

Now $k_2 = k_r'10^{14}K_{\text{ion}}K_{\text{add}} = 2200 M^{-2} \text{sec}^{-1}$. This yields $k_r' \sim 0.1 \text{sec}^{-1}$ which seems rather small but not impossible.

If this very speculative analysis is valid, it is to be expected that general base catalyzed reactions which can be formulated according to structure II will fall into two classes, one involving proton transfer as the rate-determining step and the other observing the solvation rule,⁵ the choice depending on the stability of the leaving group. Compounds with good leaving groups should react by a pathway analogous to that of mutarotation, while those with poor leaving groups should follow a route similar to the one deduced here. We hope our studies of heavy-atom isotope effects and structural influences in this system will elucidate these problems.

Isotope Effect on the Addition Step. The absence of an isotope effect on the addition step, in spite of a possible maximum inverse secondary effect of $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 1.7$ (see above), is surprising but explicable in several ways. It is possible that bonding of the hydroxide to the substrate has not proceeded to a great degree at the activated complex for addition and that the resulting small inverse effect is canceled to within experimental error by a regular effect arising from solvent reorganization. However, the similarity of the activation parameters for formation of the addition-activated complex (eq 3) and for formation of the solvent-catalyzed elimination-activated complex (eq 4) indicates similar structures for the two activated complexes,² favoring a strong hydroxide-substrate bond. If this is indeed the case, an inverse isotope effect of nearly 1.7 must be canceled by a regular effect of about the same magni-

tude, presumably from solvent reorganization. We have no data now which permit a choice between these possibilities, but if the latter is the correct explanation, some revision of the estimated isotope effects given above is required. Assuming $K_{\text{a}}^{\text{H}_2\text{O}}/K_{\text{a}}^{\text{D}_2\text{O}} = 1.0$, for the addition equilibrium, we obtain $(k_1^{\text{H}_2\text{O}}/k_1^{\text{D}_2\text{O}})_{\text{sec}} = 1.27$ and $(k^{\text{H}_2\text{O}}/k^{\text{D}_2\text{O}})_{\text{sec}} = 0.82$ for the secondary contributions, and $(k^{\text{H}_2\text{O}}/k^{\text{D}_2\text{O}})_{\text{pri}} = 2.6 \pm 1$ and $(k_2^{\text{H}_2\text{O}}/k_2^{\text{D}_2\text{O}})_{\text{pri}} = 2.6 \pm 1$ for the primary effects. These results do not support the conclusion that rate-determining proton transfer is occurring, since the primary isotope effects yield $n_1 \sim 0.15$ (Figure 1), no longer in agreement with the value of the Brønsted β . We hope our further work will resolve the dilemma.

Experimental Section

An approximately decinormal solution of sodium deuterioxide in heavy water was prepared by the method of Morgan²¹ and standardized. From this stock solution, the various deuterioxide solutions used for the kinetic runs were prepared by suitable dilutions with heavy water, adding in every case the calculated amount of dry potassium chloride. The 2,2,2-trifluoro-N-methylacetanilide was also dissolved in heavy water inside the drybox. The kinetic methods were identical with those reported previously.⁸

Acknowledgments. We are happy to thank Professor C. Gardner Swain (Massachusetts Institute of Technology) for permission to use unpublished results from his laboratory and Professor Edward R. Thornton (University of Pennsylvania) for his very valuable comments.

(21) C. R. Morgan, Ph.D. Thesis, Massachusetts Institute of Technology, 1963, p 19.

Catalysis of a Cycloaddition Reaction by Rhodium on Carbon

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Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. Received June 2, 1966

Abstract: The catalysis of a cycloaddition reaction by a noble metal hydrogenation catalyst is described. Refluxing norbornadiene with 5% rhodium on carbon converts the hydrocarbon in nearly quantitative yield to a product of which 70 to 80% is a mixture of dimers and 20 to 30% a trimer. The dimers consist mainly of two products, which the nmr spectra indicate are stereoisomers of structure IV. Small amounts of dimer I are also formed. The nmr spectrum of the trimer indicates that it is VI. The stereochemistry of IV and VI are discussed. The remarkable efficacy of rhodium in catalyzing the oligomerization of norbornadiene is shown by its ability to effect the reaction quickly and quantitatively at reflux (and slowly at room temperature) and to effect formation of the trimer.

The catalysis of reactions that outwardly appear to be simple cycloadditions is unusual because these are not generally subject to catalysis and significant because they are of considerable utility in synthesis.² Such outwardly simple cycloaddition reactions as the cyclooligomerization of acetylenes,³ butadiene,⁴ and

norbornadiene⁵ are catalyzed by a variety of transition metal complexes. In the case of norbornadiene, the

p 380 ff; (c) G. N. Schrauzer, *Chem. Ber.*, **94**, 1403 (1961); (d) E. M. Arnett and J. M. Bollinger, *J. Am. Chem. Soc.*, **86**, 4729 (1964); (e) U. Krüerke and W. Hübel, *Chem. Ber.*, **94**, 2829 (1961); (f) A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962); (g) J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.*, 3488 (1962).

(4) G. Wilke, *Angew. Chem. Intern. Ed. Engl.*, **2**, 105 (1963).

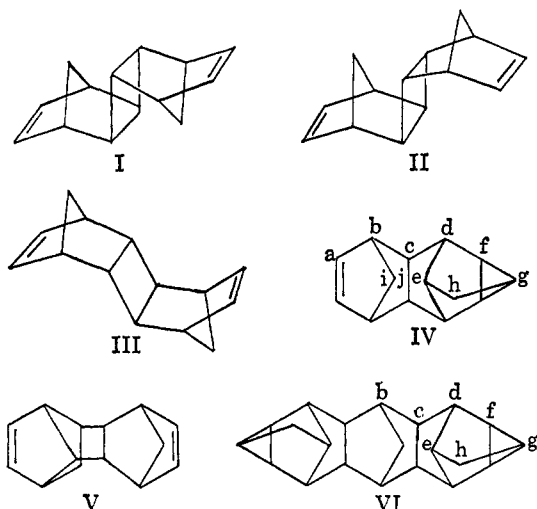
(5) (a) R. Pettit, *J. Am. Chem. Soc.*, **81**, 1266 (1959); (b) C. W. Bird, R. C. Cookson, and J. Hudec, *Chem. Ind. (London)*, 20 (1960); (c) C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Letters*, 373 (1961); (d) G. N. Schrauzer and S. Eichler, *Chem. Ber.*, **95**, 2764 (1962); (e) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2596 (1965); (f) P. W. Jolly, F. G. A. Stone, and K. MacKenzie, *J. Chem. Soc.*, 6416 (1965).

(1) To whom inquiries should be sent.

(2) R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of the Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 739 ff.

(3) (a) G. N. Schrauzer, P. Glockner, and S. Eichler, *Angew. Chem. Intern. Ed. Engl.*, **3**, 185 (1964); (b) H. Zeiss, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960,

following complexes—the iron carbonyls,^{5a-c} Ni(CO)₄,^{5b} Co₂(CO)₈,^{5c} Co₂(CO)₆[(C₆H₅)₃P]₂,^{5e} Fe(CO)₂(NO)₂,^{5f} Co(CO)₃NO,^{5f} and substances related to Ni(CH₂=CHCN)₂^{5d}—have been found to dimerize the hydrocarbon. The products formed are varying mixtures of I,^{5a,c-f} II,^{5e} III,^{5c,e} a caged saturated dimer,^{5c,6} and two uncharacterized substances asserted to have structure IV.^{5c,d,f} (A dimer asserted to be V^{5b,d,f} now appears to be II.⁷) The catalytic activity of the group VIII



metals, whose complexes bring about these dimerizations, is most commonly associated with hydrogenation.⁸ But although hydrogenation can be effected by these or similar complexes,⁹ it is usually the metal itself that is employed as the catalyst. The use of a metal to effect a cycloaddition is rare.¹³ An example is described below.

Results and Discussion

Refluxing norbornadiene (90°) with 5% rhodium on carbon converts the hydrocarbon, in up to 90% yield, to a product of which 70 to 80% is a mixture of dimers and 20 to 30% a trimer. The dimer mixture in turn consists mainly (96%) of two liquids in the ratio 7:1, probably stereoisomers, assigned on the basis of data presented below the structure IV. The trimer, a crystalline solid, mp 176–178°, appears to have the related structure VI.¹⁴ The remainder of the dimer (4%) is the known compound, mp 67–68°,^{5a,c-f} assigned structure I.^{5e}

The rhodium catalyst is remarkably effective: it effects dimerization of norbornadiene quickly and quantitatively at reflux (and also slowly at room tem-

perature¹⁵); it effects not only dimerization, but also trimerization.¹⁸ In giving almost exclusively the Diels–Alder-type products,² IV and VI, rather than 1,2 adducts, such as I, II, and III, the rhodium catalyst is unlike the complexes that are reported⁵ to dimerize norbornadiene. Preliminary experiments to test whether other metal hydrogenation catalysts would effect similar reactions were, in contrast, unsuccessful. A reaction of norbornadiene with 30% palladium on carbon gave 0.1% of dimer I, while both 5% platinum on charcoal and a nickel catalyst¹⁹ failed altogether.

The formation of the trimer suggested the possibility that in the presence of the rhodium catalyst norbornadiene would add to norbornene, but an attempt to effect such a reaction failed; the only products recognized were the dimers and the trimer of norbornadiene. (Also unsuccessful was an attempt to dimerize norbornene in the presence of the catalyst.)

Structural Assignments

The assignment of structure IV to the dimers and VI to the trimer is based on the carbon, hydrogen, and molecular weight analyses and on the nmr spectra shown in Figure 1. Both dimers, but not the trimer, exhibit absorption at τ 4 and 7.4, similar to that of the olefinic and bridgehead protons of norbornenes.^{5e,20} All show a doublet above τ 9, ascribable to the cyclopropyl protons,^{21,22} H_f, split only by H_g.^{24,25} All show peaks at τ 8.8 attributable to the methylene bridge of a nortricyclene (H_b, split by H_e).^{22,26} The infrared spectra of the compounds, described in part in the Experimental Section, are in accord with these structures. The dimers exhibit absorptions characteristic of norbornenes^{5e,27} at 1568 cm⁻¹ and between 700 and 750 cm⁻¹, and of nortricyclenes²⁸ near 800 cm⁻¹. The trimer shows only these last absorptions.

The stereochemistry of the dimer (IV) and the trimer (VI) cannot now be unquestionably assigned, but a derivation based on an analysis given by Mrowca^{16a} of the nmr spectra of the hydrocarbons is outlined below. The simplicity of the trimer's spec-

(15) The reported catalysts⁵ were used above room temperature; others are effective in the cold.^{16,17}

(16) (a) J. J. Mrowca, Dissertation, Columbia University, 1966; (b) also unpublished work from this laboratory.

(17) Belgian Patent 626,407 (June 21, 1963); *Chem. Abstr.*, **60**, 13164g (1964).

(18) No other catalyst is reported to give a trimer, except one described in a patent,¹⁷ tetrakis(triphenylphosphine)nickel, which gives a different trimer, an unsaturated compound, mp 201°.

(19) H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.*, **84**, 1493, 1494 (1962).

(20) P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964).

(21) (a) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p 52; (b) S. Forsén and T. Norin, *Tetrahedron Letters*, No. 39, 2845 (1964).

(22) The nmr spectrum of nortricyclene consists of a singlet at τ 9.03 due to the three cyclopropyl protons, a doublet ($J = 1.4$ cps) at 8.81 due to the six methylene protons, and a broad peak at 8.08 due to the remaining bridgehead proton.²³

(23) R. A. Finnegan and R. S. McNeese, *J. Org. Chem.*, **29**, 3234 (1964).

(24) The lines of the doublet are separated by 4.5 cps in both dimers and by 4.8 cps in the trimer.

(25) If the resonance of H_f is a doublet, then that of H_g should be a triplet. This absorption presumably contributes to the peaks between τ 8.7 and 8.8, but is obscured by other resonances.

(26) The splittings observed in the τ 8.8 peaks in the spectra of the dimers, $J = 1.4$ cps, are the same as in nortricyclene.

(27) (a) R. C. Lord and R. W. Walker, *J. Am. Chem. Soc.*, **76**, 2518 (1954); (b) P. von R. Schleyer, *ibid.*, **80**, 1700 (1958); (c) H. E. Simmons, *ibid.*, **83**, 1657 (1961).

(28) G. E. Pollard, *Spectrochim. Acta*, **18**, 837 (1962).

(6) D. M. Lemal and K. S. Shim, *Tetrahedron Letters*, 368 (1961).

(7) J. C. Carnahan, Jr., repeating the dimerization with bisacrylonitrilenickel,^{5d} found III and IV,^{5e} not III and VI. Stone^{5f} compared his VI with Schrauzer's, Schrauzer^{5d} his with Cookson's.^{5b}

(8) R. L. Augustine, "Catalytic Hydrogenation," M. Dekker, New York, N. Y., 1965.

(9) Hydrogenation can be effected by iron, cobalt, and rhodium carbonyls¹⁰ and by other complexes of rhodium^{11,12} and iridium.¹²

(10) (a) C. W. Bird, *Chem. Rev.*, **62**, 283 (1962); (b) B. Heil and L. Marko, *Chem. Ber.*, **99**, 1086 (1966).

(11) (a) F. H. Jardine, J. A. Osborn, G. Wilkinson, and J. F. Young, *Chem. Ind. (London)*, 560 (1965); (b) J. A. Osborn, G. Wilkinson, and J. F. Young, *Chem. Commun.*, 17 (1965).

(12) L. Vaska and R. E. Rhodes, *J. Am. Chem. Soc.*, **87**, 4970 (1965).

(13) Palladium on charcoal effects the trimerization of dimethyl acetylenedicarboxylate to hexamethyl mellitate: D. Bryce-Smith, *Chem. Ind. (London)*, 239 (1964).

(14) Decacyclo[9.9.1.0^{2,10}.0^{3,8}.0^{4,5}.0^{5,9}.0^{12,20}.0^{13,17}.0^{14,19}.0^{16,18}]heneicosane.

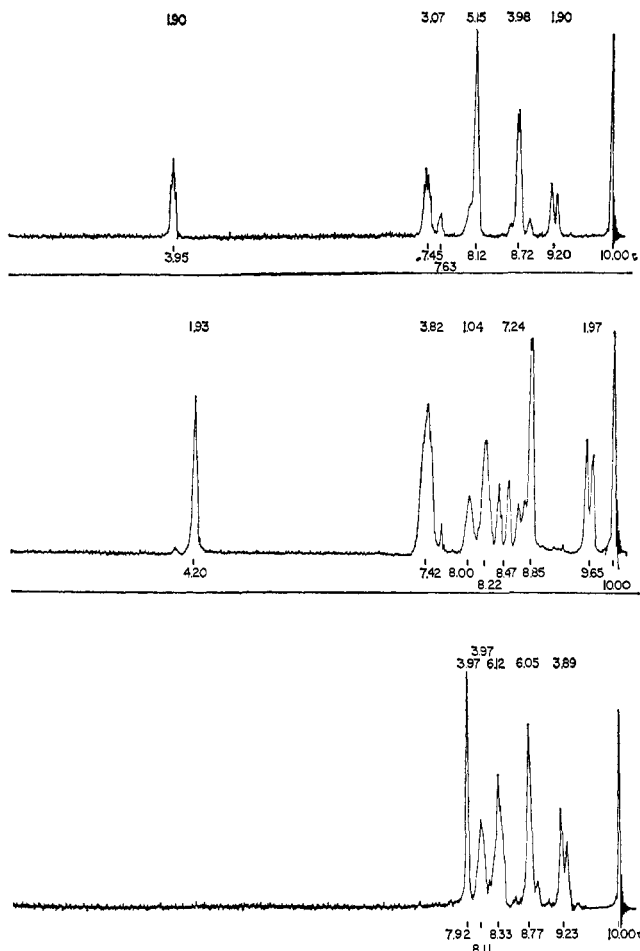
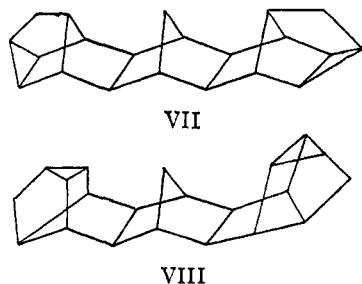


Figure 1. Nmr spectra (60 Mc/sec) of IVa (predominant dimer), IVb (minor dimer), and VI. Intensities are above the peaks. TMS is present (τ 10).

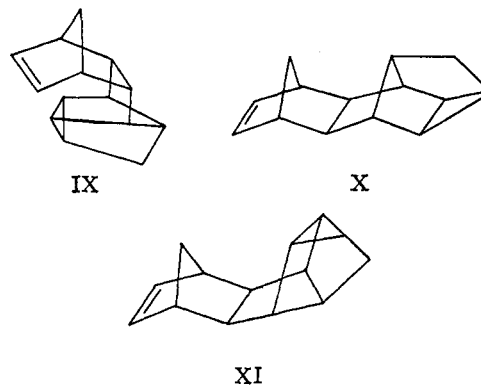
trum, in particular above τ 9 where only one doublet is observed, suggests that the trimer has one of the four structures with two symmetry planes. Of these, the two structures in which both nortricyclene rings are attached to the *endo* positions of the central norbornane are probably too sterically crowded²⁹ to represent such an easily formed molecule. Therefore, the probable structure of the trimer is VII or VIII.



There are only four stereochemistries possible for IV. If in IVb (the minor isomer) the τ 9.65 doublet is at such high field relative to IVa (the major isomer) and VI because of shielding due to the magnetic anisotropy of the double bond,³⁰ then IVb is IX. If IVa were also an *endo*-norbornene, it would be difficult to account for

(29) We could not make noninterpenetrating molecular models of these structures.

(30) Reference 21a, Chapter 7.



the different appearance of the resonances of protons i and j in it and in IVb. In IVb these resonances presumably appear as an AB quartet centered about τ 8.47.^{6e,20,27c} In IVa no AB quartet is apparent, but the intensities suggest that the peaks are among those at τ 8.7 and 7.5.³¹ The two structures with the nortricyclene *endo* to the norbornene are, therefore, unlikely for IVa. If, however, the structure of IVa were one of the two with the nortricyclene fused to the *exo* positions of the norbornene, then the resonance of one of the bridgehead protons might well be shifted to low field because of its proximity to the nortricyclene moiety, a result either of steric compression³² or of the magnetic anisotropy of the cyclopropyl group.^{21b} The probable structures for IVa are, therefore, X or XI. This assignment is supported by the appearance of the sharp peak (half-width 2 cps) at τ 8.12, which is likely to be H_c and H_d superimposed,³³ the absence of appreciable bc coupling implying^{6e,20,34} that IVa is one of the *exo* isomers.

Experimental Section

Noble metal catalysts were purchased from Engelhard Industries, Newark, N. J. Norbornadiene (Matheson Coleman and Bell) was distilled (bp 89°) immediately before use.

Dimerization and Trimerization of Norbornadiene with Rhodium on Carbon. An early experiment proceeded as follows. Norbornadiene (20 g) and 5% rhodium on charcoal (3.0 g) were stirred and heated (bath temperature 110°) in an argon atmosphere for 23 hr. Pentane (150 ml) was added, the mixture was filtered, and the solvent was evaporated at reduced pressure. Distillation of the residue gave 10.52 g (53% yield) of a mixture of norbornadiene dimers, bp 76–77° (0.8 mm), that vapor phase chromatography (vpc)³⁵ at 175° showed to be three dimers in the ratio 4:84:12. These three, I, IVa, and IVb, were isolated by preparative vpc at 190°.

Dimer I, characterized by its melting point (67–68°), was identified by comparing its infrared spectrum and vpc retention times with a sample of the dimer having the same melting point obtained by dimerizing norbornadiene with iron pentacarbonyl.^{5a,c,e}

Dimer IVa is a colorless, viscous liquid.

Anal. Calcd for C₁₄H₁₆: C, 91.30; H, 8.70. Found: C, 91.17; H, 8.64; mol wt (mass spectrum), 184.

(31) Bridgehead protons *syn* to the double bond of norbornenes appear at τ 8.92 in norbornene itself,^{27b} 8.31 in I, 8.98 in III,^{5c} and 8.90 and 8.28 in the two benzene adducts of norbornadiene.^{27c}

(32) S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Am. Chem. Soc.*, **87**, 5247 (1965).

(33) Except for H_e all the other protons have been accounted for, and H_e can give neither a peak that intense (it is only one proton) nor that sharp (it must couple to H_h). The only alternative is that H_i and H_j are at τ 8.12.

(34) (a) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962); (b) J. C. Davis, Jr., and T. V. Van Auken, *J. Am. Chem. Soc.*, **87**, 3900 (1965); (c) D. F. O'Brien and J. W. Gates, Jr., *J. Org. Chem.*, **30**, 2593 (1965); (d) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961); (e) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).

(35) 20 ft \times $\frac{3}{8}$ in. 30% SE-30 on 45/60 Chromosorb W.

Its infrared spectrum (neat between NaCl plates) is similar to that of dimer IVb. It shows absorptions at 1566 (m) ($\nu_{C=C}$), 709 (vs) (*cis*-olefinic C-H out-of-plane deformation), and 791 (vs), 799 (vs), 808 cm^{-1} (vs) (nortricyclene system).

Dimer IVb is a colorless, viscous liquid.

Anal. Calcd for $\text{C}_{14}\text{H}_{16}$: C, 91.30; H, 8.70. Found: C, 91.43; H, 8.92; mol wt (mass spectrum), 184.

Its infrared spectrum (neat between NaCl plates) is similar to that of dimer IVa. It shows absorptions at 1570 (w) ($\nu_{C=C}$), 735 (vs) (*cis*-olefinic C-H out-of-plane deformation), and 779 (s), 786 (vs), 802 cm^{-1} (s) (nortricyclene system).

The pot residue from the distillation of the dimers solidified on cooling to room temperature. It was washed from the distillation flask with ethanol. Filtration and recrystallization from ethanol afforded 2.52 g (13% yield) of the trimer VI, white crystals, mp 176–178°. Recrystallization from ethanol failed to raise the melting point. The analytical sample was prepared by sublimation (130° at 5×10^{-3} mm).

Anal. Calcd for $\text{C}_{21}\text{H}_{24}$: C, 91.30; H, 8.70. Found: C, 91.52; H, 8.62; mol wt (mass spectrum), 276.

Its infrared spectrum (Nujol mull) showed absorptions at 800 (vs), 814 (vs), and 829 (s) (nortricyclene system), but no absorptions between 1500 and 1700 ($\nu_{C=C}$) and near 700 cm^{-1} (*cis*-olefinic C-H out-of-plane deformation).

In a subsequent similar experiment,³⁶ 20.5 g of norbornadiene and 3.0 g of the catalyst gave 13.6 g of dimers (66%) and 5.3 g of trimer (26%), a total yield of isolated product of 92%.

The reaction was also conducted on a larger scale without the use of much more catalyst. Thus 325 g of norbornadiene and 4.0 g of catalyst gave the same yield of dimer (218 g).³⁶

Air was excluded from the reaction mixture in most experiments, but this precaution does not appear necessary.³⁶

The dimerization could also be effected at room temperature.

(36) This experiment was performed by J. Carnahan.

Norbornadiene (30 g) and 5% rhodium on charcoal (4.0 g) were shaken together in an evacuated sealed glass tube for 5 days. Addition of pentane, filtration, and distillation of the filtrate gave 2.3 g (8% yield) of a mixture of norbornadiene dimers, which vpc showed to be 20% I, 74% IVa, and 6% IVb.

Attempted Dimerization of Norbornadiene with Other Catalysts.
(a) **30% Palladium on Carbon.** Norbornadiene (23 g) and the catalyst (2.0 g) were refluxed in a nitrogen atmosphere for 2 days. Filtration, evaporation of excess norbornadiene, and chromatography on silicic acid (hexane eluent) gave 25 mg (0.1% yield) of I, identified by its nmr spectrum.

(b) **55% Platinum on Charcoal.** Norbornadiene (20 g) and catalyst (3 g) were refluxed under argon for 1 day. Filtration with the aid of pentane and evaporation of solvent left no residue.

(c) **Nickel.** The catalyst, prepared using the procedure of Brown and Brown¹⁹ from 1.0 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, was stirred with norbornadiene at 80° for 2 days. Filtration and evaporation of solvent left no residue.

Attempted Dimerization of Norbornene with 5% Rhodium on Carbon. Norbornene (20 g) and catalyst (3 g) were stirred under argon in a bath at 90–95° for 5 days. Filtration and evaporation left no residue.

Attempted Addition of Norbornadiene to Norbornene. Norbornadiene (10 g, 0.11 mole), norbornene (40 g, 0.43 mole), and 5% Rh-C (4.4 g) were stirred under argon for 44 hr in a bath at 110°. Addition of pentane, filtration, and distillation gave 1.5 g (15%) of a mixture of norbornadiene dimers, identified by the nmr spectrum, and 0.6 g (6%) of the trimer VI after recrystallization of the pot residue.

Acknowledgments. We are grateful to James C. Carnahan, Jr., for his assistance, and to the National Science Foundation (GP-748 and GP-5537), the Alfred P. Sloan Foundation, and the National Institutes of Health for their support.

Catalysis of Anhydride Formation in Aqueous Solutions of Dicarboxylic Acids¹

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Contribution from the School of Pharmacy, University of Wisconsin, Madison, Wisconsin 53706. Received May 12, 1966

Abstract: The rate of anhydride formation in aqueous solutions of dicarboxylic acid is shown to be significantly increased by the presence of sulfite species. The catalytic effect determined directly on both succinic and methylsuccinic acid by the aniline method was expected on thermodynamic grounds.

There now seems to be ample evidence which suggests mediation of many hydrolytic reactions involving esters^{3–5} and amides⁶ by transient formation of corresponding acid anhydrides. In earlier publications,^{7–9} we have shown also that formation of amides in aqueous solutions of certain polycarboxylic acids

involves again, in all probability, intermediate formation of such acid anhydride species. The experimental data strongly suggested existence in the latter instance of relatively sluggish equilibria between the dicarboxylic acids and their corresponding cyclic anhydrides. The present report concerns evidence which apparently indicates that the rate of such anhydride formation can be significantly increased by certain catalytic species.

As has been previously shown, the rate of amide formation in solutions of amines and dicarboxylic acids exhibits a zero-order dependence with respect to the amines at higher free-amine concentration, the rate-limiting step apparently being the rate of conversion of carboxylic acid to its anhydride. It is evident that the catalytic activity of added species would be reflected by increase in the zero-order component. This somewhat tedious approach can and has, as a part of the present study, been used to measure the catalytic rate constants.

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(2) Author to whom reprint requests should be directed.

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(5) L. Ebersson, *Acta Chem. Scand.*, **18**, 2015 (1964).

(6) M. L. Bender, Y. L. Chow, and F. Chloupek, *J. Am. Chem. Soc.*, **80**, 5380 (1958).

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