The Preparation of Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene and the Dimerization of It and of Benzonorbornadiene by Rhodium on Carbon[1]

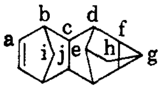
THOMAS J. KATZ, JAMES C. CARNAHAN, JR., AND ROY BOECKE

Department of Chemistry, Columbia University, New York, New York 10027

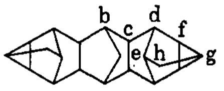
Received November 7, 1966

Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (IV), prepared by pyrolysis of the dimers of structure I formed from norbornadiene and rhodium on carbon, is dimerized by rhodium on carbon to V. Benzonorbornadiene is similarly dimerized to VI. The nmr spectra of V and VI indicate that they have the *exo,trans,exo* stereochemistry (VII and VIII). Addition of cyclopentadiene to IV gives a hydrocarbon of structure I, presumably IX, different from either of the dimers formed when rhodium on carbon dimerizes norbornadiene.

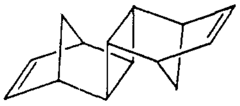
In the presence of 5% rhodium on carbon, norbornadiene self-condenses to yield quantitatively a mixture of dimers, consisting almost entirely of two stereoisomers of structure I, and a trimer of structure II.[2] (The remainder of the dimer mixture is the substance melting at 68°[3] assigned structure III.[3e]) This is the only simple formal cycloaddition, and one of only two cycloadditions known to be catalyzed by a metal.[4]



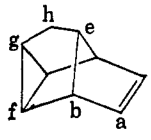
I



II



III



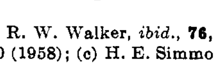
IV

Hydrocarbons similar to norbornadiene might also be expected to dimerize in the presence of rhodium on carbon: one is benzonorbornadiene, another is the unusual compound IV. The latter should be preparable if cyclopentadiene can be thermally cleaved from I in a retro-Diels–Alder reaction,[5a] and readily available since hydrocarbons of structure I are now easily made. (Norbornadiene dimers of structure I have been prepared previously, but in only 1 to 15% yield and mixed with isomers from which they are not easily separated.[3a–d]) Described below is the synthesis of hydrocarbon IV, its dimerization by rhodium on carbon, its reaction with cyclopentadiene to give a third isomer of structure I, and the dimerization of benzonorbornadiene by rhodium on carbon.[5b,c]

Results

Upon pyrolysis at 550° the dimers formed from norbornadiene and rhodium on carbon gave hydrocarbon IV in 28% yield. Its composition was indicated by its analysis, its molecular weight was indicated by the mass of the parent ion in the mass spectrum, and its structure was indicated by the following spectroscopic data: its infrared spectrum exhibiting a peak at 1572 cm^{-1} characteristic of the C=C stretching vibration of norbornenes,[2,3e,6,7] and at 797 and 816 cm^{-1} where nortricyclenes absorb;[2,8,9] its near-infrared spectrum exhibiting a maximum at 1.666 μ (ϵ 1.339) characteristic of nortricyclenes;[10] and its nmr spectrum (Figure 1) exhibiting peaks at τ 8.85 (a doublet $|J| = 4.8$ cps)[11] attributable to H_f,[2,12] at 8.53 attributable to H_h,[2,12] at 8.40 (a triplet $|J| = 4.8$ cps split further into quartets, $|J| = 1.5$ cps) attributable to H_g,[2] at 8.17 attributable to H_e,[2,12] at 7.52 attributable to H_b,[2,3e,6c,13] and at 4.06 (a triplet, $|J| = 1.9$ cps) attributable to H_a.[2,3e,6c,13]

Hydrocarbon IV is dimerized by rhodium on carbon in only low yield (5% after 2 days at 185°) and is not dimerized in the absence of the catalyst. Although the yield is low, the dimer is easily isolable and easily characterized. It is a crystalline solid, mp 142°, identified as V by its analysis, molecular weight (mass spectrum), and spectroscopic properties. The absence of olefinic protons is shown in the nmr spectrum by the absence of absorption below τ 7, and the presence of the cyclopropyl protons of a nortricyclene by the presence of an AB_2 absorption pattern (Figure 2), with τ_A 9.08, τ_B 9.37, and $|J_{AB}| = 4.6$ cps.[11] These structural fea-



V

---

(1) Supported by grants from the National Science Foundation (NSF-GP-5537) and the Alfred P. Sloan Foundation.

(2) J. J. Mrowca and T. J. Katz, *J. Am. Chem. Soc.*, **88**, 4012 (1966).

(3) (a) R. Pettit, *ibid.*, **81**, 1266 (1959); (b) C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Letters*, No. 11, 373 (1961); (c) G. N. Schrauzer and S. Eichler, *Chem. Ber.*, **95**, 2764 (1962); (d) P. W. Jolly, F. G. A. Stone, and K. Mackenzie, *J. Chem. Soc.*, 6416 (1965); (e) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2596 (1965).

(4) D. Bryce-Smith, *Chem. Ind.* (London), 239 (1964).

(5) (a) R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of the Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 906 ff. (b) The name "deltacyclane" has been suggested for the dihydro derivative of IV [by Alex Nickon at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 4–9, 1965; Abstracts of Papers, p 2P; A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Am. Chem. Soc.*, **87**, 1613 (1965)] and hence "deltacyclene" for IV itself (by Alex Nickon, to whom we are grateful). Since this manuscript was submitted, a preparation of IV (mixed with other isomers) has been described which is similar to that given here [L. G. Cannell, *Tetrahedron Letters*, 5967 (1966)]. Also preparations of the precursor I from norbornadiene using metal carbonyls have been elaborated further (G. N. Schrauzer, B. N. Bastian, and G. A. Fosselius, *J. Am. Chem. Soc.*, **88**, 4890 (1966)]. (c) NOTE ADDED IN PROOF.—Hydrocarbon IV in methanol containing platinum oxide absorbs 1 mole of hydrogen and gives a saturated hydrocarbon whose nmr and infrared spectra are identical with those of deltacyclane provided by A. Nickon. The experiment was performed by Dr. N. Acton.

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

(7) There is a strong peak at 696 cm^{-1}, which might also be ascribed to a norbornene olefin proton vibration.[2,3e]

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

(9) G. N. Schrauzer and P. Glockner, *Chem. Ber.*, **97**, 2451 (1964).

(10) (a) P. G. Gassman and W. M. Hooker, *J. Am. Chem. Soc.*, **87**, 1079 (1965); (b) H. Weitkamp and F. Korte, *Tetrahedron*, **20**, 2125 (1964).

(11) This is the same splitting observed in the spectra of the isomers of structure I and in that of the trimer of structure II (*cf.* footnote 24 in ref 2).

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

(13) K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Letters*, 9 (1966).

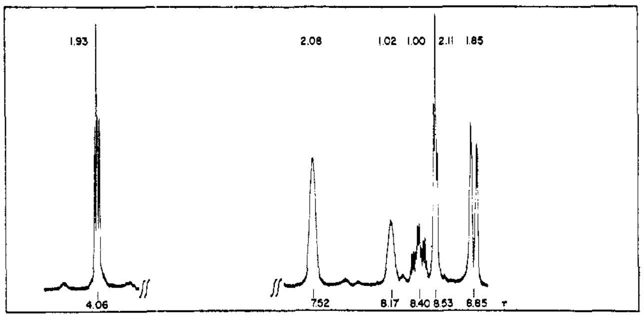


Figure 1.—Nmr spectrum (100 Mcps) of IV in CCl_4 with tetramethylsilane as the internal standard. Intensities are above the peaks.

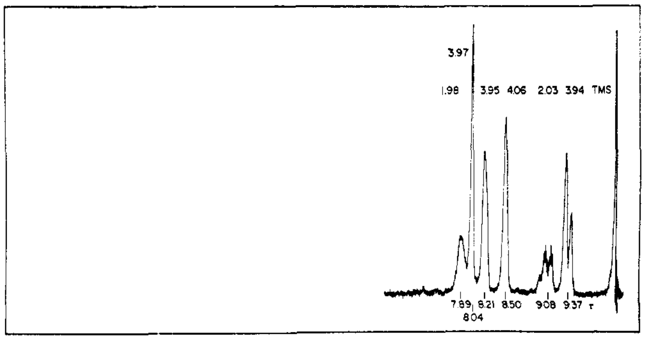


Figure 2.—Nmr spectrum (60 Mcps) of V in CS_2 with TMS as internal standard. Intensities are above the peaks.

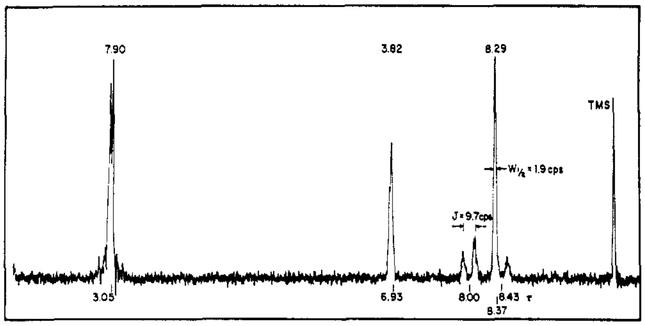


Figure 3.—Nmr spectrum (100 Mcps) of I, the cyclopentadiene adduct of IV. The solvent is CCl_4; TMS is the internal standard. Intensities are above the peaks.

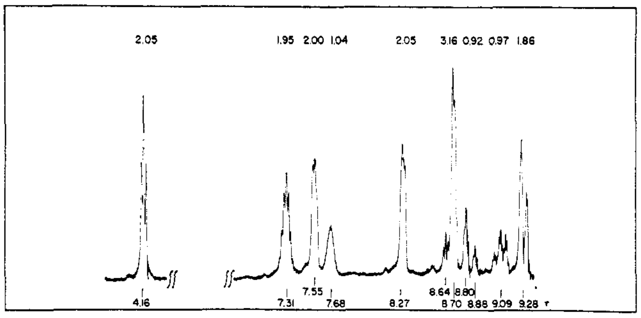


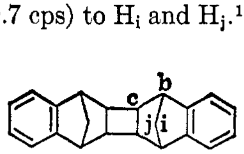
Figure 4.—Nmr spectrum (60 Mcps) of VI in CS_2 with TMS as internal standard. Intensities are above the peaks.

tures are also indicated in the infrared spectrum by the absence of the peaks characteristic of norbornenes,[2,3e,6,7] usually found near 1570 and 700 cm^{-1}, and the presence of strong absorption at 800 and 810 cm^{-1} characteristic of nortricyclenes.[2,8,9] The four remaining peaks in the nmr spectrum can be assigned to the remaining four kinds of protons in structure V. The peak at 8.50 is presumably due to the protons at h,[2,12] that at 8.21 to those at d,[2] and that at 8.04 to those at c. Because of the intensity, that at 7.89 is assigned to e.

An attempt to condense norbornadiene with IV failed. When these two hydrocarbons were heated together at 145° for 15 hr in the presence of 5% rhodium on carbon, the dimers of norbornadiene and the dimer of IV were detected by vapor phase chromatography, but a substance with intermediate retention time was not.

An adduct of IV with cyclopentadiene is formed in 77% yield when IV is heated with dicyclopentadiene at 190° for 2 days.[14] The adduct is a liquid that vapor phase chromatography indicates is homogeneous. Its composition is shown by its analysis and mass spectrum. The nmr spectrum (Figure 3) indicates that it has structure I, but the substance is different from the two known stereoisomers of I.[2] The peaks at τ 4.16 can be ascribed to H_a, those at 7.31 to H_b,[3c,6c,13,15,16] and the AB quartet partially visible at 8.69 and 8.83 ($|J_{AB}| = 8$ cps) to H_i and H_j.[13,15,16] [The splitting at τ 8.64 ($|J| = 1.7$ cps) is presumably attributable to J_{ib}[15,16] and is similar to a splitting in the spectrum of the minor isomer of structure I formed in the rhodium-catalyzed dimerization.[2]] The triplet and doublet ($|J| = 4.9$ cps)[11] at 9.09 and 9.28 appear to be characteristic of the cyclopropyl protons, H_f and H_g,[2] and the peak at 7.68 is assigned to H_e according to its intensity. Of the remaining peaks, 8.70 is assigned to H_h by analogy with peaks in the spectra of nortricyclene,[12] the other isomers of structure I,[2] the trimer II,[2] and hydrocarbons IV and V; the peak at 8.27 is assigned to H_d by analogy with the other isomers of structure I; and the peak at 7.55 is assigned to the remaining proton, H_c. The infrared spectrum shows peaks characteristic of norbornenes[2,3e,6,7] at 1572 and 740 cm^{-1} and of nortricyclenes[2,8,9] at 797 and 805 cm^{-1}.

When benzonorbornadiene is heated at 138° for 2 days it undergoes no reaction, but under the same conditions in the presence of 5% rhodium on carbon it gives a crystalline dimer in 80% yield. The dimer was identified as VI by the nmr spectrum shown in Figure 4. The peaks at τ 3.05 are ascribed to the phenyl protons, those at 6.93 to H_b,[13] the singlet at 8.37 to H_c,[3e,13] and the partially visible AB quartet (τ_A 8.43, τ_B 8.00, $|J_{AB}| = 9.7$ cps) to H_i and H_j.[13,15,16]



VI

Discussion

Since the only derivative of norbornene previously known to be dimerized by rhodium on carbon is norbornadiene,[17] it is significant that benzonorbornadiene also gives a high yield of a dimer, and the hydrocarbon

---

(14) (a) J. K. Stille and D. A. Frey, *J. Am. Chem. Soc.*, **81**, 4273 (1959); (b) S. B. Soloway, *ibid.*, **74**, 1027 (1952).

(15) J. C. Davis, Jr., and T. V. Van Auken, *ibid.*, **87**, 3900 (1965).

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

(17) Unlike norbornadiene, norbornene fails to be dimerized by rhodium on carbon,[2] and neither dimerizes in the presence of nickel tetracarbonyl[18] nor adds diphenylacetylene in the presence of $Ni(CN)_2[(C_6H_5)_3P]_2$ or $Ni(CO)_2[(C_6H_5)_3P]_2$.[9]

(18) C. W. Bird, R. C. Cookson, and J. Hudec, *Chem. Ind.* (London), 20 (1960).

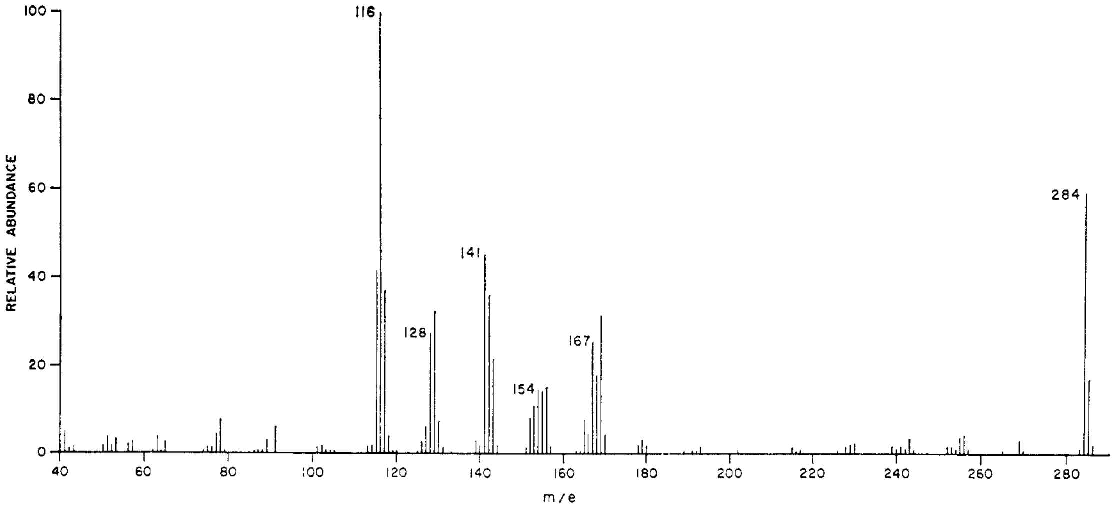
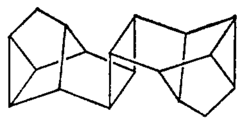


Figure 5.—Mass spectrum (75 v) of VI.

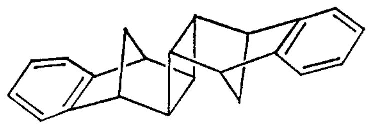
IV some. However, like norbornene, IV does not give detectable cross products with norbornadiene.

Stereochemistry of V.—There are six stereoisomers of structure V in which the four-membered ring is not fused *trans* to the bridged rings. Only four have a twofold axis of symmetry, and unless the simplicity of the nmr spectrum of V (Figure 2) is fortuitous, the dimer is one of these. The following analysis of the nmr spectrum implies that V is the *exo,trans,exo* isomer (VII). The only nmr resonances that can not be assigned on the basis of their intensities or multiplicities are the peaks at 8.04, 8.21, and 8.50, which are due to protons H_c, H_d, and H_h. The peak at 8.50 was assigned to H_h since other nortricyclenes exhibit their resonances between τ 8.72 and 8.85.[2,12] By analogy with the resonance of the bridgehead proton of norbornene, whose position appears almost invariant to whether an adjacent substituent at C-5 is *exo* or *endo*,[19] the position of the resonances of H_d in the compounds I and V should be approximately the same,[19] and the peaks observed between τ 8.12 and 8.27 in all the compounds of structure I and the peak at 8.21 in V are assigned to this proton. Therefore the peak in V at 8.04 is due to H_c. For the resonance of H_c to be so narrow—it has a half-width of 1.7 cps—the coupling constant (J_{dc}) must be small. Since in norbornanes the analogous coupling is very small only when the proton at c is in the *endo* position,[20] dimer V is the *exo,trans,exo* isomer (VII).[22]



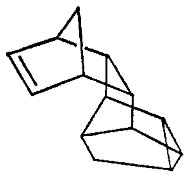
VII

Stereochemistry of VI.—For the same reasons[23] the dimer of benzonorbornadiene (structure VI) has stereochemistry VIII. Like dimer III it is the *exo,-trans,exo* isomer.



VIII

Stereochemistry of I.—By analogy with the stereochemistry of the single adducts formed upon addition of cyclopentadiene to norbornene[14b] and norbornadiene,[14a] the stereochemistry of the cyclopentadiene adduct of IV should be IX. The assignment of this stereochemistry to neither of the norbornadiene dimers of structure I[2] is confirmed by the observation that neither is identical with the adduct of cyclopentadiene and IV.



IX

Mass Spectra.—The mass spectra (75 v) of the six isomers of $C_{14}H_{16}$, the three isomers of structure I, the dimer of structure III, and the latter's *endo,trans,endo* and *endo,trans,exo* isomers,[3e] all show as their most prominent peaks, in order of decreasing intensity, those at 117 ($C_9H_9^+$), 118 ($C_9H_{10}^+$), and 91 ($C_7H_7^+$). Since the spectra of two isomers of C_9H_{10}, bicyclo[6.1.0]nonatriene, and 8,9-dihydroindene are similar, the norbornadiene dimers appear to fragment through loss of cyclopentadiene. The benzonorbornadiene dimer (VI) appears to fragment similarly (Figure 5) since the peak at 116 (C_9H_8, indene) is most prominent.

---

[19] In the three known stereoisomers of III, the position of the resonances of the bridgehead protons vary by 0.16 ppm,[3e] and in the two "benzyne-adducts" of norbornadiene by 0.12.[6c] In the 5-carbomethoxybicyclo[2.2.1]-heptenes the variation is 0.26 ppm.[15]

[20] The coupling constants between bridgehead and 2-*exo* protons are between 3 and 5 cps, while between bridgehead and 2-*endo* protons they are approximately 0. See references in ref 16, p 1177, and ref 2, 3e, 15, and 21.

[21] P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).

[22] Even if the assignment of the resonances of protons c and d were reversed, the implication would remain, for J_{dc} would still have to be small.

[23] For the peak at τ 8.37 to be so narrow, J_{bc} must be very small, and all the protons H_c should therefore be attached to *endo* positions of the norbornane skeletons.

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 × 10^5), 211 (2.3 × 10^4), 252 (shoulder, 880), 259 (1.6 × 10^3), 265 (2.7 × 10^3), 272 (3.5 × 10^3).[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.

Registry No.—IV, 7785-10-6; benzonorbornadiene, 4453-90-1; V, 7781-75-1; I, 7781-74-0; VI, 10026-43-4.

Acknowledgment.—We are grateful to Nancy Acton for determining the 100-Mc 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

M. P. Cava[1a] and F. M. Scheel[1b]

Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio

Received November 29, 1966

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 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°.

---

[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).

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

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