only with vigorous shaking; no color ever developed. The tube was opened and the contents were dissolved in 50 ml of acetone. The solution was filtered, 100 ml of 30–60° petroleum ether was added, and the precipitated polymer was collected, washed well with petroleum ether, and thoroughly dried under vacuum. Isolated was 70 mg (4.2%) of optically inactive white material identical with known polymethyl methacrylate by ir. The polymer was analyzed for sulfur and nitrogen: S, 0.00 ± 0.20%; N, 0.00 ± 0.20%. An average molecular weight of 4620 was determined osmometrically by Galbraith Laboratories. The acetone–petroleum ether soluble portion (<10 mg) was almost entirely (−)-**3** by tlc (50% ether–pentane eluent, uv developer), and ir, and had a specific rotation of $[\alpha]^{25}{}_{\mathrm{D}}$ $-100°$ (*c* 0.65, chloroform), >90% optically pure.

A control run conducted in the absence of (−)-**3** was carried out in parallel. Into a sample tube was distilled 1.8 ml of purified methyl methacrylate. After warming to room temperature and setting 2928 hr, the tube was opened and the residual monomer was removed by low-temperature vacuum distillation. No material remained in the pot. The monomer collected was identical with known material by tlc (50% ether–pentane eluent, uv developer) and ir.

Dimerization and Trimerization of Norbornadiene by Soluble Rhodium Catalysts

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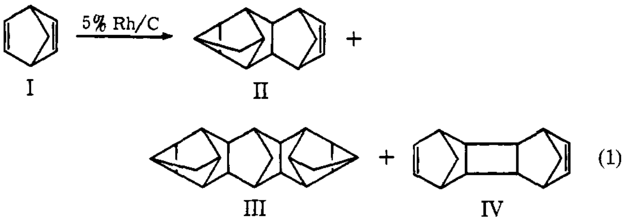
Abstract: Norbornadiene is dimerized and trimerized by catalytic amounts of $[(C_6H_5)_3P]_3RhCl$, giving eight structurally complex molecules, which have been isolated and characterized. Their structures are assigned as V–XII by X-ray crystallography, by proton nmr spectroscopy, and by analysis of their chemical reactions. The structure of a crystalline derivative of one dimer, VI, was determined previously; that of another, VII, is determined here. The stereochemistries of the four stereoisomers of structure II were assigned by comparing their proton nmr spectra and by chemically interconverting them. These interconversions were effected by the addition of hydriodic acid to XIII followed by its elimination giving V, as shown in Scheme I, and by the addition of bromine to XVI followed by dehydrohalogenation and reduction giving XVII, as shown in Scheme II. The structure of the saturated dimer was assigned as IX, rather than XXII, because it was possible to synthesize it by treating XIII with hydriodic acid. The structures of the products, V–XII, although complex, share a common architecture, suggesting that in rhodium-catalyzed reactions an intermediate intervenes that gives a variety of products.

Rhodium is a useful element in organic synthesis for it catalyzes a number of reactions, such as cycloadditions, that cannot be effected in other ways. None of these reactions is understood well although those that involve XY adding to olefins, or rearranging, where Y is H,[2] CHO,[3] or alkenyl[4] and X is hydrogen, have been known the longest and studied the most. Less is known about such reactions when X and Y are both carbon. The first of these, discovered in our laboratory in 1966, was a cycloaddition, the quantitative dimerization and trimerization of norbornadiene (I) to structures II, III, and IV effected by rhodium on carbon (eq 1).[5] Since its discovery few rhodium-catalyzed reactions (other than that giving IV) have been found in which the starting materials and products are related by 2 + 2 cycloadditions. Examples are now known of additions of olefins to olefins giving cyclobutanes[6,7] and of cyclopropanes to olefins giving cyclopentanes,[8] and when thermodynamics requires it, the reverse.[9] No rhodium-catalyzed reactions have been described, other than those giving II and III, in which the starting materials and products are formally related by a Diels–Alder reaction although a few have been discovered in our laboratory.[7] Other related reactions that have been found are some electrocyclic reactions[10] and the apparent subtraction of a carbene from a cyclopropane.[11]



(1)

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[1] (a) Columbia University; (b) University of Illinois.

[2] (a) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966); (b) P. N. Rylander, "Catalytic Hydrogenation Over Platinum Metals," Academic Press, New York, N. Y., 1967.

[3] (a) D. Evans, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 3133 (1968); (b) R. L. Pruett and J. A. Smith, *J. Org. Chem.*, **34**, 327 (1969).

[4] R. Cramer, *Accounts Chem. Res.*, **1**, 186 (1968).

[5] J. J. Mrowca and T. J. Katz, *J. Amer. Chem. Soc.*, **88**, 4012 (1966).

[6] T. J. Katz, J. C. Carnahan, Jr., and R. Boecke, *J. Org. Chem.*, **32** 1301 (1967).

[7] S. A. Cerefice, Dissertation, Columbia University, 1969.

[8] (a) H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeek, *J. Amer. Chem. Soc.*, **91**, 218 (1969); (b) T. J. Katz and S. Cerefice, *ibid.*, **91**, 2405 (1969); (c) T. J. Katz and S. A. Cerefice, *Tetrahedron Lett.*, 2561 (1969).

[9] (a) T. J. Katz and S. A. Cerefice, *ibid.*, 2509 (1969); (b) H. Hogeveen and H. C. Volger, *J. Amer. Chem. Soc.*, **89**, 2486 (1967); (c) H. Hogeveen and H. C. Volger, *Chem. Commun.*, 1133 (1967); (d) L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 3515 (1970); (e) *ibid.*, **92**, 6366 (1970); (f) P. E. Eaton and S. A. Cerefice, *Chem. Commun.*, 1494 (1970).

[10] (a) H. C. Volger and H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **86**, 830 (1967); (b) J. Wristers, L. Brener, and R. Pettit, *J. Amer. Chem. Soc.*, **92**, 7499 (1970).

Table I. Products of Norbornadiene Oligomerizations

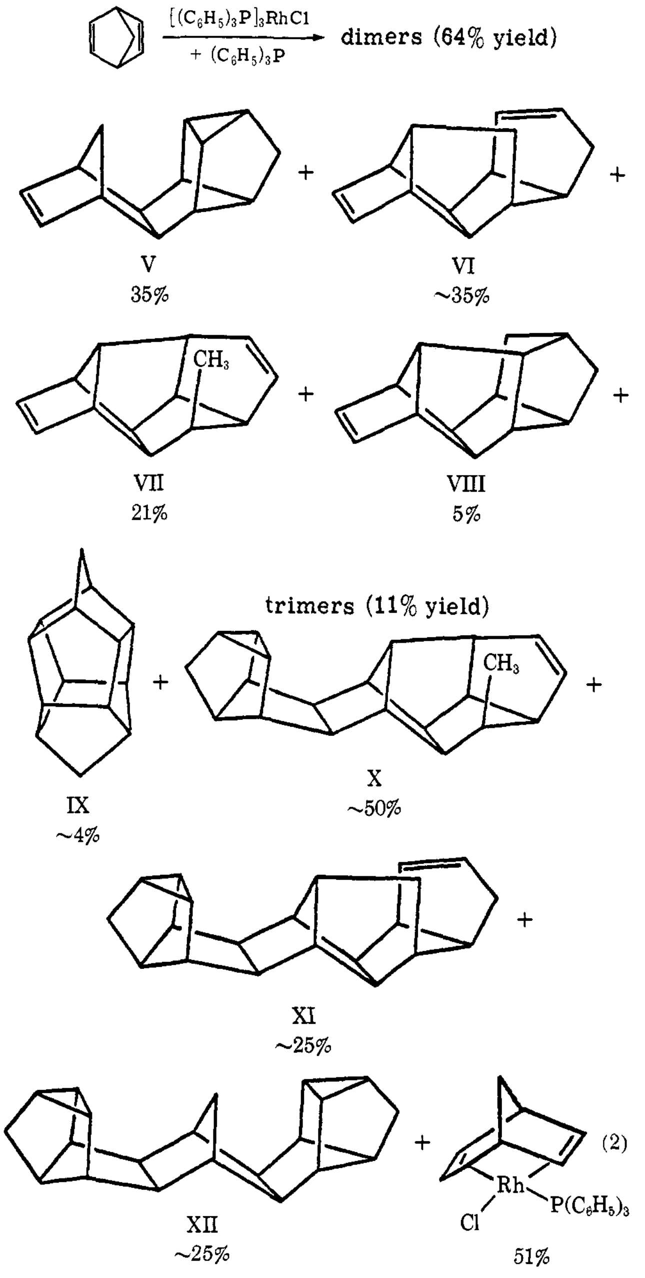
NBD, mmol	Rhodium complex (mmol)	Temp, °C	Time, days	% yield	Product ratio							
					VII	V	VI	IX	VIII	X[c]	XI[c]	XII[c]
1130	$[(C_6H_5)_3P]_3RhCl$ (12) + $(C_6H_5)_3P$ (20)	90	4	60% dimers[a,d]	21	35	35	4	5			
				11% trimers[a,e]						50	25	25
108	$[(C_6H_5)_3P]_3RhCl$ (1.03)	90	4	53[b,f]	3	36	55	*k*	6			
54	$[(C_6H_5)_3P]_2Rh(CO)Cl$ (0.57)	90	4	33[b,g]	1	40	56	0.5	2.5			
152	$[(C_6H_5)_3P]Rh(NBD)Cl$ (1.4)	90	4	17[a,h]	Trace	54	24	3	19	0	0	0
108	$[(C_6H_5)_3P]Rh(NBD)Cl$ (1.01) + $(C_6H_5)_3P$ (1.01)	90	3	41[b,i]	2	37	53	*k*	7			
108	$[(C_6H_5)_3P]Rh(NBD)Cl$ (1.01) + $(C_6H_5)_3P$ (2.02)	90	3	45[b,i]	4	33	56	*k*	6			
100	$(C_8H_{14})_2RhCl$ (0.071) + $(C_6H_5)_3P$ (0.38)	90	1	*k,j*	Trace	37	53	*k*	10			
100	$(C_8H_{14})_2RhCl$ (0.071) + $(C_6H_5)_3P$ (19.0)	90	1	*k,j*	33	29	31	*k*	7.5			
30	$(C_8H_{14})_2RhCl$ (0.215)	130	4	0[j]								

[a] Purified by distillation. [b] Purified by column chromatography on silica gel. [c] Where no yield is shown, the trimers were not sought. [d] Analysis on glpc column A (see Experimental Section, 230°) and by proton nmr. [e] Analysis on column B (270°) and by proton nmr. [f] Analysis on column D (190°). [g] Analysis on column D (195°) and by proton nmr. [h] Analysis on column C (210°) and by proton nmr. [i] Analysis on column E (240°). [j] Analysis on column F (175°). [k] Not determined.

To find out more about these reactions we asked two questions about the reaction described above in eq 1: (1) can the dimerization of norbornadiene also be effected by soluble rhodium-containing catalysts[12] like $[(C_6H_5)_3P]_3RhCl$, which is effective for hydrogenation,[2a] and if so are the products the same as those of eq 1; and (2) what are the stereochemistries of the products shown in eq 1?[15]

Results

When norbornadiene (121 g) is refluxed for 5 days with 0.9 atom % of $[(C_6H_5)_3P]_3RhCl$[17] plus 1.5 mol % of $(C_6H_5)_3P$ it gives the products shown in eq 2. When the $(C_6H_5)_3P$ is not added, the dimer mixture consists of the same materials, but the product ratios are changed, the major difference being that the yield of VII is reduced. The same dimers are formed when the reagent used is (norbornadiene)$[(C_6H_5)_3P]$RhCl,[18] or $[(C_6H_5)_3P]_2(CO)RhCl$,[19] or $[(c\text{-}C_8H_{14})_2RhCl]_2$ plus varying amounts of triphenylphosphine,[20] and it is likely that the catalytically active species have the same structures whichever of the reagents specified above is used. The likelihood of this is also indicated



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(11) (a) P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, **92**, 7631 (1970); (b) P. G. Gassman and T. J. Atkins, *ibid.*, **93**, 1042 (1971); (c) P. G. Gassman, T. J. Atkins, and F. J. Williams, *ibid.*, **93**, 1812 (1971); (d) P. G. Gassman and E. A. Armour, *Tetrahedron Lett.*, 1431 (1971); (e) P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, **93**, 4597 (1971); M. Sakai and S. Masamune, *ibid.*, **93**, 4610 (1971); M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *ibid.*, **93**, 4611 (1971).

(12) Part of this work was reported in a preliminary communication,[13] and there have since been two other reports of the dimerization of norbornadiene by soluble rhodium-containing catalysts.[14]

(13) T. J. Katz, N. Acton, and I. C. Paul, *J. Amer. Chem. Soc.*, **91**, 206 (1969).

(14) (a) G. N. Schrauzer, R. K. Y. Ho, and G. Schlesinger, *Tetrahedron Lett.*, 543 (1970); (b) R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc.*, **93**, 3089 (1971).

(15) Part of this work is reported in a preliminary communication.[16] See also ref 5 and 6.

(16) T. J. Katz and N. Acton, *Tetrahedron Lett.*, 2601 (1967).

(17) J. A. Osborn and G. Wilkinson, *Inorg. Syn.*, **10**, 67 (1967).

(18) M. A. Bennett and G. Wilkinson, *J. Chem. Soc.*, 1418 (1961).

(19) (a) L. Vallarino, *J. Chem. Soc.*, 2287 (1957); (b) J. Chatt and B. L. Shaw, *Chem. Ind. (London)*, 290 (1961); (c) A. Rusina and A. A. Vlček, *Nature (London)*, **206**, 295 (1965); (d) J. A. McCleverty and G. Wilkinson, *Inorg. Syn.*, **8**, 214 (1966); (e) D. Evans, J. A. Osborn, and G. Wilkinson, *ibid.*, **11**, 99 (1968).

(20) S. Montelatici, A. van der Ent, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1054 (1968).

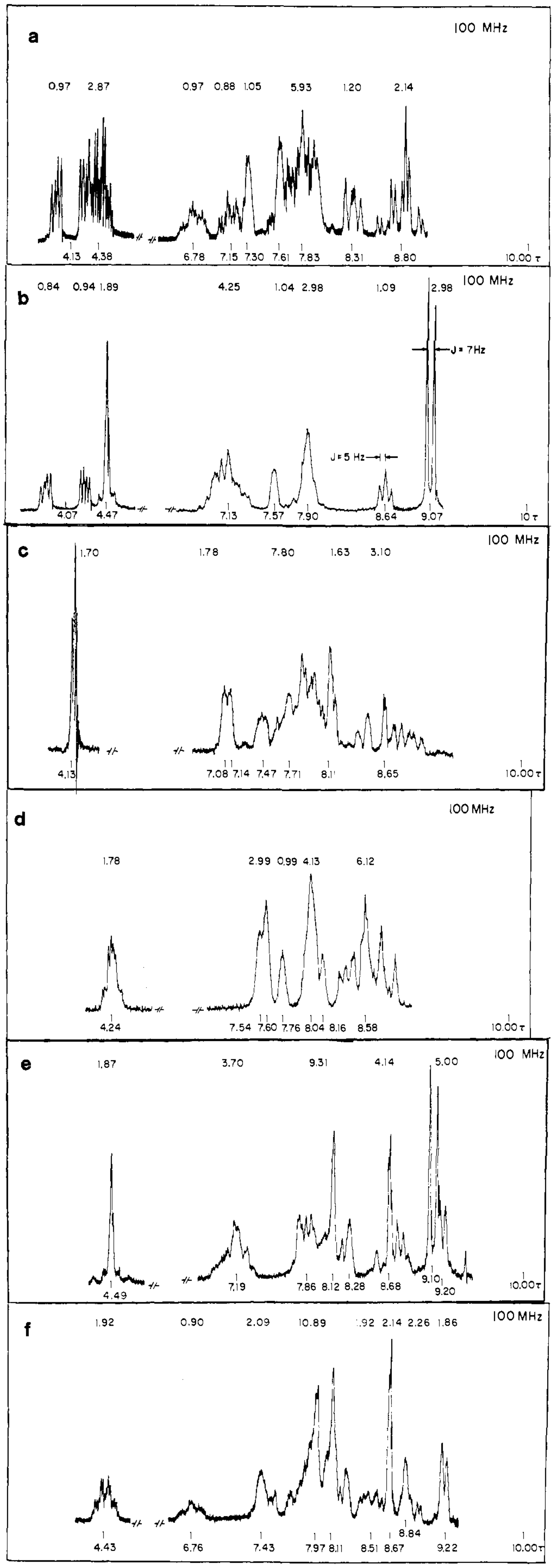
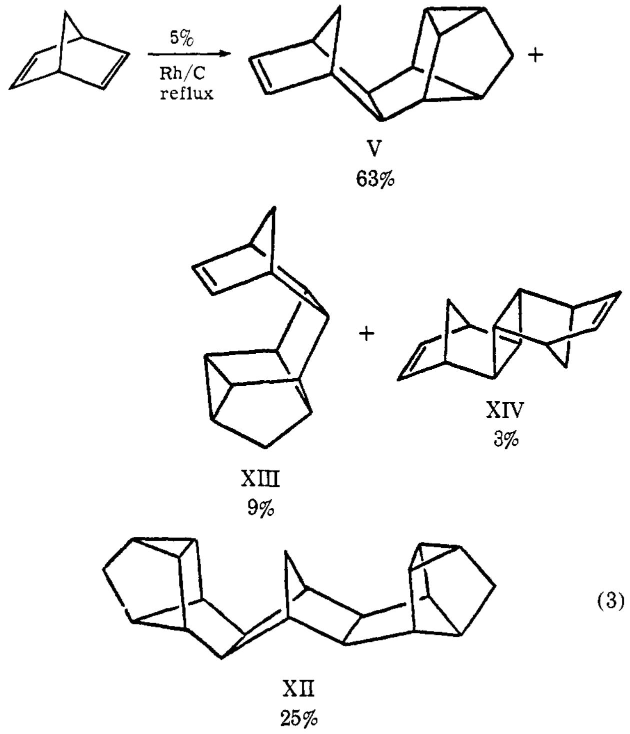


Figure 1. Proton nmr spectra (100 MHz) of norbornadiene dimers in CCl_4. Intensities are above the peaks; (a) VI, (b) VII, (c) VIII, (d) product B $\overset{?}{=}$ XXV, (e) X, (f) XI.

by the recovery of the same rhodium-containing product, (norbornadiene)[$(C_6H_5)_3P$]RhCl, whether it, [$(C_6H_5)_3P$]$_3$RhCl, or [$(C_6H_5)_3P$]$_2$(CO)RhCl was the reagent used. These results are summarized in Table I.

The products differ from those formed, when 5% rhodium on carbon[5] is the catalyst (eq 3), except that



(3)

V and XII are common to both reactions.

That the structures of the products formed by these soluble rhodium catalysts are more complex than those formed by rhodium on carbon appears not to be because the simple cycloaddition dimers V and XIII are transformed into the complex dimers VI, VII, and VIII (or even IX), as attempts to effect these transformations using [$(C_6H_5)_3P$]$_3$RhCl or (norbornadiene)-[$(C_6H_5)_3P$]RhCl failed.[21] Even in experiments in which V or XIII was added to a reaction mixture of norbornadiene and [$(C_6H_5)_3P$]$_3$RhCl, the added V or XIII could still be accounted for in the product mixture.

Determination of Structures. Dimer VI. The parent peak in the mass spectrum shows that the dimer is an isomer of the simple dimers of structure II or IV, but the complexity of its structure is indicated by the complexity of its proton nmr spectrum (Figure 1). To determine the structure we sought a suitable crystalline derivative whose structure could be determined by X-ray diffraction, and a 1 :1 complex of the hydrocarbon and $AgNO_3$ proved satisfactory. That no rearrangement had occurred when the complex formed was demonstrated by decomposing it with aqueous ammonia back to the parent hydrocarbon (VI). The crystal structure shows the hydrocarbon molecule VI with its double bonds attached to silver ions and is pictured in another paper.[13]

Dimer VII. Again the mass spectrum shows the material to be an isomer of the norbornadiene dimers, and again its proton nmr spectrum (Figure 1) is complex. A bizarre feature of the structure, the presence of

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(21) An attempt to convert VIII into VII using [$(C_6H_5)_3P$]$_3$RhCl also failed. VIII was recovered, implying that VIII is not VII's precursor.

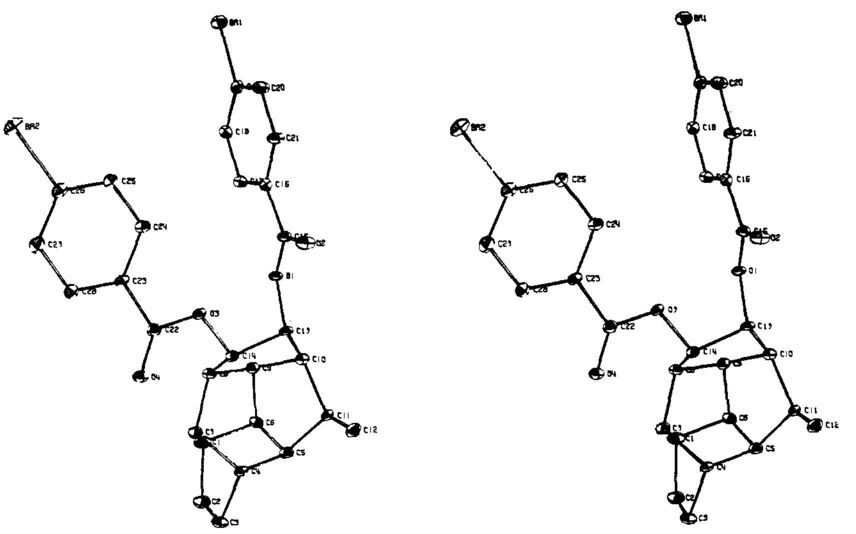
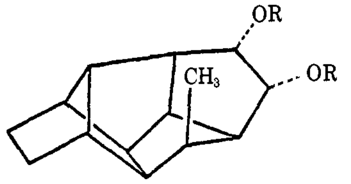


Figure 2. Stereoscopic drawing of a single molecule of XVb. The ellipsoids show the thermal motions of the atoms with a probability of 10%.

a methyl group, is revealed by the presence of a three-proton resonance, a doublet ($|J| = 7$ Hz) at τ 9.07, and again to solve the structure we sought a suitable crystalline derivative whose structure could be determined by X-ray crystallography. A 1:1 crystalline complex with $\mathrm{AgNO_3}$ proved unsatisfactory. A satisfactory derivative was prepared by allowing the dimer to react in methanol, using a platinum catalyst, with 1 mol of hydrogen, by hydroxylating the remaining double bond with osmium tetroxide, and by esterifying the diol with 2 mol of *p*-bromobenzoyl chloride. The structure of the di-*p*-bromobenzoate as determined by X-ray diffraction (see below) is shown in Figure 2 and structure XVb, and the only possible structure for the hydrocarbon dimer, consistent with this and the requirements of the hydrocarbon's proton nmr spectrum that there be two disubstituted double bonds and a $-\mathrm{CH(CH_3)}-$ group, is VII.

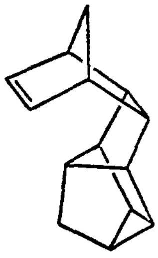
Dimers of Structure II. There are four possible stereoisomers of structure II, but only two (V and XIII) are products of the dimerizations described above. To determine their stereochemistries the other two stereoisomers, XVI and XVII, were synthesized, and the structures of all assigned on the basis of methods that interconvert them and by a comparison of their proton nmr spectra. The preparation of XVI and the assignment of its stereochemistry is described elsewhere.[6] The synthesis of XVII is described below.

The stereochemistry of the minor Diels–Alder dimer of reaction 3 was initially assigned as XIII and the major dimer as V or XVII on the basis of the proton nmr spectra.[5] The proton nmr spectra of all four stereoisomers have been published,[22] but to compare and summarize them the chemical shifts and possible assignments are presented in Table II. It is interesting to note that now that all four stereoisomers are known the basis for the initial assignment remains valid. The structure XIII was initially assigned because of the unusual shielding of the proton f,[5] and the position of that resonance is still unique. The structure V or XVII was initially assigned to the major product of reaction 3 because of the unusually large difference in chemical shift between the protons i and j,[5] and the shift difference is still unusually large.

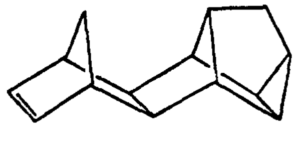


XVa, R = H

b, $\mathrm{R} = \underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{C_6H_4}\text{-}p\text{-}\mathrm{Br}$



XVI



XVII

The stereochemistry of the major Diels–Alder dimer of reaction 3 is proven to be V and the stereochemistry of the minor Diels–Alder dimer confirmed by the sequence of reactions in Scheme I. When the minor dimer (XIII) is shaken for 10.75 hr at 65–70° with 47–50% aqueous HI, it gives a mixture of substances from which was isolated in 11% yield the iodide XVIII, which was identified by its analysis and its spectroscopic properties, and which with alcoholic potassium hydroxide at 80° for 25 hr gives in 78% yield the major dimer. By analogy with the transformation of *endo*- into *exo*-dicyclopentadiene, upon which this plan was modeled,[23] the major and minor isomers must be related as shown in Scheme I.

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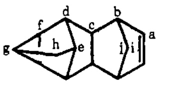
(22) That of V and XIII is in ref 5, XVI is in ref 6, and that of XVII' although not identified, is Figure 1e in the following reference: A. Greco, A. Carbonaro, and G. Dall'Asta, *J. Org. Chem.*, **35**, 271 (1970). There is an error in the way the spectrum of XVI is published. The figure captions numbered 3 and 4 in ref 6 were mistakenly interchanged on publication, so that the spectrum of XVI is the one over the caption for Figure 4.

(23) (a) P. D. Bartlett and I. S. Goldstein, *J. Amer. Chem. Soc.*, **69**, 2553 (1947); (b) G. T. Youngblood and P. Wilder, Jr., *J. Org. Chem.*, **21**, 1436 (1956).

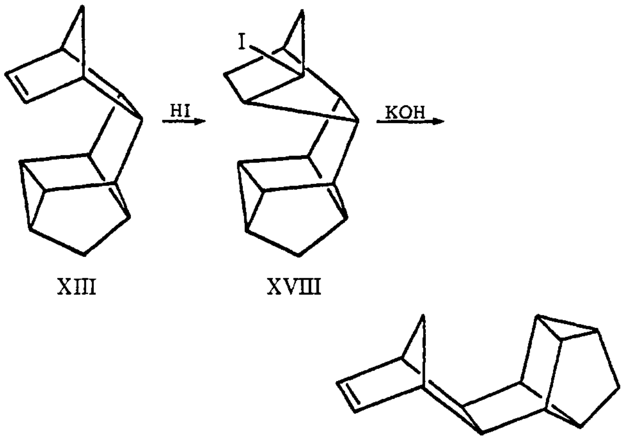
Table II. Assignment of Proton Chemical Shifts in Norbornadiene Dimers of Structure II



	V	XIII	XVI	XVII
a	3.90	4.12	4.16	3.99
b	7.43	7.33^c	7.31	7.45
c	8.13	7.43^{c,d}	7.55^d	8.2
d	8.13	8.21^d	8.27^d	8.2
e	8.05	7.98	7.68^f	7.78
f	9.22	9.67	9.28	9.18
g	8.79^a	8.76	9.09	8.86
h	8.71	8.83	8.70	8.49
i	8.71^a	8.36^e	8.69	8.9
j	7.56^b	8.59^e	8.83	8.2^g

[a] The assignments for protons g and i might be reversed. [b] In the 60-MHz spectrum published (ref 5), the peak is buried under the resonance of b; at 100 MHz it is clearly isolated as a doublet ($|J| = 9$ Hz). [c] Although overlapped at 60 MHz in the published spectrum (ref 5), these peaks are separated at 100 MHz. [d] The assignments for protons c and d might be reversed, but norbornene endo protons usually resonate at 0.6–0.8 ppm higher field than exo protons (A. P. Marchand and J. E. Rose, *J. Amer. Chem. Soc.*, **90**, 3724 (1968)). Thus compare protons c in the four compounds. [e] Protons i and j are assigned because by analogy with other norbornenes, i should be less shielded than j (B. Franzus, W. C. Baird, Jr., N. F. Chamberlain, T. Hines, and E. I. Snyder, *ibid.*, **90**, 3721 (1968); Marchand and Rose, footnote *d*), and because the resonances assigned to i are split into clean triplets (by b), unlike those of j, which should also be weakly coupled to the a protons (*cf.* J. R. Edman and H. E. Simmons, *J. Org. Chem.*, **33**, 3808 (1968); Marchand and Rose, footnote *d*). [f] Note the deshielding (compared to compounds V and XIII) by the double bond (*cf.* Edman and Simmons, footnote *e*). [g] The deshielding (compared to XIII and XVI) may have a steric origin, but the analogous effect on proton e in XVII (compared to that in V and XIII) is small (*cf.* Edman and Simmons, footnote *e*).

Scheme I

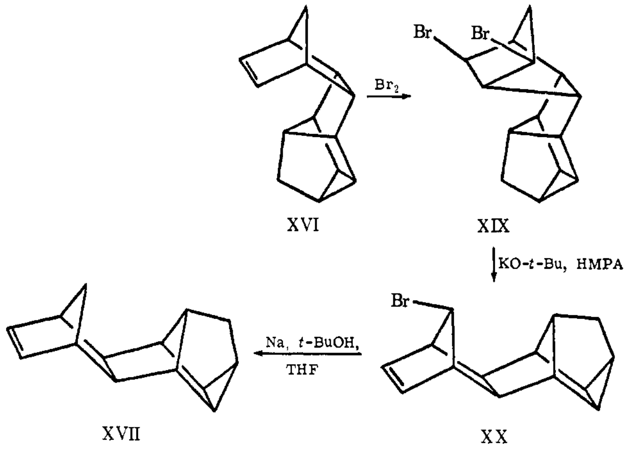


XIII XVIII

V

Attempts to convert XVI into the fourth dimer, XVII, by an exactly analogous sequence of reactions were unsuccessful, but the interconversion was accomplished using a variant, shown in Scheme II, based on the known procedure for converting bicyclo[2.2.1]heptene into its *syn*-7-bromo derivative.[24] Thus the isomer XVI reacts with bromine in carbon tetrachloride to give in 39% yield the dibromide XIX, which is dehydrohalogenated by potassium *tert*-butoxide in hexamethylphosphoramide in 96% yield to XX,[25] which in turn is reduced by sodium and *tert*-butyl alcohol in tetrahydrofuran[26] to give in 63% yield the fourth stereoisomer, XVII.

Scheme II

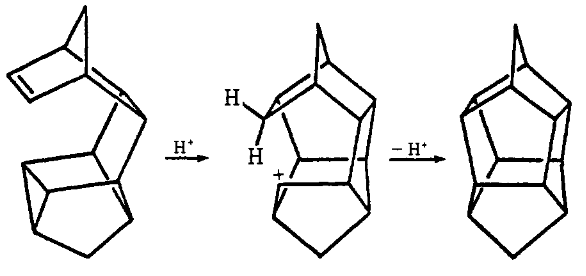


XVI XIX

XVII XX

Dimer IX. This dimer is the same as the saturated dimer first prepared by the reaction of norbornadiene with $Fe(CO)_5$ and light or with $Fe_2(CO)_9$ in the dark.[27] The simplicity of its proton nmr spectrum indicates it has either structure IX or XXII[27] and we choose IX on the basis of the observation that the reaction described above of the minor dimer (XIII) with hydriodic acid gives besides the iodide XVIII (and isomeric material described below) this same saturated hydrocarbon in 8.5% yield. As shown in Scheme III, structure IX is drived from the hydrocarbon XIII by protonation of either the olefin or the cyclopropane and reorganization of neighboring bonds,[28] but the structure XXII is not related to the starting material simply. The formation of the hydrocarbon IX in this reaction also supports the assignment of structure XIII to the minor dimer.

Scheme III



XIII XXI IX

Dimer VIII. The mass spectrum shows the dimer to be isomeric with the others, and its proton nmr spectrum (Figure 1) shows its structure to be complex. Because only small amounts of it were available, no thorough study was made to determine its structure. However, the following experiments, although not definitive, suggest that structure VIII might be correct. When the minor dimer is shaken with HI as described above, it gives, in addition to the 11% yield of XVIII and 8.5% yield of IX, a liquid whose analysis for carbon, hydrogen, and iodine shows it to be isomeric with XVIII, and which is dehydrohalogenated by alcoholic KOH

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[24] H. Kwart and L. Kaplan, *J. Amer. Chem. Soc.*, **76**, 4072 (1954).

[25] These are the reagents used for an elimination by S. J. Cristol and G. W. Nachtigall, *J. Amer. Chem. Soc.*, **90**, 7132 (1968).

[26] P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

[27] (a) D. M. Lemal and K. S. Shim, *Tetrahedron Lett.*, 368 (1961); (b) C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Lett.*, 373 (1961).

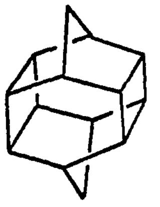
[28] (a) S. Winstein, *Experientia, Suppl.*, *II*, 137 (1955); (b) L. de Vries and S. Winstein, *J. Amer. Chem. Soc.*, **82**, 5363 (1960).

Table III. Final Positional and Thermal Parameters[a]

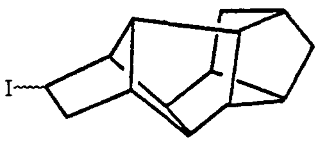
	x	y	z	$b_{11}(\times 10^4)$	$b_{22}(\times 10^4)$	$b_{33}(\times 10^4)$	$b_{12}(\times 10^4)$	$b_{13}(\times 10^4)$	$b_{23}(\times 10^4)$
Br(1)	0.01352 (9)	0.5188 (2)	0.40337 (8)	49 (1)	205 (2)	45 (1)	37 (2)	39 (1)	47 (2)
Br(2)	0.26032 (10)	0.0192 (1)	0.23935 (7)	75 (1)	129 (2)	34 (1)	−23 (2)	14 (1)	−14 (1)
C(1)	0.8919 (9)	0.6128 (13)	0.7523 (8)	47 (8)	112 (16)	55 (6)	−56 (17)	45 (12)	1 (16)
C(2)	1.0182 (9)	0.6117 (15)	0.8038 (8)	44 (8)	166 (20)	55 (7)	−67 (20)	47 (12)	−17 (18)
C(3)	1.0455 (8)	0.4641 (14)	0.8359 (8)	35 (7)	161 (18)	50 (6)	−30 (18)	41 (11)	−11 (17)
C(4)	0.9362 (7)	0.4104 (12)	0.8160 (7)	29 (6)	135 (15)	27 (5)	−5 (15)	15 (9)	−13 (13)
C(5)	0.9066 (8)	0.4965 (11)	0.8689 (7)	39 (7)	86 (13)	34 (5)	−15 (15)	31 (10)	−21 (13)
C(6)	0.8509 (8)	0.6157 (12)	0.8097 (7)	39 (7)	114 (15)	43 (5)	−40 (16)	49 (11)	−2 (14)
C(7)	0.8602 (8)	0.4670 (11)	0.7247 (7)	44 (7)	92 (13)	38 (5)	−46 (16)	39 (10)	−15 (13)
C(8)	0.7400 (7)	0.4629 (12)	0.6926 (7)	33 (6)	104 (15)	36 (5)	−9 (15)	34 (9)	3 (13)
C(9)	0.7329 (8)	0.5636 (11)	0.7529 (7)	43 (7)	97 (13)	34 (5)	−23 (15)	36 (10)	−18 (13)
C(10)	0.7117 (8)	0.4732 (12)	0.8082 (7)	41 (7)	102 (14)	33 (5)	−9 (16)	33 (10)	−4 (13)
C(11)	0.8264 (8)	0.4414 (11)	0.8878 (6)	36 (6)	110 (14)	23 (4)	−6 (15)	23 (9)	−13 (12)
C(12)	0.8469 (9)	0.3024 (13)	0.9214 (7)	59 (9)	122 (16)	36 (5)	12 (19)	34 (11)	40 (15)
C(13)	0.6502 (7)	0.3545 (11)	0.7528 (6)	23 (6)	97 (13)	31 (4)	−21 (14)	19 (9)	−19 (12)
C(14)	0.6987 (8)	0.3316 (10)	0.7015 (6)	40 (7)	77 (12)	27 (4)	−27 (14)	29 (9)	−11 (11)
C(15)	0.4616 (7)	0.3154 (11)	0.6702 (6)	32 (6)	90 (13)	34 (5)	−14 (14)	34 (9)	−10 (12)
C(16)	0.3548 (8)	0.3660 (11)	0.6028 (6)	47 (7)	97 (14)	31 (4)	0 (15)	49 (10)	0 (12)
C(17)	0.3439 (8)	0.4921 (12)	0.5702 (7)	39 (7)	134 (16)	37 (5)	−2 (16)	41 (10)	8 (14)
C(18)	0.2390 (8)	0.5366 (12)	0.5080 (7)	50 (7)	121 (14)	36 (5)	11 (16)	53 (10)	11 (13)
C(19)	0.1527 (8)	0.4546 (12)	0.4837 (6)	49 (7)	135 (15)	28 (4)	16 (16)	41 (9)	−5 (13)
C(20)	0.1641 (8)	0.3296 (12)	0.5146 (8)	42 (7)	128 (16)	51 (6)	−2 (16)	44 (11)	12 (15)
C(21)	0.2668 (8)	0.2854 (12)	0.5752 (7)	34 (6)	118 (14)	47 (5)	−31 (15)	31 (10)	−5 (14)
C(22)	0.6424 (8)	0.2255 (11)	0.5733 (6)	45 (7)	89 (13)	32 (5)	−16 (15)	33 (10)	−1 (12)
C(23)	0.5474 (7)	0.1759 (10)	0.4921 (6)	36 (6)	73 (12)	29 (4)	−26 (13)	19 (9)	−11 (11)
C(24)	0.4430 (8)	0.1875 (12)	0.4748 (7)	44 (7)	121 (15)	34 (5)	−27 (16)	31 (10)	−8 (13)
C(25)	0.3565 (9)	0.1402 (13)	0.3977 (7)	55 (8)	146 (16)	32 (5)	−27 (18)	44 (11)	−24 (14)
C(26)	0.3763 (8)	0.0857 (10)	0.3430 (6)	61 (8)	73 (11)	32 (4)	−12 (15)	35 (10)	15 (12)
C(27)	0.4787 (9)	0.0743 (12)	0.3580 (7)	73 (9)	112 (15)	38 (5)	−15 (18)	54 (12)	−15 (14)
C(28)	0.5664 (8)	0.1192 (12)	0.4362 (7)	53 (8)	122 (15)	34 (5)	−14 (17)	43 (10)	−31 (13)
O(1)	0.5397 (4)	0.4025 (7)	0.6961 (4)	24 (4)	96 (8)	33 (3)	−6 (9)	25 (6)	−6 (8)
O(2)	0.4758 (6)	0.2062 (8)	0.6966 (5)	47 (5)	93 (10)	59 (4)	−1 (11)	40 (8)	21 (10)
O(3)	0.6129 (5)	0.2800 (7)	0.6209 (4)	32 (4)	122 (9)	27 (3)	−26 (10)	23 (6)	−39 (8)
O(4)	0.7334 (5)	0.2157 (8)	0.5936 (4)	37 (5)	146 (11)	40 (3)	−21 (11)	38 (7)	−32 (10)

[a] Anisotropic thermal parameters expressed as exp $-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$.

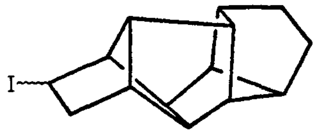
n 65% yield giving a 15:85 mixture of two hydrocarbons, A and B, isomeric with the norbornadiene dimers, the minor one of which (A) is identical with the product formed in 5% yield in eq 2. The other (B) is not identical with any known norbornadiene dimer, and its nmr spectrum (Figure 1) appears too complex to be analyzed easily. Supposing the reason the dehydrohalogenation gives two hydrocarbons is that the liquid precursor is a mixture of two isomeric iodides; it seems possible that one might be XXIII, and hence the hydrocarbon formed on dehydrohalogenation VIII. The reason XXIII seems plausible is that it can be derived simply from XIII by protonation of the double bond, cleavage of the cyclopropyl bond, and quenching by iodide, or by a Wagner–Meerwein rearrangement of XXI followed by quenching. A possible structure for the other iodide could be XXIV, and B could thus be XXV, but this speculation is unsubstantiated. A virtue of these assignments is that they account for a distinctive feature of the nmr spectra of A and B: that each has only one disubstituted double bond.



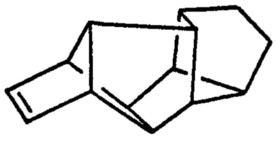
XXII



XXIII



XXIV



XXV

Trimer X. The mass spectrum shows it to be a trimer of norbornadiene, and because the proton nmr spectrum (Figure 1), although complex, shows some peaks resembling those in the spectrum of VII (the τ 4.49, 7.19, and 9.10 peaks in the spectrum of the trimer) and others resembling those in the spectrum of V[5] (the τ 8.12, 8.68, 9.20 peaks in the trimer), the structure is assigned as X.

Trimer XI. Similarly the mass spectrum shows it to be a trimer, and because the proton nmr spectrum (Figure 1) shows peaks (τ 4.43, 6.76) resembling those in the spectrum of VI, as well as peaks (τ 8.11, 8.67, 9.22) resembling those in V,[5] the structure is assigned as XI.

X-Ray Analysis of the Di-*p*-bromobenzoate (XVb) of Dimer (VII). Crystal data for $C_{28}H_{26}O_4Br_2$ showed $M = 583.3$, $a = 14.991(13)$, $b = 10.317(6)$, $c = 19.236(14)$ Å, $\beta = 123°\ 45'(4')$, $V = 2474 \times 10^{-24}$ cm^3, $D_{\text{meas}} = 1.51$ g cm^{-3}, $Z = 4$, $D_{\text{calcd}} = 1.566$ g cm^{-3}, $F(000) = 1200$, μ(Cu Kα) = 206 cm^{-1}. Systematic absences, $h0l$, when $l = 2n + 1$, and $0k0$, when $k = 2n + 1$, indicate that the space group is $P2_1/c$.

The structure was solved by the heavy atom method on a set of photographic data, but has been refined by least-squares methods to an R factor of 0.085 on 2759 nonzero reflections collected on an automatic diffractometer. The final atomic coordinates and thermal parameters are listed in Table III. A stereoscopic drawing of the molecule is shown in Figure 2.

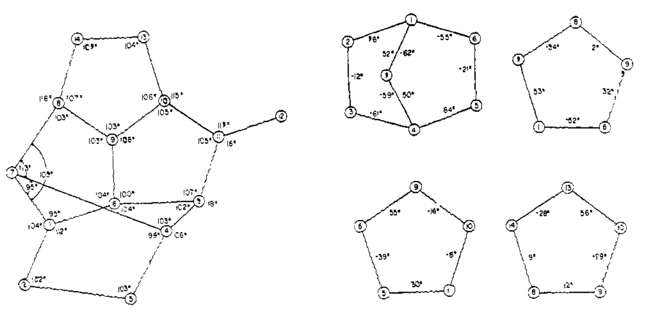


Figure 3. (a) Bond angles (deg) in the fused ring system of XVb. The esd's range from 0.8 to 1.2°. (b) Torsion angles (deg) in some of the constituent rings in XVb. The angles shown on the C(1)–C(2), C(3)–C(4), C(1)–C(6), and C(4)–C(5) bonds do not involve the bridge atom C(7).

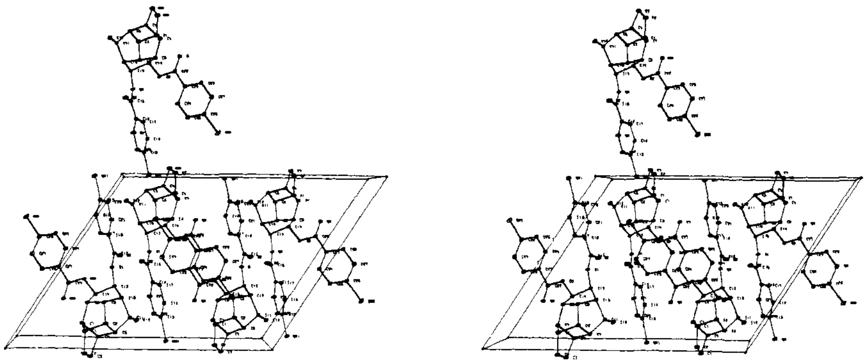


Figure 4. Stereoscopic drawing illustrating the packing of XVb. The origin is at the near top left hand corner of the drawing, and the view is along the +*b* axis. The +*c* axis is horizontal from left to right and the +*a* axis from top to bottom.

The C–C bond lengths in the fused ring system range from 1.53 to 1.61(2) Å, the C–C (aromatic rings) from 1.36 to 1.42(2) Å, the C(aromatic)–C(carbonyl) from 1.49 to 1.50(2) Å, the C═O from 1.20 to 1.21 (1) Å, the C(carbonyl)–O from 1.33 to 1.34(1) Å, and the C(sp^3)–O from 1.46 to 1.47(1) Å, while the C–Br lengths are 1.90(2) Å. The full list of bond lengths is given in the microfilm edition.[29] The C–C–C bond angles in the fused ring system and the torsion angles around many of the bonds are shown in Figure 3. These dimensions indicate the highly strained and unsymmetrical nature of the hydrocarbon moiety. The "norbornane" skeleton (C(1)–C(7)) adopts a *synchro* twist,[30] with quite large torsion angles about the C(2)–C(3) and C(5)–C(6) bonds. Two of the cyclopentane rings in the molecule [C(8), C(9), C(10), C(13), C(14) and C(5), C(6), C(9), C(10), C(11)] have distorted half-chair conformations, while the ring [C(1), C(6), C(9), C(8), C(7)] has an envelope conformation.

Intermolecular contacts <3.80 Å are listed in Table IV. A packing diagram showing the contents of the unit cell is shown in Figure 4. There is a Br(1)···Br(2)^{V} contact of 3.44 Å which is about 0.5 Å less than twice the van der Waals radius for bromine.[31] Other examples of Br···Br contacts less than 3.90 Å have been noted previously.[32]

Discussion

Thus (norbornadiene)[$(C_6H_5)_3P$]RhCl and related substances do catalyze the oligomerization of norbornadiene, and the products do differ from those obtained when rhodium on carbon is the catalyst. However, the products are enormously more complicated than had been anticipated. This might mean that metal catalyzed oligomerizations are not uninterrupted electrocyclic reactions as has been speculated,[33] but more complicated processes.

Although the structures of the products of eq 2 are complicated, it is interesting that essentially all, even the simple V, share a common architecture. Thus the carbon atoms in all the dimers are arranged as shown in structure XXVI, and the only differences occur among the dotted carbon–carbon bonds. This unity of structure may be chance, but it suggests that on the path of the reaction there is one intermediate, or one kind of intermediate with minor variants giving rise to all the products. A conceivable intermediate is XXVII

Table IV. Intermolecular Contacts (<3.80 Å)[a]

Br(2)···C(16)^{I}	3.80	C(23)···C(25)^{III}	3.72
Br(2)···C(21)^{I}	3.79	C(24)···C(28)^{III}	3.64
C(27)···O(1)^{I}	3.71	C(27)···O(2)^{III}	3.28
C(15)···C(27)^{II}	3.66	C(18)···O(4)^{IV}	3.38
Br(2)···C(14)^{III}	3.74	Br(1)···Br(2)^{V}	3.44
C(22)···C(26)^{III}	3.67	C(10)···O(2)^{VI}	3.66
C(23)···C(24)^{III}	3.79	C(2)···O(4)^{VII}	3.28

[a] Superscripted roman numerals refer to atom transformations. I refers to transformation x, $1/2 - y$, $-1/2 + z$. II refers to transformation x, $1/2 - y$, $1/2 + z$. III refers to transformation $1 - x$, $-y$, $1 - z$. IV refers to transformation $1 - x$, $1 - y$, $1 - z$. V refers to transformation $-x$, $1/2 + y$, $1/2 - z$. VI refers to transformation $1 - x$, $1/2 + y$, $1.5 - z$. VII refers to transformation $2 - x$, $1/2 + y$, $1.5 - z$.

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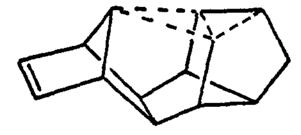
(29) A list of the calculated bond lengths and the observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-5446. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(30) C. Altona and M. Sundaralingam, *J. Amer. Chem. Soc.*, **92**, 1995 (1970).

(31) L. Pauling, in "The Nature of the Chemical Bond," 3rd Edition, Cornell University Press, Ithaca, New York, 1960, pp 257–264.

(32) M. G. Newton, M. C. McDaniel, J. E. Baldwin, and I. C. Paul, *J. Chem. Soc. B*, 1117 (1967).

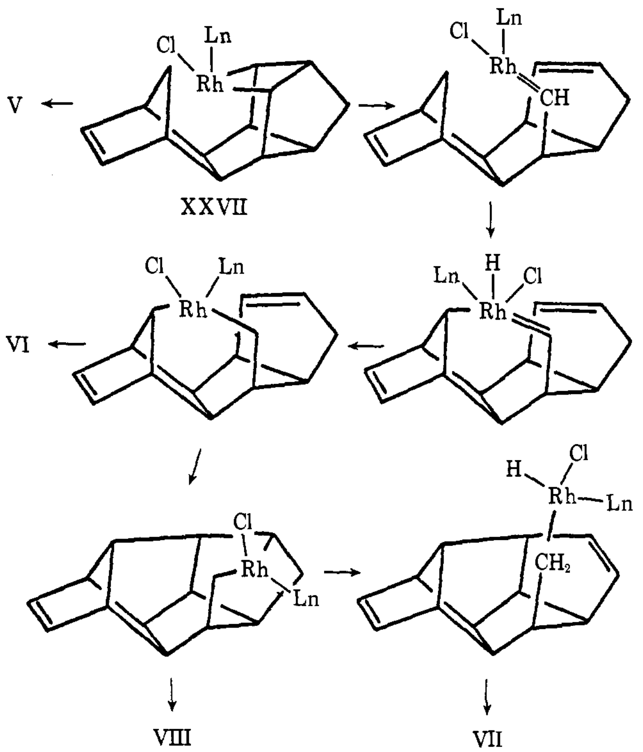
(33) (a) F. D. Mango, *Advan. Catal.*, **20**, 291 (1969); (b) F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **93**, 1123 (1971); (c) R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, **47**, 71 (1969); (d) J. Wristers, L. Brener, and R. Pettit, *J. Amer. Chem. Soc.*, **92**, 7499 (1970); (e) W. Th. A. M. van der Lugt, *Tetrahedron Lett.*, 2281 (1970); (f) G. N. Schrauzer, *Advan. Catal.*, **18**, 373 (1968).



XXVI

which, as adumbrated in Scheme IV, can be imagined

Scheme IV



to proceed to almost all the products.[34] The intermediate XXVII is consistent with ideas of how the metal-catalyzed dimerization of norbornadiene proceeds,[13] but alternatives can be imagined.

However, the idea that in rhodium-catalyzed cycloaddition reactions a kind of an intermediate forms that can give a variety of products is consistent with the results of studies of other systems.[8b, 11e, 35]

The trimers in eq 2 probably arise by addition of a third norbornadiene residue to V, VI, or VII, but we have not determined whether X arises from VII, and XI from VI, or whether both arise from V. That such additions occur is consistent with studies showing that rhodium catalysts can add norbornadiene to a variety of simple norbornenes.[7]

Experimental Section

Spectra were determined using the following instruments: nmr, Varian A-60-A or HA-100; ir, Perkin-Elmer 421 or 621 (unless noted otherwise); mass spectra, Perkin-Elmer-Hitachi RMU-6D. Peaks of less than 10% relative intensity in the mass spectra are excluded from the tabulations below. Melting and boiling points are uncorrected. Analyses are by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The following glpc columns were used: A, 13 ft × $^3/_8$ in. 20% Apiezon J on 60–80 Chromosorb W, reg; B, 4 ft × 0.25 in. 20% Apiezon L on 60–80 Chromosorb W, reg; C, 10 ft × $^1/_8$ in. 20% Apiezon L on 100–120 Chromosorb W, reg; D, 13 ft × $^3/_8$ in. 20% phenyldiethanolamine succinate on 60–80 Chromosorb P; E, 13 ft × $^3/_8$ in. 20% Apiezon L on 60–80 Chromosorb W, reg; F, 5 ft × $^1/_8$ in. 20% Apiezon L on 100–120 Chromosorb W, reg. The glpc instruments were a Varian Aerograph 1200 and a Varian Aerograph A 90 P3.

Norbornadiene is abbreviated NBD.

NBD + $[(C_6H_5)_3P]_3$RhCl. A mixture of 121 g of NBD (1.31 mol), 10.6 g of $[(C_6H_5)_3P]_3RhCl$ (0.012 mol), and 6 g of Ph_3P (0.02 mol) was stirred under nitrogen at reflux for 5 days. The mixture was poured into 600 ml of pentane, filtered from 3 g of rhodium complex,[36] and the solvent was removed under reduced pressure. Distillation gave 77.5 g (64%) of a dimer mixture, bp 70–80° (0.1 mm), consisting of five components. These could be fractionated by spinning-band distillation[37] and are (in order of glpc retention time on column A, 230°) VII (21%), V[5] (35%), a mixture of VI[13] and IX[27] (39%, not resolved by glpc, but estimated from the proton nmr spectrum to be a 9:1 mixture of VI and IX), and VIII (5%).

VII: ir (neat, cm^{-1}) 3135 m, 3054 s, 2954 s, 2920 s, 2874 s, 1617 m, 1598 w, 1564 m, 1453 s, 1372 s, 1357 s, 1348 s, 1331 s, 1320 s, 1292 m, 1282 m, 1267 s, 1252 w, 1223 m, 1213 m, 1202 s, 1195 w, 1170 w, 1156 w, 1115 m, 1093 w, 1053 m, 1040 m, 1010 m, 993 w, 980 w, 971 w, 945 m, 934 m, 817 m, 878 s, 867 s, 835 s, 810 s, 788 m, 763 s, 743 w, 725 w, 698 s, 665 w, 641 w; mass spectrum (75 eV) *m/e* (relative intensity) 41 (20.3), 51 (19.2), 63 (14.0), 65 (27.1), 66 (19.2), 77 (39.0), 78 (21.7), 79 (22.9), 91 (99.5), 92 (37.5), 93 (19.6), 103 (18.9), 104 (17.3), 105 (21.2), 106 (20.2), 115 (45.7), 116 (25.2), 117 (99.5), 118 (85.3), 119 (100.0), 128 (24.9), 129 (21.2), 130 (17.1), 141 (20.2), 142 (13.8), 143 (15.3), 153 (10.3), 155 (17.0), 156 (10.8), 169 (32.5), 184 (91.8), 185 (13.8).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 90.95; H, 8.90.

VI: ir (neat, cm^{-1}) 3050 s, 2940 s, 2867 s, 2845 s, 1603 w, 1560 w, 1449 m, 1440 m, 1353 s, 1332 s, 1321 m, 1302 m, 1280 m, 1268 m, 1262 w, 1252 s, 1220 m, 1202 m, 1185 m, 1165 w, 1152 m, 1130 w, 1112 w, 1100 w, 1072 m, 1048 m, 1040 w, 1015 m, 1009 m, 982 m, 972 m, 952 m, 942 m, 930 m, 905 m, 895 m, 887 w, 865 s, 837 w, 830 m, 812 m, 795 s, 785 m, 770 s, 765 m, 713 s, 700 s, 650 s; mass spectrum (75 eV) *m/e* (relative intensity) 66 (10.8), 77 (23.8), 78 (16.8), 79 (27.0), 91 (29.0), 104 (16.5), 105 (52.2), 115 (15.5), 117 (51.3), 118 (100.0), 119 (14.5), 184 (35.8).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.03; H, 8.89.

Continued distillation of the residue through a short column (pot temperature = 180° (0.1 mm)) gave an additional 20 g of material, a mixture of $(C_6H_5)_3P$, $(C_6H_5)_3PO$, and trimers. Most of the phosphine was removed by diluting with pentane and filtering. The filtrate was chromatographed on alumina (hexane) to give 14 g (11%) of trimer mixture. Glpc (column B, 270°) showed two peaks of about equal intensity. The first trimer to be eluted is X, a viscous oil after bulb-to-bulb distillation at 120° (0.05 mm).

X: ir (neat cm^{-1}) 3042 s, 2920 s, 1694 w, 1667 w, 1613 m, 1451 s, 1366 s, 1351 m, 1343 m, 1332 m, 1318 m, 1305 w, 1289 m, 1280 w, 1261 m, 1258 m, 1220 m, 1205 m, 1190 m, 1152 m, 1140 w, 1114 m, 1103 w, 1091 w, 1069 m, 1045 w, 1037 w, 1025 w, 1011 m, 980 m, 970 w, 954 w, 937 m, 924 w, 900 m, 893 w, 844 w, 855 m, 828 m, 812 m, 805 s, 800 s, 792 s, 777 s, 768 w, 749 s, 722 s, 688 m, 680 w, 642 w, 624 w; mass spectrum (75 eV) *m/e* (relative intensity) 39 (19.0), 41 (21.0), 65 (18.0), 67 (10.0), 77 (32.5), 78 (13.0), 79 (24.0), 91 (58.0), 92 (27.0), 93 (26.0), 105 (17.5), 115 (24.5), 116 (13.5), 117 (33.0), 118 (16.5), 128 (20.0), 129 (25.0), 130 (10.0), 131 (11.0), 141 (14.0), 143 (24.0), 155 (13.0), 158 (13.0), 167 (11.0), 169 (10.0), 181 (12.0), 210 (17.0), 211 (15.0), 247 (10.0), 276 (100.0), 277 (24.0).

Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.29; H, 8.59.

The second peak consisted of a trimer tentatively identified as XI mixed with about an equal amount of XII.[5] XI could be obtained pure by recrystallization from 95% ethanol, mp 118.5–119.5°; ir (CS_2, cm^{-1}) 3054 m, 3044 m, 3027 m, 2969 m, 2926 s, 2861 s, 2843 m, 1369 w, 1353 m, 1339 w, 1331 w, 1315 w, 1306 w, 1297 w, 1291 w, 1276 w, 1261 w, 1254 m, 1196 m, 1150 m, 1137 w, 1114 w, 1081

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(34) It does not get to IX.

(35) (a) T. J. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, **91**, 6519 (1969); (b) L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, **92**, 3515 (1970); (c) L. Cassar and J. Halpern, *Chem. Commun.*, 1082 (1970).

(36) The ir spectrum of this material was identical with that of $[(C_6H_5)_3P]Rh(NBD)Cl$ prepared from $[(NBD)RhCl]_2$ + $(C_6H_5)_3P$ in CH_2Cl_2 using the procedure described by Bennett and Wilkinson.[18] After recrystallization from 95% ethanol and sublimation at 170° (5 × 10^{-6} mm) it showed mp (vac) 224.5–225.5° dec (lit.[18] 163–164°). *Anal.* Calcd for $C_{25}H_{23}ClPRh$: C, 60.93; H, 4.70. Found: C, 61.07; H, 4.89.

(37) Nester Faust Teflon spinning band column, 24 in. × 8 mm, boiling range 119–140° (15 mm). V, VI, and VII could be obtained about 95% pure. VIII was obtained as an approximately 50:50 mixture with VI.

w, 1071 w, 1058 w, 1047 w, 991 w, 976 w, 962 w, 949 w, 943 w, 932 m, 898 m, 804 m, 839 w, 822 m, 812 m, 802 sh, 782 s, 761 s, 715 s, 687 m, 661 w; mass spectrum (75 eV) *m/e* (relative intensity) 77 (14.5), 79 (16.5), 91 (29.5), 92 (15.0), 105 (15.0), 115 (13.3), 117 (21.5), 118 (12.7), 128 (10.5), 129 (16.0), 130 (10.0), 210 (17.5), 235 (17.0), 276 (100.0), 277 (23.0).

Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.32; H, 8.82.

NBD + Bis(cyclooctene)chlororhodium(I) + $(C_6H_5)_3P$. When a mixture of NBD (9.1 g, 100 mmol), $[(C_8H_{14})_2RhCl]_2$ (25 mg, 0.035 mmol), and $(C_6H_5)_3P$ (100 mg, 0.38 mmol) was refluxed under nitrogen with stirring for 24 hr, the ratio of dimers obtained in order of retention time on column F (175°) was VII (trace), V (37%), VI (53%), VIII (10%). When the same amounts of NBD and $[(C_8H_{14})_2RhCl]_2$ were refluxed with $(C_6H_5)_3P$ (5 g, 19 mmol), the ratio of dimers obtained was VII (33%), V (29%), VI (31%), VIII (7.5%). NBD (2.7 g, 30 mmol) and $[(C_8H_{14})_2RhCl]_2$ (76 mg, 0.108 mmol) in the absence of $(C_6H_5)_3P$, when heated in a tube at 130° for 4 days, gave back NBD and no dimers.

Preparation of a Crystalline Derivative of VII. (a). VII + H_2. A mixture of 206 mg (1.12 mmol) of VII and 24 mg of PtO_2 in 25 ml of absolute methanol was allowed to react with 1 equiv of hydrogen. After removal of the catalyst and solvent, bulb-to-bulb distillation at 65° (0.1 mm) gave 174 mg (84%) of dihydro VII which was 85% pure by glpc (column C, 220°); nmr (60 MHz; CCl_4) broad singlets at τ 4.44 (1.80 H), 7.10 (2.00 H), 7.76 (2.90 H), 8.17 (2.90 H), broad multiplet 8.57 (4.78 H), doublet 9.09 (3.60 H, $J = 7$ Hz).

(b). **Preparation of XVa.**[38] A solution of 248 mg (1.33 mmol) of dihydro VII in 3 ml of ether was added to a solution of 342 mg (1.35 mmol) of OsO_4 in 3 ml of ether and 0.5 ml of pyridine. After 5 days at room temperature the solid was collected and dissolved in 40 ml of dioxane, and H_2S was bubbled through the solution. The mixture was filtered and the filtrate clarified with Norit. Removal of the solvent under reduced pressure left a dark green oily residue, which solidified on dilution with pentane. Sublimation at 80–100° (0.1 mm) gave 140 mg (47%) of a white solid XVa, mp 116–121°; ir (KBr, cm^{-1}, Perkin-Elmer Model 137 instrument) 3410 m, 3230 m, 3070 m, 2900 s, 2840 m, 1450 w, 1420 w, 1375 w, 1365 w, 1335 w, 1320 w, 1280 w, 1260 w, 1247 w, 1240 w, 1210 m, 1185 w, 1155 w, 1140 w, 1110 m, 1070 m, 1065 m, 1055 m, 1045 m, 1005 m, 943 w, 932 w, 915 w, 893 w, 877 w, 860 w, 845 w.

(c). **XVb.** A solution of 78 mg (0.354 mmol) of *p*-bromobenzoyl chloride in 1 ml of dry pyridine was added to 39 mg (0.177 mmol) of XVa in 1 ml of pyridine. After a few minutes at room temperature the solution was boiled for 2 min, then poured onto ice. The product was collected, and washed with 5% Na_2CO_3, then water. Recrystallization from 95% EtOH, then from MeOH gave 32 mg of product, mp 155–156°; ir (KBr, cm^{-1}) 2983 w, 2957 s, 2946 s, 2933 s, 2925 s, 2914 m, 2905 m, 2880 m, 2860 s, 1786 m, 1723 s, 1676 m, 1590 s, 1485 s, 1460 m, 1445 w, 1402 s, 1376 m, 1366 w, 1316 s, 1312 s, 1304 s, 1289 s, 1279 s, 1270 s, 1250 m, 1228 m, 1205 w, 1176 s, 1144 w, 1125 s, 1114 s, 1104 s, 1095 s, 1070 s, 1030 m, 1014 s, 964 w, 955 w, 944 w, 916 m, 910 w, 896 m, 840 m, 834 w, 828 w, 855 m, 850 m, 830 m, 810 w, 795 m, 770 m, 760 s, 756 s, 740 m, 705 m, 683 m, 680 m, 648 w, 625 m, 600 w, 570 w, 535 m, 525 m, 494 m, 482 m, 470 m, 464 m, 414 m, 350 m, 312 w.

Anal. Calcd for $C_{28}H_{26}Br_2O_4$: C, 57.35; H, 4.47; Br, 27.25. Found: C, 57.09; H, 4.54; Br, 27.35. Well formed crystals were obtained from acetone (hexagonal plates) or methanol (rods).

NBD + $[(C_6H_5)_3P]_2Rh(CO)Cl$. A mixture of 5 g of NBD (54 mmol) and 396 mg of $[(C_6H_5)_3P]_2Rh(CO)Cl$ (0.57 mmol)[39] was refluxed under nitrogen for 4 days. The mixture was diluted with hexane and the precipitated rhodium complex (244 mg) collected, mp (vac) 200–240° dec. The ir spectrum indicates this to be a mixture of $[(C_6H_5)_3P]_2Rh(CO)Cl$ and $[(C_6H_5)_3P]Rh(NBD)Cl$. The filtrate was washed with water, dried (Na_2SO_4), concentrated, and then chromatographed on silica gel (40 g). Elution with hexane gave 1.65 g (33%) of the following dimer mixture (in order of elution from column D, 195°): VII (1%), V (40%), VI (56%), and VIII (3.0%, contaminated by about 10% of IX).

NBD + $[(C_6H_5)_3P]_3RhCl$. A mixture of 10 g (108 mmol) of NBD and 964 mg (1.03 mmol) of $[(C_6H_5)_3P]_3RhCl$ was refluxed under nitrogen for 4 days. Dilution with hexane precipitated the rhodium complex (295 mg).[36] Concentrating the filtrate and chromatography on silica gel (hexane) gave 5.3 g (53%) of product; glpc (in order of retention time on column D, 190°) VII (3%), V (36%), VI (55%), and VIII (6%).

NBD + $[(C_6H_5)_3P]Rh(NBD)Cl$. A mixture of 14 g of NBD (152 mmol) and 700 mg (1.4 mmol) of $[(C_6H_5)_3P]Rh(NBD)Cl$[36] was refluxed under nitrogen for 4 days, diluted with pentane, and filtered, and the solvent evaporated. Distillation gave 2.4 g (17%) of product (bp 70–75° (0.1 mm)); glpc (in order of retention time on column C, 210°) VII (trace), V (54%), VI (27% containing about 10% IX), and VIII (19%). No trimers could be detected.

NBD + $[(C_6H_5)_3P]Rh(NBD)Cl$ + $(C_6H_5)_3P$. (a). A mixture of 10 g of NBD (108 mmol), 497 mg (1.01 mmol) of $[(C_6H_5)_3P]Rh(NBD)Cl$, and 265 mg (1.01 mmol) of $(C_6H_5)_3P$ was refluxed under nitrogen for 3 days, diluted with hexane, and filtered, and the filtrate concentrated. Chromatography on silica gel (hexane) gave 4.1 g (41%) of product; glpc (in order of retention time on column E, 240°) VII (2%), V (37%), VI (53%), and VIII (7%).

(**b**). A mixture of 10 g of NBD (108 mmol), 497 mg (1.01 mmol) of $[(C_6H_5)_3P]Rh(NBD)Cl$, and 529 mg (2.02 mmol) of $(C_6H_5)_3P$ was refluxed under nitrogen for 3 days. Chromatography on silica gel (hexane) gave 4.5 g (45%) of product; glpc (in order of retention time on column E, 240°) VII (4%), V (33%), VI (56%), and VIII (6%).

Preparation of VI·$AgNO_3$. Shaking a sample of VI with saturated aqueous $AgNO_3$ produced a complex which dissolved in the silver nitrate solution. The aqueous solution was washed with pentane and a few drops of water were then added. The product crystallized, was collected, washed with water, dried, and recrystallized from acetone, mp (vac) 153–154.5° dec.

Anal. Calcd for $C_{14}H_{16}AgNO_3$: C, 47.48; H, 4.55; Ag, 30.45; N, 3.95. Found: C, 47.51; H, 4.26; Ag, 30.58; N, 4.44, 4.20.

The silver nitrate complex (52 mg) was treated with dilute aqueous NH_4OH and extracted three times with pentane. The pentane solution was washed with water and dried, and the solvent was removed. Bulb-to-bulb distillations (70° (0.1 mm)) gave 26 mg (96%) of VI, identified by its proton nmr spectrum.

Preparation of VII·$AgNO_3$. VII (271 mg) was mixed with 5 ml of saturated aqueous silver nitrate. After standing overnight in the refrigerator, the mixture was diluted with a little water and the precipitate collected and washed with water, giving 476 mg (92%), mp (vac) 200–203° dec. Taken up in 40 ml of 95% ethanol and left for 1 day at room temperature it gave 184 mg of crystals (rods).

Anal. Calcd for $C_{14}H_{16}\cdot AgNO_3$: C, 47.48; H, 4.55; Ag, 30.45; N, 3.95. Found: C, 47.36; H, 4.36; Ag, 30.33; N, 3.76.

VII·$AgNO_3$ (100 mg) was shaken with dilute aqueous NH_4OH and extracted twice with pentane, and the pentane solution was washed with water. After drying over KOH, removal of the solvent and bulb-to-bulb distillation gave 46 mg of VII (89%), identified by its proton nmr spectrum.

Preparation of VIII·$AgNO_3$. VIII (133 mg) was shaken with 1 g of saturated aqueous silver nitrate solution. After standing at room temperature for 1 hr, the mixture was diluted with a little water, and the precipitate was collected and washed with water, giving 215 mg (84%) of complex. Dissolving in 5 ml of boiling acetone, clarification with Norit, and cooling quickly at −10° gave 77 mg of thin plates.

Anal. Calcd for $C_{14}H_{16}\cdot AgNO_3$: C, 47.48; H, 4.55; Ag, 30.45; N, 3.95. Found: C, 47.66; H, 4.80; Ag, 30.55; N, 3.85. Attempts to recrystallize from acetonitrile or to grow crystals by slow evaporation of the solvent resulted in decomposition.

Control Experiments. The following experiments indicate that V, XIII, and VIII are not precursors of the products in eq 2.

(**a**). **VIII + $[(C_6H_5)_3P]_3RhCl$.** An evacuated sealed glass tube containing 95 mg (0.52 mmol) of VIII and 13 mg (0.014 mmol) of $[(C_6H_5)_3P]_3RhCl$ was shaken at 97° for 4 days. Glpc analysis (column F, 170°) showed only VIII.

(**b**). **XIII + $[(C_6H_5)_3P]_3RhCl$.** A tube containing 100 mg of $[(C_6H_5)_3P]_3RhCl$ and 200 mg of XIII was shaken at 90–95° for 2.5 days. Bulb-to-bulb distillation gave 142 mg of recovered XIII which was pure by proton nmr and glpc.

(**c**). **V + $[(C_6H_5)_3P]_3RhCl$.** A tube containing 150 mg of $[(C_6H_5)_3P]_3RhCl$ and 300 mg of V was shaken at 95° for 4 days. Proton nmr of the reaction mixture showed only starting material.

(**d**). **V + $[(C_6H_5)_3P]Rh(NBD)Cl$.** A tube containing 50 mg of $[(C_6H_5)_3P]Rh(NBD)Cl$ and 300 mg of V was shaken at 95° for 4 days. Proton nmr of the reaction mixture showed only starting material.

(e). **XIII + $[(C_8H_{14})_2RhCl]_2$ + $(C_6H_5)_3P$.** A tube containing 27 mg of $[(C_8H_{14})_2RhCl]_2$, 40 mg of $(C_6H_5)_3P$, and 162 mg of XIII was

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(38) The procedure is modeled on that of D. H. R. Barton and D. Elad, *J. Chem. Soc.*, 2085 (1956).

(39) Prepared as described in ref 19c, mp (vac) 295–300° dec (lit. dec, 195–200°,[19a] and 195–197°[19d]).

shaken at 100° for 4 days. Proton nmr of the reaction mixture showed only XIII and cyclooctene.

(f). **XIII + $[(C_6H_5)_3P]_3RhCl$ + NBD.** A tube containing 240 mg of XIII, 35 mg of CH_2Cl_2 as internal standard, 83 mg of $[(C_6H_5)_3P]_3RhCl$, and 200 mg of NBD was shaken at 85–95° for 4 days. Proton nmr integration of the CH_2Cl_2 and of the τ 9.65 doublet of XIII gave a ratio of 1:2.9 before the reaction and 1:3.0 after, indicating no loss of XIII. The ratio of the intensity of the resonance at τ 9.65 and of all olefinic protons was 2.2. Glpc (column F, 170°) of the reaction mixture showed VII, V, VI, XIII (not resolved), and VIII in the ratio 2.4:20:76:1.6. These figures imply that while no loss of XIII occurred, 88% of the NBD was converted into VII, V, VI, and VIII in the ratio 6:47:43:4.

(g). **V + $[(C_6H_5)_3P]_3RhCl$ + NBD.** A tube containing 250 mg of V, 35 mg of CH_2Cl_2 as internal standard, 94 mg of $[(C_6H_5)_3P]_3RhCl$, and 220 mg of NBD was shaken at 85–95° for 4 days. Proton nmr integration of the CH_2Cl_2 and of the τ 3.95 multiplet of V gave a ratio of 1:2.6 before the reaction and 1:2.9 after. Glpc (column F, 170°) of the reaction mixture showed VII, V, VI, and VIII in the ratio of 3:69:27:1. These figures mean the amounts of VII, V, VI, and VIII formed are 12, 29, 109, and 4 mg. The amount by which V is low should be no more than 25 mg, or 10% of that put in originally, while 62% of the NBD was consumed. Thus V does not appear to be a precursor of the other products.

XIII + Aqueous HI.[40] A tube containing 2.0 g of XIII[41] and 3.0 g of 47–50% aqueous HI was shaken at 65–70° for 10.75 hr. Work-up (pentane extraction followed by washing with aqueous $NaHCO_3$, water, then drying) gave 3.2 g of an oil which was chromatographed on 610 g of acid-washed alumina, eluting with pentane, then benzene, then chloroform. The first fractions contained 170 mg (8.5%) of IX.[42] Continued elution yielded 462 mg of iodide XVIII, which was recrystallized from cold pentane and sublimed at 65° (10^{-6} mm), giving 364 mg (10.6%) of material, mp 50–56°; nmr (100 MHz, CCl_4) broad multiplets at τ 6.25 (0.92 H), 7.4–7.7 (1.92 H), 7.8–8.45 (9.35 H), triplet 8.68 (2.08 H, J = 1 Hz), broad triplet 8.75 (0.92 H, J = 4.6 Hz), broad doublet 9.18 (1.83 H, J = 4.6 Hz); ir (CS_2, cm^{-1}) 3068 m, 3050 m, 2973 s, 2931 s, 2903 s, 2890 s, 2863 s, 1365 w, 1340 w, 1318 w, 1303 m, 1285 w, 1275 w, 1255 w, 1248 m, 1238 w, 1221 m, 1220 m, 1212 s, 1170 s, 1147 w, 1140 w, 1125 m, 1108 m, 1063 w, 1025 w, 1003 w, 978 w, 951 w, 937 m, 927 m, 915 w, 902 w, 882 m, 872 m, 830 m, 814 s, 800 s, 767 w, 655 w; mass spectrum (75 eV) *m/e* (relative intensity) 41 (15), 64 (11), 65 (14.5), 66 (17.2), 77 (15.5), 79 (25.0), 91 (47.0), 105 (19.0), 115 (12.5), 117 (26.0), 119 (40.5), 129 (18.0), 143 (12.5), 185 (100.0), 186 (16.0), 312 (0.8).

Anal. Calcd for $C_{14}H_{17}I$: C, 53.86; H, 5.49; I, 40.65. Found: C, 54.04; H, 5.43; I, 40.64.

Continued elution gave a mixture of isomeric iodides, which was rechromatographed on 460 g of acid-washed alumina, eluting with pentane. Bulb-to-bulb distillation at 80° (10^{-5} mm) gave 289 mg (8.8%) of iodides XXIII and XXIV; nmr (100 MHz, CCl_4) broad multiplets at τ 5.75–6.2 (0.87 H) and at 7.15–8.90 (16.13 H); ir (neat, cm^{-1}) 3022 w, 2865 s, 2713 s, 1455 m, 1440 s, 1282 s, 1244 m, 1220 s, 1203 s, 1191 s, 1150 s, 1120 w, 1097 w, 943 w, 896 m, 870 w, 750 m, 708 w, 692 w; mass spectrum (75 eV) *m/e* (relative intensity) 41 (14.0), 67 (20.0), 77 (18.5), 78 (13.5), 79 (25.2), 91 (34.7), 93 (10.0), 105 (20.5), 117 (23.3), 119 (31.0), 128 (15.5), 129 (15.0), 143 (10.5), 185 (100.0), 186 (17.7), 312 (0.1).

Anal. Calcd for $C_{14}H_{17}I$: C, 53.86; H, 5.49; I, 40.65. Found: C, 54.12; H, 5.78; I, 40.40.

V.[43] A tube containing 262 mg of iodide XVIII (0.84 mmol) and 220 mg of KOH in 1.4 ml of absolute ethanol was shaken at 80° for 25 hr. Work-up (pentane extraction then washing with water) followed by bulb-to-bulb distillation at 70° (0.1 mm) gave 120 mg (78%) of dimer V,[5] which was pure by proton nmr and glpc.

VIII and XXV.[43] A tube containing 150 mg (0.48 mmol) of iodides XXIII and XXIV and 117 mg of KOH in 1 ml of absolute ethanol was shaken at 80° for 24 hr. After work-up, bulb-to-bulb distillation at 75° (0.3 mm) gave 58 mg (65%) of a 15:85 mixture (by glpc on column A, 240°) of two norbornadiene dimers. These were separated by glpc (column A, 240°) and are tentatively assigned structures VIII and XXV, respectively.

VIII. Ir (neat, cm^{-1}) 3054 s, 3012 s, 2942 s, 2880 s, 2870 s, 1610 w, 1587 m, 1489 s, 1459 m, 1352 s, 1327 m, 1317 m, 1306 s, 1278 s, 1259 m, 1219 m, 1207 m, 1190 w, 1169 w, 1073 w, 1026 w, 984 w, 966 w, 957 w, 938 m, 924 w, 914 m, 853 m, 820 m, 800 m, 775 s, 764 s, 748 m, 703 s, 659 w; mass spectrum (75 eV) *m/e* (relative intensity) 41 (26.3), 44 (18.8), 51 (20.4), 53 (10.1), 63 (12.1), 65 (29.0), 66 (14.7), 67 (10.4), 77 (48.2), 78 (41.0), 79 (46.0), 80 (28.7), 91 (93.2), 92 (18.5), 93 (14.6), 103 (19.0), 104 (39.0), 105 (64.2), 106 (44.4), 115 (53.5), 116 (38.2), 117 (100.0), 118 (63.8), 119 (22.1), 128 (33.0), 129 (29.5), 130 (28.7), 141 (25.0), 142 (25.0), 143 (22.8), 155 (21.3), 156 (14.0), 169 (16.3), 184 (69.5), 185 (10.2).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.03; H, 8.64.

Its proton nmr spectrum is identical with that of the product obtained by reacting NBD with $[(C_6H_5)_3P]_3RhCl$ (see above).

XXV. Ir (CS_2, cm^{-1}, Perkin-Elmer Model 137) 3080 w, 2740 s, 2840 w, 1320 w, 788 s, 785 s, 768 s, 703 s; mass spectrum (75 eV) *m/e* (relative intensity) 41 (14.5), 51 (10.0), 65 (14.0), 77 (23.5), 78 (24.0), 79 (20.0), 80 (39.0), 91 (46.3), 92 (17.0), 93 (20.8), 104 (16.7), 105 (20.5), 106 (43.4), 115 (22.1), 116 (12.7), 117 (100.0), 118 (33.1), 119 (36.5), 128 (15.3), 129 (20.0), 130 (16.0), 141 (15.5), 142 (26.1), 143 (32.0), 155 (16.0), 156 (14.0), 169 (13.2), 184 (87.4), 185 (13.8).

XIX. Bromine (1.1 ml, 16.8 mmol) in 50 ml of CCl_4 was added in drops to a stirred solution of 2.35 g (12.8 mmol) of XVI in 100 ml of CCl_4 maintained at *ca.* 0°. The temperature was allowed to rise to *ca.* 20° and the solution washed (25 ml of 0.1 *N* $Na_2S_2O_3$, then H_2O) and dried ($MgSO_4$). Solvent was removed and the product distilled evaporatively at 10^{-6} mm between 100 and 200°. After two recrystallizations from pentane–acetone, 1.70 g (39%) of white crystals was obtained, mp 102–104.5°. The sample for analysis was sublimed; nmr (100 MHz, $CDCl_3$) broad singlet at τ 5.25 (0.95 H), multiplet 6.05 (0.85 H), multiplet 7.41 (1.95 H), multiplet 7.66 (1.80 H), multiplet 8.00 (5.30 H), broad singlet 8.43 (2.05 H), multiplet 8.97 with overlapping doublet 9.15 (3.14 H, J = 5 Hz); ir (KBr, cm^{-1}) 3039 w, 2972 w, 2941 m, 2929 s, 2851 m, 1436 m, 1352 w, 1319 w, 1290 s, 1232 w, 1196 w, 1106 m, 1042 w, 1017 w, 963 m, 920 m, 896 w, 803 s, 772 s, 694 w, 639 w; mass spectrum (75 eV) *m/e* (relative intensity) 51 (45), 52 (10), 53 (23), 56 (12), 63 (21), 75 (14), 77 (45), 78 (29), 79 (53), 89 (32), 90 (21), 91 (45), 92 (16), 94 (15), 103 (11), 105 (38), 115 (30), 116 (12), 117 (100), 118 (38), 119 (51), 128 (22), 129 (35), 142 (11), 145 (15), 147 (14), 155 (16), 183 (73), 184 (19), 262 (15), 264 (15), 342 (0.6), 344 (1.1), 346 (0.6).

Anal. Calcd for $C_{14}H_{16}Br_2$: C, 48.87; H, 4.69; Br, 46.45. Found: C, 48.99; H, 4.95; Br, 46.65.

XX. Hexamethylphosphoric triamide (40 ml, freshly distilled from CaH_2) was injected into a 200-ml, round-bottomed flask equipped with reflux condenser, stirrer, and thermometer, and which contained 790 mg (2.3 mmol) of XIX under a N_2 atmosphere. KO-*tert*-C_4H_9 (1.1 g, 9.9 mmol) was added, the flask warmed to 65°, and stirred at 50° for 1 hr. After cooling, water was added. Extraction with ether, washing with water, drying ($MgSO_4$), and removal of solvent yielded 576 mg (96%) of white crystals, which were sublimed for analysis; nmr (100 MHz, $CDCl_3$) broad singlet at τ 3.92 (1.94 H), broad singlet 5.16 (0.93 H), multiplet 7.14 (1.92 H), broad singlet 7.82 (1.05 H), sharp singlet 7.94 (2.01 H), broad singlet 8.03 (1.91 H), broad singlet 8.41 (1.98 H), broad triplet 8.85 (1.16 H, J = 5 Hz), broad doublet 9.12 (2.13 H, J = 5 Hz); ir (KBr, cm^{-1}) 3063 m, 3009 m, 2986 m, 2947 m, 2931 m, 2865 m, 1356 s, 1319 s, 1286 s, 1260 s, 1237 s, 1167 m, 1105 m, 1056 w, 1036 w, 991 m, 953 m, 896 m, 868 m, 837 s, 815 s, 796 s, 766 s, 714 s, 603 m; mass spectrum (75 eV) *m/e* (relative intensity) 39 (33), 51 (14), 63 (11), 65 (30), 67 (15), 77 (20), 78 (10), 79 (24), 91 (38), 103 (10), 105 (48), 115 (23), 116 (12), 117 (100), 118 (60), 130 (15), 142 (17), 156 (10), 183 (58), 262 (5.6), 264 (5.5).

Anal. Calcd for $C_{14}H_{15}Br$: C, 63.89; H, 5.75; Br, 30.37. Found: C, 63.60; H, 5.68; Br, 30.37.

XVII. Sodium metal (in excess, *ca.* 1 g) was added in small pieces to a stirred solution of 393 mg (1.5 mmol) of XX, 15 ml of tetrahydrofuran, and 3 ml of *tert*-butyl alcohol under N_2 and refluxed overnight. The solution was decanted (from Na and NaO-*tert*-Bu) and 150 ml of H_2O added. The product was extracted with ether (3 × 30 ml), washed with H_2O (2 × 50 ml), and dried ($MgSO_4$). Bulb-to-bulb distillation at 70° (0.5 mm) yielded 172 mg (63%) of XVII, a liquid.

The proton nmr spectrum is the same as that published elsewhere;[22] ir (neat, cm^{-1}) 3050 s, 3010 m, 2959 s, 2937 s, 2862 s, 1467 m, 1357 m, 1320 s, 1286 m, 1244 w, 1168 w, 1016 w, 895 m, 869 m,

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(40) The procedure is modeled on that of H. A. Bruson and T. W. Riener, *J. Amer. Chem. Soc.*, **67**, 1178 (1945).

(41) Isolated by distilling the mixture of dimers obtained from norbornadiene and rhodium on carbon through a Nester and Faust annular Teflon spinning band distillation column. In the original preparation the isolation was effected by glpc.[5]

(42) The proton nmr, ir, and melting point are identical with those reported.[27]

(43) The procedure is modeled on that in ref 23b.

809 s, 715 s; mass spectrum (75 eV) m/e (relative intensity) 66 (18), 91 (18), 115 (11), 117 (100), 118 (81), 184 (16).

X-Ray Diffraction. Needle crystals of XVb suitable for X-ray diffraction studies were obtained from methanol. The intensity data on which the refinement was carried out were collected on a needle (along b axis) with dimensions 0.07 × 0.05 mm and length 0.5 mm, mounted on a Picker FACS-1 diffractometer with Cu Kα radiation and using the $\theta - 2\theta$ scan technique. The intensities were measured with a scintillation counter with background counts being made at each limit of the scan. A total of 2759 reflections was considered nonzero out to a 2θ limit of 130° using the criteria that the net count be greater than 0.06 times the total background count and/or 50 counts whichever is greater. No corrections were made for absorption. The range of transmission coefficients was calculated as 0.26–0.36.

Full-matrix least-squares refinement, varying positional and isotropic thermal parameters for the nonhydrogen atoms, gave values of R and R_2 ($R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$) of 0.182 and 0.166. All reflections were given unit weights and the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$. Least-squares refinement on positional and anisotropic thermal parameters for the nonhydrogen atoms reduced R and R_2 to 0.085 and 0.084. A difference map calculated at this point revealed several positive peaks in the range 0.2–0.4 electron/Å^3, some of which could represent hydrogen atoms. As the location of all of the hydrogen atoms could not be made with certainty, however, we decided to neglect the contribution of the hydrogen atoms and to terminate refinement.

The list of h, k, l, F_o and F_c values will appear in the microfilm edition.[29] The atomic scattering curves used for Br, C, and O were those tabulated by Cromer, *et al.*[44]

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(44) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

Acetamidomethyl. A Novel Thiol Protecting Group for Cysteine

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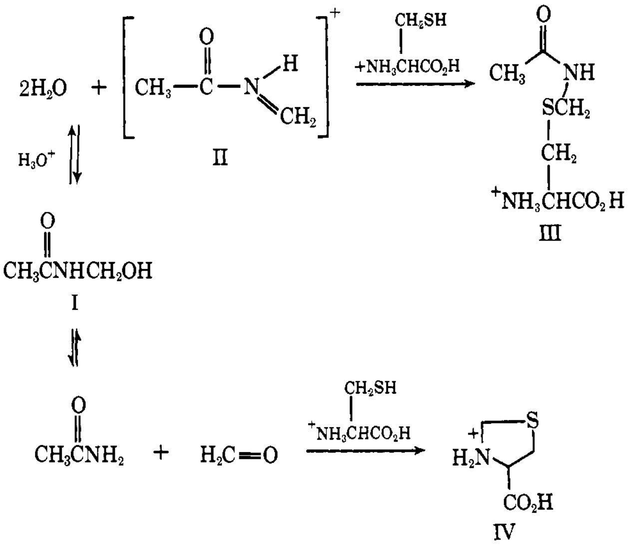
Abstract: The acetamidomethyl group has been found to be a useful protecting group for the thiol of cysteine. It was added to the thiol of cysteine and to the eight cysteines of the reduced S-protein of ribonuclease under acidic conditions. It is stable under the conditions commonly used in peptide synthesis and is removed by mercuric ion under mild conditions. The mercuric ion may be removed by treatment with H_2S for small peptides and by gel filtration in the presence of mercaptoethanol for large peptides and proteins.

In a preliminary communication[1] we have reported a novel derivative of cysteine in which the sulfur is protected by the acetamidomethyl (Acm) group.[2,3] This protecting group has been found to be useful both in the synthesis of peptides and proteins and in the reversible protection of a natural protein. In this report we describe in greater detail the preparation, properties, and utility of this derivative of cysteine.

Preparation of S-Acm-cysteine and Octa-S-Acm-octahydro-S-protein. S-Acm-Cys (III) was conveniently prepared in about 50% yield by treatment of cysteine with a 10% excess of N-hydroxymethylacetamide (I) in aqueous medium at pH 0.5. A minor by-product, thiazolidine-2-carboxylic acid (IV), was removed by recrystallization. III was found to be stable at pH 0.5. We believe, therefore, that IV arose *via* the decomposition of I to formaldehyde and acetamide. Scheme I indicates that anhydrous conditions should shift the equilibrium between I and II to the right, and thus minimize the formation of IV.

Scheme I



Indeed, when cysteine was allowed to react with a 20% excess of I in anhydrous HF at 0°, III was formed in nearly quantitative yield, and IV was not detectable in the reaction mixture. More importantly, the use of liquid HF as solvent proved to be particularly useful when we applied it to the S-alkylation of reduced S-protein,[4] since acetamidomethylation of this protein in anhydrous but not in aqueous medium led to a product

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(1) D. F. Veber, J. D. Milkowski, R. G. Denkewalter, and R. Hirschmann, *Tetrahedron Lett.*, 3057 (1968).

(2) A related class of protecting groups has been reported by F. Weygand, W. Steglich, I. Lengyel, F. Fraunberger, A. Maierhofer, and W. Oettmeier, *Chem. Ber.*, **99**, 1944 (1966).

(3) All amino acids are of the L configuration. Abbreviations used: Acm = acetamidomethyl; Boc = *tert*-butyloxycarbonyl.

(4) (a) E. Haber and C. B. Anfinsen, *J. Biol. Chem.*, **236**, 422 (1961); (b) S-protein is the protein obtained on treatment of ribonuclease-A with subtilisin (F. M. Richards, *Proc. Nat. Acad. Sci. U. S.*, **44**, 162 (1958)).