Experimental Section

Rhodium on carbon was purchased from Engelhard Industries, Newark, N. J.

Preparation of IV.—The apparatus consisted of a pressure-compensated addition funnel attached to a prevaporizer leading into a quartz pyrolysis tube packed with quartz chips and enclosed in a vertical furnace. The product was collected at liquid nitrogen temperature in a three-necked flask and trap. The prevaporizer consisted of a short tube packed with Pyrex helices, wrapped outside with nichrome wire, and heated to approximately 200°. The addition funnel was attached to a source of N_2 through a micrometer needle valve, and the traps were connected via a manometer to a vacuum pump. The glassware was pumped to 0.1 mm while being heated to operating temperature. The pressure was raised to atmospheric pressure by bleeding in N_2. The funnel was filled with 92 g (0.5 mole) of a mixture of norbornadiene dimers prepared by refluxing norbornadiene with 5% rhodium on carbon. The pressure was lowered to 10 mm (60 ml/min of N_2 flow) and the column was heated to 550°. The dimers were pyrolyzed at the rate of 3 drops/sec. The pyrolysate was dissolved in pentane (~200 ml), treated with 50 g (0.51 mole) of maleic anhydride, and warmed until reaction took place. The mixture was cooled (0°), filtered (to remove much of the maleic anhydride adduct and unreacted maleic anhydride), then treated with 500 cc of a 2 M KOH solution. The layers were separated and the aqueous layer was washed with pentane (one 60-cc portion). The combined organic layers were washed with water and dried over KOH pellets. The solvent was removed and the product was distilled at 145° at atmospheric pressure yielding 18.7 g (27.6%) of IV.

Samples for analysis and for spectroscopic study were purified by vpc (20 ft × ³/₈ in. SE-30 on 45–60 Chromosorb W, 150°). The mass spectrum shows a parent peak at 118 and the base peak at 117. The near infrared spectrum (in CCl_4) shows a maximum at 1.666 μ (ε 1.339).

Anal. Calcd for C_9H_{10}: C, 91.47; H, 8.53. Found: C, 91.36; H, 8.52.

Dimerization of IV to V.—Hydrocarbon IV (0.59 g) and 5% rhodium on carbon (0.10 g) sealed in an evacuated glass tube were shaken in an oil bath at 185° for 42 hr. After cooling, the contents of the tube were solid. The sample was dissolved in CH_2Cl_2 and the catalyst was filtered. Distillation gave a liquid that vpc showed to be only starting material and solvent, and a solid that was sublimed at 60° (0.8 mm). The yield was 29 mg (5%) of V, mp 140–142°. The mass spectrum shows a parent peak at 236 and the base peak at 118.

Anal. Calcd for $C_{18}H_{20}$: C, 91.52; H, 8.47. Found: C, 91.27; H, 8.35.

A similar sample of IV without rhodium on carbon was sealed in an evacuated glass tube and heated simultaneously with that containing IV and the catalyst. The content of the former remained colorless and fluid. Analysis by vpc indicated that no reaction had occurred.

Attempted Reaction of IV with Norbornadiene.—Hydrocarbon IV (1.18 g, 0.01 mole), norbornadiene (2.75 g, 0.03 mole), and 5% rhodium on carbon (200 mg) were sealed in an evacuated glass tube and heated at 145° for 15 hr while being shaken. The reaction mixture was filtered and distilled. Analysis by vpc showed the characteristic peaks expected for the three dimers of norbornadiene,[2] and that for V (the dimer of IV), but none for a cross product.

Addition of Cyclopentadiene to IV to Give I.—Hydrocarbon IV (1.0 g, 0.085 mole) and freshly distilled dicyclopentadiene (0.56 g, 0.0425 mole) were heated in an evacuated glass ampoule at 190° for 48 hr. Distillation at reduced pressure yielded 1.2 g (77%) of I, a clear liquid, which vpc analysis (20 ft × ³/₈ in., 30% SE-30 on 45–60 chromosorb W at 200°) showed to be homogeneous. The mass spectrum showed a parent peak at 184 and the base peak at 117.

Anal. Calcd for $C_{14}H_{16}$: C, 91.30; H, 8.70. Found: C, 91.03; H, 8.62.

Dimerization of Benzonorbornadiene to VI.—Benzonorbornadiene (1 g) and 5% rhodium on carbon (0.2 g) sealed in an evacuated glass tube were heated for 2 days at 138°. After cooling, the contents of the tube were solid. This was placed in a Soxhlet tube and extracted with n-hexane for 3 days. Removal of the solvent left 0.8 g (80%) of crystalline dimer, which in the nmr showed only the peaks characteristic of the purified material. No extraneous resonances that could be attributed to a stereoisomer were detected. The melting point after recrystallization from n-hexane was 251.5–252.5°. The parent peak in the mass spectrum was at 284 and the base peak at 116. The ultraviolet spectrum in n-hexane showed the following: λ_{max} 197 mμ (ε 1.2 × 10⁵), 211 (2.3 × 10⁴), 252 (shoulder, 880), 259 (1.6 × 10³), 265 (2.7 × 10³), 272 (3.5 × 10³).[24]

Anal. Calcd for $C_{22}H_{20}$: C, 92.25; H, 7.04. Found: C, 92.58; H, 7.30.

A sample of benzonorbornadiene without the catalyst was heated in a tube simultaneously with the sample described above. No reaction occurred as evidenced by the absence of change in the infrared and nmr spectra.

(24) The spectrum is similar to that of other *ortho* xylenes. See ref 6c and 25.

(25) K. Kitahonoki and Y. Takano, *Tetrahedron Letters*, 1597 (1963).

The Reaction of Norbornadiene with 1,3-Diphenylisobenzofuran

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Norbornadiene reacts with 1,3-diphenylisobenzofuran to give a single 1:1 adduct, assigned the *exo,exo* structure IIIa on the basis of its chemical properties and nuclear magnetic resonance (nmr) spectrum. The oxygen bridge of IIIa exerts considerable shielding and deshielding effects on the methylene bridge protons which are separated from each other by a value of 1.76 ppm. Norbornadiene also reacts with 1,3-diphenylisobenzofuran to give a mixture of two isomeric 1:2 adducts; the principal bisadduct is assigned the *exo,exo,exo* structure VIIIA.

1,3-Diphenylisobenzofuran (I) (Scheme I) is a particularly reactive and versatile diene component in the Diels–Alder reaction. On the one hand, it has proved to be very useful as a trapping agent for highly reactive and nonisolable intermediates such as benzyne[2] and

(1) (a) Department of Chemistry, Wayne State University, Detroit, Mich. 48202. (b) National Science Foundation Undergraduate Research Participant, 1964–1965.

(2) G. Wittig, W. Stils, and E. Knauss, *Angew. Chem.*, **70**, 166 (1958).

benzocyclobutadiene;[3] on the other hand, it adds, albeit slowly, even to unconjugated olefins such as cyclopentene and cyclohexene.[4] We now report the results of a study of the reaction of I with norbornadiene (II).
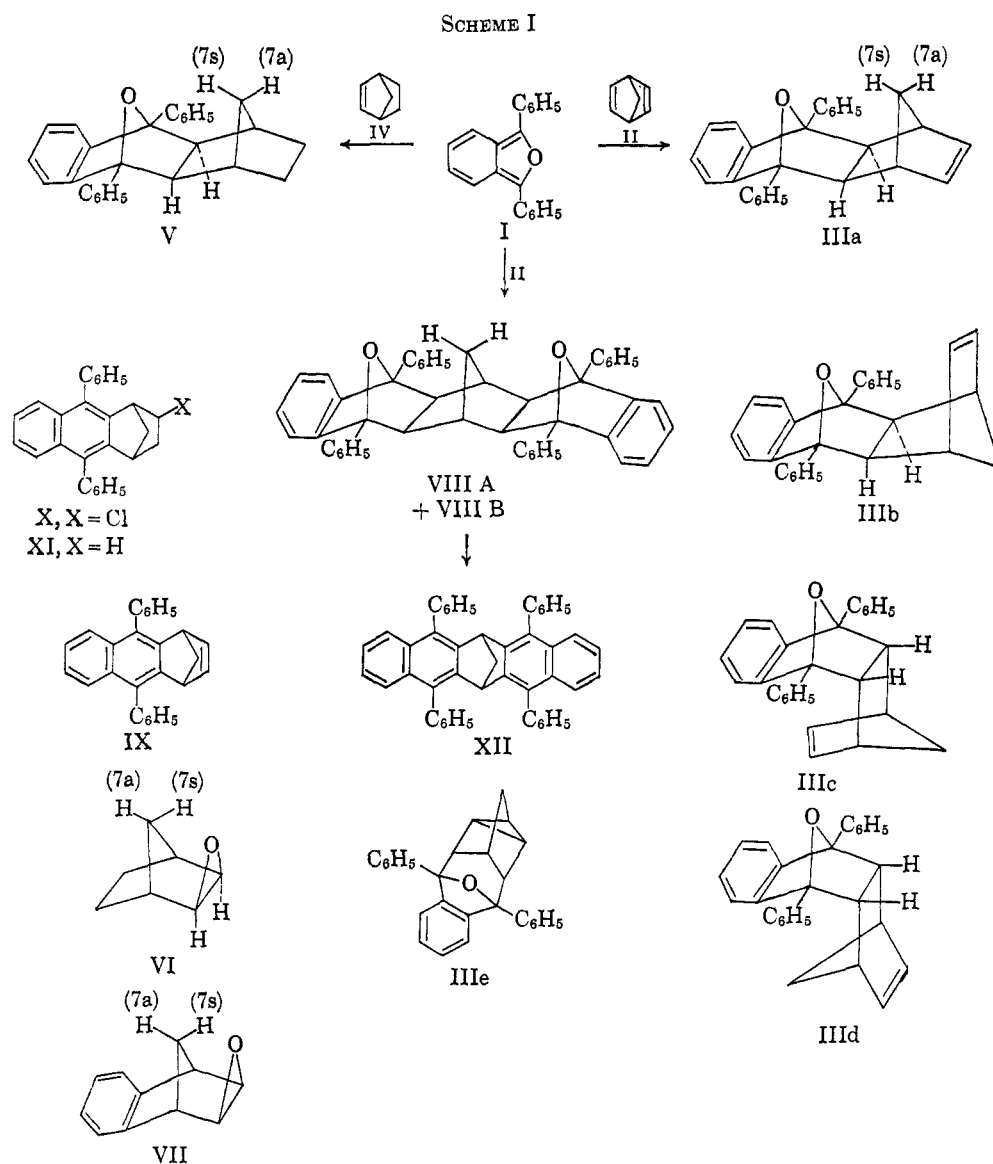
Equimolar amounts of I and norbornadiene react cleanly in refluxing benzene solution to give, in quantitative yield, a single adduct (III), mp 198–200°.

(3) M. P. Cava and R. Pohlke, *J. Org. Chem.*, **27**, 1564 (1962).

(4) G. Wittig and T. F. Burger, *Ann.*, **632**, 85 (1960).

SCHEME I

Four possible structures (IIIa–d) may be written for III, assuming that it is produced by a normal Diels–Alder reaction involving I and one of the double bonds of II. A less probable fifth structure (IIIe), formed by a 1,5 addition of I across both double bonds of II, may also be written.

The Diels–Alder addition of I to norbornene (IV) affords a single adduct (V), mp 236–237°, in good yield. This same compound (V) is obtained by the catalytic reduction of III, thus eliminating structure IIIe from further consideration. The above conversion of III to V indicates also that the second double bond in norbornadiene plays no role in determining the stereochemistry of adduct III.

Adduct III was assigned the structure of the *exo,exo* isomer IIIa on the basis of its nmr spectrum. The most striking feature of the nmr spectrum of III is the fact that the protons of the methylene bridge (7a and 7s) are clearly in very different environments. They appear as an AB-type quartet ($J = 8.5$), with the individual proton absorptions centered at τ 7.32 and 9.08. Such a large difference in the chemical shifts of the methylene bridge protons of a norbornene or norbornane derivative is, to our knowledge, unprecedented. A similar phenomenon of comparable

magnitude is found in the nmr spectrum of the saturated adduct V, in which the methylene bridge protons appear centered at τ 7.73 and 9.40. The corresponding methylene bridge protons of norbornene appear only slightly separated (at τ 8.92 and 8.67);[5] structures IIIb and c can be immediately eliminated from further consideration, therefore, since their methylene bridge protons are in an environment similar to that in norbornene. Construction of a Drieding model of structure IIId indicates that *both* methylene protons should be shielded by the central aromatic ring to a considerable degree, a prediction incompatible with the observed spectrum of III. Structure IIIa, on the other hand, is wholly in accord with the observed nmr spectrum. It has been shown that the oxygen atom in *exo*-1,2-epoxynorbornane (VI) causes a small deshielding of the *syn* proton at C-7 (7s, appearing at τ 8.65) and a larger shielding of the *anti* proton at C-7 (7a, appearing at τ 9.30) relative to the normal position for the methylene bridge protons (τ 8.80) in norbornane.[6]

(5) K. Tori, Y. Hata, R. Mumeyuki, Y. Tokano, T. Tsuji, and H. Tanida, *Can. J. Chem.*, **42**, 926 (1964).

(6) K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Letters*, 559 (1964).

By analogy, the deshielded methylene bridge proton of IIIa (or V) is assigned the configuration 7s (*syn* to the oxide bridge), while the corresponding shielded methylene bridge proton is assigned the configuration 7a (*anti* to the oxide bridge). The much greater deshielding of the 7s proton in IIIa and V relative to the epoxide VI is clearly due to the greater proximity of this proton to the oxygen atom in IIIa and V. The somewhat greater deshielding of the 7s proton (τ 7.32) in the unsaturated adduct IIIa compared with the 7s proton (τ 7.73) in the saturated analog V may be attributed to the deshielding effect of the olefinic double bond in IIIa superimposed upon the similar but greater deshielding effect of the oxide bridge. It is interesting to note that the 7a proton of the unsaturated adduct IIIa appears at lower field (τ 9.08) than that of the saturated adduct V (τ 9.40) rather than at higher field, as might have been expected on the basis of shielding of the 7a proton of IIIa by the olefinic double bond. This behavior finds analogy, however, in the relative chemical shifts of the corresponding methylene bridge protons of *exo*-epoxynorbornane (VI) and *exo*-epoxybenzonorbornene (VII).[6]

The reaction of norbornadiene with two equivalents of 1,3-diphenylisobenzofuran afforded a mixture of two bisadducts (A and B), from which bisadduct A, mp 305–306°, was readily separated by crystallization. Structure VIII was assigned to this compound, since its nmr spectrum showed two methylene protons as a singlet at τ 8.17; no protons appeared at higher fields. The lack of splitting of the methylene protons is consistent with their symmetrical environment in structure VIII.[7] Furthermore, the observed chemical shift of these protons is very close to that predicted (τ 8.33) on the basis of simple additivity of the shielding and deshielding effects of the two oxygen bridges in VIII, using the 7a and 7s protons of V and of norbornane as models. The isomeric bisadduct (B), mp 319–321°, was isolated in pure form by preparative thin layer chromatography; its nmr spectrum was not studied due to its sparing solubility.

Dehydration of the 1:1 norbornadiene adduct (IIIa) with sulfuric acid in acetic acid afforded a good yield of the corresponding naphthonorbornadiene (IX), mp 200–202°. An attempt to prepare IX from IIIa using hydrochloric acid in acetic acid led to the formation of the aromatized hydrogen chloride adduct X, mp 147–148° (stereochemistry of the chlorine undetermined). Dehydrochlorination of X by potassium *t*-butoxide proceeded readily, affording IX in high yield.

Catalytic reduction of IX afforded the corresponding dihydro derivative XI, mp 240–241°. Compound XI was also obtained by direct acid-catalyzed dehydration of norbornene adduct V and, more surprisingly, by reaction of V with phosphorus pentasulfide.

The phosphorus pentasulfide dehydration method afforded a smooth route (in contrast to acid treatment) for the dehydration of bisadduct A (VIII) and its isomer to the corresponding dinaphthonorbornadiene XII, mp 344–345°.

The nmr spectra of the aromatized adducts XI and IX were not analyzed in detail, but they were found to be qualitatively similar to those reported for benzonorbornene and benzonorbornadiene, respectively.[5] Thus, the bridge methylene protons of the naphthonorbornene XI formed part of a complex series of bands in the τ 8.0–8.8 region; the corresponding protons of the naphthonorbornadiene IX formed a narrow multiplet centered at lower field (τ 7.82). The most deshielded methylene bridge protons in the aromatized series, however, appeared at τ 7.45 in the spectrum of the dinaphthonorbornadiene XII.

Finally, it was noticed that the nmr spectra of adducts IIIa, V, and VIII each showed four (eight in the case of VIII) relatively high-field aromatic protons (τ 2.90–3.00) which were absent from the spectra of the corresponding aromatized adducts IX, XI, and XII. This effect appears to be due to shielding of the *ortho* protons of the phenyl substituents by the oxide bridge.

Experimental Section[8]

Adduct V of 1,3-Diphenylisobenzofuran with Norbornene.—A solution of 1,3-diphenylisobenzofuran (I, 4.015 g) and excess norbornene (IV, 13.0 g) in benzene (50 ml) was refluxed for 55 hr. Evaporation of the solvent left a pale yellow residue which was crystallized from chloroform–ethanol to yield (in three crops) white crystals of adduct V (4.860 g, 91%), mp 236–237°.

Anal. Calcd for $C_{27}H_{24}O$: C, 88.97; H, 6.64. Found: C, 89.25; H, 6.72.

1:1 Adduct (IIIa) of 1,3-Diphenylisobenzofuran with Norbornadiene.—A solution of 1,3-diphenylisobenzofuran (I, 4.001 g) and excess norbornadiene (II, 8 ml) in benzene (50 ml) was refluxed for 40 hr. Evaporation of the solvent left a yellow residue which was decolorized by passing its solution in benzene through a column of grade II neutral alumina. Evaporation of the benzene eluent, followed by crystallization from chloroform–ethanol, yielded (in three crops) white crystals of adduct IIIa (5.205 g, 97%), mp 198–200°.

Anal. Calcd for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found: C, 89.20; H, 6.31.

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

Dehydration of Adduct V. A.—A solution of adduct V (0.500 g) in carbon disulfide (250 ml) was stirred with phosphorus pentasulfide (4 g) at room temperature for 48 hr. The filtered solution was evaporated to dryness and the residue was taken up in benzene and purified by chromatography over neutral alumina. Crystallization from benzene–ethanol afforded the naphthonorbornene XI (4.160 g, 84%), mp 238–240°. The analytical sample of XI, mp 240–241°, was prepared by recrystallization from ethanol.

Anal. Calcd for $C_{27}H_{22}$: C, 93.60; H, 6.40. Found: C, 93.64; H, 6.69.

B.—A mixture of adduct V (1.00 g), concentrated hydrochloric acid (2 ml), and acetic acid (15 ml) was heated overnight on the steam bath. Filtration of the cooled yellow-brown suspension gave crude XI (0.816 g); crystallization of the latter from ethanol afforded pure XI, identical (mixture melting point and infrared comparison) with authentic material.

Dehydration of Adduct IIIa. A.—A mixture of adduct IIIa (2.50 g), concentrated hydrochloric acid (42 ml), and acetic acid (375 ml) was heated on the steam bath for 4 days. The solvent was evaporated *in vacuo* and the brown residue was purified by chromatography over neutral alumina (benzene eluent). The crude chloro derivative X (1.71 g, 62%), mp 145–147°, was crystallized from ethanol to give the analytical sample, mp 147–149°.

Anal. Calcd for $C_{27}H_{21}Cl$: C, 85.16; H, 5.51; Cl, 9.31. Found: C, 85.23; H, 5.67; Cl, 9.31.

(7) The spectrum of the sparingly soluble VIII was not sufficiently resolved to permit observation of the expected fine splitting of the methylene bridge protons by the bridgehead protons. We are grateful to a referee for bringing this point to our attention.

(8) All melting points were taken on a Fisher-Johns apparatus and are uncorrected. Nmr spectra were measured in deuteriochloroform solution with a Varian Associates A-60 spectrophotometer. Analyses were carried out by Dr. A. Bernhardt, Mulheim, Germany, and by Midwest Microlab, Inc., Indianapolis, Ind.

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 chro-

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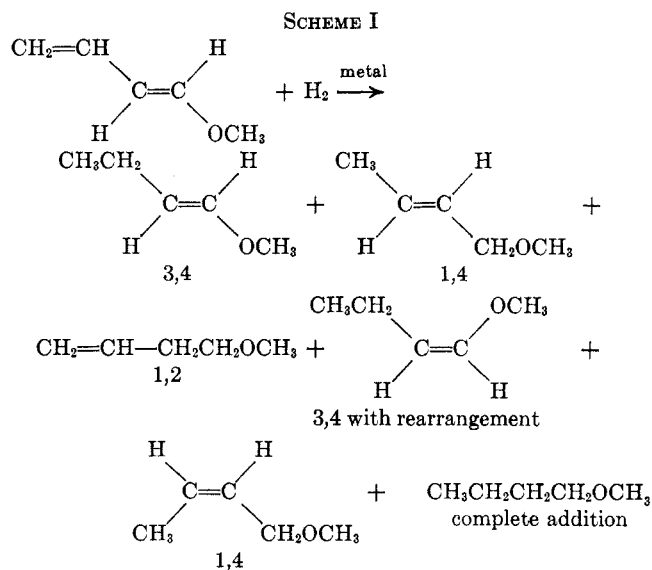
The hydrogenation of *trans*-1-methoxy-1,3-butadiene with platinum oxide at 30 and 50° under low pressure yields methyl butyl ethyl and all five possible methyl

(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).