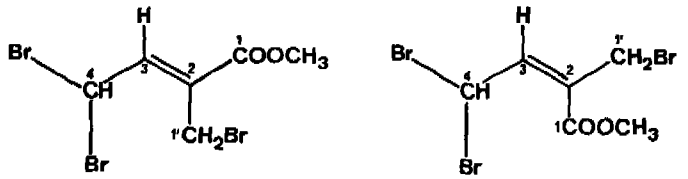
18 **19**

3. Reductive route: *via* methyl 4-bromo-2-bromomethyl-2-butenoate. We had previously reported [14] that methyl 2(*E*)-2-methyl-2-butenoate (**20**) undergoes a rapid (1 h) monobromination with N-bromosuccinimide to give a



20 **21**

mixture of two constitutionally isomeric monobromo esters [14] and that the introduction of a second bromine atom to give the dibromo ester **21** proceeds much more slowly. Under still more energetic conditions (20 h) the tribromo-ester can be obtained as a 3:1 mixture of two stereomers, **22**/**23**.

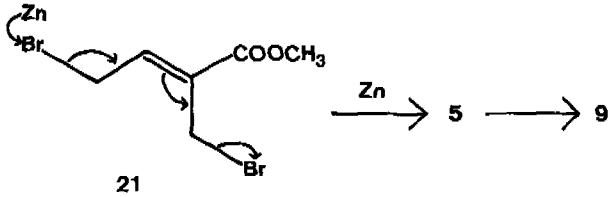


22 **23**

The constitution of the dibromo-ester, which appears as a single stereoisomer, as the product of bromination of both methyl groups (**21**) follows from the ^{1}H-NMR.-signals at 7.00/*t* (J = 8.5), 4.21/*s*, 4.08/*d* (J = 8.5) and 3.80/*s* in the ratios of 1:2:2:3, and its 2(*Z*)-configuration is made likely by the low field absorption of the vinylic hydrogen atom (H–C(3), *cis* to $COOCH_3$) [14], with the reservation that the other stereoisomer was not available for comparison. The constitution of the two isomeric tribromo-esters as methyl 2(*Z* + *E*)-4,4-dibromo-2-bromomethyl-2-butenoates (**22** and **23**) was deduced from the ^{1}H-NMR.-signals in the mixture, namely δ = 7.19 and 7.21 / both *d* (J = ~11), 6.42 and 6.70 / the first *d* (J = 11), the second *d* × *t* (J = ~11 and 1), 4.16 and 4.10 / the first *s*, the second *d* (J = 1), 3.85/*s* in the ratios of 1:1:2:3 and every pair in the ratio of 3:1. The 2(*Z*)-configuration (**22**) may be assigned to the major isomer, if it is assumed that the deshielding of H–C(4) in **23** (δ = 6.70) as compared to **22** (δ = 6.42) is due to the *cis*-location of $COOCH_3$ in **23**. Here it must be noted, that the vinyl hydrogen atoms H–C(3) are deshielded to the same extent (δ = 7.19 and 7.21) in both stereoisomers **22** and **23** (with H–C(3) *trans* and *cis* to $COOCH_3$, compare [14]); this may be due to a dominating deshielding of H–C(3) by the two vicinal bromine atoms (Br_2–C(4)) which must be located *syn* to H–C(3) since the coupling of 11 Hz between H–C(3) and H–C(4) shows these hydrogen atoms to be in an *anti*-conformation in both stereoisomers.

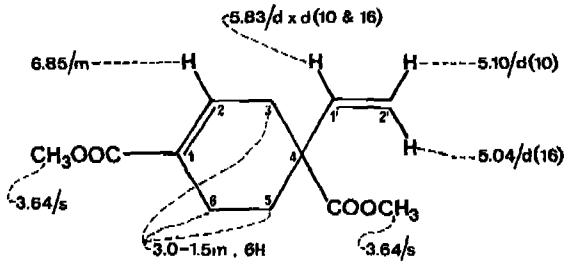
The optimum conditions of dibromination of **20** avoiding as much as possible mono- and tri-bromination, namely 2.2 mol equivalents N-bromosuccinimide, 7 h reflux over a lamp, gave a 25% yield of methyl 2(*Z*)-4-bromo-2-bromomethyl-2-

butenoate (**21**). When this dibromo-ester **21** was treated with zinc powder in tetrahydrofuran[8]), in methanol or in acetic acid the dimethyl ester of mikanecic acid (**9**)



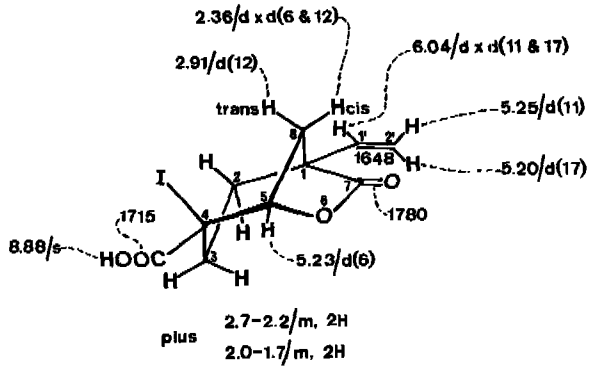
21

was obtained in about 50% yield. Evidently, reductive debromination (as shown) converts **21** to methyl 1,3-butadiene-2-carboxylate (**5**), which dimerizes to **9** *in situ*. A careful analysis of the ^{1}H-NMR.-spectrum of **9** is given below.



9

The dimethyl ester (**9**) was saponified to mikanecic acid (**8**), m.p. 240°, and the latter reesterified to **9** with diazomethane. Treatment of mikanecic acid (**8**) with iodine and aqueous sodium hydrogen carbonate resulted in iodolactonization to give (69%) 4-iodo-7-oxo-1-vinyl-6-oxabicyclo[3.2.1]octane-4-*endo*-carboxylic acid (**24**), m.p 174°. Several signals of its ^{1}H-NMR.-spectrum can be interpreted to support structure **24** as follows:

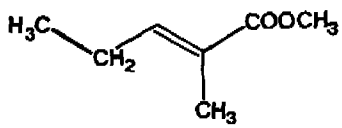


24

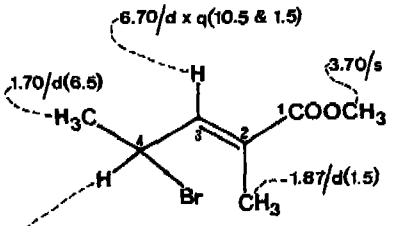
[8]) Since this reaction was first tried in an attempt to achieve a *Reformatsky* type condensation (compare [20]) 3-methyl-2-cyclohexenone was present in the mixture. It was later found that the debromination of **21** to **9** did not proceed as well in aprotic media when the ketone was absent.

The mode of formation and the IR.-band at 1780 cm^{-1} confirm that **24** is a γ-lactone. Its ease of formation suggests that lactonization took place at the olefinic carbon atom β- (and not α-) to the carboxylic acid. This offers independent confirmation that mikanecic acid has structure **8** (and not **7**) and that, therefore, the dimerization of isoprenoic acid (**4**) is of the head-to-head *Diels-Alder* type.

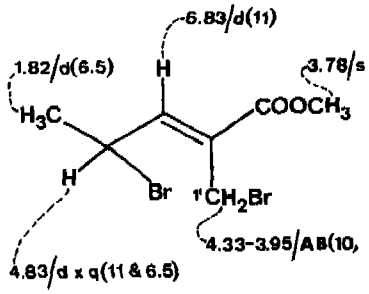
4. Dimethyl ester of 3,2'-dimethylmikanecic acid. – The dibromination *plus* zinc debromination sequence was also applied to the synthesis of a dimethyl derivative of an ester of mikanecic acid. Treatment of methyl 2(*E*)-2-methyl-2-pentenoate (**25**) with 1.1 and with 2.5 mol equivalents N-bromosuccinimide for $2^1/_2$ and for 16 h, respectively, gave a single stereoisomer in each case, namely methyl 2(*E*)-4-



25

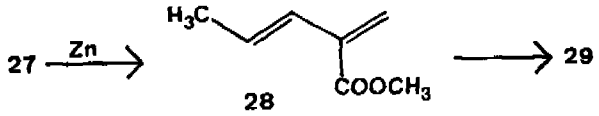


26



27

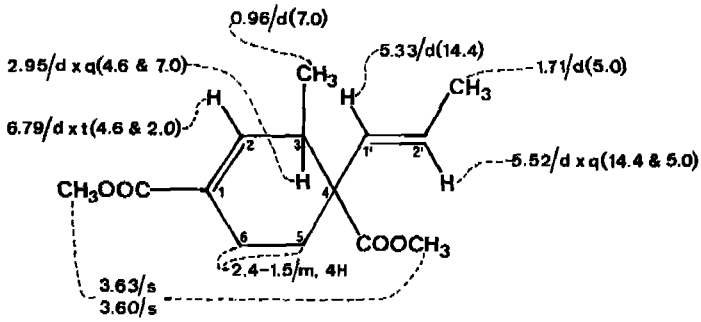
bromo-2-methyl-2-pentenoate (**26**, 75%) and methyl 2(*Z*)-4-bromo-2-bromomethyl-2-pentenoate (**27**, 46%), respectively. The ^{1}H-NMR.-signals shown on the formulae **26** and **27** clearly confirm the constitutions and probably (chemical shifts of H–C(3), see above) also the configurations given. Evidently the C=C–CH_3-group of the 2-methyl-2-pentenoate system (**25**) is more susceptible to NBS-bromination than the C=C–CH_3-group; for the monobromination product contains only the 4-bromo-isomer **26**, whereas the previously described [14] bromination of the 2-methyl-2-butenoate system produced the 4-bromo- and the 2-bromomethyl-isomers in a 2:1 ratio.



28

Reduction of the dibromo-ester **27** with granulated zinc in ether afforded 48% of dimethyl 3-methyl-4-(prop-(*E*)-enyl)-cyclohex-1-ene-1,4-dicarboxylate (**29**), presumably *via* dimerization of methyl 1,3-pentadiene-2-carboxylate (**28**).

The ^{1}H-NMR.-spectrum of the dimer confirms structure **29** as follows:



29

The absence of additional coupling in the signal due to H–C(3) ($\delta = 2.95$) beyond the one with the methyl protons ($J = 7$) and the one with the vinyl proton ($J = 4.6$), both confirmed by decoupling, shows that C(4) is fully substituted and thus establishes that the dimerization in this case was also of the head-to-head *Diels-Alder* type, as in the formation of the esters of mikanecic acid **9** and **10**.

This work was supported in part by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* and by *Sandoz AG*, Basel. We thank Messrs. *H. Hilpert*, *R. Martin* and *H. P. Rüesch* for their technical assistance.

Experimental Part

1. General. – Symbols, abbreviations and other indications used here have been described in [21] apart from the following modifications or additions: The IR.-spectra were measured on a *Perkin-Elmer* 21, 421 or 457 IR.-spectrometer. The mass spectra were measured on a *CEC* 21–110B, *Atlas* CH-5 or *AEI* MS 902 instrument and only selected peaks are reported. The ^{1}H-NMR.-spectra were measured with either a *Varian* A-60A or *Varian* HA-100 instrument with relative integration in H units.

2. Thermal route to dimethyl 4-vinyl-cyclohex-1-ene-1,4-dicarboxylate (9). – 2.1. *Methyl 2,2-dibromo-1-methylcyclopropanecarboxylate* (**12**). Reaction similar to [16] between 50 g (500 mmol) of methyl methacrylate and 150 g (600 mmol) of bromoform, but using 1.5 g of triethylbenzylammonium chloride [17] and 95 ml of 50% aqueous sodium hydroxide yielded 53.5 g (39%) of *methyl 2,2-dibromo-methylcyclopropanecarboxylate* (**12**), b.p. 49°/0.23 Torr, n_D^{24} 1.5170 (Lit. [16] b.p. 106–109°/25 Torr, n_D^{25} 1.5173) and 55 g (42%) of *2,2-dibromo-1-methylcyclopropanecarboxylic acid* (**11**), m.p. 109° (Lit. [16] m.p. 110–112.5°). – The IR.- and ^{1}H-NMR.-spectra of the ester **12** and acid **11** are in agreement with those reported in [16].

2.2. *Ethyl 2,2-dibromo-1-methylcyclopropanecarboxylate* (**13**). The reaction described above was repeated using 114 g (1000 mmol) of ethyl methacrylate, 300 g (1200 mmol) of bromoform, 3.0 g of triethylbenzylammonium chloride [16, 17] and 190 ml of 50% aqueous sodium hydroxide to give 224 g (78%) of *ethyl 2,2-dibromo-1-methylcyclopropanecarboxylate* (**13**), b.p. 66°/0.16 Torr, n_D^{24} 1.5065. – IR. (Film): 1730 *s* (C=O); 1450 *m*; 1365 *m*; 1305 *s*; 1270 *s*; 1175 *s*; 1155 *s*; 1030 *m*; 685 *m*. – ^{1}H-NMR. (60 MHz, CCl_4): 4.20/*q* (J = 7), 2 H (CH_2 of ethoxy); 2.36/*d* (J = 7.5), 1 H (H–C(3)); 1.57/*s*, 3 H (CH_3–C(1)); 1.50/*d* (J = 7.5), 1 H (H–C(3)); 1.31/*t* (J = 7), 3 H (CH_3 of ethoxy).

$C_7H_{10}Br_2O_2$ (285.975) Calc. C 29.40 H 3.52% Found C 29.10 H 3.43%

2.3. *Methyl 2-bromo-1-methylcyclopropanecarboxylates* **14** and **15**. Reduction of 13.6 g (50 mmol) methyl 2,2-dibromo-1-methylcyclopropanecarboxylate (**12**) with 14.5 g (50 mmol) tributyltin hydride according to [18] gave a 88% yield of a 6:4 mixture of the *trans*- and *cis*-stereoisomers of

methyl 2-bromo-1-methylcyclopropanecarboxylate (**14** and **15**) b.p. 31°/0.7 Torr, n_D^{24} 1.4809. – IR. (Film): 1725 *s* (C=O); 1450 *m*; 1434 *m*; 1382 *w*; 1317 *s*; 1230 *m*; 1190 *s*; 1160 *s*; 1149 *s*. – The ^{1}H-NMR.-spectrum of the mixture is described as if the two isomers were observed separately as follows: ^{1}H-NMR. of **14** (*trans*, 60%) (60 MHz, CCl_4): 3.65/*s*, 3 H (—OCH_3); 3.46/*q* – *X* part of an *ABX* system, 1 H (H—C(2)); 2.0–0.8/*m* overlapping with the corresponding signal due to the *cis*-isomer, 2 H (2 H—C(3)); 1.45/*s*, 3 H (CH_3—C(1)). – ^{1}H-NMR. of **15** (*cis*, 40%) (60 MHz, CCl_4): 3.71/*s*, 3 H (OCH_3); 2.88/*q* – *X* part of an *ABX* system, 1 H (H—C(2)); 2.0–0.8/*m* overlapping with the corresponding signal due to the *trans*-isomer, 2 H (2 H—C(3)); 1.37/*s*, 3 H (CH_3—C(1)). – MS. of mixture (70 eV): 194/192 (5.1/4.9, M^+).

$C_6H_9BrO_2$ (193.047) Calc. C 37.33 H 4.70% Found C 37.58 H 4.90%

2.4. *Ethyl 2-bromo-1-methylcyclopropanecarboxylates* **16** *and* **17**. Reduction of 28.6 g (100 mmol) ethyl 2,2-dibromo-1-methylcyclopropanecarboxylate (**12**) in the same way with 29.1 g (100 mmol) tributyltin hydride [18] gave a 83% yield of a 7:3 mixture of the *trans*- and *cis*-stereoisomers of *ethyl 2-bromo-1-methylcyclopropanecarboxylate* (**16** and **17**), b.p. 31°/0.08 Torr, n_D^{25} 1.4710. – IR. (Film): 1720 *s* (C=O); 1450 *w*; 1382 *w*; 1363 *m*; 1311 *s*; 1228 *m*; 1173 *s*; 1155 *s*; 1088 *w*; 1040 *w*; 1018 *w*. – The ^{1}H-NMR.-spectrum of the mixture is described as if the two isomers were observed separately as follows: ^{1}H-NMR. of **16** (*trans*, 70%) (60 MHz, CCl_4): 4.09/*q* (*J* = 7), 2 H (CH_2 of ethoxy); 3.44/*q* – *X* part of an *ABX* system, 1 H (H—C(2)), 1.9–0.8/*m*-overlapping with the corresponding signal due to the *cis*-isomer, 2 H (2 H—C(3)); 1.45/*s*, 3 H (CH_3—C(1)); 1.25/*t* (*J* = 7), 3 H (CH_3 of ethoxy). – ^{1}H-NMR. of **17** (*cis*, 30%) (60 MHz, CCl_4): 4.17/*q* (*J* = 7), 2 H (CH_2 of ethoxy); 2.85/*q* – *X* part of an *ABX* system, 1 H (H—C(2)); 1.9–0.8/*m*-overlapping with the corresponding signal due to the *trans*-isomer, 2 H (2 H—C(3)); 1.36/*s*, 3 H (CH_3—C(1)); 1.28/*t* (*J* = 7), 3 H (CH_3 of ethoxy).

$C_7H_{11}BrO_2$ (207.074) Calc. C 40.59 H 5.35% Found C 40.75 H 5.32%

2.5. *Pyrolysis of methyl 2-bromo-1-methylcyclopropanecarboxylates* **14** *and* **15**. 0.27 g (1.4 mmol) of methyl 2-bromo-1-methylcyclopropanecarboxylate **14** and **15** was passed through a pyrex tube (18 cm long, 0.8 cm diameter) packed with 0.1 g of pyrex wool and sodium carbonate and maintained at 482°/1.7 Torr. The product was collected at –78° in a flask containing some sodium carbonate. After warming to room temperature 0.18 g (67%) *dimethyl 4-vinyl-cyclohex-1-ene-1,4-dicarboxylate* (**9**) was isolated. It was identical by mass-, IR.-, and ^{1}H-NMR.-spectra with the compound described in 3.3 and was pure to the extent of > 90%.

2.6. *Pyrolysis of ethyl 2-bromo-1-methyl-cyclopropanecarboxylates* **16** *and* **17**. 2.0 g (9.7 mmol) of ethyl 2-bromo-1-methyl-cyclopropanecarboxylate **16** and **17** was pyrolysed at 480°/1.7 Torr in essentially the same way as described above for the methyl derivatives (**14** and **15**). Isolation of the product after warming to room temperature gave 1,2 g (100%) of *diethyl 4-vinyl-cyclohex-1-ene-1,4-dicarboxylate* (**10**). – IR. (CCl_4): 1775 *w*; 1732 *s* (O—C—(4)); 1720 *s* (O=C—C(1)); 1655 *w*; 1255 *s*; 1080 *m*; 990 *w*; 918 *w*; 908 *w*. – ^{1}H-NMR. (60 MHz, CCl_4): 6.84/*m*, 1 H (H—C(2)); 6.20–5.85/*m*, 3 H (H—C(1'), 2 H—C(2')); 4.13/2×*q* (*J* = 7). 4 H (2 CH_2 of 2 ethoxy); 3.10–1.60/*m*, 6 H (2 H—C(3), 2 H—C(5), 2 H—C(6)); 1.27/*t* (*J* = 7), 3 H (CH_3 of ethoxy); 1.23/*t* (*J* = 7), 3 H (CH_3 of ethoxy). – MS. (70 eV): 252 (5.1, M^+).

2.7. *Ethyl 1,3-butadiene-2-carboxylate* (**6**, *ethyl isoprenoate*) *and its 4-phenyl-1,2,4-triazoline-3,5-dione adduct* (**19**). The thermolysis of ethyl 2-bromo-1-methylcyclopropanecarboxylate (**16** and **17**) was performed as described in the preceeding experiment. The material in the cold trap, diluted with some $CDCl_3$ and allowed to warm to –60° only, showed the following ^{1}H-NMR.-signals, next to those of unreacted starting material (**16** and **17**) (55%): ^{1}H-NMR. (100 MHz, $CDCl_3$): 6.32/*q* = *X* part of an *ABX* system, 1 H (H—C(3); 5.92/br. *s*, 1 H (H—C(1)); 5.62/br. *s*, 1 H (H—C(1)); 5.50–4.95/*m* = *AB* part of *ABX* system, 2 H (2 H—C(4)); 4.05/*q* (*J* = 7), 2 H (CH_2 of ethoxy); 1.27/*t* (*J* = 7), 3 H (CH_3 of ethoxy). These signals are considered to belong to *ethyl 1,3-butadiene-2-carboxylate* (**6**). After this solution had been permitted to stand at room temperature for 12 h, the signals in the 4.95–6.80 region due to **6** had disappeared while those of the dimer **10** had appeared.

The thermolysis of 0.69 g (3,3 mmol) of the **16**/**17** mixture was repeated but this time the product was diluted with methylene chloride at –78° and a solution of 4-phenyl-1,2,4-triazoline-

3,5-dione (**18**) [19] in methylene chloride was added at this temperature until the red colour persisted. Evaporation of the solvent gave an oily residue which was purified by column chromatography over silica gel using benzene/acetone 8:1. Recrystallization from hexane/acetone 7:1 gave 0.55 g (55%) of *3-ethoxycarbonyl-8-phenyl-1,6,8-triaza-bicyclo[4.3.0]non-3-ene-7,9-dione* (**19**), m.p. 139°. – IR. (KBr): 1775 *m*; 1720 *s* (C=O); 1660 *w* (C=C); 1595 *w*; 1495 *m*; 1420 *s*; 1310 *m*; 1270 *s*; 1245 *s*; 1125 *s*; 760 *m*; 720 *m*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 7.5/*m*, 5 H (aromatic H's); 7.12/*m*, 1 H (H—C(4)); 4.38/*m*, 4 H (2 H—C(2), 2 H—C(5)); 4.31/*q* (J = 7), 2 H (CH_2 of ethoxy); 1.35/*t* (J = 7), 3 H (CH_3 of ethoxy). – MS. (70 eV): 301 (100, M^+).

$C_{15}H_{15}N_3O_4$ (301.306) Calc. C 59.80 H 5.02% Found C 59.99 H 4.90%

The residue from the crystallization mother liquor was shown to contain ~10% yield of the dimer **10** as well as starting material **16** and **17**.

When the thermolysis of the **16/17** mixture was carried out at 450°/0.1 Torr and the distillate treated with **18**, the product consisted of 65% of starting material **16** and **17**, 30% of the triazolinedione adduct **19** and 5% of the dimer **10**.

3. Reductive route. – 3.1. *Methyl 2(Z)-4-bromo-2-bromomethyl-2-butenoate* (**21**). A solution of 24.5 g (215 mmol) of methyl 2(*E*)-2-methyl-2-butenoate (**20**) and 85.44 g (480 mmol) of N-bromosuccinimide in 200 ml of dry, redistilled carbon tetrachloride was refluxed over a 150 W bulb for 7 h. The reaction mixture was cooled, the succinimide filtered off and the carbon tetrachloride removed under reduced pressure to give 38.08 g of a yellow oil, shown by TLC. to consist of three species. The mixture was fractionally distilled under vacuum. The first fraction, b.p. 45–68°/0.04 Torr, consisted of 6.25 g (16%) of a mixture of the monobromo esters, *methyl 2*(E)*-4-bromo-2-methyl-2-butenoate* and *methyl 2*(E)*-2-bromomethyl-2-butenoate*, the properties of which have been described earlier [14]. After discarding a second fraction of 1.40 g containing a complex mixture of bromo compounds, b.p. 68–77°/0.04 Torr, 19.08 g of a yellow oil b.p. 77–81°/0.04 Torr was collected. This last fraction was refractionated to give 15.23 g of product b.p. 80–81°/0.07 Torr. After filtering off a small amount of polymeric material the oil was redistilled using a short-path distillation technique to give 14.80 g (25%) of *methyl 2*(Z)*-4-bromo-2-bromomethyl-2-butenoate* (**21**) as a pale yellow oil, b.p. 80°/0.07 Torr. – IR. (Film): 1725 *s* (C=O); 1650 *m* (C=C); 1290 *s*; 1205 *s*; 1175 *m*; 1050 *w*; 965 *w*; 775 *m*; 758 *w*. – ^{1}H-NMR. (60 MHz, CCl_4): 7.00/*t* (J = 8.5), 1 H (H—C(3)); 4.21/*s*, 2 H (2 H—C(1')); 4.08/*d* (J = 8.5), 2 H (2 H—C(4)); 3.80/*s*, 3 H (CH_3O).

3.2. *Methyl 2* (Z)- *and 2*(E)*-4,4-dibromo-2-bromomethyl-2-butenoate* (**22** *and* **23**). When a solution of 24.5 g (215 mmol) of methyl 2(*E*)-2-methyl-2-butenoate (**20**) and 85.44 g (480 mmol) of N-bromosuccinimide in 200 ml of dry, redistilled carbon tetrachloride was refluxed over a 150 W bulb for 20 h two additional products were obtained from the fractional distillation. After collecting 29.50 g of a mixture of mono- and dibromo-esters (see 3.2 above), 6.31 g of a yellow oil distilled, b.p. 105–115°/0.03 Torr. Redistillation under vacuum using a short path distillation technique gave 4.96 g (7%) of a pale yellow oil, b.p. 113°/0.03 Torr, consisting, according to the ^{1}H-NMR.-spectrum (see below), of a 3:1 mixture of *methyl 2*(Z)*-4,4-dibromo-2-bromomethyl-2-butenoate* (**22**) and *methyl 2*(E)*-4,4-dibromo-2-bromomethyl-2-butenoate* (**23**). – IR. (Film): 1725 *s* (C=O); 1635 *w* (C=C); 1595 *w* (C=C); 1285 *s*; 1225 *m*; 1205 *m*; 1160 *m*; 1050 *w*; 960 *w*; 910 *w*; 835 *w*; 776 *m*. – The ^{1}H-NMR.-spectrum of the mixture is described as if the two isomers were observed separately as follows: ^{1}H-NMR. of **22** (60 MHz, CCl_4): 7.19/*d* (J = 11), 1 H (H—C(3)); 6.42/*d* (J = 11), 1 H (H—C(4)); 4.16/*s*, 2 H (2 H—C(1')); 3.85/*s*, 3 H (—OCH_3). – ^{1}H-NMR. of **23** (60 MHz, CCl_4): 7.21/*d* (J = 10.5), 1 H (H—C(3)); 6.70/*d* × *t* (J = 10.5 and 1), 1 H (H—C(4)); 4.10/*d* (J = 1), 2 H (2 H—C(1')); 3.85/*s*, 3 H (CH_3O).

3.3. *Dimethyl 4-vinyl-cyclohex-1-ene-1,4-dicarboxylate* (**9**, *dimethyl ester of mikanecic acid*). – 3.3.1. *Under* Reformatsky *reaction conditions.* A solution of 3.2 g (12 mmol) of methyl 2(*Z*)-4-bromo-2-bromomethyl-2-butenoate (**21**) and 10.57 g (96 mmol) of 3-methylcyclohex-2-enone in 40 ml of tetrahydrofuran was heated under nitrogen at 90° for 16 h with 1.0 g (15 mmol) of zinc powder. After filtering off the white solid formed the solution was poured into 200 ml water and extracted with 2 × 50 ml of ether. The ether extract was washed thoroughly with 5 × 100 ml of water, dried and evaporated to give 1.87 g of a pale yellow oil. The ^{1}H-NMR.-spectrum of this crude product showed, in addition to the strong signals of the major product (see below), the following minor

signals: 6.17/*s*; 5.98/*s* and 5.90/*s*. Purification by column chromatography over 100 g of silica gel using ethyl acetate/pentane 1:9 separated 0.11 g of a less polar product (discarded) and 0.76 g of a colourless oil which was collected and distilled under vacuum to give *dimethyl 4-vinyl-cyclohex-1-ene-1,4-dicarboxylate* (**9**) as a colourless liquid, b.p. 115–120°/0.05 Torr, yield 0.62 g (47%). – UV. (C_2H_5OH): 223 (8200). – IR. (CCl_4): 1741 *s* (O=C–C(4)); 1725 *s* (O=C–C(1)). – IR. (Film): 1740–1720/*s*, br. (2× ester C=O); 1660 *m* (C=C); 1640 *w* (C=C); 1260 *s*; 1090 *s*; 930 *m*; 775 *w*; 750 *w*; 720 *m*. – ^{1}H-NMR. (100 MHz, CCl_4): 6.85/*m* with fine coupling (J = 2), 1 H (H–C(2)); 5.83/*d*×*d* (J = 10 and 16), 1 H (H–C(1')); 5.10/*d* (J = 10), 1 H (H(*E*)–C(2')); 5.04/*d* (J = 16). 1 H (H(*Z*)–C(2')); 3.64/*s*, 6 H (2× OCH_3, occasionally appearing as two very close singlets); 3.0–1.5/*m* 6 H (2 H–(3), 2 H–C(5), 2 H–C(6)). This spectrum is identical to that of the diester **9** obtained by esterification of the purified diacid **8** (see 3.4). – MS. (70 eV): 224 (16, M^+); 192 (80); 165 (88); 133 (92); 105 (100); 91 (25); 77 (31); 59 (32).

The reaction did not proceed under the above conditions in the absence of 3-methylcyclohex-2-enone. When the reaction was performed in benzene instead of tetrahydrofuran by refluxing for 18 h and working-up as described above, the diester **9** was obtained in a yield of only 10%.

3.3.2. *With zinc in methanol or acetic acid.* A chilled solution of 1.00 g (4 mmol) of methyl 2(*Z*)-4-bromo-2-bromomethyl-2-butenoate (**21**) in 12 ml methyl alcohol or acetic acid was treated with 1.2 g (18.5 mmol) zinc powder and then stirred for 12 h at room temperature. After filtration it was diluted with 200 ml water and extracted with ether. The extracts were washed with aqueous sodium carbonate (not necessary when methyl alcohol was solvent) and water, dried and evaporated to leave 0.35 g of a pale yellow oil. Purification by preparative TLC. on silica gel with ethyl acetate/hexane 3:17 yielded 0.24 g (58%) of *dimethyl 4-vinyl-cyclohex-1-ene-1,4-dicarboxylate* (**9**). The ^{1}H-NMR.-spectrum of this crude product was almost identical to the spectrum of the crude material described under 3.3.1 above.

3.4. *4-Vinyl-cyclohex-1-ene-1,4-dicarboxylic acid* (**8**. *mikanecic acid*). A solution of 0.34 g (1.6 mmol) of dimethyl 4-vinyl-cyclohex-1-ene-1,4-dicarboxylate (**9**) in 5 ml ethanol and 5 ml of 15% (18.8 mmol) aqueous sodium hydroxide was refluxed for 2 h, cooled, diluted with 50 ml water and extracted with ether. The aqueous phase was acidified with 10% hydrochloric acid and extracted with ether. The combined extracts were washed with water, dried and evaporated to leave a pale yellow solid which was recrystallized from acetone to give 0.2 g (65%) of *4-vinyl-cyclohex-1-ene-1,4-dicarboxylic acid* (**8**) as colourless plates, m.p. 239–240° (Lit. [5] m.p. 238–239). – UV. (C_2H_5OH): 225 (7100). – IR. (KBr): 3700–2300 *s*, br. (OH); 1700 *s* (COOH); 1650 *m* (C=C); 1290 *s*; 950 *m*; 930 *m*; 770 *w*; 740 *m*; 711 *w*. – ^{1}H-NMR. (60 MHz, CD_3COCD_3): 7.03–6.86/br. *s*, 1 H (H–C(2)); 5.95/*d*×*d* (J = 10 and 18), 1 H (H–C(1')); 5.25/*d*×*d* (J = 2 and 10), 1 H (H(*E*)–C(2')); 5.05/*d*×*d* (J = 2 and 18), 1 H (H(*Z*)–C(2')); 3.2–1.5/*m*, 6 H (2 H–C(3), 2 H–C(5), 2 H–C(6)).

A sample of the diacid **8**, m.p. 239–240, was esterified with diazomethane to give the diester **9** whose ^{1}H-NMR.-spectrum was identical to that described in 3.3.1.

When the reaction was repeated using 0.4 g of the crude diester **9**, obtained as described under 3.3.1, 0.224 g of the impure acid **8** was obtained. Recrystallization from acetone afforded 0.17 g *4-vinyl-cyclohex-1-ene-1,4-dicarboxylic acid* (**8**), identical with the sample described above. The ^{1}H-NMR.-spectrum of the residue from the crystallization mother liquor showed that it consisted mostly of the same diacid **8**; however, two additional signals (less than $^1/_3$ H) were present namely: 6.07/*s*, 5.63/*s*.

3.5. *Iodolactonization of 4-vinyl-cyclohex-1-ene-1,4-dicarboxylic acid* (**8**). A solution of 0.103 g (0.53 mmol) of 4-vinyl-cyclohex-1-ene-1,4-dicarboxylic acid (**8**) in 10 ml of 7% aqueous sodium hydrogen carbonate was added to a solution of 0.268 g (1.06 mmol) iodine and 0.524 g (3.16 mmol) potassium iodide in 4 ml water. The resulting solution was allowed to stand in the dark for 48 h with occasional swirling and was then diluted with 50 ml water and extracted with chloroform. The aqueous layer was cautiously acidified to pH ~4 with dilute hydrochloric acid and extracted with chloroform. The combined extracts were washed with aqueous sodium thiosulfate, dried and evaporated to leave 0.117 g (69%) of *4-iodo-7-oxo-1-vinyl-6-oxabicyclo[3.2.1]octane-4*-endo-*carboxylic acid* (**24**), m.p. 161–165°, as a pale yellow solid. Recrystallization from chloroform/petrol ether gave 0.09 g (53%) of **24**, m.p. 171.5–174° as white needles. – IR. ($CHCl_3$): 3600–2300 *s*, br.

(OH); 1780 *s* (lactone C=O); 1715 *s* (acid C=O); 1648 *w* (C=C); 1460 *w*; 1450 *w*; 1290 *m*; 1270 *m*; 1140 *m*; 1075 *w*; 1040 *m*; 985 *m*; 930 *s*; 865 *m*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 8.88/*s*, 1 H (CO_2H); 6.04/*d* × *d* (*J* = 11 and 17), 1 H (H–C(1')); 5.25/*d* (*J* = 11), 1 H (H(*E*)–C(2')); 5.23/*d* (*J* = 6), 1 H (H–C(5)); 5.20/*d* (*J* = 17), 1 H (H(*Z*)–C(2')); 2.91/*d* (*J* = 12), 1 H (H *trans*–C(8)); 2.7–2.2/*m*, 3 H (H *cis*–C(8), H–C(2), H–C(3)); 2.0–1.7/*m*, 2 H (H–C(2), H–C(3)). A part of the multiplet at 2.7–2.2 can be interpreted as follows: 2.58/*d* × *d* × *d* (*J* = 2, 6 and 13), 1 H (H–C(2) or H–C(3)); 2.36/*d* × *d* (*J* = 6 and 12), 1 H (H *cis* C(8)).

$C_{10}H_{11}IO_4$ (322.10) Calc. C 37.28 H 3.44 I 39.41% Found C 37.06 H 3.43 I 39.34%

The ^{1}H-NMR.-spectrum of the iodo-lactone **24** prior to purification was the same as that described above for the purified sample with the only exception of three very weak singlets at 6.37, 6.17 and 5.97.

4. Reductive route applied to dimethyl derivative. – 4.1. *Methyl 2*(E)*-4-bromo-2-methyl-2-pentenoate* (**26**). A solution of 0.40 g (3.1 mmol) of methyl 2(*E*)-2-methyl-2-pentenoate (**25**) and 0.61 g (3.4 mmol) of N-bromosuccinimide in 5 ml of dry, redistilled carbon tetrachloride was refluxed over a 150 W bulb for 2.5 h. After cooling, the succinimide was filtered off, the carbon tetrachloride was evaporated and the product distilled twice under reduced pressure over a short path to give 0.48 g (75%) of *methyl 2*(E)*-4-bromo-2-methyl-2-pentenoate* (**26**) as a colourless liquid, b.p. 175–180°/23 Torr. – IR. (Film): 1760 *m*; 1715 *s* (C=O); 1650 *m* (C=C); 1435 *s*; 1305 *s*; 1250 *s*; 1195 *s*; 1150 *s*; 1115 *s*; 1020 *s*; 905 *w*; 825 *w*; 750 *s*. – IR. (CCl_4): 1765 *m*; 1715 *s* (C=O); 1648 *s* (C=C). – ^{1}H-NMR. (60 MHz, CCl_4): 6.70/*d* × *q* (*J* = 10.5 and 1.5), 1 H (H–C(3)); 4.80/*d* × *q* (*J* = 10.5 and 6.5), 1 H (H–C(4)); 3.70/*s*, 3 H (OCH_3); 1.87/*d* (*J* = 1.5), 3 H (H_3C–C(2); 1.70/*d* (*J* = 6.5), 3 H (H_3C–C(4)).

4.2. *Methyl 2*(Z)*-4-bromo-2-bromomethyl-2-pentenoate* (**27**). A solution of 2.0 g (15.06 mmol) of methyl 2(*E*)-2-methyl-2-pentenoate (**25**) and 7.60 g (42.7 mmol) of N-Bromosuccinimide in 250 ml of dry, redistilled carbon tetrachloride was refluxed over a 150 W bulb for 16 h. The reaction product was cooled, the succinimide filtered off and the carbon tetrachloride distilled at 25° under reduced pressure to give 5.43 g of a yellow oil, shown by TLC. to consist of two species. The mixture was separated into its two components by preparative TLC. on silica gel using ethyl acetate/pentane 1:3. The less-polar fraction was distilled under vacuum to give 0.41 g of a colourless liquid, b.p. 85–90°/0.4 Torr, which was not identified. – IR. (Film): 1745 *m*; 1730 *s*; 1600 *m*; 1320 *s*; 1240 *s*; 770 *m*; 750 *w*. The more-polar material was distilled under vacuum to give 2.05 g (46%) of *methyl 2*(Z)*-4-bromo-2-bromomethyl-2-pentenoate* (**27**) as a pale yellow oil, b.p. 102–105°/0.4 Torr. – IR. (Film): 1720 *s* (C=O); 1645 *m* (C=C); 1438 *s*; 1315 *s*; 1265 *s*; 1195 *s*; 1150 *s*; 1010 *m*; 830 *m*; 770 *s*. – ^{1}H-NMR. (60 MHz, CCl_4): 6.83/*d* (*J* = 11), 1 H (H–C(3)); 4.83/*d* × *q* (*J* = 11 and 6.5), 1 H (H–C(4)); 4.33–3.95/second order *AB* system (*J* = 10), 2 H (2 H–C(1')); 3.78/*s*, 3 H (OCH_3); 1.82/*d* (*J* = 6.5), 3 H (H_3C–C(4)).

4.3. *Dimethyl 3-methyl-4-*(*prop-*(E)*-enyl*)*-cyclohex-1-ene-1,4-dicarboxylate* (**29**). A mixture of 0.55 g (1.92 mmol) of methyl 2(*Z*)-4-bromo-2-bromomethyl-2-pentenoate (**27**) and 0.13 g (2 mmol) of granulated zinc in 20 ml of anhydrous ether was refluxed for 4 h and then stirred at room temperature for a further 36 h. A grey solid, which had formed as the zinc disappeared, was filtered off and the filtrate evaporated under reduced pressure to give 0.35 g of a pale yellow oil. This was fractionated by preparative TLC. on silica gel using ethyl acetate/pentane 1:3. Two less-polar bands (Rf = 0.6 and 0.55) containing 2 mg and 30 mg respectively of oils were discarded. Extraction with ether of the product from the major band (Rf = 0.5), followed by evaporation of the solvent yielded 0.10 g (80%) of a pale yellow oil, which was purified by short path distillation under vacuum to give 0.06 g (48%) of *dimethyl 3-methyl-4-*(*prop-*(E)*-enyl*)*-cyclohex-1-ene-1,4-dicarboxylate* (**29**) as a colourless oil, b.p. 80–86°/0.01 Torr. – UV. (C_2H_5OH): 218 (12,300). – IR. (Film): 1725 *s* (C=O); 1660 *m* (C=C); 1240–1260 *s*, br.; 1195 *m*; 1170 *m*; 1100 *m*; 1050 *m*; 980 *m*; 792 *s*; 770 *m*; 750 *m*; 730 *w*. – ^{1}H-NMR. (100 MHz, CCl_4): 6.79/*d* × *t* (*J* = 4.6 and 2.0), 1 H (H–C(2)); 5.52/*d* × *q* (*J* = 14.4 and 5.0), 1 H (H–C(2')); 5.33/*d* (*J* = 14.4), 1 H (H–C(1')); 3.63/*s*, 3 H (OCH_3); 3.60/*s*, 3 H (OCH_3); 2.95/*d* × *q* (*J* = 4.6 and 7.0), 1 H (H–C(3)); 2.4–1.5/*m*, 4 H (2 H–C(5), 2 H–C(6)); 1.71/*d* (*J* = 5.0), 3 H (CH_3–C(2')); 0.96/*d* (*J* = 7.0), 3 H (CH_3–C(3)). Irradiation at δ = 0.96 simplified 2.95/*d* × *q* to a doublet (*J* = 4.6). Irradiation at δ = 6.79 simplified 2.95/*d* × *q*

to a quartet ($J = 7$). Double irradiation at $\delta = 0.96$ and 6.79 simplified *2.95/d* × *q* to a singlet. – MS. (70 eV): 252 (80, M^+); 220 (70); 193 (96); 161 (70); 133 (70); 126 (100); 119 (30); 111 (40); 105 (60); 91 (90).

$C_{14}H_{20}O_4$ (252.32) Calc. C 66.64 H 7.99 Found C 66.08 H 7.83%

0.14 g of a fraction with Rf = 0, probably polymeric, was also present in the mixture.

REFERENCES

[1] *T. Posner*, Ber. deutsch. chem. Ges. *34*, 2643 (1901).
[2] *E. A. Braude & E. A. Evans*, J. chem. Soc. *1956*, 3238.
[3] a) *W. Reppe*, 'Acetylene Chemistry', Mayer, New York 1949, p. 158; *W. Reppe*, Liebigs Ann. Chem. *582*, 1 (1953); b) *A. Yakubovich & E. V. Volkova*, Doklady Akad. Nauks. S.S.R. *84*, 1183 (1952); Chem. Abstr. *47*, 3278 (1953).
[4] *C. C. Price, G. A. Cypher & I. V. Krishnamurti*, J. Amer. chem. Soc. *74*, 2987 (1952).
[5] *R. Pummerer, F. Aldebert, F. Büttner, F. Graser, E. Pirson, H. Rick & H. Sperber*, Liebigs Ann. Chem. *583*, 161 (1953).
[6] *C. S. Marvel & N. O. Brace*, J. Amer. chem. Soc. *71*, 37 (1949).
[7] *R. H. F. Manske*, Canad. J. Res. *14B*, 6 (1936).
[8] *R. Adams & M. Gianturco*, J. Amer. chem. Soc. *79*, 166 (1957).
[9] *C. C. J. Culvenor & T. A. Geissman*, Chem. and Industry *1959*, 366; *C. C. J. Culvenor & T. A. Geissman*, J. org. Chemistry *27*, 3045 (1961).
[10] *J. D. Edwards, T. Matsumoto & T. Hase*, J. org. Chemistry *32*, 244 (1967).
[11] *H. E. Hennis*, J. org. Chemistry *28*, 2570 (1963); *E. F. Lutz & G. M. Bailey*, J. Amer. chem. Soc. *86*, 3899 (1964); *T. Inukai & T. Kojima*, J. org. Chemistry *31*, 1121 (1966); *32*, 869 (1967); *K. L. Williamson & Y-F. L. Hsu*, J. Amer. chem. Soc. *92*, 7385 (1970).
[12] *J. Sauer*, Angew. Chem. *79*, 76 (1967); *R. Sustmann*, Tetrahedron Letters *1971*, 2721; *R. A. Firestone*, J. org. Chemistry *37*, 2181 (1972); *K. N. Houk*, J. Amer. chem. Soc. *95*, 4092 (1973); *P. V. Alston, R. M. Ottenbrite & D. D. Shillady*, J. org. Chemistry *38*, 4075 (1973); *N. T. Anh & J. Seyden-Penne*, Tetrahedron *29*, 3259 (1973); *O. Eisenstein & N. T. Anh*, Bull. Soc. chim. France *1973*, 2721 and 2723.
[13] *T. Inukai & T. Kojima*, J. org. Chemistry *35*, 1342 (1970); ibid. *36*, 924 (1971); *P. V. Alston, R. M. Ottenbrite & D. D. Shillady*, J. org. Chemistry *38*, 4075 (1973); *N. D. Epiotis*, J. Amer. chem. Soc. *95*, 5624 (1973).
[14] *A. Löffler, R. J. Pratt, H. P. Rüesch & A. S. Dreiding*, Helv. *53*, 383 (1970); *A. Löffler, N. Norris, W. Taub, K. L. Svanholt & A. S. Dreiding*, ibid. *53*, 403 (1970).
[15] *L. Skattebøl*, J. org. Chemistry *31*, 1554 (1966); *L. Skattebøl*, ibid. *35*, 3200 (1970); *L. K. Sydnes & L. Skattebøl*, unpublished work.
[16] *W. von E. Doering & A. K. Hoffmann*, J. Amer. chem. Soc. *76*, 6162 (1954); *C. A. Stein & T. H. Morton*, Tetrahedron Letters *1973*, 4933.
[17] *M. Makosza & W. Wawrzyniewicz*, Tetrahedron Letters *1969*, 4659; *E. V. Dehmlow & J. Schönefeld*, Liebigs Ann. Chem. *744*, 42 (1971).
[18] *D. Seyferth, H. Yamazaki & D. L. Alleston*, J. org. Chemistry *28*, 703 (1963).
[19] *J. C. Stickler & W. H. Pirkle*, J. org. Chemistry *31*, 3444 (1966).
[20] *A. Löffler, R. D. Pratt, J. Puchnat, G. Gelbard & A. S. Dreiding*, Chimia *23*, 413 (1969).
[21] *C. B. Chapleo & A. S. Dreiding*, Helv. *57*, 2420 (1974).