second fraction (bp 134–136°) was better than 95% monchloride (3.2 g, 80%). It could be used as such for further reaction. On vpc examination (Silicone oil column 20 ft, or Ucon-550 column 6 ft, or diisodecyl phthalate column 6 ft) the material was found to consist of three monochlorides which were in the ratio 2.5:95.0:2.5. The major component was separated by chromatography, The minor components were not identified. The purified monochloride, n^{25}D 1.4725, had strong infrared absorptions (μ, neat liquid) at 3.35, 7.78, 10.85, and 14.10; mol wt 116, 118 (mass spectrometry). (For the nmr spectrum, see Results.) *Anal.* Calcd for C_6H_9Cl: C, 61.79; H, 7.78; Cl, 30.40. Found: C, 61.83; H, 7.73; Cl, 30.28.

From the residue, two dichlorides could be separated by vapor phase chromatography.

2,2-Dichlorobicyclo[2.1.1]hexane gave the following data: mp 11.5°; $n^{25.5}$D 1.4885; infrared spectrum (μ, neat liquid) 3.33, 10.45, and 13.45. *Anal.* Calcd for $C_6H_8Cl_2$: C, 47.72; H, 5.34; Cl, 46.96. Found: C, 47.83; H, 5.33; Cl, 46.92.

trans-2,3-Dichlorobicyclo[2.1.1]hexane showed bp 158–160°; infrared spectrum (μ, neat liquid) 3.30, 7.77, 12.10, and 13.20. *Anal.* Calcd for $C_6H_8Cl_2$: C, 47.72; H, 5.34; Cl, 46.96. Found: C, 47.57; H, 5.47; Cl, 46.85.

Chlorination can also be carried out in neat bicyclo[2.1.1]hexane or in trichlorotrifluoroethane solution. The composition of the monochloride and the yields were comparable. The principal advantages in using a solvent are: (i) the loss of bicyclo[2.1.1]-hexane through vaporization is reduced; and (ii) in distilling the partially chlorinated material, the solidification of the bicyclo-[2.1.1]hexane does not cause difficulties. CCl_4 is a better solvent than $C_2Cl_3F_3$ since its boiling point is closer to that of bicyclo-[2.1.1]hexane.

Chlorination at the boiling point of CCl_4 did not give a different distribution of monochlorides. There was some indication that the bicyclo[2.1.1]hexane underwent decomposition.

Chlorination in the vapor phase was carried out in a 1-l. Pyrex flask which was filled successively with bicyclo[2.1.1]hexane vapor and chlorine gas. Oxygen was carefully excluded. On exposure to a source of 3130 A, the reaction was over in a few seconds when a 1:1 ratio of materials was used. When the chlorine ratio was increased to 2:1, the reaction produced a blue flame. Mixtures of mono- and dichlorides, and carbon were produced.

Reduction of 2-Chlorobicyclo[2.1.1]hexane. *n*-Butyl alcohol (20.0 g) and 2-chlorobicyclo[2.1.1]hexane (1.0 g, 8.6 mmoles) were heated under nitrogen in a 100-ml flask equipped with a condenser. To the boiling solution sodium (2.0 g, 87 g-atoms) cut into small pieces was added over a period of 30 min. Reflux was maintained for an additional hour. Most of the liquid was then removed by distillation. Due to the high solid content, the mixture had to be stirred during this operation. An additional quantity (5 ml) of butyl alcohol was added to the almost solid residue and distilled out. The combined distillates were fractionated through a 10-cm column packed with glass beads. The first fraction (bp 70–105°, 0.57 g) contained all of the bicyclo[2.1.1]hexane. A small portion of the hydrocarbon was separated by vpc. It was found to be identical with the authentic material in its melting point, retention time, and infrared spectrum, total yield (calculated by calibrating the vpc for bicyclo[2.1.1]hexane) 47%.

Rate Studies. Standard solutions (solvent, CCl_4) of bicyclo-[2.1.1]hexane and cyclohexane in equimolar ratio as well as 2-chloro-bicyclo[2.1.1]hexane and cyclohexane in equimolar ratio were prepared. Chlorinations were carried out with chlorine gas in the presence of a 75-w tungsten lamp. No special effort was made to degas the solution before irradiation, but the positive pressure of chlorine and HCl would have prevented additional oxygen from diffusing in.

Analyses were carried out by vpc (Ucon-550 X, 6-ft column) at several temperatures so that maximum resolution between the two reactants or products could be obtained. The rate of chlorination of bicyclo[2.1.1]hexane was followed both by the disappearance of the hydrocarbon (relative to C_6H_{12}) and the appearance of the mono-chloride (relative to $C_6H_{11}Cl$). The chlorination of C_6H_9Cl could be followed relative to the appearance of $C_6H_{11}Cl$. In a separate experiment the chlorination of C_6H_9Cl could be followed relative to its formation from C_6H_{10}. The three rates checked with each other within 25%.

Anomalous Reductions of 7-Substituted Norbornadienes with Diimide[1a]

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Contribution from the Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey 07036. Received September 6, 1966

Abstract: The diimide reduction of several 7-substituted norbornadienes yields *anti*-7-substituted norbornenes rather than the corresponding *syn* isomers whose formation would be anticipated on the basis of theoretical and stereochemical considerations. Reductions utilizing deuteriodiimide yield deuterated *anti*-7-substituted norbornenes in which the deuterium atoms exhibit an *exo,exo* configuration. A similar reduction of the parent hydrocarbon, nor-bornadiene, also involves the introduction of *exo*-deuterium. Competitive diimide reductions show that this preferential reduction is characteristic of the *syn* double bond of 7-substituted norbornenes as well as that of 7-substituted norbornadienes.
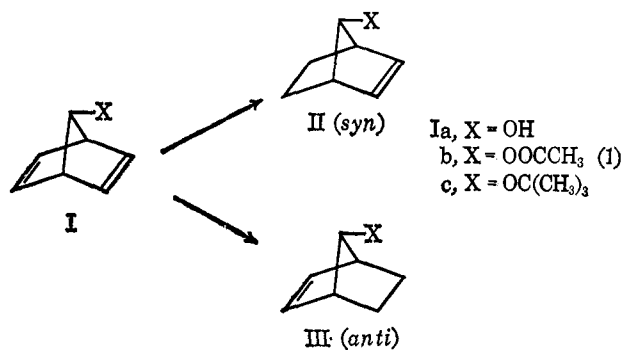
As part of a study of the chemistry of 7-substituted norbornadienes and norbornenes, convenient syntheses for the *syn* and *anti* isomers of the latter compounds were desired. Reasonable routes to these structures appeared to be the specific reduction of either the *anti* or the *syn* double bond of the corresponding norbornadienes[2] (eq 1) by means of the prop-erly selected catalytic[3] or chemical reducing system. The reducing agent, diimide (N_2H_2), suggested itself as a useful reagent which, for stereochemical reasons, would selectively attack the *anti* double bond of 7-

(1) (a) Presented in part at the 148th National Meeting of the American Chemical Society, Aug 1964, p 91S. (b) Enjay Chemical Intermediates Laboratory, Linden, N. J. 07036.

(2) These compounds may be readily prepared according to published synthetic procedures: P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

(3) B. Franzus, E. I. Snyder, and W. C. Baird, Jr., "Reductions In the 7-Substituted Norbornyl System; A Convenient Synthesis of *Syn*- and *Anti*-7-Substituted Norbornenes," in preparation; presented in part at the Regional Metropolitan American Chemical Society Meeting, New York, N. Y., Feb 1965.

II (syn)   Ia, X = OH
           b, X = OOCCH$_3$ (1)
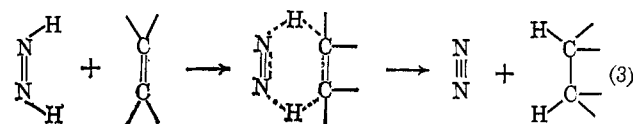   c, X = OC(CH$_3$)$_3$

I

III (anti)

substituted norbornenes. This paper reports the anomalous results encountered during the reduction of these compounds with diimide.

While the ability of diimide to reduce olefinic and acetylenic bonds had been sporadically demonstrated over a period of several decades,[4] the synthetic utility of this reagent was first made clearly apparent by the fundamental studies reported by Corey[5] and van Tamelen[6] and co-workers. From these reports two basic principles regarding the chemistry of diimide reductions of olefins have evolved; both assume considerable importance when applied to the reduction of the 7-substituted norbornyl systems being discussed here. The first of these is the fact that reductions of olefinic bonds with diimide exhibit a very high degree of stereospecificity,[5b,6c,7] cis addition of hydrogen predominating to the extent of 97–98%.[5b] This point is unambiguously demonstrated by the cis addition of deuterium through the use of N$_2$D$_2$[5b] (eq 2). Since this observed stereospecificity is independent of olefin structure and of the source of diimide, it follows that the hydrogenation is effected by the same reagent in every

$$>C=C< + N_2D_2 \longrightarrow \underset{D\ \ D}{>C-C<} + N_2 \qquad (2)$$
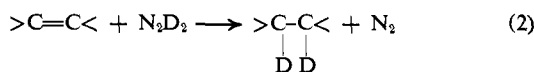
case and that both hydrogen atoms are simultaneously transferred to carbon. Consequently, Corey[5b] has proposed that the reduction occurs via a concerted reaction in which the critical step is the formation of a six-membered ring transition state which subsequently collapses to nitrogen and the stereospecifically reduced hydrocarbon (eq 3).[8]

Secondly, it has been shown that diimide reductions are remarkably sensitive to steric approach control.[6d] While such an effect might be anticipated on the basis of the steric requirements of the cyclic transition state (eq 3), the magnitude of this sensitivity toward steric factors has been reflected in the formation of the thermodynamically less stable stereoisomers resulting from diimide approach from the less hindered side of various olefinic substrates. This steric influence is most readily apparent from reductions of cyclic and bicyclic olefins. For example, α- and β-pinene have been reduced to the less stable cis-pinane in yields of 99 and 96%, respectively;[6d] similarly, 2-norbornene-2,3-dicarboxylic acid has yielded only the endo–cis isomer (exo–cis addition of hydrogen), endo approach of diimide being hindered by the endo-hydrogen atoms on carbons 5 and 6.[6d] Steric effects have also been noted to be significant in diimide reductions of acylic olefins in that trans double bonds are reduced more rapidly than cis double bonds.[4a,b] The discriminating ability of diimide toward cis–trans reductions is convincingly illustrated by the selective formation of cis-cyclododecene from the reduction of cis,trans,trans-1,5,9-cyclododecatriene.[9] This distinction between the relative rates of reduction of cis and trans olefinic bonds is also attributed to steric factors operating in the transition state, the cyclic complex derived from the trans olefins being less crowded and accordingly requiring a lower activation energy.[10]

If these principles of diimide reduction, i.e., stereospecific cis addition via a cyclic transition state and steric approach control, are applied to the reduction of 7-substituted norbornadienes (I), a reasonable conclusion results. The steric interference of the 7 substituents should seriously inhibit the formation of the exocyclic transition state[11] with the syn double bond and hence suppress the formation of anti-7-substituted norbornenes (III). Calculations based on models of 7-t-butoxy- and acetoxynorbornadiene[12] and diimide[13] taking into account unfavorable entropy effects (restricted rotation of the 7 substituent) and bond compression in the syn-exocyclic transition state lead to the conclusion that reduction of the anti double bond should be favored to the extent that the product mixture should consist of 96% syn isomer and 4% anti. Consequently, reduction of the anti double bond leading to syn product (II) should proceed readily and provide a convenient route to these compounds (eq 1). The subsequent testing of this hypothesis experimentally produced a completely unexpected and totally opposite result.

Treatment of the 7-substituted norbornadienes (Ia–c) with potassium azodicarboxylate in methanol–acetic acid[6b] yielded only small amounts of the anticipated syn products (II); most reductions gave rise to the anti isomers (III) as the exclusive norbornene derivative. The results of these reactions are summarized in Table I. The reduction of 7-norbornadienol (Ia, X = OH) was complicated by the apparent decomposition of starting material and/or product during the reaction,

(4) For reviews on the chemistry of diimide, see (a) C. E. Miller, J. Chem. Educ., 42, 254 (1965); (b) S. Hünig, H. R. Müller, and W. Thier, Angew. Chem. Intern. Ed. Engl., 4, 271 (1965); (c) F. Aylward and M. Sawistowska, Chem. Ind. (London), 484 (1962).

(5) (a) E. J. Corey, W. L. Mock, and D. J. Pasto, Tetrahedron Letters, 11, 347 (1961); (b) E. J. Corey, W. L. Mock, and D. J. Pasto, J. Am. Chem. Soc., 83, 2957 (1961); (c) E. J. Corey and W. L. Mock, ibid., 84, 685 (1962).

(6) (a) E. E. van Tamelen, R. S. Dewey, and R. J. Timmons, ibid., 83, 3725 (1961); (b) R. S. Dewey and E. E. van Tamelen, ibid., 83, 3729 (1961); (c) E. E. van Tamelen, R. S. Dewey, M. F. Lease, and W. H. Pirkle, ibid., 83, 4302 (1961); (d) E. E. van Tamelen and R. J. Timmons, ibid., 84, 1067 (1962); (e) E. E. van Tamelen, M. Davis, and M. F. Deem, Chem. Commun., 71 (1965).

(7) S. Hünig, H. R. Müller, and W. Thier, Tetrahedron Letters, 353 (1961).

(8) While this mechanism has not been proven unequivocably, the chemistry of the reduction and the properties of the reagents involved impart to it substantial credibility. See ref 4a and b.

(9) M. Ohno and M. Okamoto, Tetrahedron Letters, 2423 (1964).

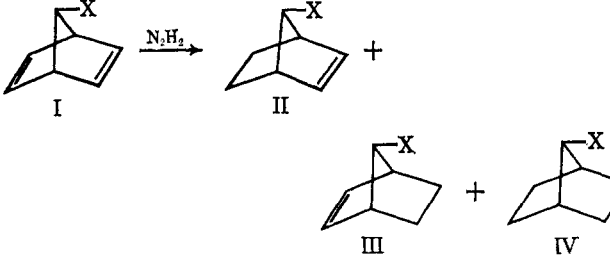(10) S. Hünig and H. R. Müller, Angew. Chem., 74, 215 (1962).

(11) The formation of an endocyclic transition state is prevented by the 5–6 hydrogens. See ref 6d.

(12) C. F. Wilcox, Jr., J. Am. Chem. Soc., 82, 414 (1960).

(13) G. W. Wheland and P. S. K. Chen, J. Chem. Phys., 24, 67 (1956).

and poor reaction yields were realized as a result. Vapor phase chromatography utilizing internal standards demonstrated that the reduction of 7-acetoxy- and 7-*t*-butoxynorbornadiene (Ib, Ic) were quantitative in that both starting material and products were stable under the reaction conditions. In all cases, the reduction products were identified by comparative vpc, nmr, and infrared techniques with authentic compounds.[14] An excess of potassium azodicarboxylate was generally employed to counter partially the moderate efficiency of diimide as a reducing agent.[15] Inspection of Table I reveals that the selectivity to the *anti* isomers (III) is independent of this variable.

Table I. Diimide Reduction of 7-Substituted Norbornadienes

Initial diene (I)	N2H2 : diene, moles	I	II (*syn*)	III (*anti*)	IV
X = OH	1.8:1	37	8	27	28
X = OOCCH3	1.9:1	25	0	50	25
	1.3:1	24	0	49	27
	0.5:1	88	0	12	0
X = OC(CH3)3	1.2:1	25	0	63	12
	1.5:1	17	3	65	15
	2.0:1	0	0	38	62

The preferential diimide reduction of *syn* double bonds as opposed to *anti* was also apparent from the competitive reduction of *syn-* and *anti*-7-acetoxynorbornene (IIb and IIIb) (eq 4). Reduction of an equal molar mixture of these isomeric esters with a slight excess of diimide gave a product mixture containing none of the *syn*-acetate while 50% of the *anti* isomer remained unreduced. When the reduction of the ester mixture was performed using only 50% of the theoreti-

(4)
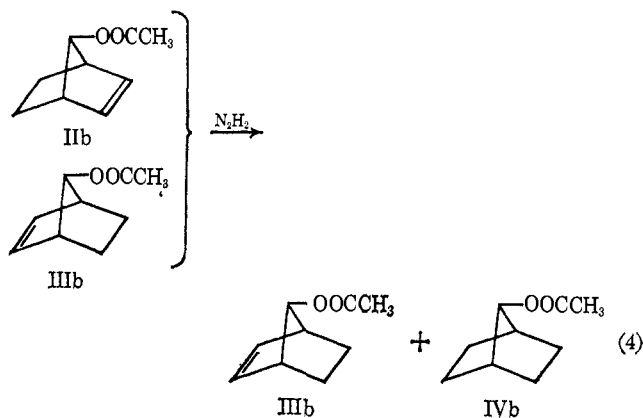
cal quantity of diimide, none of the *anti* isomer was reduced while 50% of the *syn*-acetate was converted to 7-

acetoxynorbornane (IVb). The partial reduction of the pure *syn* ester (IIb) with 50% of the stoichiometric amount of diimide did not produce any of the *anti*-acetate (IIIb); consequently, the products of the diene reductions arise from a kinetically controlled reaction rather than through an isomerization reaction.

Reduction of 7-norbornadienyl acetate (Ib) with deuteriodiimide led to a reaction mixture containing 50% *anti*-7-acetoxynorbornene (see Table I). Isolation of this compound by preparative vpc and analysis of its nmr spectrum[14] showed this material to be *exo,exo*-5,6-dideuterio-*anti*-7-acetoxynorbornene (V, eq 5). Total

(5)
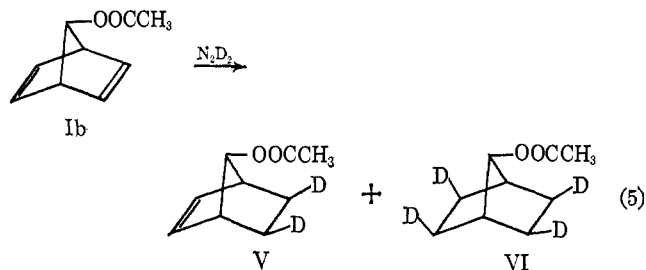
reduction of the 7-acetoxydiene gave tetradeuterio-7-acetoxynorbornane (VI, eq 5), in which all four deuterium atoms exhibited an *exo* configuration.[14] These results are totally consistent with the previously proposed stereospecific *cis*-addition mechanism.[5b] Furthermore, they also demonstrate the preferential formation of the cyclic transition state complex with the *syn* double bond in an exocyclic manner in spite of the adverse steric effects presented by the 7 substituents.

In order to establish that the presence of a 7 substituent is not a necessary condition for *exo-cis* addition, the parent hydrocarbon, norbornadiene (VII), was treated with deuteriodiimide (eq 6). From the reac-

(6)
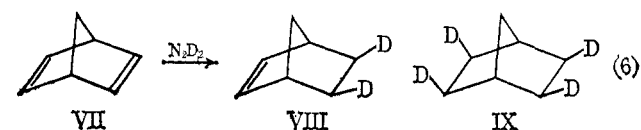
tion mixture dideuterionorbornene (VIII, 26%) and tetradeuterionorbornane (IX, 44%) were isolated by preparative vpc. The nmr spectra of these compounds revealed that all of the deuterium atoms had been introduced by *exo-cis* addition.[16] The spectrum of *exo,-exo*-5,6-dideuterionorbornene (VIII)[17] exhibited the following pattern: vinyl triplet (2 H), 360 cps; bridgehead hydrogens, broad singlet (2 H), 170 cps; bridge hydrogens, complex multiplet (2 H), 63–90 cps; *endo* hydrogens, broad singlet (2 H), 58 cps. *exo,exo,exo,-exo*-2,3,5,6-Tetradeuterionorbornane (IX) showed a broad singlet at 131 cps for the two bridgehead protons and a second broad singlet at 69 cps for the remaining four *endo* protons and the two bridge protons. Neither VIII nor IX absorbed in the 100–120-cps region indicating the absence of *exo* hydrogens, which would have arisen from *endo* addition of deuterium. It is obvious that these results are also consistent with the *cis*-addition mechanism and occur in an exocyclic manner; the presence or absence of a 7 substituent would appear then to have little bearing on this point.

(14) E. I. Snyder and B. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964).
(15) The reagent experiences decomposition to yield nonreducing species. See ref 4.

(16) A similar stereochemical reduction of norbornadiene by deuterium over palladium on charcoal has been reported by D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2596 (1965).
(17) A detailed analysis of the nmr spectrum of this compound has been completed and will be reported in the near future.

The mechanistic implications of the unusual results observed here regarding the diimide reduction of 7-substituted norbornadienes and norbornenes are obvious. While theoretical and stereochemical principles point toward the selective reduction of the *anti* double bond, the observed preferential reaction of the *syn* double bond reveals that a potent electronic effect is significantly superceding any adverse steric factors. Although statements regarding the reasons for this preferential, stereospecific reduction of the *syn* double bonds of these compounds must remain speculative for the time being, two possible rationales may be considered. The first of these involves an electronic activation of the *syn* double bond by the 7 substituent thereby enhancing its relative reactivity. An alternate and potentially more attractive explanation is the stabilization of the exocyclic transition state by the coordination of an electron-donating atom in the 7 position with the partially positive diimide nitrogen–nitrogen bond.[5b,6a,18] Calculations based on models of 7-*t*-butoxy- or acetoxynorbornadiene[12] and diimide[13] indicate that in the assumed *syn*-exocyclic transition state the oxygen bonded to C_7 and the nitrogen–nitrogen bond are separated by approximately 2.05 Å, a distance over which electronic stabilization could be operative. In any event, the factors controlling the selective reduction of the *syn* double bond must be appreciable. The 99:1 predominance of the *anti* isomer found in these reductions indicates that formation of the *syn* transition state relative to that involving the *anti* double bond is preferable by approximately 4.5 kcal/mole.

Experimental Section

Infrared spectra were determined using a Beckman IR-5 spectrophotometer and a Baird Model 4-55 recording spectrophotometer. Vapor phase chromatographic analysis was carried out on a Perkin-Elmer Model 154-D fractometer. Preparative gas chromatography was performed using an Aerograph Autoprep Model A-700. Nmr spectra were determined with a Varian Associates A-60 spectrometer using tetramethylsilane as an internal standard.

7-Norbornadienol (Ia), 7-norbornadienyl acetate (Ib), 7-*t*-butoxynorbornadiene (Ic), and *anti*-7-norbornenol (IIIa) were prepared by the method of Story.[2] *syn*-7-Norbornenol (IIa) was prepared in these laboratories;[19] *syn*- and *anti*-7-acetoxynorbornene (IIb and IIIb) were prepared by treating the corresponding alcohols with acetic anhydride.[14] The structures of the isomeric 7-*t*-butoxynorbornenes (IIc and IIIc) have been determined by these laboratories.[3] The stereochemistry of the deuterated 7-acetoxynorbornenes and 7-acetoxynorbornane has been reported by Snyder and Franzus.[14]

The products of the reduction reactions were identified by comparison of their infrared and nmr spectra and their vpc retention times with those of the authentic compounds.

Diimide Reduction of 7-Norbornadienol (Ia). To a stirred suspension of 754.2 mg (3.88 mmoles) of potassium azodicarboxylate (Aldrich Chemical Co.) in 10 ml of methanol containing 113.8 mg (1.05 mmoles) of 7-norbornadienol was added dropwise with stirring a solution of 472.6 mg (7.88 mmoles) of acetic acid in 5 ml of methanol. The reaction was stirred at room temperature for 30 min. The reaction mixture was diluted with water and extracted with pentane. The pentane extract was dried over magnesium sulfate and was analyzed on a 1 m × 0.25 in. 5% polypropylene glycol column at 80° and a helium flow of 90 cc/min. The product had the following composition: 7-norbornadienol (Ia, 3.6 min),

(18) A similar "chelating" effect is believed to be responsible for the enhanced stability of the silver nitrate–*syn*-7-acetoxynorbornene complex relative to that of the *anti*-7-acetate complex. Determination of the equilibrium constants for these complexes have shown $K_{syn}/K_{anti} = \sim 10$; ref 3.
(19) W. C. Baird, Jr., *J. Org. Chem.*, 31, 2411 (1966).

37%; *syn*-7-norbornenol (IIa, 4.7 min), 8%; *anti*-7-norbornenol (IIIa, 12.6 min), 27%; 7-norbornanol (IVa, 13.6 min), 28%.

Diimide Reduction of 7-Norbornadienyl Acetate (Ib). To a stirred suspension of 245.5 mg (1.26 mmoles) of potassium azodicarboxylate in 0.5 ml of methanol containing 150.9 mg (1.0 mmole) of 7-norbornadienyl acetate was added dropwise a solution of 154.4 mg (2.58 mmoles) of acetic acid in 0.5 ml of methanol. Stirring was continued for 20 min; the reaction was diluted with water and extracted with pentane. The pentane extract was dried over magnesium sulfate and was analyzed by vpc. The product had the following composition: 7-norbornadienyl acetate (Ib), 24.0%; *anti*-7-acetoxynorbornene (IIIb), 49.5%; 7-acetoxynorbornane (IVb), 26.5%. The *anti* and saturated acetates were isolated by preparative vpc and identified by their infrared spectra. Vpc analyses utilized a 2 m × 0.25 in. 20% diethylene glycol succinate column (125°, 25 psig helium) in conjunction with a 2 m × 0.25 in. 5% polypropylene glycol column (80°, 10 psig). Analyses were also performed on a 2 m × 0.25 in. 30% FFAP[20] column at 124° and 25 psig. Retention times from air for the acetate esters on the substrates cited are summarized in Table II.

Table II

Ester	Diethylene glycol succinate	Polypropylene glycol	FFAP
Ib	11.2	10.6	13.7
IIb	9.5	10.6	12.4
IIIb	6.9	8.6	9.6
IVb	7.1	10.4	10.2

Diimide Reduction of 7-*t*-Butoxynorbornadiene (Ic). To a stirred suspension of 232.3 mg (1.20 mmoles) of potassium azodicarboxylate in 1.0 ml of methanol containing 167.7 mg (1.02 mmoles) of 7-*t*-butoxynorbornadiene was added a solution of 163.0 mg (2.72 mmoles) of acetic acid in 1.0 ml of methanol. After stirring had been continued for 20 min, the reaction was diluted with water, and the product was extracted with pentane. The pentane extract was dried over magnesium sulfate and analyzed by vpc (20% polypropylene glycol column, 126°, 25 psig). The product had the following composition: 7-*t*-butoxynorbornadiene (Ic, 17.3 min), 25.0%; *anti*-7-*t*-butoxynorbornene (IIIc, 12.8 min), 63.3%; 7-*t*-butoxynorbornane (IVc, 15.2 min), 11.6%. *syn*-7-*t*-Butoxynorbornene (IIc) and the diene (Ic) exhibited identical retention times but could be resolved on a 300-ft capillary column. Analyses on this column showed that the amount of *syn* isomer formed in the diimide reduction did not exceed 3%.

Partial Reduction of 7-Norbornadienyl Acetate with Deuteriodiimide. Experiments involving deuterated materials were conducted in a drybox. To a stirred suspension of 2.23 g (11.5 mmoles) of potassium azodicarboxylate in 10 ml of methanol-*d* (Volk Chemical Co.) containing 1.50 g (10.0 mmoles) of 7-norbornadienyl acetate was added dropwise a solution of 1.62 g (27.0 mmoles) of acetic acid-*d* (from deuterium oxide and acetic anhydride) in 5 ml of methanol-*d*.[21] The reaction mixture was cooled to maintain the temperature at 25°. Stirring was continued for 15 min. The reaction was diluted with water and extracted with pentane. The pentane extract was dried over magnesium sulfate, and the solvent was removed under vacuum at room temperature. The residue (780 mg) contained 50% (by vpc) of *exo,exo*-5,6-dideuterio-*anti*-7-acetoxynorbornene. The ester was separated by preparative vpc, and its structure was confirmed by its nmr spectrum.[14]

The above experiment was repeated, but the quantities of the reagents employed were reduced by a factor of 10. *p*-Cymene was added as an internal standard. Analysis of the reaction mixture demonstrated that the reaction was quantitative in that neither starting material nor products were destroyed under the reaction conditions.

Total Reduction of 7-Norbornadienyl Acetate with Deuteriodiimide. The total reduction of 1.50 g (10.0 mmoles) of 7-norbornadienyl acetate with N_2D_2 was accomplished by treating the ester in 10 ml of methanol-*d* with a 4–5 mole excess of potassium azodicarboxylate and acetic acid-*d*. The reaction work-up yielded 800

(20) Wilkens Instrument, Walnut Creek, Calif.
(21) Isotopic purities: acetic acid-*d*, 98.1 mole %; methanol-*d*, 99.9 mole %.

mg of product. The *exo,exo,exo,exo*-2,3,5,6-tetradeuterio-7-ace-toxynorbornane was isolated by preparative vpc and identified by its nmr spectrum.[14]

Competitive Reduction of *syn*- and *anti*-7-Acetoxynorbornene with Diimide. A blend of 80.5 mg (0.53 mmole) of *syn*-7-acetoxynorbornene (IIb) and 83.4 mg (0.55 mmole) of *anti*-7-acetoxynorbornene (IIIb) was prepared. Vpc analysis of this mixture (diethylene glycol succinate column, 125°, 15 psig) gave the following composition: 52.3% *anti* isomer; 47.7% *syn* isomer. The acetate mixture was reduced by treatment with 232.7 mg (1.20 mmoles) of potassium azodicarboxylate and 134.0 mg (2.23 mmoles) of acetic acid in 1.0 ml of methanol. Vpc analysis of the product mixture gave the following composition: *syn*-7-acetoxynorbornene (IIb), 0%; *anti*-7-acetoxynorbornene (IIIb), 24.3%; 7-acetoxynorbornane (IVb), 75.7%.

When an identical blend of *syn*- and *anti*-acetates (0.97 mmole) was reduced with 79.8 mg (0.41 mmole) of potassium azodicarboxylate and 68 mg (1.13 mmoles) of acetic acid, the following product mixture was isolated: *syn*-7-acetoxynorbornene, 20.6%; *anti*-7-acetoxynorbornene, 47.7%; 7-acetoxynorbornane, 31.7%.

Partial Reduction of *syn*-7-Acetoxynorbornene with Diimide. To a stirred suspension of 75.8 mg (0.39 mmole) of potassium azodicarboxylate in 0.5 ml of methanol containing 107.8 mg (0.72 mmole) of *syn*-7-acetoxynorbornene was added a solution of 52.5 mg (0.88 mmole) of acetic acid in 0.5 ml of methanol. Stirring was continued for 15 min, and the reaction was worked up according to the normal procedure. No *anti*-7-acetoxynorbornene was detected in the vpc of the product.

Reduction of Norbornadiene with Deuteriodiimide. To 1.84 g (20 mmoles) of freshly distilled norbornadiene and 4.70 g (24.2 mmoles) of potassium azodicarboxylate in 10 ml of methanol-*d* was added a solution of 4.40 g (73.1 mmoles) of acetic acid-*d* in 5 ml of methanol-*d*. The reaction was stirred at 10–25° for 2 hr. The reaction mixture was diluted with 60 ml of water and extracted with pentane (two 40-ml portions). The pentane extract was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed by distillation; the residue was analyzed by vpc (2 m × 0.25 in. squalane column, 70°, 25 psig) and shown to have the following composition: norbornadiene (VII, 8.4 min), 20.1%; *exo,exo*-5,6-dideuterionorbornene (VIII, 11.1 min), 23.8%; *exo,exo,exo,exo*-2,3,5,6-tetradeuterionorbornane (IX, 16.0 min), 46.6%. Compounds VIII and IX were separated by preparative vpc, and their structures were determined by nmr.

Calculation of Relative Energies of *syn* and *anti* Transition States. The fact that diimide reductions are highly exothermic[5a] and proceed at a rapid rate permits describing these reactions in terms of the Hammond postulate:[22] if a one-step reaction is fast and exothermic, the structure of the transition state should resemble that of the reactants more closely than that of the products. This condition has led to the selection of Wheland's model of diimide,[13] shown below, and of Wilcox's model of norbornane[12] as the structural units on which to base calculations of transition-state energies. The distance between the *exo* hydrogens of norbornane can be calculated to be 2.30 A;[12] thus, only minor alternations of the
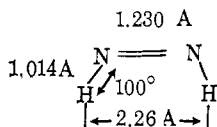
diimide geometry can be anticipated in passing through the transition state. On this basis two different exocyclic transition states may be constructed, the *anti* A and the *syn* B, which are simply depicted below. These transition states shall now be considered with respect to (a) entropy effects and (b) bond compression energies.

(22) G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955).

A *(anti)*   B *(syn)*

$$Y = CH_3CO,\ (CH_3)_3C$$
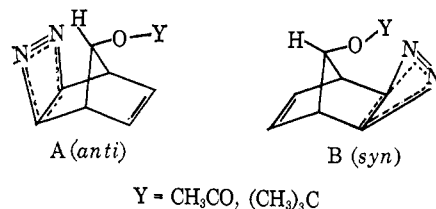
Entropy Effects. Inspection of the transition states A and B reveals that in the *syn*-model rotation of the Y portion of the 7 substituent will be restricted by the approach of the diimide molecule to the *syn* double bond. If this restriction amounts to *only* 50% of the original rotation (360°) of this group, the minimum, unfavorable entropy introduced at this point amounts to 1.372 eu ($\Delta S = R \ln 2$), or $T\Delta S = 409$ cal at 25°. If it is assumed that no additional complicating factors exist, then by means of the expression, $-T\Delta S = \Delta G = -RT \ln K$, the value of K is calculated as being 2. Consequently, on the basis of entropy considerations alone the diimide reduction of these dienes would be expected to produce a mixture containing 66% of the *syn* isomer (*anti* double bond reduced) and 33% of the *anti* compound.

Compressional Energies. Simple geometry shows that the distance from the C_7 hydrogen to the azo bond in A is 2.14 A; the distance from the C_7 oxygen to the nitrogen–nitrogen bond in B is 2.05 A. The van der Waals distances between these atoms may be calculated as being for $H \cdots N$, 2.7 A, and for $O \cdots N$, 2.9 A. Thus, in A, the $H \cdots N$ distance is compressed by 0.56 A while, in B, the $O \cdots N$ distance is compressed by 0.85 A. The net compression difference between A and B then is ~0.3 A, with the *anti*-exocyclic transition state again being favored. These effects may be related to energies by the method outlined by Westheimer.[23] A crude approximation of the van der Waals potential can be made by assuming that the shape of the van der Waals curve for any two atoms will approach that for the rare gas with the same interatomic separation at the energy minimum, *i.e.*, where the van der Waals radius of the rare gas equals the average of the van der Waals radii of the interacting atoms. By using helium as a model system, the difference in the repulsion energies between $O \cdots N$ and $H \cdots N$, or between B and A, is computed to be 254 cal. This value plus the entropy term calculated above (409 cal) leads to a total energy difference of 663 cal and to a $K \cong 3.1$, which would be reflected in a product composition of 75% *syn* and 25% *anti*. Basing a similar calculation on neon gives a repulsion energy difference of 1.92 kcal, a total energy difference of 2329 cal, a K value of ~52, and a product mixture of 98% *syn* and 2% *anti*. The most realistic situation is to "correct" the neon potential curve by displacing it by the van der Waals internuclear distances (2.7 A for $H \cdots N$ and 2.9 A for $O \cdots N$) and reading the compression energy for the calculated distances (2.14 A for $H \cdots N$ and 2.05 A for $O \cdots N$). This approach yields a repulsion energy difference of 1.44 kcal, a total energy of 1849 cal, a K of ~23, or a product containing 96% *syn* and 4% *anti*. Experimental results have produced a mixture containing >99% *anti* isomer/1% *syn* isomer. This composition reflects a minimum energy of 2723 cal ($\Delta G = -RT \ln K$). As the preceding calculations indicate, the formation of the *syn* isomer should be favored by 1849 cal. Consequently, the electronic effect operating in these reductions must approach 4.5–4.6 kcal in magnitude.

(23) F. H. Westheimer, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp 529–532.