keeping with the generally faster deuteration of the free phenol relative to the ether,[5] followed by acid-catalyzed exchange of the free enol ether function, which has many precedents.[4,13] In summary we have observed rapid exchange reactions of various naphthols and their ethers which may be of use for the preparation of polyalkoxynaphthalenes by a process of aryl oxygen fission.

Experimental Section[14]

Melting points were measured on a Kofler hot stage and are uncorrected. Ultraviolet spectra were recorded in MeOH on a Coleman-Hitachi 124 double-beam spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer. Nmr spectra were recorded on a Varian A-60 spectrometer with tetramethylsilane as internal reference. Mass spectra were measured on an AEI MS 9 mass spectrometer.

Alcoholic hydrogen chloride solutions were prepared by absorbing dry HCl gas (1.0 g) in 9.0 g of the respective alcohol. The three naphthols **2**, **3**, and **8** were characterized as the colorless crystalline acetate derivatives **11**, **12**, and **13**, respectively. The acetates **11**, **12**, **13**, and **14** were readily formed by heating the parent naphthol in Ac_2O in the presence of 2 equiv of NaOAc for 10 min at 80°.

2,4-Dimethoxy-1-naphthol (2).—**1** (0.5 g) was dissolved in 10 ml of methanolic HCl. The solution was heated to 60° for 1 min and then evaporated to yield pinkish crystals. This product was then redissolved in 10 ml of MeOH and evaporated down again in order to remove any remaining HCl gas. Another aliquot of MeOH was added to the product and then again evaporated off to yield a colorless crystalline compound **2**: mp 77–82°; uv max 242 mμ (ϵ 27,400), 313 (4080); ir ($CHCl_3$) 3560 (OH), 2940, 2840 (OMe), 1640, 1600, 1590 cm^{-1}; nmr ($CDCl_3$) δ 3.85 (s, 3), 3.90 (s, 3), 5.10 (bs, 1), 6.60 (s, 1), 7.40 (m, 2), 8.15 (m, 2); mass spectrum (70 eV) *m/e* (relative intensity) 204 (25), 189 (17), 174 (2), 161 (5).

2,4-Dimethoxy-1-naphthol acetate (11) had mp 90.5–91.5°; uv max 253 mμ (ϵ 40,200), 301 (4680); ir ($CHCl_3$) 2940, 2840 (OMe), 1760 (ester C=O), 1640, 1600, 1560 cm^{-1}; nmr ($CDCl_3$) δ 2.34 (s, 3), 3.76 (s, 3), 3.80 (s, 3), 6.47 (s, 1), 7.35 (m, 2), 7.56 (m, 1), 8.08 (m, 1); mass spectrum (70 eV) *m/e* (relative intensity) 246 (5), 204 (22), 189 (12).

Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.36; H, 5.85.

2,4-Diethoxy-1-naphthol (3).—Ethanolic HCl was substituted for methanolic HCl and the preparation proceeded as that for **2**: nmr ($CDCl_3$) δ 1.40 (t, 3), 1.46 (t, 3), 4.10 (q, 2), 4.12 (q, 2), 5.20 (bs, 1), 6.64 (s, 1), 7.35 (m, 2), 8.12 (m, 2).

2,4-Diethoxy-1-naphthol acetate (12) had mp 110.5–111.5°; uv max 236 mμ (ϵ 35,400), 301 (4130); ir ($CHCl_3$) 2980–2900 (m), 1760 (ester C=O), 1640, 1600, 1570 cm^{-1}; nmr ($CDCl_3$) δ 1.37 (t, 3), 1.48 (t, 3), 2.40 (s, 3), 4.14 (q, 4), 6.64 (s, 1), 7.36 (m, 2), 7.66 (m, 1), 8.20 (m, 1); mass spectrum (70 eV), *m/e* (relative intensity) 274 (3), 231 (11), 175 (16).

Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 69.96; H, 6.84.

2-Chloro-4-methoxy-1-naphthol (8).—1,4-Naphthoquinone (0.5 g) was substituted for **1** and the preparation proceeded as that for **2**: nmr ($CDCl_3$) δ 3.90 (s, 3), 5.55 (bs, 1), 6.67 (s, 1), 7.50 (m, 2), 8.16 (m, 2).

2-Chloro-4-methoxy-1-naphthol acetate (13) had mp 74–75.5°; uv max 235 mμ (ϵ 43,000), 295 (9200); ir (CCl_4) 3180–2950 (m), 2850 (OMe), 1790 (ester C=O), 1630, 1590; nmr ($CDCl_3$) δ 2.36 (s, 3), 3.82 (s, 3), 6.67 (s, 1), 7.40 (m, 2), 7.58 (m, 1), 8.14 (m, 1); mass spectrum (70 eV) *m/e* (relative intensity) 252 (3), 250 (10), 210 (30), 208 (50), 195 (20), 193 (55), 157 (10).

Anal. Calcd for $C_{13}H_{11}ClO_3$: C, 62.28; H, 4.42; Cl, 14.14. Found: C, 62.57; H, 4.37; Cl, 14.00.

Registry No.—**2**, 20352-27-6; **3**, 20352-28-7; **8**, 20352-29-8; **11**, 20352-30-1; **12**, 20352-35-6; **13**, 20352-36-7.

Acknowledgment.—We would like to thank Eli Lilly and Co. for generous financial support.

---

[13] W. F. Gannon and H. O. House, *Org. Syn.*, **40**, 41 (1960).

[14] Elemental analyses were performed by the Midwest Microlab Inc., Indianapolis, Ind. 46226.

The Stereochemistry of the Hydroformylation of Norbornene

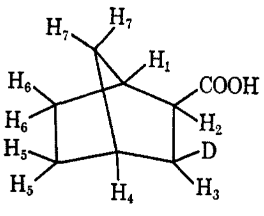
William E. Fichteman and Milton Orchin

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

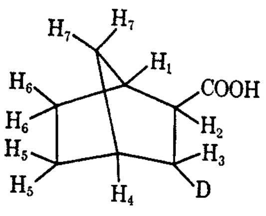
Received September 4, 1968

We recently reported that the hydrogenation of 1,2-diphenylcyclobutene with cobalt hydrocarbonyl, $HCo(CO)_4$, is primarily a *cis* process.[1] The stereochemistry of the stoichiometric hydroformylation of olefins has never been established, although two previous studies of the high-pressure catalytic oxo reaction indicated a cleanly *cis* hydroformylation of unsaturated carbohydrates possessing a vinyl ether structure.[2,3] We now wish to report that the stoichiometric hydroformylation of an olefin, norbornene, is largely, if not entirely, a *cis* process.

When a hexane solution of $DCo(CO)_4$ was added to norbornene under an atmosphere of carbon monoxide at room temperature, slow absorption of carbon monoxide occurred and deuterated norbornane-2-carboxaldehyde[4] was isolated in about 20% yield. The product was oxidized with potassium permanganate to give *exo*-norbornane-2-carboxylic acid which, were the hydroformylation *cis*, would have structure **1**, and were it *trans*, would have structure **2**. The nmr of the acid from the hydroformylated product was essentially identical with that of an authentic sample[5] of **1** (Figure 1). We consider it quite unlikely that **2** would give a spectrum identical with **1**, since the coupling constant $J_{H_2\text{-}H_3}$ between two *endo* hydrogens in norbornyl systems is about 8 cps and that between an *endo,exo* pair is about 2 cps.[6]



1



2

Experimental Section

Melting points were taken on a Fisher–Johns block and are uncorrected. Nmr spectra were obtained with a Varian A-60 spectrometer and infrared spectra were determined with a Perkin-Elmer Infracord 337. Norbornene was purchased from Aldrich Chemicals.

---

[1] W. Fichteman and M. Orchin, *J. Org. Chem.*, **33**, 1281 (1968). Although a small amount of *trans* product was observed, it can be accounted for by olefin isomerization, followed by *cis* addition.

[2] A. Rosenthal and D. Abson, *Can. J. Chem.*, **42**, 1811 (1964).

[3] A. Rosenthal and H. J. Koch, *ibid.*, **43**, 1375 (1965).

[4] Y. Colleuille and P. Perras, French Patent 1,352,841, *Chem. Abstr.*, **61**, 593*a* (1964), reports that when norbornene is treated with dicobaltoctacarbonyl in cyclohexane solvent under high carbon monoxide pressure, a low yield of norbornane-2-carboxaldehyde is obtained along with other products. We found that under catalytic oxo conditions using dicobaltoctacarbonyl as catalyst, norbornene hydroformylates quite readily to give a good yield of norbornane-2-carboxaldehyde.

[5] Supplied by Dr. John Hudec; see C. W. Bird, R. C. Cookson, J. Hudec, and R. O. Williams, *J. Chem. Soc.*, 410 (1963), who report here the *cis* hydrocarboxylation of norbornene by $Ni(CO)_4$ and H_2O.

[6] A. Factor and T. G. Traylor, *J. Org. Chem.*, **33**, 2607 (1968).

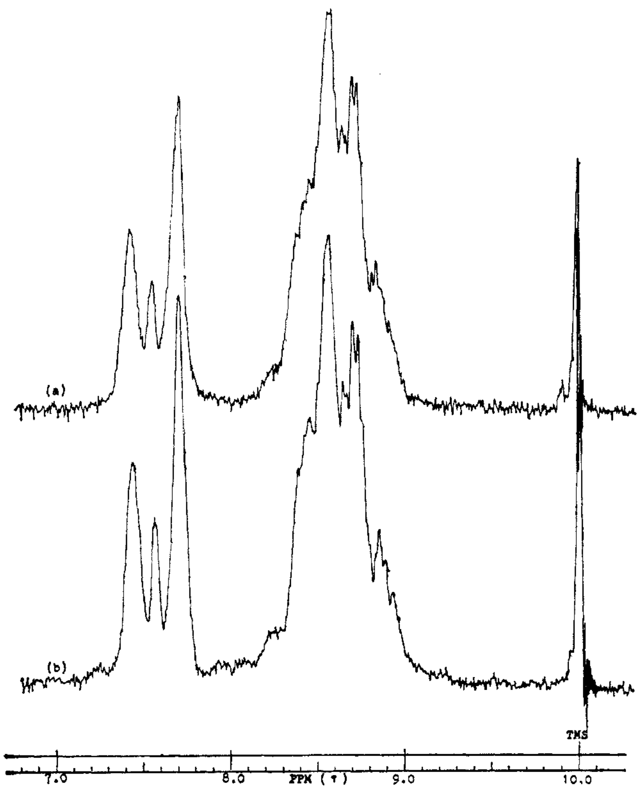


Figure 1.—(a) 60-Mc nmr spectrum of *exo*-norbornane-2-carboxylic acid from deuterioformylated norbornene. (b) 60-Mc nmr spectrum of authentic sample of 1, 30% by weight in $DCCl_3$; TMS reference.

Stoichiometric Reaction of $DCo(CO)_4$ with Norbornene.—Norbornene (2.42 g, 24.8 mmol) was dissolved in 50 ml of hexane and a small amount of some insoluble impurity was removed by filtration. About 75 ml of a hexane solution[7] of $DCo(CO)_4$ was injected in 10-ml portions over a period of 6 hr into the hexane solution of norbornene. The reaction was carried out in a serum stoppered flask connected to a gas buret, under an atmosphere of carbon monoxide and at room temperature. A total of 57.1 mmol of $DCo(CO)_4$ was used, and about 13 mmol of carbon monoxide was absorbed slowly. The reaction mixture was stirred for 24 hr, and 25 ml of dimethylformamide was added to destroy the dicobaltoctacarbonyl. About 50 ml of water was then added and the mixture was extracted with ether. The ether solution was dried with magnesium sulfate and evaporated to dryness on a rotary evaporator. The light pink viscous oil was vacuum distilled at 3 mm to give 0.65 g of clear distillate: bp 42–52°, 20% yield. The infrared spectrum of the distillate showed C-D stretching bands at 2163 and 2048 cm^{-1} and the C=O stretching band at 1713 cm^{-1}. The nmr ($DCCl_3$ solution, TMS reference) showed a multiplet from τ 7.23–7.83 (2.9 H) assigned to protons at positions 1, 2, and 4 and a multiplet from 8.08–8.97 (7.1 H) assigned to the protons at positions 3, 5, 6, and 7. An unsymmetrical doublet (J = 1 cps) at τ 0.36 due to the aldehydic proton indicated that about 7% of the product had no deuterium on the carbonyl carbon.

The aldehyde was oxidized with potassium permanganate to yield 0.13 g of the acid 1 (mp 52.0–53.5°, mmp with authentic sample, 53–54°). The nmr spectrum of the acid was taken in $DCCl_3$ (~30% by weight) and is shown in Figure 1. The carboxyl proton absorbed at τ −1.5; the carboxyl to norbornyl proton ratio was 1.0:10.0.

Registry No.—Norbornene, 498-66-8; deuterated *exo*-norbornane-2-carboxaldehyde, 20238-57-7.

Acknowledgment.—The authors are grateful to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this work. The authors are especially grateful to Drs. C. W. Bird and John Hudec for supplying us with an authentic sample of the deuterated *exo*-2-norbornanecarboxylic acid.

---

[7] L. Roos and M. Orchin, *J. Amer. Chem. Soc.*, **87**, 5502 (1965).

Use of N,N-Dimethylvinylamine in an Improved Synthesis of Derivatives of Thietane and Thiete[1]

PETER L.-F. CHANG AND DONALD C. DITTMER

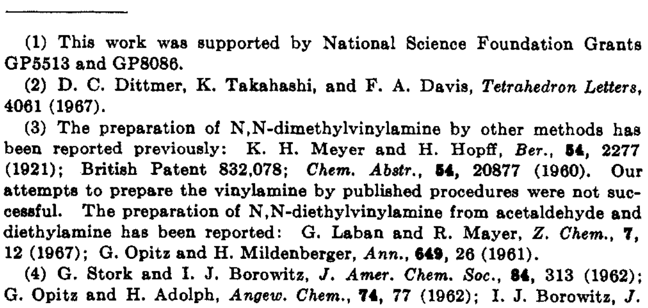
Department of Chemistry, Bowne Hall,
Syracuse University, Syracuse, New York 13210

Received March 6, 1969

The original synthesis of thiete (thiacyclobutene) involved a long, multistep sequence starting with epichlorohydrin, and the over-all yield was relatively low.[2] Because large quantities of thiete were desired in order to study its chemical and physical properties, a new synthesis was devised utilizing the addition of "sulfene" to N,N-dimethylvinylamine, which was obtained conveniently and in high yield by dehydrohalogenation of N,N-dimethyl-N-β-chloroethylamine.[3] The addition of sulfenes to enamines is an efficient method of preparation of β-aminothietane sulfones.[4]

Both N,N-dimethyl- and N,N-diethylvinylamines were obtained by the dehydrohalogenation procedure in 84–87% yields as colorless liquids, stable below −20°. They are sensitive to air and become brown and resinous at room temperature. The nmr spectrum shows clearly the vinyl protons at τ 6.35–6.65 ($CH_2=$) and 3.95–4.10 (>C=C—H). The infrared spectrum shows absorption at 1630–1640 cm^{-1} attributed to the carbon–carbon double bond.

A chemical proof of the structure of N,N-dimethylvinylamine consists of its addition to sulfene to give 3-(N,N-dimethylamino)thietane 1,1-dioxide in 86% yield. The adduct can be converted either to thiete by



---

[1] This work was supported by National Science Foundation Grants GP5513 and GP8086.

[2] D. C. Dittmer, K. Takahashi, and F. A. Davis, *Tetrahedron Letters*, 4061 (1967).

[3] The preparation of N,N-dimethylvinylamine by other methods has been reported previously: K. H. Meyer and H. Hopff, *Ber.*, **54**, 2277 (1921); British Patent 832,078; *Chem. Abstr.*, **54**, 20877 (1960). Our attempts to prepare the vinylamine by published procedures were not successful. The preparation of N,N-diethylvinylamine from acetaldehyde and diethylamine has been reported: G. Laban and R. Mayer, *Z. Chem.*, **7**, 12 (1967); G. Opitz and H. Mildenberger, *Ann.*, **649**, 26 (1961).

[4] G. Stork and I. J. Borowitz, *J. Amer. Chem. Soc.*, **84**, 313 (1962); G. Opitz and H. Adolph, *Angew. Chem.*, **74**, 77 (1962); I. J. Borowitz, *J. Amer. Chem. Soc.*, **86**, 1146 (1964). The reaction is reviewed in L. L. Müller and J. Hamer, "1,2-Cycloaddition Reactions," Interscience Publishers, New York, N. Y., 1967.