The chloro derivative X (0.225 g) was heated on the steam bath for 10 hr with 60 ml of a 15% solution of potassium *t*-butoxide in *t*-butyl alcohol. Work-up in the usual manner afforded a neutral organic residue which was crystallized from chloroform–ethanol to give hydrocarbon IX (0.181 g, 90%), mp 200–202°.

Anal. Calcd for $C_{27}H_{20}$: C, 94.15; H, 5.85. Found: C, 93.87; H, 5.80.

Catalytic reduction of a sample of IX in ethanol solution (10% palladium–charcoal catalyst) afforded hydrocarbon XI, identical (mixture melting point) with a sample prepared from adduct V.

B.—A suspension of adduct IIIa (1.77 g) in acetic acid (167 ml) containing 2 drops of sulfuric acid was stirred at room temperature for 24 hr. During this period the starting material dissolved completely, and the product then precipitated out. The filtered and dried precipitate was crystallized from benzene–cyclohexane to give material (1.20 g) which was identical (melting point and infrared) with pure IX prepared from chloride X.

2:1 Adducts of 1,3-Diphenylisobenzofuran with Norbornadiene.—A solution of 1,3-diphenylisobenzofuran (I, 4.00 g, 14.8 mmoles) and norbornadiene (0.756 g, 7.4 mmoles) in benzene (30 ml) was heated on the steam bath in a sealed tube for 1 week. Evaporation of the solvent, followed by crystallization of the residue from ethanol, yielded 3.43 g of crystals, which were shown to be a mixture of two products by thin layer chromatography. Three recrystallizations from ethanol afforded the pure isomer VIIIA, mp 305–306°.

Anal. Calcd for $C_{47}H_{36}O_2$: C, 89.16; H, 5.74. Found: C, 89.28; H, 5.70.

Preparative thin layer chromatography of the original product mixture (benzene–cyclohexane on silica plates) afforded a sample of pure isomer VIIIB, mp 319–321°.

Anal. Calcd for $C_{47}H_{36}O_2$: C, 89.16; H, 5.74. Found: C, 88.88; H, 5.60.

Dehydration of Bisadducts VIIIA and VIIIB.—A solution of an approximately 1:1 mixture of adducts VIIIA and VIIIB (0.500 g) in carbon disulfide (95 ml) was stirred with phosphorus pentasulfide (4 g) at room temperature for 5 days. The filtered solution was evaporated to dryness and the residue was taken up in benzene and purified by chromatography on neutral alumina. Crystallization from benzene–ethanol afforded the dinaphthonorbornadiene XII (0.447 g, 95%), mp 344–345°.

Anal. Calcd for $C_{47}H_{32}$: C, 94.63; H, 5.37. Found: C, 94.70; H, 5.38.

Registry No.—I, 5471-63-6; II, 121-46-0; IIIa, 10211-74-0; V, 10146-91-5; VIIIa, 10174-31-9; VIIIb, 10146-92-6; IX, 10146-93-7; X, 10146-94-8; XI, 10146-95-9; XII, 10146-96-0.

Catalytic Hydrogenation of *trans*-1-Methoxy-1,3-butadiene[1]

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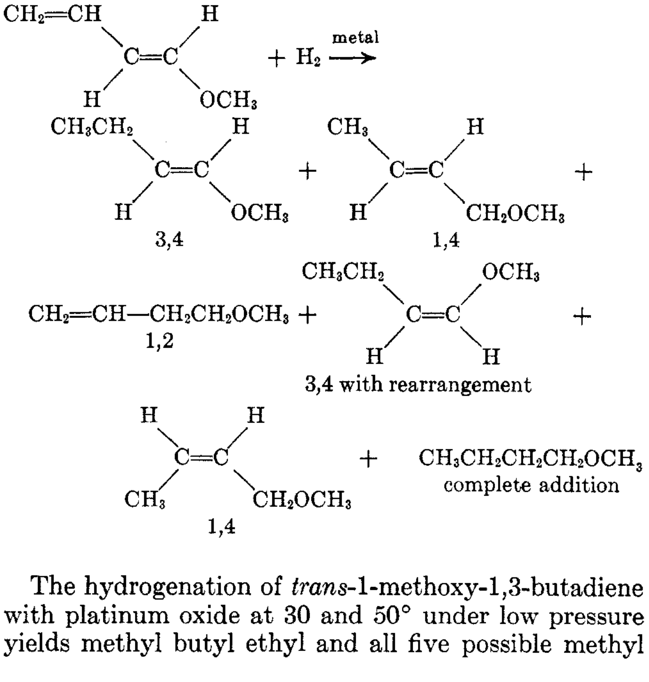
Hydrogenation of *trans*-1-methoxy-1,3-butadiene over Adams catalyst gives all possible intermediate butenyl methyl ethers, but the predominant product for the addition of 1 mole of hydrogen is *trans*-1-methoxy-1-butene. 1-Methoxy-2-butene is the source of the hydrogenolysis products and the *cis*-1-methoxy-1-butene is formed by rearrangement of *trans*-1-methoxy-1-butene. Raney nickel catalyst gives nearly equal amounts of 1,2-, 3,4-, and 1,4-addition products while Lindlar catalyst gives a greater proportion of the 3,4-addition product than Adams catalyst. Both Raney nickel and Lindlar catalysts provide only small amounts of methyl butyl ether until the 1-methoxy-1,3-butadiene is consumed and the reaction ceases for all practical purposes at this point for the Lindlar catalyst. With Adams catalyst methyl butyl ether production is significant from the beginning of hydrogenation. Nickel–boron catalyst gives over-all results comparable with those of Adams catalyst except that *cis–trans* isomerism was not observed.

Studies of the addition of various reagents to 1-alkoxy-1,3-butadienes have demonstrated a marked tendency for these dienes to undergo 1,4 additions.[1,5,6] The selectivity and stereoselectivity of the addition of hydrogen to *trans*-1-methoxy-1,3-butadiene could give needed information on the relations between *cis–trans* isomerization, selectivity of hydrogen addition, and double-bond migration for 1,3-diene systems.[7] We have studied the addition of hydrogen to *trans*-1-methoxy-1,3-butadiene in the liquid phase over platinum oxide (Adams catalyst), Raney nickel, Lindlar catalyst, and nickel–boron catalyst with the greatest emphasis on studies with platinum oxide. The possible products for the addition of hydrogen to this diene and rearrangement are shown in Scheme I.

SCHEME I



The hydrogenation of *trans*-1-methoxy-1,3-butadiene with platinum oxide at 30 and 50° under low pressure yields methyl butyl ethyl and all five possible methyl

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(1) Presented in part before the Southeastern Regional Meeting of the American Chemical Society, Charlotte, N. C., Nov 1963. For previous studies of the chemistry of 1-alkoxy-1,3-butadienes, see D. G. Kubler, *J. Org. Chem.*, **27**, 1435 (1962).

(2) Undergraduate Research Participation Scholar under National Science Foundation Grant G-21603. Grateful acknowledgment is given for financial support of this work by the National Science Foundation and by Furman University.

(3) Taken in part from the thesis presented by J. M. B. to Furman University in partial fulfillment of the requirements of the College Teaching Honors Program, B.S. degree, June 1964.

(4) Author to whom inquiries should be addressed: Department of Chemistry, Furman University, Greenville, S. C.

(5) W. Flaig, *Ann.*, **568**, 1 (1950).

(6) Consortium fur Electrochemische Ind. Gmbh., British patent 757,907 (1956); *Chem. Abstr.*, **52**, 1205 (1958).

(7) R. L. Burwell, Jr., *Chem. Rev.*, **57**, 895 (1957).

TABLE I

HYDROGENATION OF *trans*-1-METHOXY-1,3-BUTADIENE OVER ADAMS CATALYST AT 30°

	% reaction[a]									
	9.5	25.0	40.0	42.8	49.8	53.0	57.3	63.3	69.3	86.4
Methyl butyl ether	4.8	15.3	21.3	24.0	27.2	30.1	29.8	44.8	52.7	92.8
4-Methoxy-1-butene	2.1	4.3	5.0	5.9	6.6	3.8	4.6	0.0	0.0	0.0
cis-1-Methoxy-1-butene	1.7	3.5	6.4	7.1	9.8	9.1	8.6	9.5	7.1	0.0
trans-1-Methoxy-1-butene	9.7	22.7	30.9	30.8	30.0	35.5	37.8	30.1	31.9	7.2
trans-1-Methoxy-2-butene	3.4	4.7	7.1	5.9	9.2	10.1	9.5	10.4	8.5	0.0
cis-1-Methoxy-2-butene	2.5	2.1	3.5	3.4	4.4	6.2	4.1	5.1	0.0	0.0
Methanol[b]	2.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
trans-1-Methoxy-1,3-butadiene	73.5	47.4	25.9	22.9	12.7	5.7	5.5	0.0	0.0	0.0

[a] The % reaction is based on the calculated pressure drop for 2 moles of hydrogen per mole of diene. [b] Methanol was detected by glpc in one experiment, but butane and butenes were present in all of the mixtures.

TABLE II

HYDROGENATION OF *trans*-1-METHOXY-1,3-BUTADIENE OVER ADAMS CATALYST AT 50°

	% reaction[a]						
	9.5	24.8	39.8	45.3	49.3	65.1	75.0
Methyl butyl ether	11.0	12.1	17.3	21.2	23.6	59.7	75.4
4-Methoxy-1-butene	4.7	7.6	10.3	11.3	10.1	0.0	0.0
cis-1-Methoxy-1-butene	4.0	7.1	11.3	13.2	14.2	6.6	2.6
trans-1-Methoxy-1-butene	13.3	18.4	25.4	30.0	31.1	25.9	22.0
trans-1-Methoxy-2-butene	3.4	6.1	9.1	11.3	11.2	7.8	0.0
cis-1-Methoxy-2-butene	1.6	3.6	5.1	5.6	5.9	0.0	0.0
Methanol	3.5	1.1	0.0	0.0	0.0	0.0	0.0
Butane and butenes	P[b]	P	P	P	P	P	P
trans-1-Methoxy-1,3-butadiene	58.5	44.1	21.5	7.3	3.9	0.0	0.0

[a] The % reaction is based on the pressure drop for 2 moles of hydrogen per mole of diene. [b] The indication P means the compound was present; no percentage composition was recorded.

butenyl ethers. Some hydrogenolysis occurs resulting in the formation of methanol, butane, and the three butenes. The hydrogenations were carried to various extents of completion ranging from 9.5 to 86.4% of completion (for two double bonds) and the mixtures were analyzed by gas-liquid partition chromatography (glpc). No glpc peaks appeared other than the previously mentioned products. The data obtained 30° are given in Table I and the 50° data are given in Table II.

Plots of these data demonstrate that methoxybutadiene disappears and methyl butyl ether appears approximately as a linear function of the extent of reaction until the diene is depleted at about 57% of theoretical hydrogen uptake. After the diene is depleted, the slope of the curve for the concentration of methyl butyl ether *vs.* the per cent of reaction sharply increases but the curve is still a linear function of the extent of reaction. All of the reaction intermediates increase in concentration until the diene is depleted and thereafter the intermediates diminish in concentration.

Methanol appeared as a product for one experiment at 30° and for two experiments at 50°, and in these cases the extent of hydrogenation was low. It is not apparent as to why methanol is not found for greater amounts of hydrogen uptake. Methanol is probably formed in all the cases studied since trace amounts of butane and the butenes were always found. It is possible that some of the methanol added to the diene forming crotonaldehyde dimethyl acetal or its polymers with the diene, but such an occurrence was not demonstrated for these systems.[8]

The predominant intermediate product throughout the reaction is *trans*-1-methoxy-1-butene, and its concentration is nearly equal to the combined concentrations of the other intermediate ethers at all stages of reaction. This unsaturated ether also persists after all other intermediate ethers have disappeared. In contrast to the results for the vapor phase reduction of 1-butyne, 1,2-butadiene, and 1,3-butadiene over palladium on alumina catalyst and for 1,3-butadiene over several catalysts for which no butane is produced until the polyunsaturated compound disappears,[9,10] methyl butyl ether appears almost from the beginning of hydrogenation of methoxybutadiene over Adams catalyst. These results mean that the intermediate butenyl ethers compete effectively with the methoxybutadiene for the catalyst surface, or, before the partially hydrogenated ether can be desorbed and replaced by another molecule of diene, complete addition of hydrogen occurs to give significant amounts of the saturated ether. Therefore, no firm conclusions can be made about the relative extents of 1,2, 1,4, and 3,4 addition because the saturated ether could be formed from any of the intermediate ethers. While considerably greater amounts of the *trans*-1-methoxy-1-butene are found, the 1,2 and/or 1,4 adducts may give rise to most of the methyl butyl ether during the first half of the reaction.

It was hoped that the problem of orientation of addition could have been resolved by the determination of the kinetics of hydrogenation of methoxybutadiene and for each of the intermediate butenyl methyl ethers. Therefore, throughout these studies, the pressure of hydrogen was measured as a function of time and the log P_{H_2} was plotted *vs.* time.[11] In nearly all instances a straight-line plot was obtained (the rate was independent of the concentration of the diene)

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[8] D. G. Kubler, *J. Org. Chem.*, **27**, 791 (1962).

[9] E. F. Meyer and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **85**, 2881 (1963).

[10] G. C. Bond, G. Webb, P. B. Wells, and J. M. Winterbottom, *J. Chem. Soc.*, 3218 (1965).

[11] H. A. Smith and B. L. Stump, *J. Am. Chem. Soc.*, **83**, 2739 (1961).

Table III

Hydrogenation of *trans*-1-Methoxy-1,3-butadiene over Raney Nickel, Lindlar Catalyst, and Nickel–Boron

	% reaction (temp, °C)						
	Raney nickel				Lindlar		Ni–B[a]
Products[b]	10 (30)	30 (30)	45 (30)	82 (30)	50[c] (30)	30 (50)	57 (30)
Methyl butyl ether, %	0.2	2.1	3.8	61.2	5.3	0.5	16.4
4-Methoxy-1-butene, %	8.6	19.2	32.2	0.0	2.0	4.6	4.5
cis-1-Methoxy-1-butene, %	0.2	1.9	2.3	6.9	8.8	5.5	0.0
trans-1-Methoxy-1-butene, %	8.1	24.9	27.5	29.5	71.0	52.5	50.5
trans-1-Methoxy-2-butene, %	4.4	15.4	21.2	2.2	11.8	9.6	20.4
cis-1-Methoxy-2-butene, %	0.7	4.4	6.8	0.0	1.0	1.5	8.2
trans-1-Methoxy-1,3-butadiene, %	76.9	32.4	6.1	0.0	0.0	25.9	0.0

[a] Percentages are on a 100% basis not counting the ethanol in the mixture (about 75% ethanol). [b] No butane or butenes were observed for these hydrogenations. [c] The rate of uptake of hydrogen markedly decreased after about 40% of reaction and nearly ceased after 50% of reaction.

but the rate constants calculated from the slopes were not very duplicable (*ca.* ±25%). In a few instances the line deviated from linearity (the rate decreased and the line curved upward) after 10–50% completion, but the deviation was not reproducible.

The cause of the nonreproducible kinetic results was not learned. A single batch of Adams catalyst was used throughout the studies and was found to give very reproducible rates of hydrogenation of cyclohexene in acetic acid. The methoxybutadiene was freshly distilled from a single, large batch just before use and care was taken to exclude air from the containers before and during transfer (nitrogen purge). Use of methanol as a solvent did not improve the kinetic results. Furthermore the same erratic kinetic results were obtained with the intermediate ethers.[12]

To establish the source of hydrogenolysis products and to determine the extents of isomerizations, if any, major intermediate ethers were each hydrogenated to various extents of completion. The products were analyzed by glpc.

trans-1-Methoxy-1-butene (99% pure) was hydrogenated over Adams catalyst to various extents of completion (10, 25, 90%) at 30° and to 25% completion at 50°. The predominant reaction was hydrogenation to form methyl butyl ether. However, the unreacted starting material contained some *cis* isomer and the ratio of the *cis* to the *trans* isomer increased with the extent of hydrogenation (*trans* content decreased from 82.9 to 59.6 to 2.2% at 30° while the *cis* content changed from 3.7 to 6.2 to 0.9%) and as the temperature increased. The temperature effect on the isomerization is also evident from the data of Tables I and II, the ratio of the *cis* to *trans* isomer being significantly higher at 50° than at 30° to more than 60% of complete hydrogenation. The starting diene (which appears to be isomerically pure) is not likely the source of the *cis*-1-methoxy-1-butene *via* rearrangement and hydrogen addition to the 3,4 positions, since at no time were any stray chromatographic peaks observed which could have indicated the presence of *cis*-1-methoxy-1,3-butadiene. The *trans*-1-methoxy-1-butene is the only intermediate ether which shows significant double-bond rearrangement under the reaction conditions used.

The 4-methoxy-1-butene hydrogenates cleanly to methyl butyl ether. A trace of rearrangement to *trans*-1-methoxy-1-butene was detected for one reaction mixture. Under similar conditions at 30 and 50° methyl butyl ether does not dehydrogenate or undergo hydrogenolysis.

The major source of hydrogenolysis products is probably the *trans*-1-methoxy-2-butene. In all cases for the hydrogenation of *trans*-1-methoxy-2-butene (95% pure) methanol, butane, and the butenes formed, and the amount of methanol increased directly with the extent of reaction. The extent of hydrogenolysis exceeded the extent of hydrogenation based on the methanol content. The reason hydrogenolysis is not a serious problem in the hydrogenation of methoxybutadiene is because of the minor amount of 1,4 addition. The amount of double-bond migration for this intermediate was unimportant since there was formed only a small amount of 4-methoxy-1-butene. A minor point of interest is that *cis*-1-methoxy-2-butene was not detected after initiation of hydrogenation. Either this isomer undergoes hydrogenation or hydrogenolysis very rapidly or it is isomerized to the *trans* isomer.

Other Catalysts.—Hydrogenations of *trans*-1-methoxy-1,3-butadiene at 30° and 50 psi were carried to various extents of completion with Raney nickel, Lindlar catalyst,[13] and nickel–boron catalyst.[14] The data for these studies are summarized in Table III. Methyl butyl ether and all of the intermediate butenyl ethers are formed with Raney nickel and with Lindlar catalyst. The formation of methyl butyl ether over these two catalysts is curtailed significantly compared with Adams catalyst. Notable differences of these catalysts from Adams catalyst are that hydrogenolysis does not occur and Lindlar catalyst appears to be somewhat more selective in giving 3,4 addition, while Raney nickel is less selective than Adams catalyst and provides nearly equal amounts of 1,2, 3,4, and 1,4 addition. With Lindlar catalyst the hydrogenation essentially ceased after the uptake of 1 mole of hydrogen.

The nickel–boron catalyst provided, in a single experiment, methyl butyl ether and all of the methyl butenyl ethers except *cis*-1-methoxy-1-butene. This catalyst apparently fails to promote *cis–trans* isomerism which is one of the important virtues suggested for its use for the hydrogenation of alkanes.[14]

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(12) Professor Peter B. Wells, The University, Hull, England, has kindly written to these authors that he too has experienced difficulty in obtaining reproducible kinetics with Adams catalyst and suggested the use of platinum supported on charcoal.

(13) H. Lindlar, *Helv. Chem. Acta*, **35**, 446 (1952).

(14) H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.*, **85**, 1003, 1005 (1963).

Experimental Section

Hydrogenation Procedures.—The hydrogenation studies were conducted in a Parr low-pressure apparatus with a small Coca-Cola bottle as a reaction flask.[15] The bottle was surrounded by a metal water jacket which was closed at the top by a large rubber stopper. Water was circulated through the metal jacket from a constant-temperature bath (±0.1°). A standard weight of 0.04 g of Adams catalyst[16] and 10 g of freshly distilled 1-methoxy-1,3-butadiene were added to the hydrogenation bottle which had been previously flushed with nitrogen. Both components were weighed to the nearest 0.1 mg. The system was purged three times with hydrogen (National Cylinder Gas Co.) and then brought to an initial pressure of 52 ± 2 psig. The mixture was allowed to stand in the apparatus for 15 min to allow for temperature equilibration before beginning to shake the mixtures. No pressure drops were observed during this period. The pressure drop during reaction was read to ± 0.05 psi on an Ashcroft 0–60-psi test gauge[17] having scale divisions of 0.2 psi.

Hydrogenations were carried to various extents of completion calculated from the drop in pressure by the ideal gas equation. The volume of the system (4.30 l.) was determined by the hydrogenation of cyclohexene in glacial acetic acid. The pressure drop for the reactions varied from 2 to 22 psi depending upon the point at which the hydrogenation was interrupted. Zero time was taken when agitation was started and pressure was recorded against time in seconds. Hydrogen was vented from the system and the mixtures were centrifuged to settle the catalyst. The supernatant liquid was decanted and refrigerated in septum capped vials until analyzed.

For the Raney nickel studies, W-6 catalyst[18] was prepared and stored under water. The catalyst was weighed wet, washed with methanol, and transferred to the hydrogenation bottle. Complete transfer of the nickel was effected by several portions of methanol which totaled to 20 ml for each run. Several runs in the absence of methanol demonstrated that hydrogenolysis of methoxybutadiene did not occur.

The runs with Lindlar catalyst[19] were conducted as were the Adams catalyst runs. The catalyst was used in the amount of 0.6% by weight of the methoxybutadiene with a weight of quinoline equal to the weight of catalyst.[20]

The nickel-boron catalyst[14] of Brown was prepared from 1.244 g of Baker and Adams nickel acetate tetrahydrate in 40 ml of 95% ethanol and 0.380 g of sodium borohydride in 10 ml of 95% ethanol. The catalyst and alcohol solution were transferred to the hydrogenation flask along with 10.38 g of freshly distilled methoxybutadiene. The hydrogenation was interrupted after 57% of theoretical uptake of hydrogen.

Gas-Liquid Partition Chromatographic Analyses.—The hydrogenation mixtures were analyzed by glpc using a column of Carbowax 4000 on HMDS Chromosorb P with helium as the carrier gas.[21]

The components of the mixtures were identified by means of their retention times when they were compared with those of authentic samples. The chromatographic fractions also were trapped in carbon disulfide or chloroform in a Dry Ice–acetone bath and the infrared spectra were compared with the spectra of the synthetic compounds. The only product which was not independently synthesized was *cis*-1-methoxy-2-butene. This substance, however, was trapped from the chromatograph and identified by its infrared spectrum. This isomer also was present in low concentration (glpc) in the synthesized *trans*-1-methoxy-2-butene.

The sensitivity of the thermal conductivity cell for each component was determined by the use of synthetic mixtures. The area percentages were then corrected for the detector sensitivity. All of the peaks were cleanly resolved expect for 4-methoxy-1-butene and *cis*-1-methoxy-1-butene, the latter always appearing as a shoulder on the former peak.

Materials. *trans*-1-Methoxy-1,3-butadiene.—This material was prepared by the phosphoric acid-catalyzed dealcoholation of 1,1,3-trimethoxybutane as described by Montagna and Hirsh.[22] The product boiled at 45-47° (150 mm) and had $n^{25}\text{D}$ 1.4602. Analysis by glpc indicated no impurities even in trace amounts using various size samples for injection and various instrumental operating conditions through the following 0.25-in. columns: a 12-ft silver nitrate-triethylene glycol on Chromosorb P, a 12-ft D. C. Silicone 710 on Chromosorb W, a 50-ft didecyl phthalate on Chromosorb W, and a 20-ft Carbowax 4000 on HMDS Chromosorb P. The infrared spectrum (Perkin-Elmer Model 21) showed strong absorption bands characteristic of the dienyl ether system in general and in particular for the *trans* hydrogen wag at 928 cm^{-1}.[23]

The purified methoxybutadiene was made in a sufficiently large quantity for all of the hydrogenation studies and was stored over hydroquinone and tri-*n*-butylamine to prevent either radical or ionic polymerization. Small portions were distilled under reduced pressure, bp 39° (100 mm), through a 6-in. micro Vigreaux column just before each hydrogenation. The samples were kept under nitrogen during all operations prior to hydrogenation.

Butane and Butenes.—Butane was prepared by the reaction of 2-chlorobutane and magnesium in ether followed by treatment with water. A mixture of the three butenes was prepared by the sulfuric acid catalyzed dehydration of 2-butanol. The butane showed two glpc peaks, one of which was butane and the other was air. The butenes contained at least five components, one of which was air. The butane peak and the three major butene peaks corresponded exactly in retention times to four of the peaks found in hydrogenation mixtures for which hydrogenolysis occurred.

Methyl Butyl Ether.—1-Bromobutane (205 g, 1.5 moles) was added dropwise over a period of 1 hr to a solution of 81 g (1.5 moles) of sodium methoxide in methanol. After the mixture had remained at room temperature for 1 week, it was extracted several times with water, dried over sodium sulfate, and then refluxed over sodium. Distillation provided 51 g (0.59 mole, 39%) of methyl butyl ether which boiled at 67.5–68°. The product showed no impurities by glpc with several columns.

4-Methoxy-1-butene.—The procedure of Pariselle[24] was employed to make 4-methoxy-1-butene using allyl chloride and magnesium in ether to prepare the Grignard reagent followed by the addition of freshly distilled chloromethyl methyl ether. The 4-methoxy-1-butene (16.7%) boiled at 67.5–68° and had $n^{25}\text{D}$ 1.3886. Pariselle reported bp 68–69° and $n^{20}\text{D}$ 1.398. The sample contained only a trace of impurity (less than 1%) as was determined by glpc over Carbowax 4000 on HMDS Chromosorb P. The infrared spectrum (in chloroform) showed strong ether absorption bands and the characteristic absorption due to a terminal double bond (1640, 990, and 918 cm^{-1}).

Anal. Calcd for $C_5H_{10}O$: C, 69.73; H, 11.70. Found: C, 69.84; H, 11.76.

***cis*- and *trans*-1-Methoxy-1-butene.**—Freshly distilled butyraldehyde dimethyl acetal, (bp 64–64.5° (130 mm), $n^{25}\text{D}$ 1.3863) was fed under a slight pressure of nitrogen to a 1 × 24 in. tube containing 75 ml of pelleted Celite 408 catalyst carrier[25] at the rate of 1 drop per second. The tube was heated at 300–325° by means of an electric furnace while a total of 652 g of acetal was passed. The reactor effluent was washed three times with water to remove methanol and then dried successively over sodium sulfate and Drierite. Gas chromatographic analysis of the dried product over Carbowax 4000 indicated the presence of three materials only: the *cis* and *trans* isomers of 1-methoxy-1-butene and the beginning acetal. The ratio of the *trans* to *cis* isomers was 1.5:1. The dried product was distilled on a 3-ft spinning-band column to obtain 39 fractions boiling from 68 to 75.5° which contained only the *cis*- and *trans*-1-methoxy-1-butenes (glpc). The yield of both isomers was 318 g (3.7 moles, 67%).

Analysis of the fractions indicated that none was the pure *cis* isomer. Fractions 2 through 16 were combined: 104 g, boiling range 68–71.5°, $n^{25}\text{D}$ 1.3960 (varied from 1.3944 to 1.3962 for

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(15) A very effective reaction flask used at the suggestion of Professor H. A. Smith of the University of Tennessee.

(16) The catalyst contained 83.62% PtO_2 and was obtained from E. H. Sargent Co.

(17) Ashcroft laboratory test gauge, no. 1082A.

(18) H. R. Billica and H. Adkins, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 176.

(19) Obtained from Englehard Industries, Inc., Newark, N. J.

(20) B. W. Baker, R. P. Linstead, and B. C. L. Weedon, *J. Chem. Soc.*, 2218 (1955).

(21) We wish to thank Dr. Earl Taft of Wilkens Research and Instrument Co., for his evaluation and suggestion of the use of this column for the separation.

(22) A. E. Montagna and D. H. Hirsh, U. S. Patent 2,902,722 (1959).

(23) We wish to thank Mr. Norman Colthup of American Cyanamid Co., Stamford, Conn., for generous help in the interpretation of spectrum.

(24) H. Pariselle, *Ann. Chim.*, [8] **24**, 327 (1911).

(25) Johns-Manville Corp., New York, N. Y.

the series). These combined fractions contained 60% *cis* isomer and 40% *trans* isomer. Fractions 17 through 35 were combined: 179 g, boiling range 71.5–75°, n^{25}D 1.3974 (varied from 1.3966 to 1.3979 for the series). These combined fractions contained about 38% *cis* isomer and 62% *trans* isomer. Fractions 36 through 39 were combined: 35 g, boiling range 75–75.5°, n^{25}D 1.3982. The latter combination contained less than 1% *cis* isomer and more than 99% *trans*-1-methoxy-1-butene. In a further attempt to obtain the pure *cis* isomer, fractions 2–16 were refractionated. This was unsuccessful and the best fraction contained only 80% *cis* isomer: bp 69–70°, n^{25}D 1.3930.

The *cis* and *trans* isomers have been prepared by the distillation of butyraldehyde dimethyl acetal containing sodium acid sulfate.[26] The reported yield of the mixture of isomers was 70% and the isomer ratio was 1.5 parts *trans* to 1 part *cis*. The reported physical constants were for *trans* (98%), bp 76° (754 mm), n^{20}D 1.4021; for *cis* (94%), bp 71° (749 mm), n^{20}D 1.4020.

Further evidence for the assigned structures was obtained from their infrared spectra and by their hydrogenation to methyl butyl ether. The fraction enriched in the *cis* isomer (80%) had a C=C stretch at 1640, the C—O—C stretch at 1260, and a strong, broad band characteristic of *cis* out-of-plane C—H bending at 730 cm^{-1} as well as some absorption frequencies characteristic of the *trans* isomer. The *trans* isomer exhibited a doublet at 1670 and 1650 characteristic of the C=C stretch of vinyl ethers,[27] along with a medium band at 973, and a strong band at 933 cm^{-1} characteristic of the out-of-plane bending of the *trans* C—H.

***trans*-1-Methoxy-2-butene.**—Crotyl alcohol was prepared by the sodium borohydride (60 g, 1.6 moles) reduction of water-saturated crotonaldehyde (90% crotonaldehyde, 334 g, 4.8 moles contained) in 400 ml of water containing 1 pellet of sodium hydroxide. The aqueous layer was removed and extracted three times with 200-ml portions of ether. The extracts and the alcohol layer were combined and dried over magnesium sulfate. Distillation provided 163 g (48%) of crotyl alcohol, bp 70–78° (100 mm), n^{25}D 1.4224. The alcohol was converted into crotyl chloride by reaction with 425 ml of concentrated hydrochloric acid. The mixture was shaken vigorously in a separatory funnel at 10-min intervals over a period of 1 hr. The organic layer was extracted with water and dried over calcium chloride. The mixture was first distilled through a short helices-packed column and then redistilled on a spinning-band column to obtain 79 g (39%) of crotyl chloride, bp 53–55° (290 mm), n^{25}D 1.4281.[28]

The crotyl chloride (79 g) was converted into 1-methoxy-2-butene by the procedure of Roberts[29] using 32 g of sodium and 1300 ml of methanol. There was obtained 36 g (48%) of predominantly *trans*-1-methoxy-2-butene having bp 76–77°, n^{25}D 1.3965. Analysis by glpc indicated a composition of 95% *trans*, 4.5% *cis*, and 0.5% consisting of two other substances. Infrared showed the absorption frequencies expected for the *trans*-1-methoxy-2-butene (3005, 2880, 2800, 1675, 1450, 1150, 968, and 905 cm^{-1}) with the 968-cm^{-1} band being the C–H out-of-plane deformation for the *trans* configuration. The material also showed a weak and broad band at 725 cm^{-1} which is probably due to the *cis* isomer. The 905-cm^{-1} band could be due to the presence of 3-methoxy-1-butene formed by allylic rearrangement during the preparation of crotyl chloride and/or the ether. However, we do not believe this is true because there was not a concomitant band at 990 cm^{-1} and this 905-cm^{-1} band of the same relative intensity also was present in the infrared spectrum of the *trans* isomer trapped from glpc of both the synthetic ether and from the hydrogenation of methoxybutadiene.

Registry No.—*trans*-1-Methoxy-1,3-butadiene, 10034-09-0; methyl butyl ether, 628-28-4; 4-methoxy-1-butene, 4696-30-4; *cis*-1-methoxy-1-butene, 10034-12-5; *trans*-1-methoxy-1-butene, 10034-13-6; *trans*-1-methoxy-2-butene, 10034-14-7; crotyl chloride, 591-97-9; *cis*-1-methoxy-2-butene, 10034-16-9.

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Fluoro Olefins. I. The Synthesis of β-Substituted Perfluoro Olefins[1]

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The reaction of polyfluorinated ketones with difluoromethylenetriphenylphosphorane, $(C_6H_5)_3P{=}CF_2$, generated *in situ* from sodium chlorodifluoroacetate and triphenylphosphine, provides a general, one-step route to β-substituted perfluoro olefins. Olefins containing a β-alkyl, alicyclic, phenyl, or substituted phenyl substituent were obtained in 16–78% yields. Trapping experiments with tetramethylethylene and isopropyl alcohol failed to trap any difluorocarbene in these reactions suggesting that the mechanism does not involve the trapping of difluorocarbene by triphenylphosphine. An alternative mechanism involving decomposition of an intermediate phosphobetaine salt is proposed as a route to the difluoromethylene ylid.

No simple general route to perfluoro olefins containing a β substituent, other than halogen, hydrogen, or perhaloalkyl group, has been reported. Middleton and co-workers[3] have observed the formation of 2-phenylpentafluoropropene by the pyrolysis of 7,7-bis(trifluoromethyl)-1,3,5-cycloheptatriene at 500°. The perfluorinated analog, decafluoro-α-methylstyrene, has been prepared by the defluorination of perfluoroisopropylcyclohexane over nickel gauzes at 750°.[4] A few other perfluoro olefins containing simple alkyl β substituents have also been prepared;[5] however, the reaction sequence was generally long and the yields were generally low.

Owing to the unique reactivity of fluoro olefins in fluorocarbon chemistry, we were interested in preparing perfluoro olefins containing β substituents for synthetic and mechanistic studies and required a facile route to these compounds. Previous attempts by other workers to prepare fluoro olefins containing a β substituent utilizing either free-radical[6] or ionic reactions[7] have met with little or no success. In the ionic

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