# Hydrogenation of *syn*- and *anti*-7-Acetoxynorbornenes and 7-Acetoxynorbornadiene over Platinum and Palladium Catalysts[1a]

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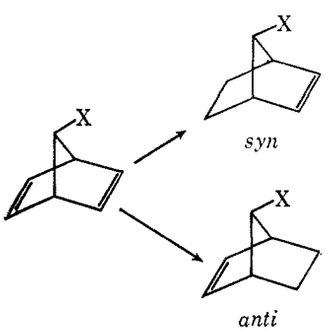
A study of the hydrogenation of *syn*- and *anti*-7-acetoxynorbornenes, 7-acetoxynorbornadiene, and related compounds over various platinum and palladium catalysts has been made. A marked sensitivity of these reductions to catalyst, catalyst prereduction, and the steric requirements of the 7 substituents has been observed. In addition to the anticipated reduction products, the hydrogenation of 7-acetoxynorbornadiene has yielded 3-acetoxynortricyclene in amounts ranging from 3–5% over platinum catalysts to 25–30% over prereduced palladium catalysts. Reductions utilizing deuterium have shown that the dienyl acetate and *syn*-7-acetoxynorbornene experience substantial *endo,cis* deuterium addition as well as the normally anticipated *exo,cis* addition. The *anti*-acetate reduces exclusively through *exo,cis* addition. The relative rates of *syn* and *anti* double-bond reduction, $k_{anti}/k_{syn}$, for *syn*- and *anti*-acetoxynorbornenes and for 7-acetoxynorbornadiene have shown that, while reduction of the monoolefins is largely controlled by steric effects, the reduction of the dienyl acetate is less sensitive to steric factors. A rationale for these observations is attributed to the direction of coordination of the olefinic substrates with the catalyst. The hydrogenation of norbornadiene and 7-acetoxynorbornadiene over prereduced palladium has revealed the anomalous behavior of the prereduced catalyst.

The preparation of *anti*-7-substituted norbornenes by the chemical reduction of readily available 7-substituted norbornadienes has been described in previous papers from this laboratory (eq 1).[2,3] Chemical reducing




(1)

X = OH, $OOCCH_3$, $OC(CH_3)_3$

agents have been found to be unsatisfactory for the synthesis of the corresponding *syn* isomers (eq 1) owing to the influence of electronic factors that direct such electrophilic additions preferentially to the *syn* double bond.[3,4] The argument was subsequently advanced that, in those reactions where electronic factors are nonoperative, then the steric shielding of the *syn* double bond of the diene by the 7 substituent should direct the reaction to the *anti* double bond.[4a] Consequently, catalytic hydrogenation of these dienes should occur primarily with the formation of *syn* product.[5] Experimental verification of this proposal resided in the reduction of 7-substituted norbornadienes over platinum and palladium catalysts to yield product mixtures enriched in the *syn* isomer.[4a,6]

Although these experimental results indicated a degree of steric control, close inspection of the details of these reductions revealed several peculiar features. First, when the 7 substituent was varied from hydroxy to acetoxy to *t*-butoxy, the observed *syn*/*anti* ratios corresponded to an order of steric requirement, $OOCCH_3 > OH > OC(CH_3)_3$, which was obviously illogical and demonstrated that the invocation of steric factors *per se* in these reductions did not account for the observed product distributions.

Secondly, it was noted that the use of the *syn*/*anti* ratio as an indicator for the true stereoselectivity of the hydrogenation reaction was misleading. This fact became apparent when the source of saturated compound (30–50% of the total) produced during these reductions was considered. The logical precursors of the saturated product were the isomeric *syn*- and *anti*-norbornenes. Since it had been qualitatively shown that the *anti* isomer is rapidly hydrogenated to saturated material,[4a] it was reasonable to expect that the reduction of the diene was producing substantially more *anti* compound than was ultimately detected in the reaction mixture.

Finally, it was apparent that the product distribution of reductions performed over prereduced palladium catalysts was completely different from those utilizing a nonprereduced catalyst. In contrast, platinum-catalyzed hydrogenations were independent of this variable.

In order to probe and define the chemistry of these reductions, a study of the hydrogenation of 7-acetoxynorbornadiene (**1**), *syn*- (**2**) and *anti*-7-acetoxynorbornenes (**3**), and related compounds over various palladium and platinum catalysts was undertaken. This report describes the results of these experiments and their implications.

## Results

The hydrogenation of 7-acetoxynorbornadiene (**1**) over platinum and palladium catalysts proceeded as illustrated by eq 2; product distributions representative of these reductions are summarized in Table I.

(1) (a) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, p 0–10. (b) Department of Chemistry, East Tennessee State University, Johnson City, Tenn.

(2) Lithium Aluminum Hydride. B. Franzus and E. I. Snyder, *J. Amer. Chem. Soc.*, **87**, 3423 (1965).

(3) Diimide. W. C. Baird, Jr., B. Franzus, and J. H. Surridge, *ibid.*, **89**, 410 (1967).

(4) (a) B. Franzus, W. C. Baird, Jr., E. I. Snyder, and J. H. Surridge, *J. Org. Chem.*, **32**, 2845 (1967); (b) G. W. Klumpp, A. H. Veefkind, W. L. deGraaf, and F. Bickelhaupt, *Ann.*, **706**, 47 (1967); (c) J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966); (d) W. C. Baird, Jr., and M. Buza, *J. Org. Chem.*, **33**, 4105 (1968).

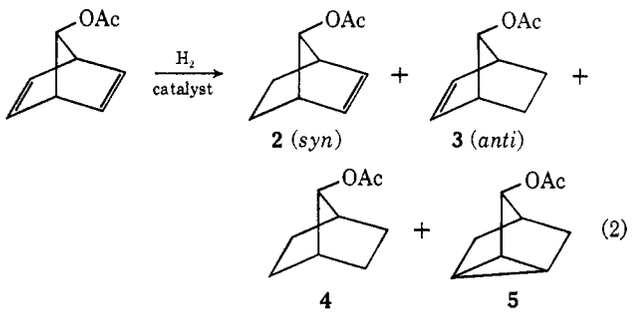
(5) (a) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Amer. Chem. Soc.*, **87**, 2596 (1965); (b) R. L. Burwell, Jr., *Chem. Rev.*, **57**, 895 (1957); (c) E. E. van Tamelen and R. J. Timmons, *J. Amer. Chem. Soc.*, **84**, 1867 (1962); (d) R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine, and R. R. Whetstone, *ibid.*, **64**, 1985 (1942).

(6) B. Franzus, W. C. Baird, Jr., and J. H. Surridge, *J. Org. Chem.*, **33**, 1288 (1968).

TABLE I

REDUCTION OF 7-ACETOXYNORBORNADIENE

| Catalyst | Product composition, % syn 2 | anti 3 | Satd 4 | Diene 1 | Nortricyclene 5 |
|---|---|---|---|---|---|
| Pd/C | 46.1 | 9.0 | 21.6 | 18.3 | 5.0 |
| HPd/C | 28.8 | 26.6 | 14.1 | 8.9 | 21.7 |
| $PtO_2$ | 37.2 | 3.2 | 27.1 | 32.5 | 4.6 |
| HPt/C | 44.2 | 4.0 | 21.3 | 23.3 | 7.2 |
| Pt/C | 35.8 | 3.0 | 29.3 | 25.6 | 6.3 |




A remarkable feature of these hydrogenations was the formation of 3-acetoxynortricyclene (**5**) in amounts ranging from 5–10% over platinum and nonprereduced palladium catalysts to 20–30% over prereduced palladium on charcoal. The formation of this nortricyclene derivative constituted the first occurrence of homoconjugative addition to a norbornadiene system during catalytic hydrogenation.[6-8] That the nortricyclic ester (**5**) is derived from 2,6 addition to the acetoxydiene (**1**) was apparent from the gradual increase of the nortricyclyl acetate content to the point at which no 7-acetoxynorbornadiene remained unreduced, and the production of the nortricyclic ceased. No 3-acetoxynortricyclene was formed during control reductions of *syn*- and *anti*-7-acetoxynorbornenes, a fact that revealed the dependence of the cyclization reaction on the presence of diene substrate. The nortricyclic acetate was stable under the reaction conditions, for the ester was not isomerized[9] or reduced by continued exposure to catalyst and hydrogen.

Table I reveals the sensitivity of the reduction to the choice of catalyst and in the case of palladium catalysts the effect of prereduction of the catalyst.[10] Product distributions obtained with platinum catalysts were essentially invariant and indicated independence of the catalyst source and its prereduced or nonprereduced state. A prereduced palladium catalyst produced *syn* (**2**), *anti* (**3**), and nortricyclic (**5**) esters in nearly equivalent amounts, but over a nonprereduced palladium catalyst the formation of *anti* isomer and nortricyclene was significantly diminished relative to *syn* compound. If the palladium-catalyzed reductions were performed at an initial hydrogen pressure of 2 atm, the relationship among *syn*, *anti*, and nortricyclic products was similar to that observed over a nonprereduced catalyst at atmospheric pressure.

The distinctive product distributions from the reduction of 7-acetoxynorbornadiene over these catalysts implied that the hydrogen addition reaction might not be occurring through *exo,cis* addition.[5] In order to explore this possibility, an examination of the direction of addition was undertaken by using deuterium as the reducing gas. This approach was not applicable to platinum-catalyzed reductions, for deuterium scrambling and/or deuterium–hydrogen exchange reactions precluded any accurate interpretation of the reduction path.[5b,11] Reductions over palladium catalysts, however, have been shown to be free of these complications,[5,6,12] and significant information was obtained from the palladium-catalyzed deuteriogenation of 7-acetoxynorbornadiene and *syn*- and *anti*-7-acetoxynorbornenes. The direction of deuterium addition to these compounds was ascertained by nmr analysis of the relative areas of the *endo* and *exo* hydrogens occurring at $\delta$ 0.80–1.30 and $\delta$ 1.50–1.85, respectively.[13,14]

Partial deuterium reduction (*ca.* 50% of theory) of 7-acetoxynorbornadiene (**1**) over palladium catalysts in ethanol proceeded in accord with Scheme I, yielding the products with the deuterium configurations illustrated. Table II summarizes the *exo,cis–endo,cis* deuterium distributions in the various products; the product compositions were comparable with those of Table I. The outstanding feature of these reactions was the significant degree of *endo,cis* deuterium addition that occurred in both steps of the reaction. The reduction of the *syn* double bond of the diene to yield *anti* isomer (**7**) involved 100% *endo,cis* addition; reduction of the *anti* double bond of **1** to *syn* product (**6**) exhibited *ca.* 15–30% *endo,cis* deuterium addition (**6b**) depending upon the reaction pressure and catalyst treatment. The formation of 3-acetoxynortricyclene (**9**) proceeded *via* homoconjugative addition to introduce the 5,7 deuteriums in an *endo,endo* configuration.[15] Analysis of the saturated product, 7-acetoxynorbornane (**8**), revealed that *ca.* 30–50% of the deuterium atoms had added *endo,cis*. Furthermore, of these *endo,cis* deuteriums, 70–80% were *syn* to the acetate group (**8a,c,d**) while the remainder were *anti* (**8d,e**). Conversely,

(7) The formation of 3-substituted nortricyclenes has also been observed during the reduction of 7-*t*-butoxynorbornadiene[4a] and 7-*t*-butylnorbornadiene; W. C. Baird, Jr., and J. H. Surridge, unpublished data.

(8) Nortricyclenes have been produced by a variety of heteropolar and homopolar additions to norbornadiene. (a) P. de Mayo, "Molecular Rearrangements," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1963, p 198; (b) S. Winstein and M. Shatavsky, *Chem. Ind.* (London), 56 (1956); (c) H. C. Kuivila and C. R. Warner, *J. Org. Chem.*, **29**, 2845 (1964), and references cited therein; (d) D. I. Davies and L. T. Parfitt, *J. Chem. Soc., C*, 2691 (1967); (e) M. Green, *ibid.*, 541 (1965); (f) H. Heaney and J. M. Jablonski, *Tetrahedron Lett.*, 2733 (1967); (g) T. V. van Auken and E. A. Rick, *ibid.*, 2709 (1968).

(9) Transition metal catalyzed cleavage of the cyclopropane ring analogous to the valence isomerization of quadricyclene to norbornadiene was not detected. H. Hogeveen and H. C. Volger, *J. Amer. Chem. Soc.*, **89**, 2486 (1967).

(10) In reactions utilizing a prereduced catalyst, the catalyst was hydrogenated prior to the injection of the acetoxydiene into the catalyst–solvent suspension. All reagents were present prior to the admission of hydrogen in nonprereduced reactions. See also ref 4a

(11) H. C. Volger and H. Hogeveen, *Rec. Trav. Chim.*, **87**, 1356 (1968).

(12) Norbornane experienced only 4% deuterium–hydrogen exchange over palladium at 75°. R. L. Burwell, Jr., B. K. C. Shim, and H. C. Rowlinson, *J. Amer. Chem. Soc.*, **79**, 5142 (1957).

(13) For the chemical shifts of *endo* and *exo* protons in norbornyl and norbornenyl compounds, see (a) E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964); (b) M. E. Brennan and M. A. Battiste, *J. Org. Chem.*, **33**, 324 (1968); (c) F. A. L. Anet, H. H. Lee, and J. L. Sudmeier, *J. Amer. Chem. Soc.*, **89**, 4431 (1967); (d) J. C. Davis, Jr., and T. V. van Auken, *ibid.*, **87**, 3900 (1965); (e) P. M. Subramanian, M. T. Emerson, and N. A. Lebel, *J. Org. Chem.*, **30**, 2624 (1965); (f) P. Laszlo and P. V. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964); (g) B. Franzus, W. C. Baird, Jr., N. F. Chamberlain, T. Hines, and E. I. Snyder, *ibid.*, **90**, 3721 (1968); (h) A. P. Marchand and J. E. Rose, *ibid.*, **90**, 3724 (1968).

(14) For the stereochemistry and nmr spectra of deuterated norbornane, norbornene, and 7-acetoxynorbornenes and -norbornane, see ref 2, 3, and 6.

(15) Deuterium decoupling experiments by Dr. E. I. Snyder, University of Connecticut, have confirmed that the deuterium atoms occupy the 5,7 positions. The chemical shifts of the 5,7 protons are consistent with those anticipated for *exo* hydrogens.

SCHEME I

STERIC COURSE OF DEUTERIUM ADDITION TO 7-ACETOXYNORBORNADIENE AND 7-ACETOXYNORBORNENES

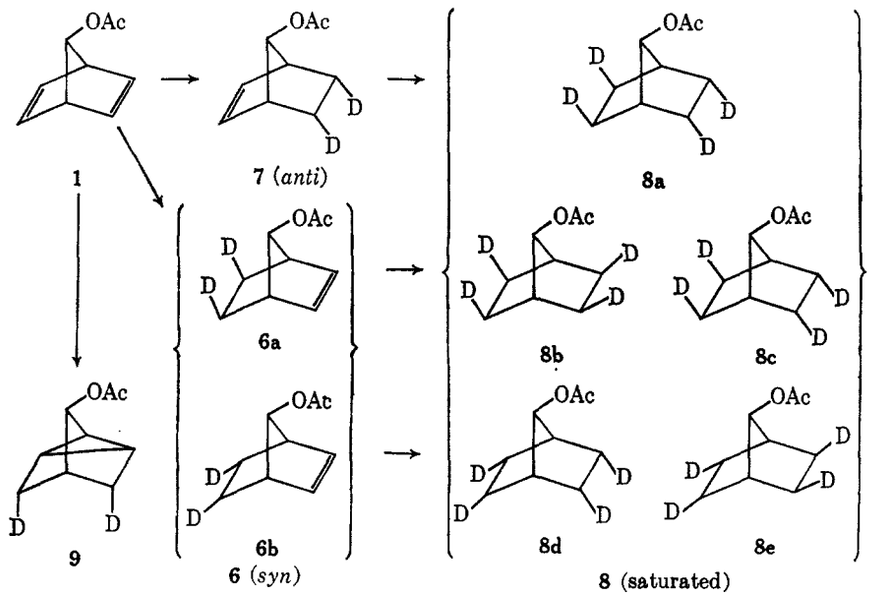



TABLE II

DIRECTION OF DEUTERIUM ADDITION TO 7-ACETOXYNORBORNADIENE

| | % distribution of deuterium | | | | | |
|---|---|---|---|---|---|---|
| | *syn* 6 | | *anti* 7 | | Saturated 8 | |
| Catalyst | *endo,cis* 6b | *exo,cis* 6a | *endo,cis* | *exo,cis* | *endo,cis* 8a,c–e | *exo,cis* 8a–c,e |
| Pd/C[a] | 21 | 79 | 100 | 0 | 52 | 47 |
| Pd/C[b] | 15 | 85 | 100 | 0 | 33 | 67 |
| HPd/C[b] | 28 | 72 | 100 | 0 | 40 | 60 |

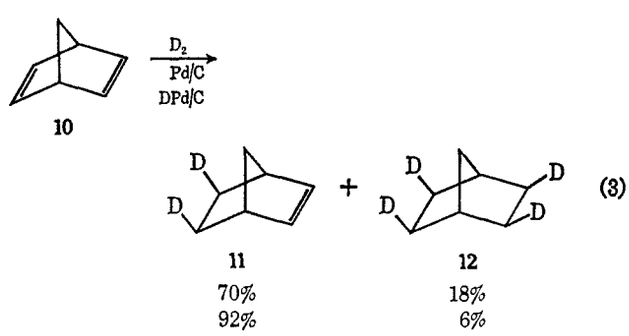
[a] 2 atm of $D_2$. [b] 1 atm of $D_2$.

60–70% of the *exo,cis* deuteriums were *anti* to the 7 substituent (**8a–c**).

The deuterium reduction of *syn*- and *anti*-7-acetoxynorbornenes revealed that the second stage of the hydrogenation reaction also involved *endo,cis* addition. That only the *syn*-acetate experienced *endo,cis* addition was shown by the reduction of 5,6-dideuterio-*syn*-7-acetoxynorbornene (**6a,b**) (Scheme I). While the initial olefin contained 21% *endo,cis* deuterium (**6b**) and 79% *exo,cis* (**6a**), reduction over a nonprereduced palladium catalyst yielded saturated ester containing 29% *endo,cis* and 71% *exo,cis* deuteriums. This change corresponded to 40% *endo,cis* deuterium addition; over a prereduced catalyst the degree of *endo,cis* reduction amounted to 30%.

Deuterium reduction of the dideuterated *anti*-acetate (**7**) gave exclusively *exo,cis* addition (Scheme I) independent of the state of reduction of the catalyst. Similarly, *syn*- and *anti*-7-hydroxynorbornenes were reduced with deuterium by exclusively *exo,cis* addition.

Unlike 7-acetoxynorbornadiene, the parent olefin, norbornadiene (**10**), undergoes reduction over either a nonprereduced[5a] or a prereduced palladium-on-charcoal catalyst[6] to yield only *exo,cis* deuterated products (eq 3). Neither reduction yielded any nortricyclene, a fact that indicates that the presence of a 7 substituent is a necessary condition for homoconjugative reduction.[7] Although these reductions exhibited the same stereochemistry, the selectivity to *exo,exo*-5,6-dideuterionorbornene (**11**) at *ca.* 50% reduction was definitely sensitive to catalyst prereduction (eq 3).




The different stereochemistry associated with the reduction of norbornadiene and 7-acetoxynorbornadiene over palladium catalysts generated a valuable experiment.[16] It was of interest to subject an equimolar mixture of the dienes to deuterium reduction, for it was conceivable that the coreduction of the diolefins over the same catalyst might change the direction of deuterium addition from that observed in the individual cases. Deuterium reduction of the diene mixture, however, did not exhibit any departures from previously observed stereochemistry; norbornadiene reduced exclusively *exo,cis* and the dienyl acetate experienced both *endo,cis*–*exo,cis* and homoconjugative addition. That the reductions occurred independent of one another was apparent.

An aspect of the coreduction of the diene mixture that was revealed after the fact was the impact that the

(16) This experiment was suggested by Professor H. C. Brown.

presence of an equimolar amount of norbornadiene, or norbornene, had on the product distribution. Determination of the relative rates of disappearance of the starting diolefins and of the appearance and disappearance of the various monoolefinic species established this reactivity order: norbornadiene $\gg$ 7-acetoxynorbornadiene $\geq$ norbornene $\gg$ *anti*-7-acetoxynorbornene > *syn*-7-acetoxynorbornene.[6] This sequence indicated that the conversion of the *syn*- and *anti*-acetates to saturated product could be effectively suppressed by the presence of norbornene. Thus, if mixtures of dienyl acetate and norbornadiene, or norbornene, were reduced until no dienyl acetate remained, the product mixture was composed only of *syn*, *anti*, and nortricyclic esters. It should be emphasized that similar selectivity effects were not realized with platinum catalysts.

The addition of norbornene and norbornadiene to reductions of 7-acetoxynorbornadiene exerted one other influence on this reaction. In those reactions where norbornadiene was present, no differences in acetate product composition were noted when a prereduced or a nonprereduced catalyst was used. With the exception of the decreased formation of saturated product due to the inhibition of its formation by norbornene, the product mixtures derived from reductions containing norbornadiene bore a strong resemblance to those obtained over a nonprereduced catalyst. The loss of the effect of catalyst prereduction is attributed to the fact that the first olefin hydrogenated by the catalyst is norbornadiene. As a result, when the dienyl acetate is finally exposed to the palladium catalyst, the catalyst is not truly "prereduced." This situation does not apply to reductions performed in the presence of norbornene, for the first olefin to be hydrogenated by the catalyst is 7-acetoxynorbornadiene, and these reductions give product mixtures characteristic of a prereduced catalyst.

The final phase of this study of the hydrogenation of 7-acetoxynorbornadiene and *syn*- and *anti*-7-acetoxynorbornenes was the determination of the relative rates of reduction of the *syn* and *anti* double bonds in these compounds. For the isomeric *syn*- and *anti*-acetates, $k_{syn}$ and $k_{anti}$ were simply defined as the rates of conversion of these olefins to saturated ester. The relative rate, $k_{anti}/k_{syn}$, was determined by competitive hydrogenation of mixtures of the *syn* and *anti* compounds over various catalysts according to the general procedure described by Hussey, Baker, and Keulks;[17] these data are summarized in Table III. From the data of Table III, it is clear that only in the reduction of *syn*- and *anti*-7-hydroxynorbornenes is no preferential reactivity observed. Competitive reduction of *syn*- and *anti*-7-acetoxynorbornenes has shown a marked preference for *anti* double bond reduction independent of the catalyst, and there can be little doubt that the reduction of these isomeric monoolefins is controlled by steric factors. The sterically hindered *syn* double bond simply cannot compete as effectively for the catalyst sites. The diminished $k_{anti}/k_{syn}$ value for the prereduced palladium catalyst relative to the nonprereduced would seem to reflect a more reactive, less discriminating nature for the former catalyst. The fact that the selectivity of the prereduced platinum catalyst tends toward that of the nonprereduced palladium catalyst is not understood.

(17) A. S. Hussey, R. H. Baker, and G. W. Keulks, *J. Catal.*, **10**, 258 (1968).

TABLE III

$k_{anti}/k_{syn}$ FOR 7-SUBSTITUTED NORBORNENES

| Substrate | Catalyst | $k_{anti}/k_{syn}$ |
|---|---|---|
| *syn*-ol + *anti*-ol | Pd/C | 0.94 |
| *syn*-acetate + *anti*-acetate | Pd/C | 16.8 |
| *syn*-acetate + *anti*-acetate | HPd/C | 5.4 |
| *syn*-acetate + *anti*-acetate | $PtO_2$ | 3.7 |
| *syn*-acetate + *anti*-acetate | Pt/C | 3.4 |
| *syn*-acetate + *anti*-acetate | HPt/C | 10.1 |

In the reduction of 7-acetoxynorbornadiene, $k_{anti}$ has been defined as the rate of reduction of the *anti* double bond to yield *syn* product, $k_{syn}$ as the rate of reduction of *syn* double bond to form *anti* product. The relative rates of these reactions, $k_{anti}/k_{syn}$, have been determined from the ratio, *syn*-acetate produced/*anti*-acetate produced. For palladium catalysts, this value is readily obtained from reductions performed in the presence of norbornadiene, or norbornene, where the conversion of the monoolefins to saturated ester is suppressed. This technique cannot be used in the case of platinum catalysts, for the subsequent reduction of the *syn* and *anti* isomers cannot be prevented by norbornene. In the case of platinum catalysts, the assumption has been made that the saturated product formed arises predominately from the *anti* isomer. This view seems reasonable in the light of Table III. The values of $k_{anti}/k_{syn}$ over platinum catalysts have therefore been determined by the ratio, *syn* acetate/*anti* acetate plus saturated acetate. While these relative rates are not so quantitative as those for palladium catalysts, they do constitute useful semiquantitative estimates. Table IV presents these $k_{anti}/k_{syn}$ data for the reduction of 7-acetoxynorbornadiene.

TABLE IV

$k_{anti}/k_{syn}$ FOR 7-ACETOXYNORBORNADIENE

| Catalyst | $k_{anti}/k_{syn}$ |
|---|---|
| Pd/C | 3.42 |
| HPd/C | 0.58 |
| $PtO_2$ | 1.2 |
| Pt/C | 1.1 |
| HPt/C | 1.8 |

Direct comparison of Tables III and IV shows that the reduction of 7-acetoxynorbornadiene is considerably less sensitive to purely steric control. Without exception, the reduction of the less sterically hindered *anti* double bond in the *anti*-acetate occurs with greater facility than reduction of the *anti* double bond in the diene. Table IV reveals a remarkable distinction between a prereduced and a nonprereduced palladium catalyst. While the latter shows a decided preference for *anti* double bond reduction of the diene, the former experiences an unanticipated reversal and preferentially hydrogenates the *syn* double bond. This dif-

ference in selectivity amounts to a factor of *ca.* 6 and certainly cannot be rationalized by steric arguments. Platinum catalysts as a group appear to demonstrate a very slight preference for *anti* double bond reduction, although these catalysts do not exhibit the pronounced tendencies observed with palladium. The results are consistent with the less selective behavior of platinum catalysts in these reductions.

## Discussion

Analysis of the experimental observations described above has permitted certain conclusions to be drawn regarding the palladium-catalyzed hydrogenation of 7-acetoxynorbornadiene. The lack of comparably significant diagnostic data for the platinum-catalyzed reductions renders the interpretation of these reactions less meaningful; however, some general statements regarding these reductions can be made.

It has become apparent that the over-all reduction of the acetoxydiene over palladium is sensitive to two factors operating in concert, steric control and coordination control. The latter is a manifestation of the direction of olefin–catalyst complexation (exocyclic *vs.* endocyclic) and has been previously invoked to resolve other reactions of these ring systems involving group VIII metals.[8c] While the impact of these factors is detectable throughout the reduction, the degree of influence of either is determined largely by the structure of the unsaturated substrate experiencing hydrogenation.[18] The palladium-catalyzed hydrogenation of the isomeric *syn*- and *anti*-7-acetoxynorbornenes to saturated ester is controlled by steric factors, as evidenced by consistently high $k_{anti}/k_{syn}$ ratios. The additional fact that the *anti* isomer is reduced exclusively by *exo,cis* addition is in accord with facile exocyclic coordination and reduction of the sterically unencumbered *anti* double bond. The olefinic bond of the *syn* isomer, shielded by the bulk of the acetate group, is impeded in its ability to compete for the catalyst sites. This steric effect is obviously dependent upon the 7 substituent exhibiting a reasonable steric requirement; in contrast to the corresponding acetate esters, *syn*- and *anti*-7-hydroxynorbornenes are both reduced totally *exo,cis* with a $k_{anti}/k_{syn}$ value of *ca.* 1.

A secondary steric effect induced by a large 7 substituent is apparent in the reduction of the *syn*-acetate, where *ca.* 30–40% of the hydrogen is added *endo,cis*. The stereochemical distinctions between the reduction of the *syn*-7-ol (100% *exo,cis*) and the *syn*-7-acetate are reminiscent of those noted in the hydrogenation of 2-cyclopentylidene-1-hydroxy- and -alkoxycyclopentanes.[19] While the alkylidenecyclopentanol is reduced to the preferred *trans* isomer, introduction of the methoxyl group and higher homologs led to the formation of the *cis* isomer. As in the present case, the existence of a substituent of increased steric capacity diverted the olefin–catalyst coordination away from that side affected by this group.

If the palladium-catalyzed reduction of the dienyl acetate were controlled solely by steric effects comparable to those observed in the reactions of the monoolefins, then the diene reduction should also be characterized by equally high $k_{anti}/k_{syn}$ values and predominant *exo,cis* addition. In fact, the values of $k_{anti}/k_{syn}$ are diminished relative to those of the monoolefins over palladium; furthermore, the *syn* bond is preferentially reduced over prereduced palladium. The formation of the three primary reduction products, *syn*-, *anti*-, and nortricyclic acetates, has also involved substantial *endo,cis* addition. Consequently, it is concluded that the hydrogenation of the acetoxydiene is sensitive to coordination control and that a significant portion of the reaction proceeds through an endocyclic palladium–diene complex.[20] A favorable argument for coordination control is found in the formation of 3-acetoxynortricyclene, whose synthesis from a diene–catalyst *endo* complex which experiences homoconjugative *endo,cis* addition of hydrogen is envisioned.[21] The totally *endo,cis* reduction of the *syn* double bond of the diene to *anti*-acetate is only consistent with endocyclic coordination, as is *endo,cis* addition to the *anti* double bond to yield *syn* product. The preferential reduction of the *syn* double bond relative to the *anti* over prereduced palladium (Table IV) is not understood, although electronic activation of the *syn* double bond by the 7 substituent is a distinct possibility. Coordination control appears to play a more predominant role in reductions over a prereduced catalyst, as evidenced by the substantially increased formation of the nortricyclene and the *anti*-acetates and the greater degree of *endo,cis* deuteration.

The reduction of the dienyl acetate is not devoid of the influence of steric factors, for the hydrogenation of the *anti* bond occurs predominately (*ca.* 80%) *exo,cis*. It is interesting to note, however, that no *exo,cis* addition takes place with the *syn* double bond. The interplay between steric and coordination effects is also obvious in the reduction of the acetoxydiene, for the parent olefin, norbornadiene, experiences neither *endo,cis* nor homoconjugative hydrogenation.[7]

*In general, the view is advanced that the reduction of 7-substituted norbornenes over palladium catalysts is considerably more sensitive to steric control than is that of the corresponding norbornadienes. Furthermore, the general principles governing the hydrogenation of the parent olefins cannot be applied indiscriminately to the reduction of their derivatives.*

The lack of suitable data precludes a detailed analysis of the platinum-catalyzed reductions. Over-all, these reactions seem to be controlled by the same factors; reduction of the dienyl acetate is sensitive to both steric and coordination control; reduction of the *syn*- and *anti*-acetates is controlled solely by steric factors. The impact of these effects is greatly diminished over platinum catalysts, and as a group these catalysts exhibited less selectivity than the palladium catalysts, in accord with previous observations.[5b,11]

A major unresolved issue raised during this study is

(18) This interpretation accepts the *cis* addition of hydrogen by transfer of the hydrogen atoms to the plane of the olefin from that side facing the catalyst.[5b]

(19) (a) T. J. Howard and B. Morley, *Chem. Ind.* (London), 73 (1967); (b) T. J. Howard, *Rec. Trav. Chim.*, **83**, 992 (1964); (c) S. Mitsui, K. Hebiguchi, and H. Saito, *Chem. Ind.* (London), 1746 (1967).

(20) (a) Palladium metal is a surface on which such olefin $\pi$ complexes are formed. G. C. Bond and P. B. Wells, *Advan. Catal.*, **15**, 125, 134, 136 (1964); (b) The palladium chloride–norbornadiene complex is endocyclic. N. C. Baenziger, J. R. Doyle, and C. L. Carpenter, *Acta Cryst.*, **14**, 303 (1961).

(21) The mechanism of this 2,6 addition is obscure; the participation of a $\pi$-homoallylic palladium–norbornadiene complex is suggested. D. R. Coulson, *J. Amer. Chem. Soc.*, **91**, 200 (1969).

the effect of prereduction of the palladium-on-carbon catalyst, for the principles controlling the chemistry of this system are obscure. The anomolous behavior of the prereduced catalyst is most apparent in two instances: (1) the marked effect of prereduction on the selectivities of the hydrogenation of both norbornadiene and 7-acetoxynorbornadiene; (2) the total influence of the prereduced catalyst on these reactions, for the olefin/catalyst ratios suggest that any special activity imparted to the catalyst by prereduction should be destroyed in the initial stages of the reaction. Inspection of the experimental data suggests that prereduction has sensitized the palladium catalyst toward preferential coordination with the diene system; as a result, hydrogenation of the diene predominates until the bulk of this substrate is removed from the reaction. This predilection for complexation of the diene is independent of the stereochemistry of the reduction, for the reduction of norbornadiene and 7-acetoxynorbornadiene exhibit different directions of deuterium addition. Consequently, this study has uncovered an unusual catalytic affect whose origins and significance are presently vague.

## Experimental Section

Infrared spectra were recorded on a Beckman IR-5A spectrophotometer. Nmr spectra were measured on a Varian Associates A-60 spectrometer using tetramethylsilane as an internal standard. Analytical vapor phase chromatography (vpc) was performed on a Varian Aerograph Model 202 chromatograph and a Perkin-Elmer Model 154D factometer. Preparative-scale gas chromatography was performed on a Varian Aerograph Model A-700.

Platinium oxide (Adam's catalyst), 5% platinum on carbon, and 10% palladium on carbon were obtained from Matheson Coleman and Bell. Matheson prepurified hydrogen and CP grade deuterium were employed for all reductions. 7-Acetoxynorbornadiene was purchased from Frinton Laboratories, Vineland, N. J. The following compounds were prepared by published procedures: *syn*-[22] and *anti*-7-norbornenol,[23] *syn*-[4a,13a] and *anti*-7-acetoxynorbornene,[13a] 7-acetoxynorbornane,[3] 3-acetoxynortricyclene,[24] *exo,exo*-5,6-dideuterio-*syn*-[6] and -*anti*-7-acetoxynorbornene,[2,3] *exo,exo,exo,exo*-2,3,5,6-tetradeuterio-7-acetoxynorbornane,[3] *exo,exo*-5,6-dideuterionorbornene,[3,6] and *exo,exo,exo,exo*-2,3,5,6-tetradeuterionorbornane.[3] Norbornadiene was distilled prior to use. All other reagents were obtained from commercial sources and were used as received.

Reductions utilizing a gas buret apparatus were carried out as previously described.[4a] Reductions requiring hydrogen or deuterium pressures of 20–40 psig were performed in a Parr low pressure hydrogenator.[25] Results derived from these hydrogenations are presented in Table I. In the majority of these reactions, hydrogen absorption was permitted to proceed until the amount theoretically required to reduce one double bond of the diene had been consumed. In other reactions, samples were periodically withdrawn in order to observe changes in composition as the reduction occurred. The reductions were not affected by a change in solvent from ethanol to methanol, nor were the product compositions altered over a range of acetoxydiene to catalyst ratios.

**Reduction of 7-Acetoxynorbornadiene with Deuterium.**—Into a Parr low pressure reactor were placed 10 g (67 mmol) of 7-acetoxynorbornadiene, 50 ml of absolute ethanol, and 0.5 g of 10% palladium on charcoal. The system was purged with nitrogen and deuterium and finally pressurized with deuterium to 31 psig. Reduction was permitted to proceed until 70 mmol of deuterium had been absorbed. The reaction mixture was filtered, and the filtrate was poured into 150–200 ml of water. The esters were extracted with pentane (three 50-ml portions), and the solution was washed with water and dried over magnesium sulfate. The solvent was removed on a rotary evaporator at 60° (14 mm) to give a crude yield of 12.6 g. The ester mixture was analyzed by vpc on a 11.5 ft × 0.25 in. 20% FFAP[26] column, 135°, helium flow 85 ml/min, detector and injector, 200°. The product had the following composition (retention time): 7-acetoxynorbornadiene (**1**, 32.0 min), 7%; 5,6-dideuterio-*syn*-7-acetoxynorbornene (**6**, 28.5 min), 43%; 5,6-dideuterio-*anti*-7-acetoxynorbornene (**7**, 21.9 min), 10%; 2,3,5,6-tetradeuterio-7-acetoxynorbornane (**8**, 24.1 min), 30%; 5,7-dideuterio-3-acetoxynortricyclene (**9**, 33.7 min), 11%.

The crude ester mixture was taken up in 100 ml of ether, and the ether solution was extracted with 5 *M* silver nitrate (four 30-ml portions).[4a] The ether layer was washed once with water and dried over magnesium sulfate. Removal of the solvent on a rotary evaporator gave 8 g of residue. Vpc analysis (see above) gave the following composition: **1**, 0%; **6**, 7%; **7**, 17%; **8**, 57%; **9**, 19%. This material was separated by preparative vpc[27] into 5,7-dideuterio-3-nortricyclylacetate (**9**) (purity by vpc, 100%) and a mixture of **7** (24%) and **8** (76%). The mixture of **7** and **8** was taken up in 10 ml of pentane and was shaken for 4 hr with 30 ml of 5 *M* silver nitrate. The pentane solution was dried over magnesium sulfate, and the solvent was removed to give 1 g of 2,3,5,6-tetradeuterio-7-acetoxynorbornane (**8**), purity by vpc, 97%. The silver nitrate solution (from the separation of **7** and **8**) was added to a chilled solution of 20 g of sodium cyanide in 50 ml of water. The aqueous solution was extracted with pentane (three 20-ml portions), and the extract was washed with water and dried over magnesium sulfate. Removal of the solvent gave 0.2 g of crystalline 5,6-dideuterio-*anti*-7-norbornenol. Vpc analysis (5 ft × 0.25 in. 20% polypropylene glycol column, 150°, helium flow 65 ml/min, detector and injector, 200°) confirmed the structure of the alcohol[23] and showed it to be 93% pure.

The original 5 *M* silver nitrate solution was added to a solution of 100 g of potassium cyanide in 300 ml of water containing *ca.* 100 g of ice. The liberated esters were extracted with ether (three 50-ml portions), and the extract was washed with water and dried over magnesium sulfate. Removal of the solvent gave 5.8 g of residue. Vpc analysis gave the following composition: **1**, 15%; **6**, 78%; **7**, 7%. Preparative vpc[27] provided a sample of 5,6-dideuterio-*syn*-7-acetoxynorbornene (**6**, purity, 100%) and a sample of 5,6-dideuterio-*anti*-7-acetoxynorbornene (**7**, purity, 95%).

Deuterium analysis of the *syn*- (**6**) and the *anti*-7-acetoxynorbornenes (**7**) by chemical ionization mass spectrometry[28] indicated a deuterium content of *ca.* 90% $d_2$ and *ca.* 10% $d_1$. Analysis of tetradeuterio-7-acetoxynorbornane (**8**) showed 90% $d_4$, 5% $d_3$, 3% $d_2$, and 2% $d_1$.

The nmr spectra of the deuterated acetate esters (**6**, **7**, **8**, **9**) were recorded on neat samples; dideuterio-*anti*-7-norbornenol was dissolved in $CDCl_3$. The relative areas of the *exo* protons ($\delta$ 1.50–1.83) and of the *endo* protons ($\delta$ 0.83–1.30)[13] served as a measure of *endo,cis* and *exo,cis* addition of deuterium. Analysis of the *endo*-proton areas indicated the relative amounts of *anti,endo* ($\delta$ *ca.* 1.18) and of *syn,endo* ($\delta$ *ca.* 1.27) protons. The nmr data for the esters (**6**, **7**, **8**, **9**) and for the alcohol are summarized in Table V. Deuterium decoupling experiments[15] on 5,7-dideuterio-3-acetoxynortricyclene (**9**) showed a sharpening of the protons at $\delta$ 1.45 and 1.75. The chemical shifts of these protons are similar to that expected for *exo* hydrogens; consequently, the two deuterium atoms have been assigned an *endo,endo*-5,7 configuration.

**3-Acetoxynortricyclene by Reduction of 7-Acetoxynorbornadiene.**—Into a Parr low pressure reactor were placed 50 ml of ethanol, 0.5 g of 10% palladium on charcoal, and 4.5 g (30 mmol) of 7-acetoxynorbornadiene. The diolefin was hydrogenated at an initial hydrogen pressure of 20 psig until no further hydrogen consumption occurred (63 mmol absorbed). The reduction mixture was filtered, the filtrate was poured into 150 ml of saturated sodium chloride solution, and the product was extracted with pentane. From the pentane extract 4.6 g of crude ester was recovered. Vpc analysis (5 ft × 0.25 in. 20% polypropylene

(22) W. C. Baird, Jr., *J. Org. Chem.*, **31**, 2411 (1966).
(23) P. R. Story, *ibid.*, **26**, 287 (1961).
(24) L. Schmerling, J. P. Luvisi, and R. W. Welch, *J. Amer. Chem. Soc.*, **78**, 2819 (1956).
(25) Parr Instrument Co., Moline, Ill.
(26) Varian Aerograph, Walnut Creek, Calif.
(27) Preparative vpc conditions: 12 ft × 3/8 in. 30% FFAP column, 125°, helium flow 110 ml/min, detector and injector, 200°.
(28) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **88**, 2621 (1966). The authors thank Dr. Field of these laboratories for obtaining and interpreting the mass spectral data.

TABLE V

NMR SPECTRA OF DEUTERATED REDUCTION PRODUCTS FROM 7-ACETOXYNORBORNADIENE

| | Proton type, δ (relative area) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Compd | CH=CH | H—C—OAc | >C—H | $CH_3CO$ | *exo* $>C<^{H}_{H}$ | *endo* $>C<^{H}_{H}$ | % *endo* $d_2$ addition | % *exo* $d_2$ addition |
| **6** | 5.95 (2) | 4.43 (1) | 2.84 (2) | 1.85 (3) | 1.75 (0.4) | 0.90 (1.6) | 21 | 79 |
| **7** | 6.00 (2) | 4.30 (1) | 2.72 (2) | 1.98 (3) | 1.72 (2) | ... | 100 | 0 |
| **8** | ... | 4.65 (1) | 2.10 (2) | 1.96 (3) | 1.75 (0.96) | 1.17 (1.04) | 52 (42 *syn*, 10 *anti*) | 48 (13 *syn*, 35 *anti*) |
| *anti*-ol | 5.95 (2) | 3.53 (1) | 2.52 (2) | 3.30 (1) (OH) | 1.78 (2) | ... | 100 | 0 |
| **9** | ... | 4.56 (1) | 1.93 (4) | | 1.45 (1)<br>1.75 (1) | 1.23 (3) (*c*-Pr H) | | |

glycol, 150°, 80 ml/min) showed the composition of the product to be 87% 7-acetoxynorbornane (**4**, $t_R$ 14.8 min) and 13% 3-acetoxynortricyclene (**5**, $t_R$ 18.4 min). Pure 3-acetoxynortricyclene was separated by preparative vpc[27] and was shown to be identical to an authentic sample[24] by comparative nmr, vpc, and infrared techniques.

**Deuterium Reduction of *syn*- and *anti*-7-Substituted Norbornenes.**—Into a gas buret apparatus were placed 124.8 mg of 10% palladium on charcoal, 3 ml of methanol, and 464.7 mg (3.01 mmol) of 5,6-dideuterio-*syn*-7-acetoxynorbornene (**6**). The deuterium distribution in the *syn*-acetate was 21% *endo,cis* and 79% *exo,cis*. The olefin was reduced with deuterium until no further gas consumption occurred. The reduction mixture was filtered and added to 10 ml of ether. The ether solution was washed twice with water and then dried over calcium chloride. Removal of the ether by distillation gave 469.3 mg of acetate ester. Purification by preparative vpc[27] gave 280 mg of tetradeuterated 7-acetoxynorbornane. Nmr analysis of the saturated ester revealed the deuterium distribution to be 29% *endo,cis* and 71% *exo,cis*, which corresponded to 40% *endo,cis* deuterium addition. Further resolution of the *exo* proton area (29%) showed the proton distribution to be *ca.* 20% *exo,syn* and *ca.* 9% *exo,anti*. Similar analysis of the *endo* proton area (71%) revealed the composition to be *ca.* 32% *endo,syn* and *ca.* 39% *endo,anti*. The ratio of *endo,anti* protons to *exo,anti* protons was *ca.* 4.3:1, which corresponded reasonably well to the 3.8:1 ratio in the initial *syn*-acetate. The ratio of *endo,syn* protons to *endo,anti* protons of 1.6:1 agreed well with the ratio of 1.5:1 calculated on the basis of 40% *endo,cis* deuterium addition.

The deuterium reduction of *syn*-7-acetoxynorbornene was repeated using 58.9 mg of prereduced 10% palladium on charcoal and 256.2 mg (1.66 mmol) of acetate. Nmr analysis of the 2,3-dideuterio-7-acetoxynorbornane showed that the reduction had occurred with 30% *endo,cis* deuterium addition.

In a gas buret apparatus, 342.6 mg (2.22 mmol) of *exo,exo*-5,6-dideuterio-*anti*-7-acetoxynorbornene (**7**) was reduced with deuterium over 52.2 mg of 10% palladium on charcoal. Nmr analysis of the tetradeuterated 7-acetoxynorbornane revealed the presence of exclusively *endo,syn* and *endo,anti* protons, in accord with 100% *exo,cis* deuterium addition.

*syn*-7-Hydroxynorbornene (240.1 mg, 2.18 mmol) was reduced with deuterium over 41.6 mg of 10% palladium on charcoal. The saturated alcohol was purified by sulbimation to give 170 mg of pure 2,3-dideuterio-7-hydroxynorbornane. Nmr analysis ($CDCl_3$) revealed the existence of two *exo* protons and four *endo* protons, indicating 100% *exo,cis* deuterium addition.

A 198.5-mg sample of *exo*-5-deuterio-*anti*-7-hydroxynorbornene[2] was reduced with deuterium over 34.5 mg of 10% palladium on charcoal. Sublimation yielded 120 mg of pure 2,3,5-trideuterio-7-acetoxynorbornane. Nmr analysis ($CDCl_3$) showed the presence of one *exo* proton and four *endo* protons, in accord with 100% *exo,cis* addition of deuterium.

**Competitive Reductions of *syn*- and *anti*-7-Hydroxy- and -Acetoxynorbornenes.**—Competitive hydrogenation studies were performed according to the general procedure described by Hussey, Baker, and Keulks.[17] Into a gas buret apparatus were placed 3 ml of ethanol, 30 mg of 10% palladium on charcoal, 114.8 mg (1.04 mmol) of *syn*-7-hydroxynorbornene, 133.3 mg (1.21 mmol) of *anti*-7-hydroxynorbornene, and 78.6 mg of isoamyl alcohol as an internal standard. The mixture was analyzed by vpc, and the response factors for the *syn* and *anti* alcohols relative to isoamyl alcohol were calculated. Vpc analyses were performed on 2 m × 0.25 in. 20% polypropylene glycol and 1 m × 0.25 in. 5% polypropylene glycol columns in series at 135° and 120 ml/min: retention times—*syn*-ol, 17.6 min; *anti*-ol, 31.0 min; isoamyl alcohol, 6.2 min. The olefin mixture was reduced with hydrogen, and samples were withdrawn periodically through a septum and were analyzed by vpc. From the vpc data the changes in the *syn*- and *anti*-alcohol concentrations were determined. The relative rate of hydrogenation was calculated from the equation[17]

$$k_{anti}/k_{syn} = \frac{\log (anti)_0/(anti)}{\log (syn)_0/(syn)}$$

The value of $k_{anti}/k_{syn}$ was also measured from the slope of the plot of $\log (anti)_0/(anti)$ *vs.* $\log (syn)_0/(syn)$. By these methods, the relative rate of hydrogenation of the *syn* and *anti* alcohols was determined to be 0.95 and 0.94, respectively.

The same general method was employed to determine $k_{anti}/k_{syn}$ for the competitive hydrogenation of *syn* and *anti* 7-acetoxynorbornenes over various platinum and palladium catalysts. Vpc analyses were performed on a 11.5 ft × 0.25 in. 20% FFAP column at 135° and 85 ml/min. The data are presented in Table III; the accuracy and precision of these data are limited by the analytical method, by the small degree of *syn* double bond reduction that occurs in the early stages of the reduction, and by the absence of *anti*-acetate in the final stages.

Control reductions were performed with pure *syn*- and *anti*-acetate to ensure that no isomerization reactions were occurring during the hydrogenation. Periodic analysis of reductions of these isomeric olefins over various catalysts showed the reaction mixture to contain only 7-acetoxynorbornane and the starting olefin. No *syn–anti* or *anti–syn* isomerizations were detected.

**Competitive Reduction of Norbornadiene and 7-Acetoxynorbornadiene.**—The general procedure for the competitive reduction of norbornadiene and 7-acetoxynorbornadiene has been described.[6] In a preparative experiment, a mixture of 890 mg (5.93 mmol) of 7-acetoxynorbornadiene, 640.1 mg (6.95 mmol) of norbornadiene, and 293.1 mg of ethylbenzene (internal standard) was reduced with deuterium in 10 ml of methanol over 302 mg of 10% palladium on charcoal. The reduction was permitted to proceed until 454 ml of deuterium (73% of theory) was absorbed. Vpc analysis of the reduction mixture[6] showed that the norbornadiene had been converted to norbornane and that the acetoxydiene had been reduced to *syn*-7-acetoxynorbornene (38%), 7-acetoxynorbornane (55%), and 3-acetoxynortricyclene (7%). The norbornane and methanol were removed by distillation, and the distillate was added to 20 ml of water. The norbornane was extracted with pentane (two 10-ml portions), and the extract was dried over magnesium sulfate. The pentane solution was reduced by distillation to *ca.* 1 ml, and the residue was subjected to preparative vpc (12 ft × 3/8 in. 20% FFAP column, 100°, 120 ml/min) to isolate 150 mg of norbornane. The nmr spectrum ($CDCl_3$) of the hydrocarbon was identical with that of an authentic sample of *exo,exo,exo,exo*-2,3,5,6-tetradeuterionorbornane; the reduction of norbornadiene had proceeded *via* 100% *exo,cis* deuterium addition.

The residue from the methanol distillation was separated by preparative vpc (12 ft × 3/8 in. 20% FFAP column, 135°, 120 ml/min) into 7-acetoxynorbornane (171 mg) and *syn*-7-acetoxynorbornene (121 mg). Nmr analysis ($CDCl_3$) of the *syn*-acetate showed it to be composed of 85% *exo,cis*-5,6-dideuterio isomer and 15% *endo,cis*-5,6-dideuterio isomer. Nmr analysis ($CDCl_3$) of 7-acetoxynorbornane revealed a deuterium distribution of 66% *exo,cis* and 34% *endo,cis*.

A sample that had been withdrawn from this reduction after the absorption of 372 ml of deuterium (60% of theory) was

analyzed for acetate ester content by vpc. The composition of the acetate fraction was shown to be 74% *syn*-7-acetoxynorbornene, 16% *anti*-7-acetoxynorbornene, 3% 7-acetoxynorbornane, and 7% 3-acetoxynortricyclene. Based on the direction of deuterium addition in forming these isomeric acetates during reduction of dienyl acetate, the mixture of norbornenyl acetates corresponded to 20% *endo,endo*-5,6-dideuterio-*anti*-7-acetoxynorbornene, 68% *exo,exo*-5,6-dideuterio-*syn*-7-acetoxynorbornene, and 12% *endo,endo*-5,6-dideuterio-*syn*-7-acetoxynorbornene. Since it had been shown (*vide supra*) that the *anti* isomer experienced 100% *exo,cis* deuterium addition and that the *syn* isomer (over a nonprereduced catalyst) underwent 40% *endo,cis* and 60% *exo,cis* deuterium addition, the deuterium distribution of tetradeuterated 7-acetoxynorbornane was predicted to be 33.6% *endo,cis* and 66.4% *exo,cis*. The values agreed with the observed distribution of 34% and 66%, respectively.

**Competitive Reduction of Norbornene and 7-Acetoxynorbornadiene.**—In a gas buret apparatus 268.5 mg of 10% palladium on charcoal in 5 ml of methanol was reduced with deuterium. Into the catalyst slurry a solution of 764 mg (4.8 mmol) of 7-acetoxynorbornadiene and 990 mg (10.5 mmol) of norbornene in 5 ml of methanol was injected. The reduction reaction was sampled periodically and analyzed by vpc.[6] The composition of the acetate mixture was determined and is summarized in Table VI below.

TABLE VI

| Reduction, % | Composition, % | | | | | |
|---|---|---|---|---|---|---|
| | Norbornene | Dienyl acetate | *syn*- | *anti*- | Satd | Nortricyclic |
| 24 | 81 | 49 | 11 | 20 | 0 | 20 |
| 48 | 56 | 11 | 23 | 37 | 0 | 30 |
| 64 | 34 | 0 | 25 | 40 | 4 | 30 |
| 80 | 6 | 0 | 26 | 38 | 7 | 30 |
| 96 | 0 | 0 | 16 | 0 | 54 | 30 |
| 100 | 0 | 0 | 0 | 0 | 70 | 30 |

**Determination of $k_{anti}/k_{syn}$ for Reduction of 7-Acetoxynorbornadiene to *syn*- and *anti*-7-Acetoxynorbornenes.**—In the reduction of 7-acetoxynorbornadiene, $k_{anti}$ is derived from the rate of reduction of the *anti* double bond to yield *syn*-7-acetoxynorbornene. Conversely, $k_{syn}$ is a measure of the rate of reduction of the *syn* double bond to produce *anti*-7-acetate. The relative rate, $k_{anti}/k_{syn}$, has been determined by the ratio, % *syn*-acetate produced/% *anti*-acetate produced. For palladium-on-charcoal catalysts, this ratio is readily calculated from reductions performed in the presence of excess norbornene or norbornadiene, where the subsequent conversion of *syn*- and *anti*-acetates to saturated product is effectively suppressed. In the case of a prereduced palladium-on-charcoal catalyst (norbornene present), $k_{anti}/k_{syn}$ = 0.56–0.61 (average 0.58). In the case of a nonprereduced palladium catalyst (norbornadiene present), $k_{anti}/k_{syn}$ = 3.22–3.52 (average 3.41).

Reductions utilizing platinum catalysts are complicated by the fact that conversion of initially formed *syn*- and *anti*-acetates to saturated ester cannot be suppressed. In these cases the assumption has been made that the saturated product formed while dienyl acetate is present arises predominately from reduction of the *anti* isomer. This rationale is predicated on the observed preference for *anti* double bond reduction in the competitive reduction of *syn*- and *anti*-acetates over platinum catalysts (see Table III). Consequently, $k_{anti}/k_{syn}$ for dienyl acetate reductions over platinum catalysts has been estimated from the ratio, % *syn* produced/% *anti* + % saturated produced. For the platinum oxide catalyst, values of $k_{anti}/k_{syn}$ were calculated to be 1.01–1.36 (average 1.19). A platinum-on-carbon catalyst gave an average value for $k_{anti}/k_{syn}$ of 1.11; a prereduced platinum catalyst gave an average value of 1.81.

**Registry No.**—**1**, 13426-49-8; **2**, 13426-52-3; **3**, 13426-55-6; **6a**, 15649-38-4; **6b**, 20843-70-3; **7**, 20843-71-4; **8a**, 20843-72-5; **8b**, 20843-73-6; **8d**, 20843-74-7; **8e**, 20843-75-8.

# The Oxymercuration–Demercuration of Cycloalkadienes

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The oxymercuration–demercuration of isomeric cyclooctadienes was studied. The major product from 1,3-cyclooctadiene is 9-oxabicyclo[4.2.1]non-7-ene (**2**). 1,4-Cyclooctadiene yields mostly 3-cycloocten-1-ol and 1,4-epoxycyclooctane. Treatment of 3-cycloocten-1-ol with mercuric acetate, followed by reduction with sodium borohydride, is a convenient preparatory method for isomerically pure 1,4-epoxycyclooctane.

Oxymercuration–demercuration of olefins has been shown to be an excellent method for obtaining alcohols.[1] Previous studies[1,2] have shown that the direction of the addition is according to Markovnikov's rule and that the addition is controlled by steric factors. Relatively little work, however, has been done on the reactions of dienes. Bordwell[3] recently reported that the oxymercuration of 1,5-cyclooctadiene yielded a cyclization product instead of a simple addition product. We wish to report our studies on the reaction of some cyclic dienes, and related olefinic alcohols. The dienes that were chosen for our studies were 1,3-,1,4,- and 1,5-cyclooctadienes and 1,3- and 1,4-cyclohexadienes.

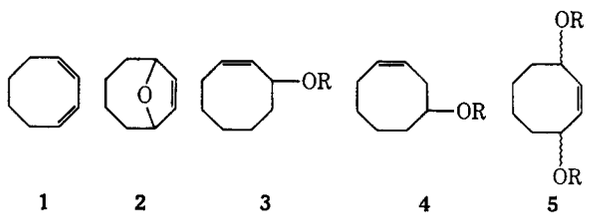
(1) For excellent review articles, see (a) J. Chatt, *Chem. Rev.*, **48**, 7 (1951); (b) N. S. Zefirove, *Russ. Chem. Rev.*, **34**, 527 (1965); (c) W. Kitchins, *Organometal. Chem. Rev.*, **3**, 61 (1968).

(2) H. C. Brown and P. Geogegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967).

(3) F. G. Bordwell and M. S. Douglass, *ibid.*, **88**, 993 (1966).

## Results and Discussion

Treatment of 1,3-cyclooctadiene (**1**) with mercuric acetate in tetrahydrofuran (THF) and water, followed, by alkaline demercuration with sodium borohydride gave 9-oxabicyclo[4.2.1]non-7-ene (**2**) in 37% yield, in




**1** **2** **3** **4** **5**

a, R = H
b, R = Ac

addition to **3a**, **4a**, and **5a**. When the diene was treated with mercuric nitrate instead of mercuric acetate, **2** was obtained in a lower yield.