gents have been chiefly responsible for the elucidation of structure-activity correlations in proteins.

Continuing work on this project is concerned with the stereochemistry of the products **12** which have been prepared from optically active carbonyl compounds and dipeptides **11**.

Experimental Section[10]

General Procedure for the Preparation of Imidazolidinyl Peptides (12).—This procedure was used for the preparation of all of the imidazolidinyl peptides listed in Table I except that prepared from diglycine and cyclopentanone. The dipeptide free acid (10.0 mmol) was dissolved (or suspended) in a small amount of water and the resultant mixture was treated with 10 ml of 1 *N* NaOH. The aqueous solvent was removed by distillation under reduced pressure and the residual solid (dipeptide sodium salt, **11**) was found to be homogeneous by thin layer chromatography (the R_f of **11** was always greater than that of the dipeptide-free acid). The dipeptide sodium salt **11** (10.0 mmol) was dissolved in about 30 ml of methanol. The resultant solution was then treated with 20–25 mmol of the appropriate aldehyde or ketone and this was followed by heating of the reaction mixture to the reflux temperature for 3 hr. Thin layer chromatographic inspection indicated that an equilibrium between the reactants and the products was established during this time period and that further heating beyond 3 hr did not increase the yield of the products (usually two new tlc zones were observed with larger R_f values than those of the reactants). The reaction mixture (now light yellow to dark brown) was concentrated by distillation under reduced pressure until all of the solvent was removed. The oily residue was then dissolved in a minimum amount of MeOH–EtOAc or MeOH–acetone (both 50:50) and this solution was placed on a column of silica gel (E. Merck, 70–375 mesh). The column was eluted with the same solvent that was used to dissolve the oily residue. The w/w ratio of adsorbent to sample was about 66 to 1. The column fractions were collected and combined according to their thin layer chromatograms. Usually the original oily reaction product which was placed on the column was separated into two homogeneous products, one of which was obtained in a much greater yield than the other. The foregoing manipulations were performed as quickly as possible in order to avoid undue decomposition which was known to occur spontaneously with some of the products. The major product eluted from the column was usually an oil. It was stored in a desiccator (hygroscopic) for several hours, during which time it usually crystallized. Recrystallization was accomplished from a mixture of methanol and petroleum ether (bp 30–60°). Infrared, elemental analysis, and melting point data for the products are listed in Table I. Accurate calculations of yields were made in the experiments involving diglycine–isobutyraldehyde (57.5%), diglycine–cyclohexanone (36.0%), and diglycine–acetone (40.2%). The yields of products from the other experiments were estimated to be in the same range.

Condensation of Diglycine and Cyclopentanone. Preparation of an Imidazolidinyl Peptide in an Aqueous Medium.—Diglycine (10.0 mmol) and an equimolar amount of CH_3ONa were mixed and stirred in a small amount of dry methanol for a few minutes. The methanol was removed under reduced pressure and the residual solid (**11**, R^1, R^2 = H) was homogeneous according to tlc. This diglycine sodium salt and 10.0 mmol of cyclopentanone were added to 15 ml of distilled water and the resultant mixture was stirred at room temperature for 24 hr. After this time, the brownish-red product was isolated, chromatographed, crystallized, and recrystallized exactly as described in the general procedure. The physical constants for this product are listed in Table I. The estimated yield was similar to the yields obtained in the general procedure.

(10) Thin layer chromatograms of the reactions mixtures were run on 20 × 20 cm glass plates coated with a 250-μ thick layer of silica gel (Camag DF-5). Spotting was performed using 2 μl of a 1% solution and the developing solvent system was one of the following: methylene chloride–methanol (70–30 or 50–50) or ethyl acetate–methanol (50–50). The eluted zones were detected as colored areas after spraying with a 0.3% solution of ninhydrin in 1-butanol–2,4,6-collidine (95–5) followed by heating.

Acknowledgment.—Support of this work under a National Institutes of Health Research Project Grant No. AM 12761-03 is gratefully acknowledged.

Reactions of 7-*tert*-Butylnorbornadiene. Synthesis of *syn*- and *anti*-7-*tert*-Butylnorbornenes[1]

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7-*tert*-Butylnorbornadiene was synthesized from the corresponding 7-*tert*-butoxy compound and *tert*-butyllithium. Hydroboration and oxymercuration of the *tert*-butyldiene occurred exclusively with the sterically unencumbered anti double bond *via* exo,cis addition. Diimide reduction and catalytic hydrogenation occurred preferentially with the anti double bond even though both exo,cis and endo,cis additions were involved. The study of these various reactions has provided synthetic routes from the *tert*-butyl diene to the isomeric *syn*- and *anti*-7-*tert*-butylnorbornenes. The chemistry of 7-*tert*-butylnorbornadiene has been contrasted with that of norbornadienes substituted in the 7 position with an oxygen radical.

Previous papers from these and other laboratories have illustrated the preference of norbornadienes and norbornenes substituted in the 7 position with an oxygen-bearing substituent to experience electrophilic addition to the syn double bond[2–7] (eq 1). This preference has been ascribed to "chelation" of the entering electrophile by the syn double bond and the 7 substituent, which stabilizes the transition state.[3–5] In this way, the potentially adverse steric inhibition presented by the syn-7 substituents was overcome by this electronic effect.

The proposition was subsequently advanced that, in reactions where this electronic effect was nonoperative, steric factors would become dominant.[4] Catalytic hydrogenation of the syn and anti isomers was shown to be controlled by steric parameters ($k_{anti} \gg k_{syn}$); similar reduction of the norbornadiene derivatives was less sensitive to steric control and was influenced primarily by coordination control.[3,9]

(1) Presented in part at the 159th National Meeting of the American Chemical Society, Houston, Tex., Feb 1970, Abstract PETR 103.

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

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

(4) B. Franzus, W. C. Baird, Jr., E. I. Snyder, and J. H. Surridge, *J. Org. Chem.*, **32**, 2845 (1967).

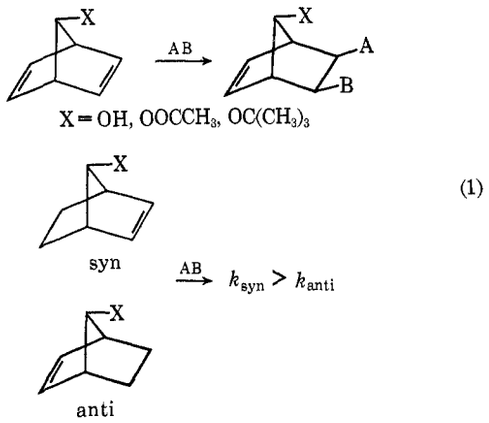
(5) W. C. Baird, Jr. and M. Buza, *ibid.*, **33**, 4105 (1968).

(6) G. W. Klumpp, A. H. Veefkind, W. L. de Graff, and F. Bickelhaupt, *Justus Liebigs Ann. Chem.*, **706**, 47 (1967).

(7) J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966).

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

(9) W. C. Baird, Jr., B. Franzus, and J. H. Surridge, *ibid.*, **34**, 2944 (1969).



(1)

Against this background an investigation of the reactions of norbornenes and norbornadiene substituted in the 7 position by a group that possessed a large steric requirement but no polar functionality was undertaken. This study was made possible by the availability of 7-*tert*-butylnorbornadiene[10] and by the development of synthetic routes to *syn*- and *anti*-7-*tert*-butylnorbornenes. This paper describes these syntheses and the various addition reactions of 7-*tert*-butylnorbornadiene that led to them. A subsequent paper will discuss the chemistry of the isomeric *tert*-butylnorbornenes.

Results and Discussion

7-*tert*-Butylnorbornadiene (**1**) was synthesized from 7-*tert*-butoxynorbornadiene and *tert*-butyllithium according to the procedure described by Wittig and Otten;[10] isolated yields ranged from 50 to 60%. The nmr spectrum of **1** (Table I) exhibited two features requiring comment. In contrast to other 7-substituted norbornadienes, both the syn (δ 6.34) and the anti (δ 6.80) vinyl hydrogens appeared as triplets; *i.e.*, the syn vinyl protons were not split by the anti-7 hydrogen as had been previously observed.[11] Since this long-range coupling was also absent in the spectrum of *syn*-7-*tert*-butylnorbornene (**2**), it was concluded that this criterion for configurational assignment of the 7 substituent with respect to the double bonds is not applicable to the 7-*tert*-butyl compounds. Secondly, the syn vinyl protons of **1** experienced a 24-Hz diamagnetic shift relative to the vinyl resonance of norbornadiene compared to an average shift of ~10 Hz for other 7-substituted norbornadienes.[10,11] The chemical shift difference between the syn and anti vinyl hydrogens of **1** was 27.6 Hz compared to an average value of 6 Hz. These spectral data clearly indicated that the 7-*tert*-butyl diene possessed unique structural features.

Catalytic hydrogenation, demonstrated previously to be sensitive to steric factors,[4,8,9] seemed a reasonable approach to the synthesis of *syn*-7-*tert*-butylnorbornene (**2**). Hydrogenation of 7-*tert*-butylnorbornadiene (**1**) proceeded as illustrated in Scheme I; product distribution as a function of catalyst is summarized in Table II. Unlike hydrogenation of the previously studied norbornadienes, reduction of the 7-*tert*-butyl compound yielded *syn*-7-*tert*-butylnorbornene (**2**) as the exclusive olefinic product. No anti isomer (**3**) was detected (within the limits of vpc analysis) at any time during

(10) G. Wittig and J. Otten, *Tetrahedron Lett.*, 601 (1963).
(11) E. I. Snyder and B. Franzus, *J. Amer. Chem. Soc.*, **86**, 1166 (1964).

TABLE I
NMR SPECTRA OF 7-*tert*-BUTYL COMPOUNDS

Compd	Proton type, δ (pattern, relative area [J]) HC=CH	CH	Exo >C<H	HC-*tert*-Bu	Endo >C<H	$(CH_3)_3C$	% exo,cis addition	% endo,cis addition
7-*tert*-Butylnorbornadiene (**1**)[a]	Anti 6.80 (t, 2 [5])							
	Syn 6.34 (t, 2 [5])	3.40 (m, 2)		2.48 (m, 1)		0.80 (s, 9)		
syn-7-*tert*-Butylnorbornene[a] (**2**)	5.66 (t, 2 [5])	2.68 (m, 2)	1.46–1.72 (m, 2)	1.39 (m, 1)	0.82–1.00 (m, 2)	0.78 (s, 9)		
anti-7-*tert*-Butylnorbornene (**3**)	6.10 (t, 2 [5])	2.71 (m, 2)	1.61–1.90 (m, 2)	1.38 (m, 1)	0.93–1.08 (m, 2)	0.88 (s, 9)		
7-*tert*-Butylnorbornane (**4**)		2.06 (m, 2)	1.36–1.90 (m, 4)	1.26 (m, 1)	1.00–1.20 (m, 4)	0.92 (s, 9)		
3-*tert*-Butylnortricyclane (**5**)		1.80 (m, 1)	1.52–1.62 (m, 1)	1.14–1.24 (m, 5)[b]	0.95–1.04 (m, 2)	0.86 (s, 9)		
5,6-Dideuterio-*syn*-7-*tert*-butylnorbornene (**6**)	5.75 (t, 2)	2.72 (m, 2)	1.63 (m, 1.2), (m, 0.8)[c]	1.41 (m, 1)	0.89 (m, 0.8), (m, 1.2)[c]	0.80 (s, 9)	40 60[c]	60 40[c]
2,3,5,6-Tetradeuterio-7-*tert*-butylnorbornane (**7**)		2.07 (m, 2)	1.40–1.76 (m, 2.8)	1.26 (m, 1)	1.06 (m, 1.2)	0.93 (s, 9)	30	70
			1.68 (m, 1.4)[c]		1.04–1.14 (m, 2.6)[c]		65[c]	35[c]
5,7-Dideuterio-3-*tert*-butylnortricyclane (**8**)		1.80 (m, 1)	1.55 (m, 1)	1.00–1.22 (m, 5)[b]		0.87 (s, 9)	0	100

[a] Nmr on neat samples; all others in $CDCl_3$. [b] *exo* $>CH_2$ (1), HC-*tert*-Bu (1), cyclopropyl H's (3). [c] Values from diimide reduction.

SCHEME I

REACTIONS OF 7-*tert*-BUTYLNORBORNADIENE

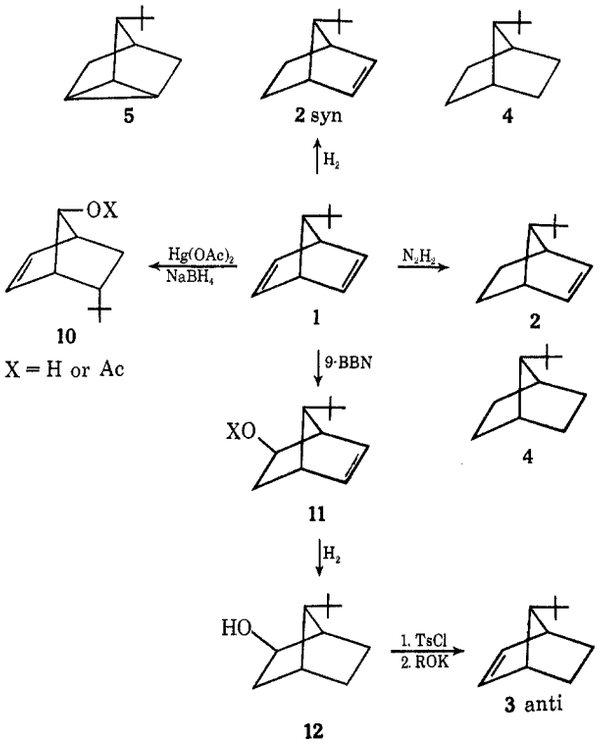


TABLE II

HYDROGENATION OF 7-*tert*-BUTYLNORBORNADIENE

	Product composition, %				
Catalyst	Diene 1	Syn 2	Satd 4	Nortricyclane 5	Method
Pd/C	17	57	14	12	*a*
HPd/C	33	38	7	22	*a, b*
HPd/C	3	91	0	7	*a, b, c*
Pd/C	0	0	88	12	*d*
HPd/C	0	0	72	28	*e*
PtO_2	21	58	18	2	*a*

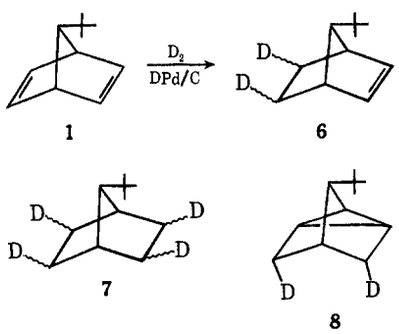
[a] Gas buret, H_2 consumption, 50–60% of theory. [b] Prereduced catalyst. [c] Norbornadiene present. [d] Parr hydrogenator, 30 psig, 100% reaction. [e] Brown hydrogenator, prereduced catalyst, 100% reaction.

the reaction, a reflection of remarkable selectivity for the sterically unhindered anti double bond of the diene. The failure to observe any anti isomer cannot be ascribed to its rapid reduction to 7-*tert*-butylnorbornane (**4**). The competitive rates of reduction of *syn*- and *anti*-7-*tert*-butylnorbornenes, $k_{anti}/k_{syn} \cong 9.6$, are too close to permit total destruction of any initially formed anti isomer by this process.[12,13]

The production of *syn*-7-*tert*-butylnorbornene (**2**) by hydrogenation was maximized by the addition of norbornadiene, or norbornene, to the reaction (Table II, line 3).[8,9] The relative rates of reduction of norbornene and **2** (~40:1) completely suppressed the hydrogenation of the latter to saturated product **4**. The synthesis of *syn*-7-*tert*-butylnorbornene by this procedure has provided isolated yields of 60–70%. Hydrogenation of the *tert*-butyl diene **1** in the presence of norbornadiene also failed to produce any anti isomer, thereby providing additional evidence for the absence of this potential reduction product.

Homoconjugative hydrogenation of 7-*tert*-butylnorbornadiene (**1**) produced 3-*tert*-butylnortricyclane (**5**) in amounts ranging from ~10% over platinum and nonprereduced palladium catalysts to ~30% over prereduced palladium. These yields and catalyst sensitivities were comparable to those observed for nortricyclene formation during the reduction of 7-acetoxy- and 7-*tert*-butoxynorbornadiene.[9] Such homoconjugative reduction is most reasonably ascribed to endocyclic catalyst–diene complexation followed by hydrogen transfer through a π-homoallylic metal–olefin complex.[14–16]

The stereochemistry of the hydrogenation of 7-*tert*-butylnorbornadiene (**1**) was assessed by utilizing deuterium as the reducing gas. The course of deuterium addition is summarized by eq 2, where the values in



(2)

	% D_2 distribution		
	6	7	8
exo,cis	40 (72)	30 (60)	
endo,cis	60 (28)	70 (40)	100 (100)

parentheses are for corresponding 7-acetoxy compounds.[9] The direction of deuterium addition was determined by nmr analysis (Table I).[17] Inspection of this comparative data has shown that this reduction has involved predominantly endo,cis addition. The results represent a departure from those obtained from the 7-acetoxy derivatives in that the roles of steric and coordination control have been reversed. The high level of endo,cis reduction of the anti olefinic bond of **1** was indicative of endocyclic coordination of this site with the catalyst. The preference of the anti bond for endo reduction is believed to reflect the development of structural strain in the exocyclic catalyst complex; the source of such strain may be bond angle deformation, or nonbonded interaction between the 7-*tert*-butyl group and the syn π orbitals. In view of this degree of endo reduction it was particularly significant that no endo,cis addition to the syn bond of the diene **1** to give anti-7-*tert*-butylnorbornene occurred. The failure to observe anti product is attributed to the desire to avoid steric repulsion between the *tert*-butyl group and the exo,cis 5,6 hydrogens generated by endocyclic reduction of the syn double bond.

The reduction of *syn*-7-*tert*-butylnorbornene (**6**) to tetradeuterated norbornane (**7**) was clearly sterically

(12) Anti product was present in cases where $k_{anti}/k_{syn} \cong 17$. See ref 9.

(13) For comparison, when the 7 substituent was methyl, $k_{anti}/k_{syn} \cong 2$: V. A. Mironov, B. D. Polkovinkov, E. P. Mikos, T. M. Fadeeva, and A. A. Akhrem, *Izv. Akad. Nauk SSSR, Ser. Khim. Nauk*, 118 (1970).

(14) D. R. Coulson, *J. Amer. Chem. Soc.*, **91**, 200 (1969).

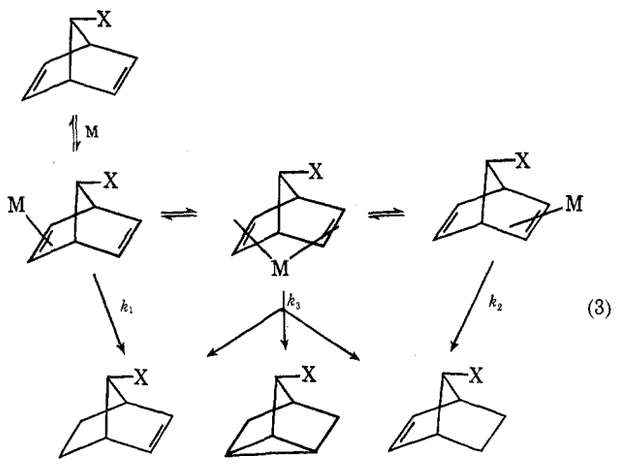
(15) M. Green and R. I. Hancock, *J. Chem. Soc. A*, 2054 (1967).

(16) H. A. Quinn, M. A. McKervey, W. R. Jackson, and J. J. Rooney, *J. Amer. Chem. Soc.*, **92**, 2922 (1970).

(17) For pertinent background, see ref 9, footnotes 12–15.

controlled and gave 80% endo,cis deuteration. The comparable reaction in the 7-acetate series occurred with 60% exo,cis addition.[9] In both cases the formation of the nortricyclic derivative was totally endocyclic.

Since the parent olefin, norbornadiene, did not experience either endocyclic or homoconjugative hydrogenation,[9] the presence of a 7 substituent must be a necessary condition for these reactions. A rationale for this behavior is suggested by eq 3, where the reacting system is considered to comprise equilibria between two isomeric exocyclic complexes and an endocyclic complex. In the case of norbornadiene (X = H), k_1 and $k_2 \gg k_3$, and homoconjugative and endocyclic reduction are not competitive. When X is acetoxy,



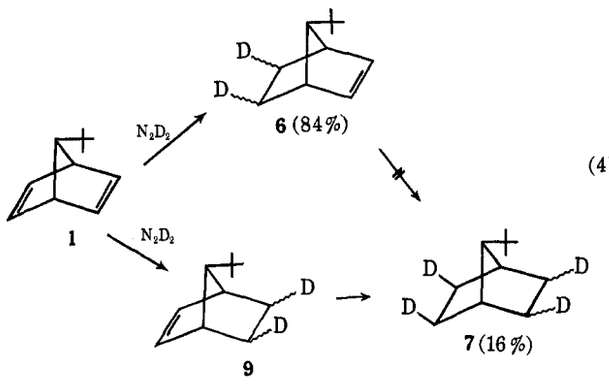
(3)

X = H, $OOCCH_3$, $OC(CH_3)_3$, $(CH_3)_3C$

tert-butoxy, or *tert*-butyl, this kinetic relationship is altered to the extent that k_3 becomes competitive and even dominant. The effect of the 7-oxy radicals on this situation may be ascribed to steric hindrance to reaction of the syn double bond and deactivation of the anti double bond through electron delocalization.[4,5] For 7-*tert*-butylnorbornadiene and other 7-alkyl derivatives,[13,18] steric shielding of the syn bond is obviously important; the influence of the 7-*tert*-butyl group on the reactivity of the anti bond cannot be ascribed to delocalization and must involve the strain factors cited above.

The reduction of 7-*tert*-butylnorbornadiene (**1**) to *syn*-7-*tert*-butylnorbornene (**2**) in 84% selectivity was accomplished with the chemical reducing agent diimide (Scheme I). While this high degree of selectivity was in accord with the sensitivity of diimide reduction to steric approach control,[19] the formation of *anti*-7-*tert*-butylnorbornene (**3**) and 7-*tert*-butylnorbornane (**4**) as by-products was totally unexpected. Control experiments showed that, although the syn olefin **2** was passive to diimide, the anti isomer **3** was reduced to 7-*tert*-butylnorbornane (**4**).

In order to study this reaction in detail the reduction was carried out using dideuteriodiimide;[3] eq 4 illustrates the results. The observed level of endo,cis reduction was without precedent and represented a



(4)

	% D_2 distribution		
	6	**9**	**7**
exo,cis	60	30	65
endo,cis	40	70	35

complete departure from normal diimide reactions. The deuterium distribution in **6** has shown that the reduction of the *tert*-butyl diene has involved endocyclic diimide attack in addition to the anticipated exocyclic reaction. While **6** was not the precursor of **7**, it has been demonstrated that this endocyclic reaction produced *anti*-7-*tert*-butylnorbornene, which was subsequently rapidly reduced to saturated product.[20] Control experiments have shown that the anti isomer is reduced with 100% exo,cis addition (eq 4). This fact, coupled with the overall deuterium distribution found in tetradeuterio-7-*tert*-butylnorbornane (**7**), has indicated that the formation of dideuterio-*anti*-7-*tert*-butylnorbornene (**9**) has involved both endocyclic (70%) and exocyclic (30%) reduction of the syn double bond of the diene.

The failure of *syn*-7-*tert*-butylnorbornene (**2**) to yield 7-*tert*-butylnorbornane (**4**) is ascribed to the hindrance to exo attack by the *tert*-butyl group and to endo attack by the endo 5,6 hydrogens. That the syn double bond of the diene **1** did experience a small degree of exocyclic reduction (5% of the total reaction) is believed to reflect a more favorable geometric disposition between the *tert*-butyl group and the six-membered cyclic transition state involved in diimide reductions.[21,22]

Since direct conversion of 7-*tert*-butylnorbornadiene (**1**) to *anti*-7-*tert*-butylnorbornene (**3**) by chemical or catalytic reduction was clearly not feasible, the reaction sequence shown in Scheme I was selected as a route to this olefin. Oxymercuration of norbornenes and norbornadienes had been shown to occur exo,cis, to be free of rearrangements, and to occur on the less hindered side of the molecule;[23] consequently, oxymercuration appeared to provide a useful synthesis of *exo*-5-hydroxy-*syn*-7-*tert*-butylnorbornene-2 (**11**). While nmr experiments[24] confirmed that the oxymercuration reaction had occurred exo,cis with the anti double bond of the *tert*-butyl diene, borohydride reduction of the

(18) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 201 (1970).

(19) 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., Int. Ed. Engl.*, **4**, 271 (1965); (c) F. Aylward and M. Sawistowska, *Chem. Ind. (London)*, 484 (1962).

(20) Such a sequence has been observed in the 7-acetoxy series.[3]

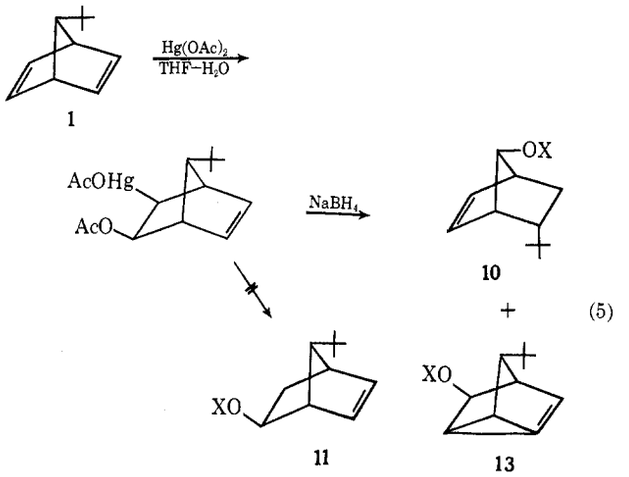
(21) E. J. Corey, W. L. Mock, and D. J. Pasto, *J. Amer. Chem. Soc.*, **83**, 2957 (1961).

(22) Diimide reduction of 7,7-dimethylnorbornene also gave exo,cis addition: H. C. Brown, J. H. Kawakami, and K.-T. Liu, unpublished results. The authors thank Professor Brown for a preprint of these data.

(23) (a) H. C. Brown and P. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967); (b) H. C. Brown and W. J. Hammar, *ibid.*, **89**, 1524 (1967); (c) H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **89**, 1525 (1967); (d) T. G. Traylor and A. W. Baker, *ibid.*, **85**, 2746 (1963).

(24) H. C. Brown, M.-H. Rei, and K.-T. Liu, *ibid.*, **92**, 1760 (1970).

organomercurial[23a] did not yield any of the desired alcohol (**11**). The reaction had proceeded as shown by eq 5 to give an 80% yield of *endo*-5-*tert*-butyl-*anti*-7-



hydroxynorbornene-2 (**10**), a product of the now well-established radical rearrangement encountered in the borohydride reduction of such norbornenyl mercurials.[25] A 12% yield of by-product was also formed, which has been arbitrarily assigned the nortricyclic structure **13**; a sample of sufficient purity to permit accurate identification could not be obtained, but the formation of **13** would be consistent with known chemistry.[5,25,26] The exclusion of **11** from the product mixture and the sixfold dominance of **10** over **13** have not been observed in the previous studies cited. Since the products are derived from hydrogen transfer to rapidly equilibrating norbornenyl $\rightleftharpoons$ nortricyclyl radicals,[25d] it was apparent that in this case the radical precursor to **10** was the preferred thermodynamic species by virtue of being the least strained configuration.

Hydroboration of 7-*tert*-butylnorbornadiene (**1**) with 9-BBN[27] produced the desired exo 5-alcohol **11** (Scheme I) in 90% yield. Catalytic hydrogenation and tosylation gave the exo tosylate of **12** in 81% yield. Attempts to induce elimination with potassium *tert*-butoxide in dimethyl sulfoxide were unsuccessful. Dehydrotosylation with the potassium salt of 2-cyclohexylcyclohexanol[28] gave a 47% yield of *anti*-7-*tert*-butylnorbornene (**3**); the overall yield from 7-*tert*-butylnorbornadiene was 34%.

In summary, synthetic routes to *syn*- and *anti*-7-*tert*-butylnorbornenes from a common precursor, 7-*tert*-butylnorbornadiene, have been realized. In general, additions to the *tert*-butyl diene have shown a marked preference for the sterically unhindered anti double bond in contrast to the syn double bond reactions experienced by 7-oxy substituted norbornadienes. Additions to the anti double bond involving cyclic transition states (hydrogenation, diimide reduction) have exhibited both exocyclic and endocyclic stereochemistry, the degree of each being determined by the steric and strain demands of the reacting species. Hydroboration with 9-BBN, which also involves a cyclic mechanism, occurred only exo due to the reluctance of the system to accommodate such a bulky reagent in an endocyclic configuration. Finally, these results have reinforced the view that the principles governing the reactions of the parent olefin, norbornadiene, cannot be applied indiscriminately to those of its derivatives.[9]

(25) (a) G. A. Gray and W. R. Jackson, *J. Amer. Chem. Soc.*, **91**, 6205 (1969); (b) G. M. Whitesides and J. San Filippo, Jr., *ibid.*, **92**, 6611 (1970); (c) V. M. A. Chambers, W. R. Jackson, and G. W. Young, *Chem. Commun.*, 1275 (1970); (d) G. A. Gray, W. R. Jackson, and V. M. A. Chambers, *J. Chem. Soc. C*, 200 (1971).

(26) K. Pande and S. Winstein, *Tetrahedron Lett.*, 3393 (1964).

(27) E. F. Knights and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 5200 (1968).

(28) H. C. Brown, J. H. Kawakami, and S. Misumi, *J. Org. Chem.*, **35**, 1360 (1970).

Experimental Section

Infrared spectra were recorded on a Beckman IR-5A spectrophotometer. Nmr spectra were recorded on Jeol Minimar, Varian Associates A-60, and Varian Associates HA-100 spectrometers using tetramethylsilane as an internal standard. Analytical vapor phase chromatography (vpc) was performed on a Perkin-Elmer 154D fractometer and a Perkin-Elmer Model 226 capillary gas chromatograph. Preparative scale vpc was performed on a Varian Aerograph Model A-700. Melting points and boiling points are not corrected. All reagents were obtained from commercial sources and were used as received.

7-*tert*-Butylnorbornadiene (1).[10]—To a 500-ml round-bottom flask equipped with a stirrer, a thermometer, a dropping funnel, and a reflux condenser were added under nitrogen 81 ml of a 1.24 *M* solution of *tert*-butyllithium in *n*-pentane (0.1 mol)[29] and 160 ml of dry *n*-pentane. A solution of 16.4 g (0.1 mol) of 7-*tert*-butoxynorbornadiene[30] in 100 ml of dry *n*-heptane was added dropwise with stirring at −20° over a period of 2 hr. The reaction mixture was allowed to warm to room temperature. The pentane was removed by distillation, and simultaneously 100 ml of dry *n*-heptane was added. The reaction was stirred and refluxed for 2 hr. The reaction was cooled to 0° and 10 ml of isopropyl alcohol was added. The heptane solution was washed twice with 125-ml portions of water and dried over magnesium sulfate. The solvent was removed on a rotary evaporator at 40° (50 mm), and the residue was distilled through a Monel spiral Todd column to give 8.0 g (54%) of 7-*tert*-butylnorbornadiene, bp 98–100° (85 mm), n^{20}D 1.4702 (lit.[10] n^{20}D 1.4718). Vpc analysis (4 m × 0.25 in. 20% squalane column, 160°, 70 ml/min helium) gave a single peak, retention time 25 min, purity 98%.

Anal. Calcd for $C_{11}H_{16}$: C, 89.18; H, 10.82. Found: C, 89.12; H, 10.86.

The nmr spectrum is included in Table I.

Hydrogenation of 7-*tert*-Butylnorbornadiene.—Into a gas buret hydrogenation assembly were placed 8 ml of methanol and 106 mg of 10% palladium on charcoal. The catalyst was exposed to hydrogen, and a solution of 2.34 g (14.2 mmol) of 7-*tert*-butylnorbornadiene in 10 ml of methanol was injected through a septum. After ~73% of the theoretical quantity of hydrogen had been absorbed, a 7-ml sample was withdrawn. The vpc analysis of the product is given in Table III.

TABLE III

Compd	Retention time (min from air) a	Retention time (min from air) b	Per cent
7-*tert*-Butylnorbornadiene (1)	25.0	14.2	0
syn-7-*tert*-Butylnorbornene (2)	26.5	13.7	57
3-*tert*-Butylnortricyclane (5)	35.0	16.5	29
7-*tert*-Butylnorbornane (4)	38.5	17.0	14

[a] 4 m × 0.25 in. 20% squalane, 160°, 70 ml/min. [b] 300 ft × 0.01 in. DC-550 silicone, 115°, 30 psig.

No *anti*-7-*tert*-butylnorbornene (**3**) was detected in an amount exceeding 1%. The syn isomer (retention time 26.5 min) was separated in >98% purity on a 12 ft × 0.375 in. 20% SE-30 silicone column at 160° and 110 ml/min and was shown to be identical with an authentic sample.

The remainder of the reaction mixture was hydrogenated to completion to give a mixture of 3-*tert*-butylnortricyclane (29%)

(29) Foote Mineral Co., Exton, Pa.

(30) Frinton Laboratories, Vineland, N. J.

and 7-*tert*-butylnorbornane (71%). The two hydrocarbons were separated by preparative vpc (20 ft × 0.375 in. 20% squalane column, 160°, 110 ml/min) to give samples of >98% purity. The nmr data are presented in Table I.

7-*tert*-Butylnorbornane (**4**) had n^{20}D 1.4650. *Anal.* Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.47; H, 13.50.

3-*tert*-Butylnortricyclane (**5**) had n^{20}D 1.4666. *Anal.* Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 87.70; H, 12.27.

The influence of various catalysts and catalyst prereduction on the hydrogenation of 7-*tert*-butylnorbornadiene was evaluated by previously described techniques.[4] Representative data are shown in Table II.

A sample of the 7-*tert*-butyl diene (**1**) was reduced with deuterium according to the procedure described above. The products were separated by preparative vpc to provide individual samples of the deuterated hydrocarbons **6**, **7**, and **8** in 98% purity. The nmr data are summarized in Table I. Analysis of the exo,endo proton areas gave a measure of the relative amounts of exo,cis and endo,cis deuterium addition;[17] these values are listed in Table I.

***syn*-7-*tert*-Butylnorbornene (2).**—In a gas buret apparatus a mixture of 215 mg of 10% palladium on charcoal, 4.0 g (43.5 mmol) of norbornadiene, and 3.0 g (20.2 mmol) of 7-*tert*-butylnorbornadiene (**1**) in 50 ml of methanol was hydrogenated at ambient conditions. The hydrogenation was taken to ~70% of completion (~2.2 l. of hydrogen). In a duplicate run 2.5 g (17.0 mmol) of **1** was reduced. The combined reaction mixtures were filtered, and the filtrate was added to 250 ml of water. The hydrocarbons were extracted with pentane (three 50-ml portions), and the combined extracts were dried over magnesium sulfate. The pentane, norbornene, and norbornane were removed by distillation through a Monel spiral Todd column. The residue (3.7 g) was heated at 100°(90 mm) on the Todd assembly to sublime residual norbornane. Distillation of the residue gave 3.5 g (64%) of *syn*-7-*tert*-butylnorbornene, bp 102° (90 mm), n^{20}D 1.4654. Vpc analysis on a capillary column (see above) gave a product peak at 13.7 min, purity 89.5%. The nmr spectrum is presented in Table I.

Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 87.63; H, 12.30.

Diimide Reduction of 7-*tert*-Butylnorbornadiene.—To a stirred solution of 2.0 g (13.5 mmol) of 7-*tert*-butylnorbornadiene (**1**) and 2.9 g (15.0 mmol) of potassium azodicarboxylate in 5 ml of methanol-d_1 was added dropwise a solution of 1.85 g (30 mmol) of acetic acid-d_1 in 10 ml of methanol-d_1. The reaction was stirred at room temperature under nitrogen for 30 min; a second charge of diimide (7.5 mmol of potassium azodicarboxylate and 15 mmol of acetic acid-d_1) was added to ensure total reduction of the diene. The reaction was poured into water and extracted with pentane. Removal of the pentane by distillation gave 1.43 g (71%) of product which contained 83.5% 5,6-dideuterio-*syn*-7-*tert*-butylnorbornene (**6**) and 16.5% 2,3,5,6-tetradeuterio-7-*tert*-butylnorbornane (**7**). The two hydrocarbons were separated by vpc (SE-30 silicone column) to give individual samples of 99% purity. The nmr spectra are given in Table I with the deuterium distribution noted.

To a mixture of 3.0 g (20.3 mmol) of 7-*tert*-butylnorbornadiene and 5.8 g (30.0 mmol) of potassium azodicarboxylate in 15 ml of methanol was added a solution of 3.6 g (60 mmol) of acetic acid in 15 ml of methanol. The acetic acid solution was added in three equal portions, and a sample of the reaction was withdrawn subsequent to each addition. The sample was shaken with water and pentane, and the pentane layer was analyzed by vpc (200 ft × 0.02 in., 50% phenylsilicone–50% nitrile silicone column, 70°, 16 psig). The results are summarized in Table IV.

TABLE IV

Sample	Product distribution, %[c] Diene (1)	syn (2)	anti (3)	Satd (4)
1	50	41	5	4
2	32	57	4	7
3	21	65	3	11
4[a]	0	83	2	15
5[b]	0	84	0	16

[a] Sampled 30 min after sample 3. [b] Additional 0.5 g of potassium azodicarboxylate added. [c] Retention time, minutes from C_5H_{12}: diene, 11.0; syn, 10.5; anti, 12.5; satd, 13.5.

The reaction mixture was added to 25 ml of water and was extracted twice with pentane. The extract yielded 2.4 g of product.

Hydroboration of 7-*tert*-Butylnorbornadiene.—To 40 ml of 0.78 *M* 9-BBN[27] in tetrahydrofuran was added dropwise a solution of 4.5 g (30.4 mmol) of *tert*-butyl diene (**1**) in 15 ml of tetrahydrofuran. The reaction was stirred under nitrogen for 20 min at room temperature; 15 ml of 6 *N* sodium hydroxide and 12 ml of 30% hydrogen peroxide were added, and the reaction was refluxed for 1 hr. The reaction mixture was saturated with sodium chloride, and the tetrahydrofuran layer was separated and dried over magnesium sulfate. The ether was removed by distillation, and the residue was slurried with pentane. The slurry was washed with water, and the pentane layer was separated and dried. The pentane was removed by distillation to give 4.5 g (90%) of *exo*-5-hydroxy-*syn*-7-*tert*-butylnorbornene-2 (**11**), crude mp 64–69°. Purification by sublimation at 80° (150 mm) gave white needles, mp 63.5–64.5°.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.34; H, 10.90. Found: C, 79.13; H, 10.72. Nmr ($CDCl_3$) δ 5.85 (m, 2, HC=CH), 3.80 (m, 1, J = 11.3 Hz, endo HCO), 2.56 (s, 1, OH), 2.50–2.83 (m, 2, >CH), 2.14 (m, 1, exo >CH_2), 1.20–1.66 (m, 2, endo >CH_2, HC-*tert*-Bu), 0.85 [s, 9, $(CH_3)_3C$].

***exo*-2-Hydroxy-*anti*-7-*tert*-butylnorbornane (12).**—The unsaturated alcohol (4.5 g) was hydrogenated in 75 ml of methanol over 200 mg of 10% palladium on charcoal. The product was isolated by dilution with water and pentane extraction; the yield of saturated alcohol was 4.3 g (98%), mp 84.5–85.5° (after sublimation). Acetylation with acetyl chloride–pyridine gave a single ester, retention time 21 min (from $CDCl_3$) on a 300 ft × 0.01 in. DC-550 silicone column, 150°, 30 psig.

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.30; H, 11.71. Nmr ($CDCl_3$) δ 3.68 (m, 1, J = 11.5 Hz, HCO), 2.16 (s, 1, OH), 1.94–2.28 (m, 2, >CH), 1.03–1.91 (m, 7, exo >CH_2, endo >CH_2, HC-*tert*-Bu), 1.00 [s, 9, $(CH_3)_3C$].

A solution of 3.6 g (21.4 mmol) of *exo*-2-hydroxy-*anti*-7-*tert*-butylnorbornane (**12**) in 60 ml of pyridine was cooled to 0°, and freshly purified tosyl chloride (8.4 g, 44 mmol) was added with stirring. The mixture was stored at 0° for 16 hr, poured into 200 ml of water, and extracted with ether (four 50-ml portions). The combined extracts were washed with cold 10% hydrochloric acid and water and were dried over magnesium sulfate. The ether was removed under vacuum at 30° to give 5.6 g (82%) of the tosylate as a viscous, pale yellow oil. The tosylate was recrystallized with difficulty from pentane at −60°; the tosylate was insufficiently stable to permit accurate elemental analysis. Nmr ($CDCl_3$) δ 7.76, 7.30 (m, 4, aromatic H's), 4.32 (m, 1, J = 11.5 Hz, HCO), 2.41 (s, 3, CH_3–), 2.19 (m, 2, >CH), 0.95–2.00 (m, 7, exo,endo >CH_2, HC-*tert*-Bu), 0.90 [s, 9, $(CH_3)_3C$].

***anti*-7-*tert*-Butylnorbornene (3).**—For preparative purposes the tosylate described above was stored at 0° in ethereal solution until needed. The dehydrotosylation was a modification of the procedure described by Brown.[28] To 20 g of 2-cyclohexylcyclohexanol and 10 ml of 1,4-diisopropylbenzene was added 2.6 g of potassium. The reaction was heated at 130° until all of the potassium had dissolved. The solution was cooled to room temperature, and a solution of the tosylate prepared from 4.7 g (28 mmol) of **12** in 10 ml of 1,4-diisopropylbenzene was added. The reaction was stirred vigorously and was rapidly heated to 140° and maintained at this temperature for 1 hr. The cooled reaction mixture was poured into 150 ml of water and extracted three times with 50-ml portions of pentane. The extract was dried over magnesium sulfate, and the pentane was removed by distillation. The residue was distilled at 130° (60 mm) through a Monel spiral Todd column; 11–12 ml of distillate was collected and redistilled to give 1.95 g of *anti*-7-*tert*-butylnorbornene, bp 107° (87 mm), vpc purity 85%. The olefin was purified by preparative vpc (10 ft × 0.375 in. 3% Dowfax on Chromosorb W, 120°, injector and detector at 250°, 200 ml/min helium) to give 1.2 g of 97% pure material, n^{20}D 1.4721. Vpc (2 m × 0.25 in. 20% polypropylene glycol column, 175°, 80 ml/min) gave a single peak, retention time 5.4 min. The yield based on starting alcohol was 47%. The nmr spectrum is listed in Table I.

Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 88.05; H, 12.07.

Oxymercuration of 7-*tert*-Butylnorbornadiene.—To a stirred suspension of 1.6 g (5 mmol) of mercury(II) acetate in 5 ml of water and 2.5 ml of tetrahydrofuran was added 700 mg (4.7 mmol) of 7-*tert*-butylnorbornadiene in 2.5 ml of tetrahydrofuran. The reaction decolorized in ~60 sec; stirring was continued for

15 min. The reaction was decomposed with sodium hydroxide–sodium borohydride[23a] and worked up in the usual manner.[5] The crude product was acetylated with acetyl chloride–pyridine to give 900 mg (92%) of acetate ester. Vpc analysis (300 ft × 0.01 in. DC-550 silicone column, 115°, 30 psig) gave a mixture of two esters, retention time 30.0 min (87%) and 34.5 min (13%). Neither ester was shown by comparative vpc to be *exo*-5-acetoxy-*syn*-7-*tert*-butylnorbornene-2 (**11**), retention time 27.5 min (from hydroboration of **1**). A pure sample of the major ester was separated by preparative vpc (10 ft × 0.375 in. 20% FFAP column, 170°, 110 ml/min) and was shown by nmr to be *endo*-5-*tert*-butyl-*anti*-7-acetoxynorbornene-2 (**10**).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.68; H, 9.57. Nmr ($CDCl_3$) δ 5.96 (m, 2, HC=CH), 4.26 (m, 1, J = 5 Hz, HCO), 2.50–2.88 (m, 2, >CH), 2.03 (s, 3, CH_3CO), 1.60–1.88 (m, 2, exo $>CH_2$), 0.95 (s, 1, endo $>CH_2$), 0.80 [s, 9, $(CH_3)_3C$].[31]

(31) The position and stereochemistry of the *anti*-7-acetoxy group was established by comparative nmr with other acetoxynorbornenes.[11]

The reaction of the 7-*tert*-butyldiene with mercury(II) trifluoroacetate in benzene-d_6 was studied by nmr.[24] The spectrum of the diene was immediately replaced by that of the exo,cis mercuration adduct of the anti double bond: δ 5.80 (dq, 2, HC=CH), 4.85 (d, 1, HCO, J = 8 Hz), 2.93 (m, 2, >CH), 2.30 (d, 1, HgCH, J = 8 Hz), 2.20 (s, 1, HC-*tert*-Bu), 0.86 [s, 9, $(CH_3)_3C$]. An identical experiment with norbornadiene gave the following nmr spectrum: δ 6.00 (dq, 2, HC=CH), 4.88 (d, 1, HCO, J = 8 Hz), 2.90 (m, 2, >CH), 2.18 (d, 1, HCHg, J = 10 Hz), 1.50 (s, 2, $>CH_2$). Both spectra were unchanged after 24 hr at room temperature.[32]

Registry No.—**1**, 32640-82-7; **2**, 32640-83-8; **3**, 32640-84-9; **4**, 32640-85-0; **5**, 32670-72-7; **10**, 32640-90-7; **11**, 32640-91-8; **12**, 32640-86-1; **12** (tosylate), 32640-87-2; exo,cis mercuration adduct of the anti double bond, 32640-89-4; adduct of norbornadiene and mercury(II) trifluoroacetate, 32640-88-3.

(32) The authors thank Dr. R. L. Hartgerink for these nmr measurements.

Notes

Formation of (Alkoxymethylene)dimethylimmonium Halides in the Reactions of Triphenylphosphine Dihalides with Alcohols in Dimethylformamide

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The reaction of triphenylphosphine dihalides with alcohols to give halides[1] is a useful synthetic procedure.[2] The reaction mechanism in acetonitrile has been proposed as shown in eq 1.[3] The reaction may also pro-

$$R_3PX_2 + R'OH \xrightarrow{\text{fast}} R_3\overset{+}{P}OR' + \overset{-}{X}HX \xrightarrow{\text{slow}} R_3P{=}O + R'X + HX \quad (1)$$

ceed satisfactorily when dimethylformamide (DMF) is used as the solvent.[1,2] We report here a second pathway followed by this reaction when done in DMF.

When *N*-benzoyl-*N*-methyl-4-hydroxyadamantan-1-amine[4] (**1**) is allowed to react with triphenylphosphine dibromide in DMF at ice-bath temperatures, a crystalline precipitate forms. The spectral and analytical properties of this relatively stable product were not consistent with the expected bromide structure **4**. Instead, elemental analysis showed that, in addition to bromine, the empirical formula had also gained the elements of C_3H_6N. The nmr spectrum suggested that part of this gain could be accounted for by two methyl groups attached to a heteroatom such as nitrogen. The infrared spectrum showed the absence of an OH bond and a new strong absorption band at 1710 cm^{-1}. These data suggested that the product had structure **2a**, an (alkoxymethylene)dimethylimmonium bromide. Structure **2** is, in fact, an immomium ether halide, a structural type for which considerable precedent exists.[5] For example, an analogous structure has been assigned to the salts obtained from the reaction of dimethylformiminium chloride with either *tert*-butyl alcohol or dimethylbenzylcarbinol, although the products were characterized by elemental analyses only.[5c] Related structures have frequently been postulated[6] and occasionally isolated[7] as intermediates in Vilsmeyer formylation reactions.

Consistent with structure **2a** was the observation that the compound was water soluble and was rapidly hydrolyzed, giving formate ester **3** as the product. The structure of **3** was apparent from the elemental analyses and the infrared spectrum (ester carbonyl at 1730 cm^{-1}), as well as the fact that it underwent further hydrolysis under alkaline conditions to give the starting alcohol **1**. The latter result shows that the configuration of the oxygen substituent in **1** has been retained throughout these transformations.

An (alkoxymethylene)dimethylimmonium iodide intermediate (**2b**) also formed when iodine was used in the reaction instead of bromine. Formate ester **3** was also obtained from this intermediate upon hydrolysis.

An intermediate of the above type apparently formed when the diol 1-benzoyl-1-methyl-4,6-dihyroxyadaman-

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