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THE ANODIC OXIDATION OF SOME CYCLOPROPANE CARBOXYLIC ACIDS

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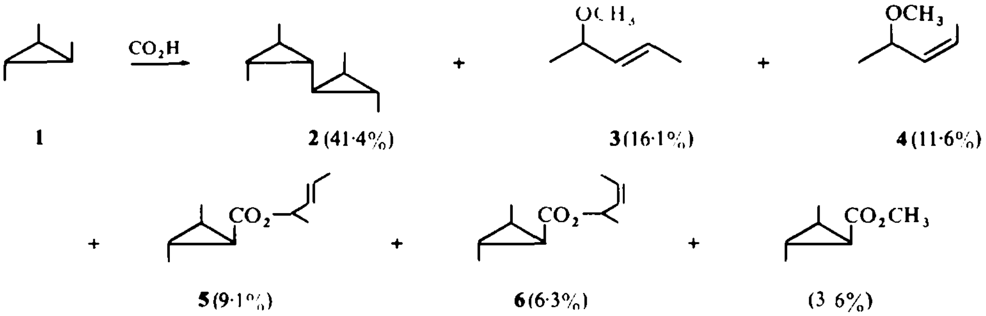
Abstract—Products, and other observations, are reported for anodic oxidation of several methyl substituted cyclopropane carboxylic acids. Implications regarding the mechanism(s) for production of cationic species are discussed.

AS PART OF an investigation into the mechanistic aspects of the anodic oxidation of carboxylic acids, a study of some substituted cyclopropane carboxylic acids has been completed.

Electrolyses were performed at −10 to 0° with parallel platinum foil electrodes on methanolic solutions *ca.* 0·4 M in carboxylic acid. Enough sodium was added to neutralize 2% of the acid present. These solutions were electrolyzed at a constant current of 0·2 amp until 1·5 unit charge/molecule of acid had been passed.

Product* results from the anodic oxidation of *trans*-2,3-dimethylcyclopropane carboxylic acid, (**1**) are summarized below. Although it has been previously reported[1] that electrolysis of cyclopropane carboxylic acid yields no products with a retained ring, we find here that the major product is the Kolbe dimer **2**, formed by coupling of two cyclopropyl radicals. Shown to be absent from the reaction mixture were the various isomers of 4,5-dimethyl-2,6-octadiene and each of the isomers of **7**, the radical coupling products expected should the cyclopropyl radicals show any tendency



1 **2** (41·4%) **3** (16·1%) **4** (11·6%)

5 (9·1%) **6** (6·3%) (3·6%)

+ 8 unidentified products totalling 11·9%

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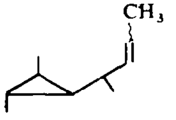
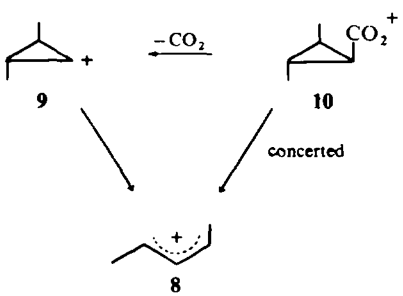
* All products reported herein, with the exception of the various bicyclopropyl compounds, were identified by glpc preparative separation and comparison of chromatographic and spectroscopic properties with those of independently synthesized authentic samples The bicyclopropyl compounds were separated by preparative glpc and identified from their spectroscopic properties which were in all cases consistent with the assigned structures.

toward ring-opening to pentenyl radicals. Products **3**–**6** must then be assumed to arise from nucleophilic attack of either carboxylate or MeOH on **8**, the anticipated[2,3] cationic intermediate, produced by disrotatory ring-opening, should either **9** or **10** be electrochemically generated. The observed *trans:cis* ratios (**3**:**4** and **5**:**6**) are 58:42, which is reasonable if **8** is the precurser to these products.

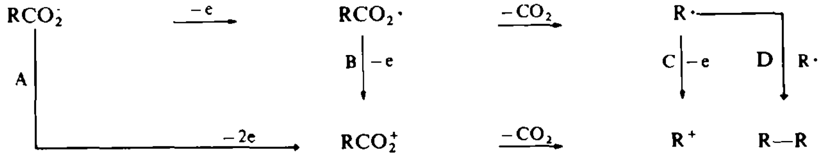


7

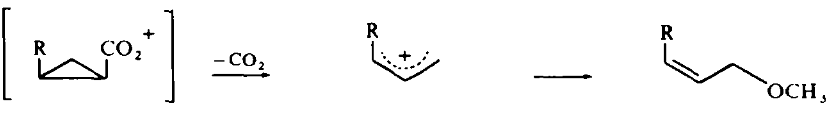


In Scheme 1 are summarized the various possible discreet stages of oxidation and chemical reaction.[4] It is possible that in some or all cases, electron transfer and decarboxylation occur simultaneously.[4a] The distinction is not important to this discussion, other than to the possible exclusion of path B if $RCO_2\cdot$ is not a discrete intermediate. Of primary interest is the question of which path A, B or C represents the operable electrode process for cation formation. Paths A and B, both leading at least transiently through RCO_2^+, are indistinguishable in work dependent on product studies.

SCHEME 1

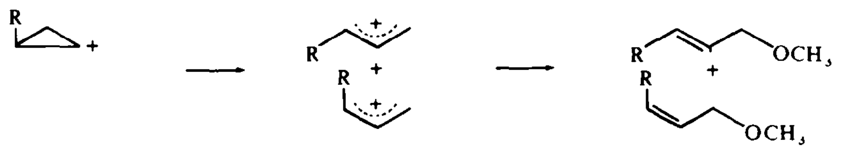


Conceivably, information pertinent to this question might be obtained from the isomer distribution among ring-opened products of substituted cyclopropane carboxylic acids. The concerted and stereospecific opening, of (incipient) cyclopropyl



(1)

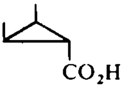
(2)



(3)

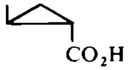
cations upon departure of the leaving group is well-documented.[3] Thus, one might anticipate results such as shown in equations (1)–(3).

Accordingly, the anodic oxidation of each of the acids **11–14** was performed. Although only partial product analyses were effected, it was established that on platinum electrodes the Kolbe dimer (mixtures of isomers in each case) was the major product from each acid. Additional results are tabulated below.



11

12



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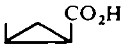

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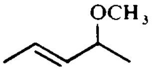

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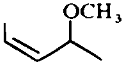

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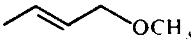

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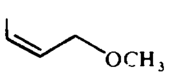

18

Starting Acid	Electrode Material	15*	16*	17*	18*
11	Pt	>99%	trace	—	—
12	Pt	>99%	trace	—	—
13	Pt	—	—	82·5%	17·4%
14	Pt	—	—	83·3%	16·7%
13	Carbon	—	—	82·0%	18·0%
14	Carbon	—	—	80·3%	19·7%

Identical *trans*:*cis* (**17**:**18**) ratios are observed for the epimeric acids **13** and **14**; the conclusion is unavoidable that a common intermediate, the 2-methylcyclopropyl cation, is traversed in each case [*eq.* (3), R = CH_3]. Had "carboxonium" ions (RCO_2^+) been formed and had they reacted according to equations (1) and (2), **13** would have produced only **17** and **14** only **18**. The results for **11** and **12**, although not as compelling, are consistent with this conclusion.

The cyclopropyl cations could be formed by either (1) oxidation of cyclopropyl radicals (path C, Scheme 1), or (2) formation of RCO_2^+ (path A, B) followed by decarboxylation *without* ring-opening. That (2) is a distinct possibility has been demonstrated by Kirmse and Schütte.[5] *cis-* and *trans*-2-Phenylcyclopropyl diazonium ions were both quite convincingly shown to decompose through a common intermediate, the 2-phenylcyclopropyl cation. The dissociative loss of CO_2 from RCO_2^+ and N_2 from RN_2^+ are both certainly expected to be highly exothermic. It is not unreasonable to anticipate that in each case ring-opening might be the slow step of a two-step process.

Although the data do not allow a provable and conclusive choice between the alternatives given in the preceding paragraph, the following observations provide tentative support for (1), path C.

If the acyloxy radical is electroactive (path B) at the anodic working potential, it is difficult to see how the majority of these radicals (*e.g.*, *ca.* 66% from 1) could escape oxidation. That is, $RCO_2\cdot$ would be produced in contact with an electrode whose

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* Percentages represent the *relative* yields of these products only.

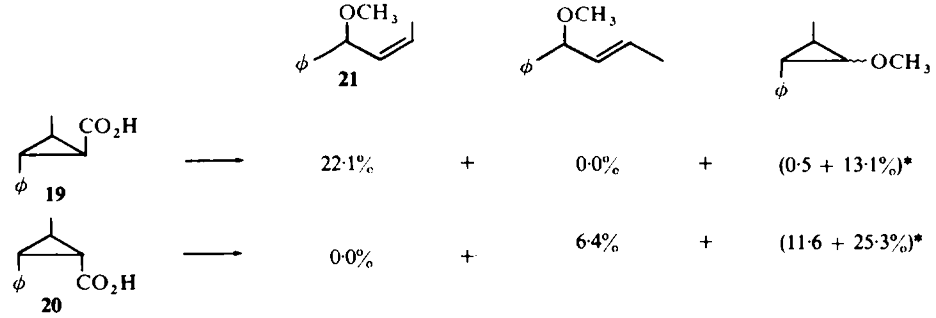
potential would thermodynamically allow further oxidation. However, the rates of electron transfer for these species are not known, and there may be kinetic competition between electron transfer and decarboxylation. This competition would be seemingly favorable only if the anode potential lies within a narrow range of that potential necessary to effect the oxidation. It is generally assumed that electron transfer rates are exponential functions of electrode potential.[6] The competitive rates of oxidation and decarboxylation should then be sensitive to changes in the anodic potential, and indeed a reduction in potential would result in an increase of the *relative* rate of decarboxylation and of the yield of Kolbe dimer.

In two additional experiments, acids **11** and **12** were electrolyzed on platinum at a constant current of 0·1 amp. Other conditions were unchanged from the previous electrolyses at 0·2 amp. In each case, the yield of Kolbe dimer was significantly reduced and the yields of carbonium ion products correspondingly increased. Since a reduction of operating current could have resulted in only a decrease of anodic overpotential, these results are opposite to those anticipated had path B been operative.

Furthermore, it is an apparently reasonable assumption that the two-electron oxidation of path A is thermodynamically less favorable than the one-electron oxidation leading to radical products. If this assumption is correct, and if *any* change in product ratios was to be observed upon reduction of operating current (and anode overpotential) one would again anticipate a relative increase in the production of radical products.

The change in product distribution observed, however, is reasonably rationalized in terms of a kinetic competition between paths C and D. Under these conditions, the localized concentration of cyclopropyl radicals would surely be proportional to current density. Since the radical coupling reaction (path D) is kinetically second-order in [R·] and path C apparently first-order, a reduction in current density, and thus [R·] would shift the product distribution, as observed, in favor of carbonium ion products. Additional support for this position may be cited from other work. Studies of the electrolytic oxidation of sodium hexanoate have indicated a trended increase (possibly linear) in the ratio of radical to cation product with current density.[7]

A considerable distinction in products has been generally observed when carboxylic acids are oxidized on carbon electrodes rather than platinum.[8] In cases where radical products are predominant on platinum, their production is greatly inhibited on carbon; cation products are almost solely produced. These results may reflect mechanistic differences which are dependent on the electrode material.

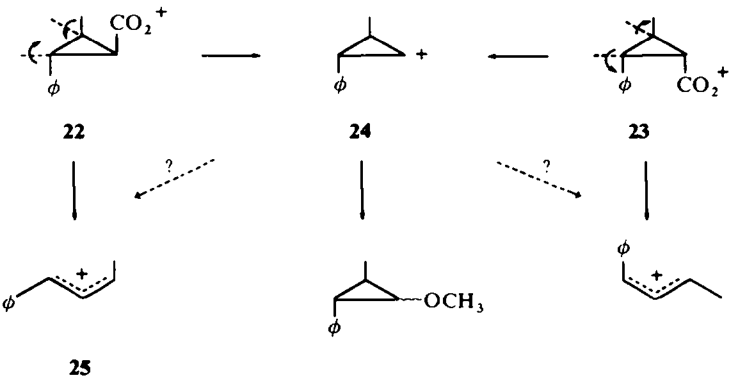


* The first number represents the yield of cyclopropylmethyl ethers, and the second the percentage yield of a secondary product shown to result from further oxidation of these ethers.

Shono *et al.*[9] have recently reported the anodic oxidation of acids **19** and **20** in MeOH and on *carbon* electrodes. These results, in part, are summarized above.

The reported stereospecific formation of allylic ethers was cited as support for the intermediacy of carboxonium ions **22** and **23**, according to Scheme 2. The high yield of cyclopropylmethyl ethers from **20** was rationalized by considering that concerted

SCHEME 2



disrotatory opening of **23** would be hindered relative to **22** for steric reasons. The bulky Ph must turn inward to a highly crowded position. In the failure to undergo concerted opening, decarboxylation to **24** would occur. The reactivity of **24** toward ring-opening should be at least as great, if not greater than **9** and little different from the 2-phenylcyclopropyl cation.[5] In these cases, allylic products are nearly exclusively formed.[*] It is then anticipated, with apparent near certainty, that **24** would predominantly isomerize to **25**, the cationic precurser of **21**. The authors have inferred (without discussion), through their lack of observation of **21**, that **24** is *totally* trapped by solvent. This surprising result, if indeed **24** is formed,[†] and the suggested mechanism are each contingent on the absence of **21** in the reaction mixture.

This possible discrepancy may be resolved by either (1) showing that the cyclopropylmethyl ethers are formed by a pathway not involving **24**,[‡] or (2) demonstration that **24**, when generated by an independent route, *e.g.*, deamination, is structurally stable. Otherwise, in our opinion, the electrode mechanism for cation formation on carbon must remain contentious. A widely held alternative point-of-view is that alkyl radicals are produced, which, owing to numerous paramagnetic centers on carbon, are strongly adsorbed on the electrode, thereby inhibiting radical combination and providing near assurance of further oxidation.[8b]

In the table above, partial results are recorded for the electrolysis on carbon of acids

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[*] From **1** we could find no evidence for formation of cyclopropylmethyl ethers, although they may have been among the eight unidentified products. The major of these was formed in 4·4% yield, and the remainder each less than 1·5%

[†] It is noteworthy that the epimeric cyclopropylmethyl ethers are formed in the same 4:1 ratio from **19** and **20**. ref 9.

[‡] An alternative pathway in which these products are formed by combination of cyclopropyl and OMe radicals is excluded by the observation that, on carbon electrodes and in MeOH, anodic oxidation of 1-methylcyclohexylacetic acid yields methyl ethers of which 99·4% are the result of carbonium ion rearrangement.[8b] When the corresponding radical is generated chemically by a variety of means, no rearrangement products are observed.[10]

13 and 14. It is apparent that, as on platinum, a common intermediate intervenes in the production of the allylic ethers **17** and **18** [eq. (3)], and that reactions such as those depicted in eqs. (1) and (2) are not important. By NMR analysis of the product mixtures, it was seen that no more than 5–6% of the product contained an intact three-membered ring. Part of this, by glpc, was Kolbe dimer and part was composed of esters of the starting acids. From a combination of these observations, it is certain that cyclopropylmethyl ethers could have been formed to no greater extent than 2–3%.

EXPERIMENTAL

M.ps and b.ps are uncorrected. NMR spectra were obtained on either a Varian HA-100 or a Varian A-60 NMR Spectrometer. IR spectra were obtained on a Perkin–Elmer Model 237B Grating Infra-red Spectrometer.

Glpc columns used are identified as follows:

(1) ⅛" × 2·5' Aluminum: 30% DC 550 Silicon oil and 3% Stearic acid on Chromosorb P.[11]
(2) ¼" × 21' Copper: 17% Carbowax and 8% $AgNO_3$ on Chromosorb P.
(3) ⅛" × 30' Aluminum: packing identical to (2).
(4) ⅛" × 10' Copper: packing identical to (2).

Preparation of starting acids

All acids were prepared by the same general procedure given for **1** below. Yields varied from 30–50%.

trans-2,3-*Dimethylcyclopropane carboxylic acid* (**1**). To *trans*-2-butene (3 moles) in a flask bearing a Dry-Ice cooled condenser, was added 1–2 g of freshly prepared CuCl,[12] followed by dropwise addition of ethyl diazoacetate (2 moles) in 100 ml CH_2Cl_2 over 12 hr. Occasional addition of CuCl in 0·2g quantities was beneficial. Upon cessation of N_2 evolution, the ethyl ester was isolated by distillation, b.p. 78–80° 47 mm. Saponification and distillation gave **1**, b.p. 122°/34 mm, shown to be free of other acids by glpc [column (1)].

2-trans-3-trans- *and* 2-cis-3-cis-*Dimethylcyclopropane carboxylic acids* (**11** *and* **12**). The mixture of epimeric esters had b.p. 73–75°/29 mm. Following saponification, the acids were partially separated by distillation. Recrystallization (3 ×) from water of the higher-boiling fractions gave **11**, m.p. 81–82·5°. Repeated elution chromatography with hexane over silica gel of the lower-boiling fractions gave **12**, m.p. 83·5–85·2°. **11** and **12** were each shown to be pure and free of contamination by the other by glpc [column (1)]. Structural assignment was based on the observation that the esters were formed in a ratio of *ca.* 7:3. It has been previously shown[13] that methyl diazoacetate adds to *cis*-2-butene to give predominantly the *anti*-isomer. The lower-boiling acid corresponds to the minor adduct.

trans- *and* cis 2-*Methylcyclopropane carboxylic acid* (**13** and **14**). The mixture of esters had b.p. 77–79°/70 mm. Following saponification, the acids were separated by distillation using a Nester-Faust 24" Spinning-band Column. Selected fractions were obtained for each compound that were shown to be pure and free of the other isomer by glpc [column (1)]. **14** was collected at 82°/10 mm and **13** at 88°/11 mm. IR spectra were identical to those previously reported.[14]

Preparation of authentic samples

trans- *and* cis-2-*Methoxy*-3-*pentene* (**3** *and* **4**). A mixture of *cis*- and *trans*-2-bromo-3-pentene, obtained from benzoyl peroxide catalyzed reaction of 2-pentene and N-bromosuccinimide, was added slowly to methanolic $AgNO_3$. The mixture of **3** and **4** obtained was separated by preparative glpc [column (2)].

3. NMR (CCl_4): 4·50τ, multiplet (2 protons); 6·37τ, pentet (1 proton); 6·77τ, singlet (3 protons); 8·29τ, doublet (3 protons); and 8·79τ, doublet (3 protons). J_{trans}: 15·1 Hz, by double resonance. IR (CCl_4, 0·1 mm cell): 967 cm^{-1} (s) and 1675 cm^{-1} (w).

4. NMR (CCl_4): 4·54τ, multiplet (2 protons); 5·87τ, multiplet (1 proton); 6·75τ, singlet (3 protons); 8·32τ, doublet of doublets, $J \simeq 2·0$, 6·6 Hz (3 protons); and 8·79τ, doublet (3 protons). J_{cis}: 11·2 Hz, by double resonance. IR (CS_2, 0·1 mm cell): 688 cm^{-1} (m) and 1662 cm^{-1} (w).

trans- *and* cis-3'-*Penten*-2'*yl* 2-cis-3-trans-*dimethylcyclopropane carboxylate* (**5** *and* **6**). A suspension of **1** (3·0 g, 0·026 mole) in water was neutralized (litmus) with aqueous KOH. To this solution was added with stirring 4·5 g (0·027 mole) $AgNO_3$ in water. The silver salt of **1** was filtered, washed well with abs. EtOH and then with anhydrous ether. The salt was dried for several days *in vacuo* in the dark, powdered to 40 mesh, and dried for several more days to give 4·3 g (0·019 mole). To an etherial suspension of this salt was slowly added, with stirring, 2·9 g (0·019 mole) 2-bromo-3-pentene in ether. After stirring for several hr, the solution was filtered, washed in order with brine (containing $AgNO_3$),$NaHCO_3$ aq, and water. The organic layer was dried (Na_2SO_4) and distilled to give a mixture of **5** and **6** [b.p. 38–40°/1 mm]. Pure samples of **5** and **6** were obtained by preparative glpc [80°, column (2)]. Although the detailed multiplet patterns were visually distinctive, the NMR spectra of **5** and **6** were grossly similar as follows (CCl_4): 4·2–5·1τ, multiplet (3 protons); 8·34τ doublet (3 protons); and 8·6–9·3τ, multiplet (12 protons). IR (**5**, neat): 3020 cm^{-1}; 1725 cm^{-1}; 1670 cm^{-1} (sh); 1185 cm^{-1}; 965 cm^{-1}. IR (**6**, neat): 3020 cm^{-1}; 1720 cm^{-1}; 1680 cm^{-1} (sh); 1180 cm^{-1}; region near 965 cm^{-1} featureless.

4,5-*Dimethyl*-2,6-*octadiene*. In dry glassware and under N_2, 10·0 g (0·067 mole) 2-bromo-3-pentene in 50 ml diethyl ether was added with stirring and cooling to 0·8 g (0·033 mole) of Mg. A copius precipitate ($MgBr_2$) formed. After 1 hr, the mixture was washed thoroughly with water and the etherial solution dried (Na_2SO_4). Distillation, b.p. 165–170°/760 mm [lit.[15] 167–168/760 mm], gave 4·1 g (90%). Glpc analysis [column (3)] showed at least five overlapping peaks; there are six possible geometric and diastereomeric isomers. NMR (mixture, CCl_4): 4·5–5·2τ, multiplet (4 protons); 8·05τ, broad (2 protons); 8·4τ, pseudo-triplet (6 protons); and 9·11τ, broad doublet (6 protons).

2-(trans-2′,3′-*Dimethylcyclopropyl*)-3-*pentenes* (**7**). (a) To KOt-Bu (44·8 g, 0·4 mole) and *trans*-2-butene (98 g, 1·7 mole) in ether was added 76 g (0·3 mole) of $CHBr_3$. After two hr, aqueous NH_4Cl was added and the etherial solution separated, washed with water and dried (Na_2SO_4). Distillation provided 53·5 g (78·0%) of *trans*-2,3-dimethyl-1,1-dibromocyclopropane, b.p. 70–72/34 mm. (b) To *trans*-2,3-dimethyl-1,1-dibromocyclopropane (53·5 g, 0·234 mole) was added with stirring 38·4 g (0·13 mole) of tri-n-butyltin hydride over 3 hr. After 1 additional hr, the colorless mixture was distilled to give 16·7 g (86%) *trans*-2,3-dimethyl-1-bromocyclopropane, b.p. 48–49°/ 73 mm, recovered dibromide, 17·0 g, b.p. 82–84°/60 mm, and tri-n-butyltin bromide, 47·7 g, b.p. 110–115°/1 mm. (c) To 1·0 g (0·041 mole) of Mg under N_2 and covered with *ca.* 5 ml of anhydrous THF maintained at reflux temp. was added *trans*-2,3-dimethyl-1-bromocyclopropane (6·0 g, 0·040 mole) in 20 ml anhydrous THF; 2 dps MeI were used for initiation. After 1·5 hr, the Grignard solution was pressure filtered (with N_2) through glass-wool plug into an addition funnel connected to a flask containing 6·0 g (0·040 mole) 2-bromo-3-pentene. Rapid addition was effected with stirring and cooling. After 1 hr, a copious precipitate ($MgBr_2$) was filtered, the etherial solution washed in turn with $AgNO_3$ aq, water, and then dried (Na_2SO_4). Distillation give 4·8 g of **7**, 86%, b.p. 47–50°/48 mm. The *cis*- and *trans*-isomers of **7** were separated by preparative glpc [50°, column (2)].

cis-**7**. NMR (CCl_4): 4·7τ, multiplet (2 protons); 7·95τ, multiplet (1 proton); 8·46τ, doublet (3 protons); 9·0τ, multiplet (9 protons); and 9·4–10·1τ, multiplet (3 protons). IR (neat): Closely similar to *trans*-**7** except 969 cm^{-1} band absent.

trans-**7**. NMR (CCl_4): 4·65τ, multiplet (2 protons); 8·2–8·5τ, multiplet (4 protons); 9·0τ, multiplet (9 protons); and 9·4–10·1τ, multiplet (3 protons). IR (neat): 969 cm^{-1} (s).

trans- *and* cis-1-*Methoxy*-2-*butene* (**17** and **18**). To 25·3 g (0·0149 moles) of $AgNO_3$ in 100 ml absolute MeOH was added with stirring 20·0 g (0·0148 mole) of 1-bromo-2-butene. After 5 hr the mixture was poured into brine, the organic layer separated, washed with brine (2x) and dried (Na_2SO_4). Distillation on a Nester-Faust 24″ Spinning Band column gave 3·2 g (25·2%) 3-methoxy-1-butene, b.p. 50–52°/760 mm and 7·8 g of **17** and **18** (61·5%), b.p. 76°/760 mm. **17** and **18** were separated by preparative glpc [40°, column (2)].

17. NMR ($CDCl_3$): 4·38 τ, multiplet (2 protons); 6·19 τ, broad doublet (2 protons); 6·71 r, singlet (3 protons); and 8·28 τ, broad doublet (3 protons). J_{trans} = 15·0 Hz, by spin decoupling. IR (CCl_4, 0·1 mm cell): 3010 cm^{-1}; 1676 cm^{-1} (w): 1115 cm^{-1} (s); and 970 cm^{-1} (s).

18. NMR ($CDCl_3$): 4·33 τ, multiplet (2 protons); 5·96 τ, broad doublet (2 protons); 6·61 τ, singlet (3 protons); and 8·26 τ, broad doublet (3 protons). J_{cis} = 11·8 Hz, by spin decoupling, IR (CS_2, 0·1 mm cell): 3015 cm^{-1}; 1663 cm^{-1} (w); 1120 cm^{-1} (s); and 690 cm^{-1} (ms).

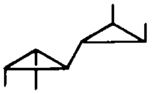
Kolbe product from **1** (**2**). Obtained by preparative glpc from electrolysis mixture. NMR (CCl_4): 8·8–9·2 τ, multiplet (12 protons) and 9·26–10·2 τ, multiplet (6 protons).

Kolbe products from **11** *and* **12**. Obtained by preparative glpc from electrolysis mixture. The same two isomers (i and ii) were obtained in nearly the same ratio from both **11** and **12**. The third possible isomer was not found; its formation is, however, uncertain.

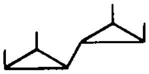
i: NMR (CCl_4): 9·01 τ, multiplet (12 protons); 9·56 τ, broad (4 protons); and 9·87 τ, broad (2 protons).

ii: NMR (CCl_4): 8·97 τ, multiplet (12 protons); 9·36 τ, broad (4 protons); 9·77 τ, quartet (1 proton); 10·34 τ, overlapping triplets (1 proton).

These spectra are consistent with the structures given below.



i



ii

Electrolyses

A cylindrical 75 ml vessel served as the electrolysis cell. A stopper, fitting this vessel, carried the following: Drawn N_2 inlet tube extending into the solution; gas outlet tube; thermometer; and two lengths of glass tubing into and through which were sealed lengths of platinum wire. Smooth platinum foil electrodes (1·5 × 2·5 cm) were joined to the wires. The electrolysis vessel was immersed into a cooling bath for temperature control. Mild magnetic stirring was employed during each electrolysis. Constant current was supplied with a Sargent Coulometric Current Source Model IV. Electrolysis solutions were prepared with 50 ml MeOH, freshly distilled from Mg. A small piece of clean Na, calculated to neutralize *ca.* 2% of the acid to be used was added, followed by the acid (usually 2 g). Electrolyses were continued until 1·5 unit charge/molecule of acid had been passed. Owing to filming of the anode (probably polymer), the electrode polarities were reversed approximately every 40 min.

Carbon rods 0·6 cm in diameter were used for electrodes in two experiments. Filming was not observed in those cases. On carbon, electrolyses were performed at −35 to −40°.

Analyses

The electrolysis mixtures were poured into water. The pH was adjusted until the solution was basic and the mixture thoroughly extracted with ether. After drying (Na_2SO_4), the solvent was stripped. The product mixtures were qualitatively and quantitatively analyzed by conventional glpc and spectroscopic techniques.

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