stated there. Recovery was essentially quantitative. The percentage composition determined by GLC was **9:10,** 90.2:9.8. The composition determined by NMR analysis was **9:10,** 87:13.

B. In Glyme. Ester **9** (1 mmol) was substituted for bromo ketone **6** in the procedure given above for the Favorskii reaction of the latter in glyme. The procedure used was identical and the recovered ester (~100%) was analyzed: by GLC, **9:10,** 58.1:41.9; by NMR, **9:10,** 60:40.

Acknowledgment. The authors thank Dr. R. S. Egan and Ms. R. Stanaszek of Abbott Laboratories for their assistance in the NMR aspects of this work.

Registry No.—**2,** 54143-19-0; **4,** 13351-26-3; **6,** 54143-20-3; **6** DNP, 54143-21-4; **7,** 54164-79-3; **7** DNP, 54164-80-6; **8,** 54143-22-5; **8** Cl, 54143-23-6; **9,** 54143-24-7; **10,** 54164-81-7; **10** free acid, 54274-40-7; 2,4-DNP derivative of (a)-2-ethoxybenzo[6,7]bicyclo[3.2.1]oct-6-en-3-one, 54143-25-8; phenyltrimethylammonium tribromide, 4207-56-1.

References and Notes

(1) Taken from the M.S. Thesis of R.R.R., 1973. Portions of this work were presented at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973, Abstracts, No. ORGN 26.
(2) Reviews: (a) R. Jacquier, *Bull. Soc. Chim. Fr.*, **17,** 35 (1950); (b) A. S. Kende, *Org. React.*, **11,** 261 (1960).
(3) E. W. Warnhoff, C. M. Wong, and W. T. Tai, *J. Am. Chem. Soc.*, **90,** 514 (1968); W. C. Fong, R. Thomas, and K. V. Scherer, Jr., *Tetrahedron Lett.*, 3789 (1971).
(4) Dr. P. J. Chenier at the University of Wisconsin—Eau claire has found that *exo*-3-bromobenzonorbornenone-2 undergoes Haller–Bauer cleavage and not Favorskii ring contraction upon treatment with sodium hydroxide in tetrahydrofuran. We thank Dr. Chenier for this information prior to publication.
(5) Stereospecificity under certain conditions has been previously observed.[6]
(6) G. Stork and I. J. Borowitz, *J. Am. Chem. Soc.*, **82,** 4307 (1960).
(7) H. O. House and W. F. Gilmore, *J. Am. Chem. Soc.*, **83,** 3980 (1961).
(8) (a) P. T. Lansbury and E. J. Nienhouse, *J. Am. Chem. Soc.*, **88,** 4290 (1966); (b) P. T. Lansbury, E. J. Nienhouse, D. J. Scharf, and F. R. Hilfiker, ibid., **92,** 5649 (1970). We thank Professor Lansbury for detailed information on this synthesis early in our studies.
(9) The formation of **2** was first noticed in our work by F. Guziec, Senior Research Report, 1968. Lansbury and Nienhouse[8a] claimed its absence.
(10) (a) C. W. Jefford and B. Waegell, *Tetrahedron Lett.*, 1981 (1963); (b) B. Waegell and C. W. Jefford, *Bull. Soc. Chim. Fr.*, 844 (1964); (c) A. Baretta, J. P. Zahra, B. Waegell, and C. W. Jefford, *Tetrahedron*, **26,** 15 (1970).
(11) J. W. Wilt and P. J. Chenier, *J. Org. Chem.*, **35,** 1562 (1970).
(12) (a) An ethyl ester, possibly the ethyl ester analog of **10,** was reported by K. Alder and M. Fremery, *Tetrahedron*, **14,** 190 (1961), as the adduct of isoindene (generated in situ) and ethyl acrylate. A 20% yield was claimed, with support for structure from an unreported spectrum. Its configuration was not discussed. We have been unable to duplicate this work. (b) J. W. Wilt and V. Narutis, *J. Org. Chem.*, submitted for publication. In brief, the sequence involved the construction of a benzo ring onto the skeletal framework of norbornene-*endo*-2-carboxylic acid, followed by esterification to **10.**
(13) Lansbury and coworkers[8b] report the allylic methylene group at δ 2.48, with no mention of the AB multiplet.
(14) It has been our experience that small amounts of **2** can go undetected in **1.** The NMR differences reported[15] between 1- and 3-methylindene which were employed as corroborative evidence by Lansbury and Nienhouse[8a] for the absence of **2** do not relate well to the differences between **1** and **2.**
(15) A. Bosch and R. K. Brown, *Can. J. Chem.*, **42,** 1718 (1964).
(16) N. B. Kupletskaya, A. V. Dombrovskii, and A. P. Terent'ev, *Zh. Obshch. Khim.*, **27,** 3041 (1957).
(17) K. E. Teo and E. W. Warnhoff, *J. Am. Chem. Soc.*, **95,** 2728 (1973).
(18) J. W. Wilt, G. Gutman, W. J. Ranus, Jr., and A. R. Zigman, *J. Org. Chem.*, **32,** 893 (1967).
(19) For a pertinent, recent article with many leading references where the spectral features of cyclic α-bromo ketones are developed in detail, see C. W. Jefford, R. McCreadie, P. Muller, and J. Pfyffer, *J. Chem. Educ.*, **50,** 181 (1973).
(20) We thank Dr. R. Egan and Ms. R. Stanaszek of Abbott Laboratories, North Chicago, Ill., for the decoupling experiments. Details of these experiments and of a LAOCN 3 computer-calculated spectrum of **6** are available in the thesis of R.R.R.
(21) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, Elmsford, N.Y., 1969, p 284. Cf. also K. G. R. Pachler, *Tetrahedron Lett.*, 1955 (1970).
(22) Cf. F. Ramirez and A. F. Kirby, *J. Am. Chem. Soc.*, **75,** 6026 (1953); **74,** 4331 (1954).
(23) For skeletal rearrangements in this system, see P. T. Lansbury and N. T. Boggs, III, *Chem. Commun.*, 1007 (1967); P. T. Lansbury and E. J. Nienhouse, ibid., 1009 (1967).
(24) Reference 21, p 289.
(25) The same effect has been observed for the methyl resonances of exo (δ 2.15) and endo (δ 1.87) 2-acetylbenzonorbornenes by R. R. Sauers and A. M. De Paolis, *J. Org. Chem.*, **38,** 639 (1973).
(26) Bordwell and coworkers have been largely responsible for the development of the detailed reaction sequence. For a recent paper, cf. F. G. Bordwell and J. G. Strong, *J. Org. Chem.*, **38,** 579 (1973).
(27) J. M. Conia and J. Salaün, *Tetrahedron Lett.*, 1175 (1963); *Bull. Soc. Chim. Fr.*, 1957 (1964).
(28) Our results do not *preclude* an "abnormal" pathway to the esters, but enolizable bromo ketones usually follow the "normal" pathway.
(29) Complete spectra may be found in the M.S. Thesis of R.R.R., 1973.
(30) Cf. (chloroallyl)indene **1,** λ_{max} (hexane) 243 nm (ϵ 13,110).

Addition of Diphenyldiazomethane to 7-*tert*-Butoxynorbornadiene. Formation of *exo*- and *endo*-3,3-Diphenyltricyclo[3.2.1.$0^{2,4}$]octene Derivatives[1,2]

James W. Wilt* and Daniel R. Sullivan

Department of Chemistry, Loyola University of Chicago, Chicago, Illinois 60626

Received October 11, 1974

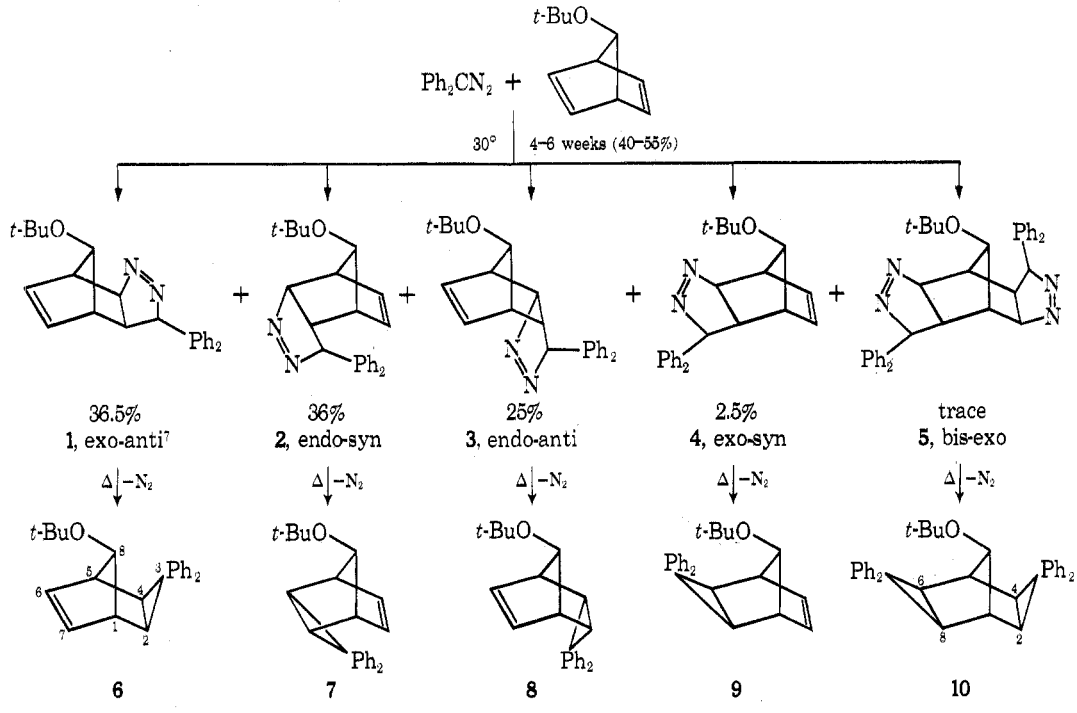
Room temperature addition of the title two reactants (diene in excess) led to all of the monoadducts possible (40–55%) in roughly comparable amounts except for the exo-syn adduct, which was formed in very low yield. Minor amounts of bis adducts were observed. Some factors involved in this nonselective 1,3-dipolar cycloaddition are discussed. Pyrolysis of the adducts led to the corresponding tricyclic ethers in high yield. These ethers serve as convenient entries into the *exo*- and *endo*-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]octane systems. As examples of some transformations possible with these ethers, the exo-anti ether was converted via acetolysis and hydrolysis to its alcohol with complete retention of configuration. Similarly, the endo-syn ether was converted to its alcohol and eventually to the interesting parent hydrocarbon, *endo*-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]octene. The endo-anti and exo-syn ethers did not behave analogously. The former underwent an apparently deep-seated change upon acetolysis, whereas the latter smoothly rearranged to a bicyclo[3.2.1]octene derivative. The pathways of these reactions are discussed briefly, along with the presentation of confirmatory physical data for the structures assigned.

Work on another aspect of this general area[3] necessitated the synthesis of alcohol **6**-OH (vide infra). The first step in its preparation was the 1,3-dipolar cycloaddition of diphenyldiazomethane to 7-*tert*-butoxynorbornadiene. This addition resulted in a variety of adducts, all of which have potential utility in the study of 3,3-diphenyltricy-

clo[3.2.1.$0^{2,4}$]octanes. We describe here the characterization of these adducts and some of the transformations that they undergo.

Results

Slow (4–6 weeks) addition of diphenyldiazomethane to excess 7-*tert*-butoxynorbornadiene (no other solvent) at room temperature afforded all of the possible monoadducts **1–4** as well as small amounts of bis adducts, of which **5** was characterized. The adducts were largely separable by column chromatography. Although these adducts had spectra consonant with the assigned structure,[4,5] the orientation of the addition in each case was better assigned by inspection of the tricyclic ether formed in high yield from each by pyrolysis at 165–175°.[6] The reactions are shown in eq 1.

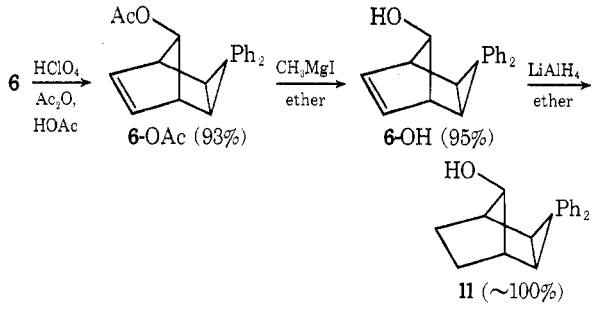


(1)

The cyclopropyl and vinyl protons in each of the ethers are unique. The exo/endo orientation of the fused cyclopropane ring can be determined by the multiplicity of the H-2,4 proton resonance and its chemical shift.[3] In **6** and **9** the H-2,4 pair is a singlet ($W_{1/2}$ = 2 Hz) whereas in **7** and **8** this pair is a multiplet. In the former cases, the H-2,4 pair is endo and does not couple with the bridgehead pair H-1,5 owing to unfavorable geometry. Some weak coupling of the long-range "W" type between H-2,4 and H-8 may broaden the singlet slightly in **9**, however. Such coupling is manifested in **10**, where the H-2,4 singlet is narrower ($W_{1/2}$ = 2 Hz) than the H-6,8 singlet ($W_{1/2}$ = 2.5 Hz). Conversely, in **7** and **8**, there is coupling due to a more favorable geometry between the now exo H-2,4 and H-1,5 pairs, resulting in distorted multiplets (three lines for **7** and four lines for **8**). As would be anticipated, the endo H-2,4 pair in **6** and **9** was upfield (δ 1.75 and 1.83, respectively) from the exo H-2,4 pair in **7** and **8** (δ 2.38 and 2.02, respectively).

The vinyl protons H-6,7 present a dramatic difference in these ethers. In **6** and **9** the vinyl resonance is at δ 6.48 and 6.51, respectively. In **7** and **8**, however, the underlying phenyl group attached to the endo cyclopropane moiety exerts a shielding effect on these vinyl protons, causing an upfield shift to δ 5.13 in **7** and δ 5.14 in **8**. Whereas this resonance was a sharp norbornene-type "triplet"[9] in **7** and **9**, additional broadening into a poorly resolved multiplet was evident in the vinyl resonance of **6** and **8**. These different resonances clearly are the result of the different orientation of the 8-*tert*-butoxy group, allowing some long-range coupling in these last two ethers.

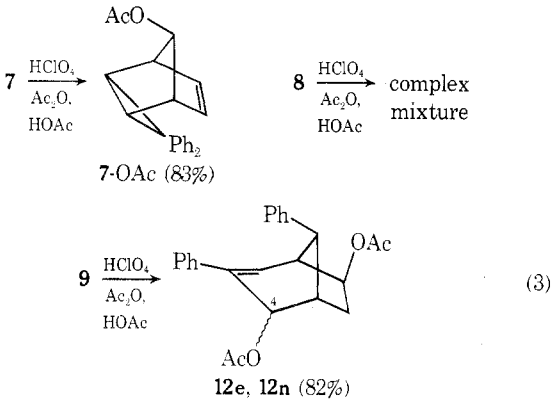
The syn/anti orientation of the *tert*-butoxy group in the endo adducts was decided by spin-decoupling results. As expected, irradiation of H-8 in **7** had no effect on the vinyl proton resonance. Irradiation of H-8 in **8**, however, cleanly sharpened the initial vinyl multiplet into a triplet. Also, irradiation of the vinyl protons in **8** changed the H-8 resonance from a complex multiplet into a triplet, $J_{1(5),8}$ = 2 Hz. So the *tert*-butoxy group is syn in **7** and anti in **8**. In the exo adducts, the *tert*-butoxy group in **6** was shown to be anti by conversion to the saturated alcohol **11** as in eq 2.[10] Alcohol **11** had been prepared earlier[3] and completely characterized. The sequence in eq 2 involved no gross structural change because in their NMR spectra both **6**-OAc and **6**-OH retained the H-2,4 singlet and complex vinyl proton multiplet characteristic of the **6** system. By elimination, the other exo adduct **9** obviously then has a syn *tert*-butoxy group.



(2)

As seen in eq 2, ether **6** smoothly afforded **6**-OAc upon acetolysis in the presence of perchloric acid. Likewise, ether **7** produced **7**-OAc. This ester showed the proper endo-type NMR spectrum. The cyclopropyl pair H-2,4 was a triplet centered at δ 2.32, as was the vinyl pair H-6,7 at δ 5.17. The syn acetoxy group orientation was assumed from the contrary behavior observed with **8** and from the generally observed retention of configuration in such reactions. Ether **8**, in this regard, gave a variety of uncharacterized products (at least seven by TLC analysis) in this reaction and the matter has not been pursued as yet.[11] Clearly, however, the endo-anti acetate expected (**8**-OAc) is unstable

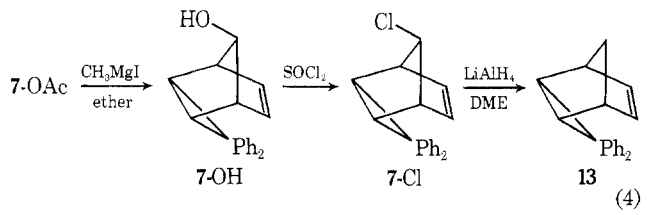
under these reaction conditions and generates other products, or *some* intermediate is formed which does so (with 8-OAc perhaps among the products). Ether **9** underwent a structural rearrangement under these acetolytic conditions to form a mixture of acetates **12.** These and the other reactions mentioned are illustrated in eq 3. Each ester in the



(3)

pair **12** had only one vinyl proton (δ 6.46 in **12e,** 6.28 in **12n**) and an unperturbed styrene chromophore [λ_{max} (EtOH) 248 nm (log ϵ 4.06) for **12e,** 249 nm (log ϵ 4.00) for **12n**]. Two CHOAc resonances were obvious in each ester but assignment was difficult. One, a broad singlet centered at δ 5.35, was assigned to H-4 in **12e** because of the geometry present in its case. Using this as the structural reference, one could then assign the remaining resonances: δ 5.31, H-4 in **12n;** 5.47, H-7 in **12e;** and 5.50, H-7 in **12n.**

One of the goals in the present study was the preparation of *endo*-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]octene itself (**13**). A comparison of its chemistry relative to that already known for its exo analog[13] should be interesting. Conversion of **7**-OAc to **7**-OH was straightforward. Because its tosylate proved to be elusive, reductive solvolysis of the *p*-nitrobenzoate ester of **7**-OH in diglyme with sodium borohydride[14] was attempted. No **13** was observed, however, and the reaction led rather to the parent alcohol and an uncharacterized oil. Alcohol **7**-OH did, nonetheless, easily form **7**-Cl upon treatment with thionyl chloride. This chloride was a reactive compound. It gave the corresponding methyl ether simply upon dissolution in warm methanol. Reduction of **7**-Cl to **13** succeeded with lithium aluminum hydride in dimethoxymethane under reflux[15] (eq 4). Reduction of **7**-Cl



(4)

with tri-*n*-butyltin hydride did not yield **13.** The crude product contained no norbornene double bond in the NMR spectrum. Hydrocarbon **13** was a crystalline solid, mp 74–75°. Its uv spectrum was similar to that of the exo isomer.[13] Their NMR spectra differed, and the shielding influence of the endo diphenylcyclopropyl ring upon the vinyl protons in **13** was pronounced. In **13** these protons appeared at δ 5.18, whereas in the exo isomer they appeared at δ 6.57.

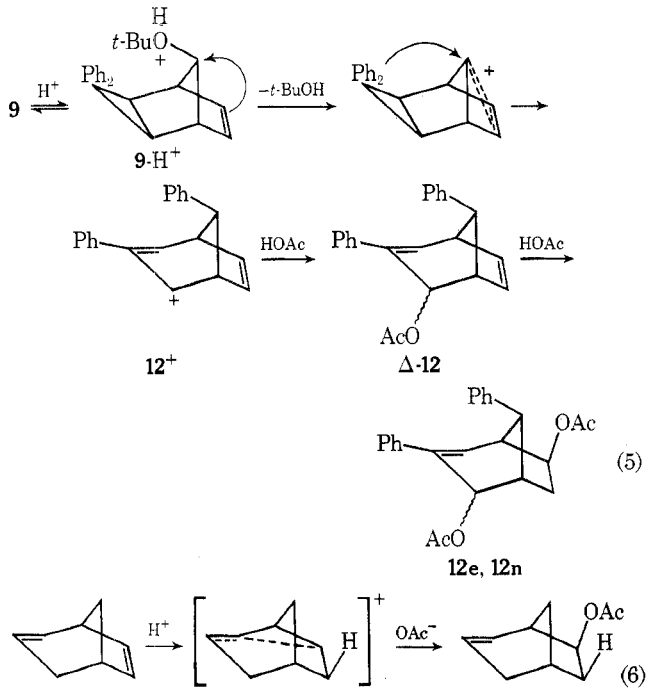
Discussion

1,3-Dipolar cycloadditions to norbornenes follow the Alder and Stein[16] "exo rule", the basis of which is still somewhat controversial. Abundant examples illustrate this rule and the matter need not be developed further here. Such additions to norbornadienes are less specific, however. Phenyl azide adds to norbornadiene preferentially exo (exo/endo = 11)[17] and diphenyldiazomethane adds exclusively exo to this diene,[13] as does diazofluorene.[18] The bis adduct from the former is also exo-exo (as would be expected once one addition had occurred because the second would then follow the "exo rule"). However, steric factors can effect the success of such reactions and cases are known where *no* addition occurs rather than endo addition.[19] Of all such additions, however, the most pertinent to the present study is the addition of phenyl azide to 7-*tert*-butoxynorbornadiene reported by Klumpp and coworkers.[20] Triazolines related to pyrazolines **1, 2,** and **4** were produced in percentage compositions of 30, 55, and 15%, respectively. No triazoline related to **3** was apparently formed. The 30% of exo-anti adduct presumably reflected the "exo rule" coupled with a favorable steric approach. On the other hand, Klumpp attributed the 15% exo-syn adduct to a "special coordination effect" between the *tert*-butoxy group and phenyl azide which compensated somewhat for the crowded transition state involved in this case. The major product, an endo-syn adduct, was postulated to result from a sterically favorable endo addition to the syn double bond. This double bond was theorized to be the more reactive because of electronic factors involving again the *tert*-butoxy group. Such results with phenyl azide are very much like those here reported for diphenyldiazomethane addition. Because the diazo compound is a more bulky dipolar reagent, however, the transition state for its addition probably involves more steric hindrance.[21] So exo-syn addition (i.e., to form **4**) is diminished. Presumably the formation of endo-anti adduct **3** also illustrates this steric influence and accounts for the mildly increased overall endo addition with the diazo compound (61%) compared with phenyl azide (55%). Our studies do not contribute to any claim of coordination effects or of enhanced reactivity of the syn norbornadiene double bond nor do they explain the absence of a triazoline product related to **3** in Klumpp's work. Clearly, steric and electronic factors are in delicate balance in these reactions and subtle shifts in these factors cause the minor differences in the two additions. However, obviously, the "exo rule" is not adhered to in these 1,3-dipolar cycloadditions.[23]

The conversions of **6** and **7** to the acetates (eq 2 and 3) exemplify the known retention of configuration that attends such ether cleavages.[3] The rest of the sequence in eq 2 mirrors that previously reported[3] for the saturated analog. The complex acetolysis of **8** is not yet understood.[11] The reaction of ether **9** may be rationalized as shown in eq 5.

Three points of interest might be mentioned concerning this sequence. First, the loss of *tert*-butyl alcohol from **9**-H^+ is believed to result from the anti double bond participation, a well-known effect. Such a loss may also be involved in the previously mentioned conversion of **7** to **7**-OAc, but *not* in the conversion of **6** to **6**-OAc. Had the latter conversion involved the creation of cationic charge at C-8, then a phenyl migration would have followed to rearrange the tricyclic system.[24] From the present and past work, it is concluded that an anti double bond or cyclopropyl group will participate in the acetolysis of such 8-*tert*-butyl ethers to cause C-8 charge creation, but a proximate 3-phenyl group will not.

The second point of interest is the complete specificity of addition of acetic acid to Δ-12. Addition of acetic acid to bicyclo[3.2.1]octadiene occurs as shown in eq 6, presumably via the delocalized cation shown.[25] This is a clear precedent for the stereospecific addition in eq 5 to form **12.** As the



(5)

(6)

last point of interest, the nonstereospecific capture of ion 12^+ by acetic acid also was observed with the 6,7-dihydro analog, and indicates that the charge in 12^+ is not delocalized over the dienic system, presumably because such delocalization would lead to antiaromatic character in the ion.

The additions of acetic acid are believed to occur in the order shown in eq 5. The possibility that addition of acetic acid to **9** preceded the acetolysis seems remote for two reasons: only unchanged **9** was isolable from purposely incomplete reactions, and the high reactivity of **9** necessitates the presence of the anti bond.

With an entry available now to these various tricyclic systems, future papers will report on efforts to explore these systems further.

Experimental Section[26]

Reaction of Diphenyldiazomethane and 7-*tert*-Butoxynorbornadiene. The diazo compound[27] was added to freshly distilled diene[28] in aliquots such that the molar ratio of diene to diazo compound was never less than 100:1. It was convenient to add 0.5 portions of the latter with stirring to ca. 100 g of the former at 25–30°. Further additions were made as the purple color of the solution faded to pale yellow. After 4–6 weeks monoadduct began to precipitate. The solution was steam distilled to recover excess diene, which was recycled. The residue was dissolved in a minimal volume of benzene and dried by azeotropic distillation. It was then chromatographed on alumina (Matheson Coleman and Bell "chromatographic grade", 80–325 mesh, used as received). A practical weight ratio of alumina to residue was 100:1. Elution with 10% ether–hexane removed a trace of diene reactant. Use of 50% ether–hexane gave adducts[29] 1 and **2**, the initial fractions being richer in **2**. Continued elution next afforded pure **1**, mp 143–144° dec.[4] Fractional crystallization of the mixed adducts above from methanol eventually gave pure **2**, mp 142.5–143.5° dec.[4] The slower eluting adduct **3** was finally obtained by longer elution with 50% ether–hexane. Recrystallization from methanol gave **3**, mp 162.5–163.5° dec.[4] Although sharp-melting, **3** was not obtained pure enough for acceptable C, H analysis. Adduct **4** was difficult to obtain also. After five reactions to obtain all of the above, the mother liquors from all recrystallizations were combined and rechromatographed. Adduct **4** was observed spectrally in those fractions rich in **1** and **2**. A pure sample of **4** was, however, not obtained.[4] Bis adduct **5** was eventually obtained by elution with 50% ether–chloroform. Recrystallization from methanol gave pure **5**, mp 186–186.5° dec.[4,5] Other bis adducts were probably present as well, but no serious effort was made to isolate them.

Owing to considerable tar formation an accurate yield of **1–4** was not determined. Based on diazo reactant, *isolated* yields ranged from 40 to 55%. The composition of the adduct mixture was determined by NMR integration of the *tert*-butoxy singlets. The NMR sample was a steam-distilled residue that had been freed from tars by rapid passage through a short alumina column.

Pyrolysis of Pyrazolines. The individual adducts **1–5** were heated in an oil bath at 165–175° (230° for **5**) until nitrogen evolution ceased. The residue was taken up in a small volume of chloroform and passed through a short alumina column with 10% ether–hexane. Evaporation of the solvent gave the colorless, crystalline ethers. The ethers were recrystallized from methanol.[4] The yields were 84–96%. The melting points of the ethers follow: **6**, 167–168°; **7**, 124.5–125.5°; **8**, 114.5–115.5°; **9**, 173.5–174.5°; **10**, 263–264° dec. Once the pyrazoline adducts had been characterized, it was found to be more economical to pyrolyze the mixture of adducts **1**, **2**, and **4** previously mentioned as the initial eluate with 50% ether–hexane through alumina. The ethers were then separated by chromatography on 200 wt % of Florisil (MCB, 100 mesh and finer). Elution with hexane readily gave ether **9**, while elution with 5% ether–hexane gave first **7** and then **6**, all of which were obtained in analytical purity.[4]

Acetolysis of the Ethers. The cleavage of ethers **6** and **7** was performed as reported[3] for the saturated analog of **6**, except that, after reaction, the acidic solution was neutralized with solid sodium carbonate and the acetate product extracted with methylene chloride. Removal of solvent from the dried extracts gave the crude acetates. Esters 6-OAc and 7-OAc were formed in 93 and 83% yield, respectively.[4] Upon recrystallization from methanol followed by hexane or pentane they both formed colorless needles: 6-OAc, mp 141–142°; 7-OAc, mp 96.5–97.5°. Ether **8** gave an off-white solid product in this cleavage. By TLC (30% ethyl acetate–hexane) analysis, seven distinct fractions were noted, but none was isolated or characterized except to the extent that the NMR spectrum showed no evidence of the parent tricyclic system. Other cleavage methods using various concentrations of sulfuric acid and another using triphenylphosphine dibromide in acetonitrile failed. Ether **8** was stable, however, to acetic acid–acetic anhydride mixtures (25°, 10 hr). Cleavage of ether **9** (300 mg) gave a mixture of esters **12** (280 mg) in the ratio of two parts **12n** to three parts **12e**. Separation was accomplished by chromatography on Florisil (80 g/g of acetates). Acetate **12n** eluted first with 4% ethyl acetate–hexane and it was recrystallized from methanol, mp 129.5–130.5°.[4] Acetate **12e** was obtained as a glass which could not be recrystallized satisfactorily, mp 45–55°.[4]

Formation of 3,3-Diphenyltricyclo[3.2.1.$0^{2,4}$]oct-6-enols, 6-OH and 7-OH. Acetates 6-OAc and 7-OAc were treated with excess methymagnesium iodide as described earlier[3] for the saturated analog of **6**-OAc. The exo-anti alcohol 6-OH (95% yield) was recrystallized from hexane, mp 126.5–127°.[4] The endo-syn alcohol 7-OH (97% yield) had mp 140–141° from hexane.[4]

Reduction of 6-OH to 11.[10] Alcohol 6-OH (100 mg) in dry ether (15 ml) was added to a slurry of lithium aluminum hydride (100 mg) in dry ether (15 ml). The mixture was stirred at 25° for 6 hr and hydrolyzed by cautious addition of water followed by sulfuric acid (10%). The ether layer was separated, washed with sodium carbonate (10%) and water, and then evaporated to afford alcohol **11** (100 mg, 100% yield, mp 153–155° from hexane). The product was identical by mixture melting point and spectra with authentic material.[3]

Reduction of 7-OH to 13. Attempted conversion of 7-OH to its tosylate in pyridine was unsuccessful (84 hr, 5–10°). However, work-up over crushed ice–10% hydrochloric acid returned only 10% of the original material. The *p*-nitrobenzoate derivative (mp 168–169° from chloroform–methanol) was prepared in pyridine with *p*-nitrobenzoyl chloride. Reaction of this ester with sodium borohydride in aqueous diglyme[12] (90°, 4 hr) gave back 7-OH (63% recovery) and an uncharacterized oil that had no spectral characteristics of the parent tricyclic system.

Treatment of 7-OH (300 mg) with purified thionyl chloride (100 mg) at 25° led to the evolution of gases which were removed in a nitrogen stream. Evaporation of the slight excess of thionyl chloride led to an off-white solid, 310 mg, mp 111–115°, which was judged by NMR analysis to be ca. 90% pure 7-Cl.[4] Attempted recrystallization of the chloride from all solvents tried was unrewarding except for methanol. However, the recrystallized product from methanol was clearly the methyl ether 7-OMe [mp 74–75°, δ 3.18 (s, OCH_3), other resonances indicative of **7** system[4]].

Chloride 7-Cl (unrecrystallized, 500 mg) in dry 1,2-dimethoxyethane (DME, 10 ml) was added dropwise to a slurry of lithium aluminum hydride (200 mg) in DME (50 ml) at 25°.[15] The solution was heated to reflux, whereupon it turned deep blue. After a 14-hr

heating period (TLC analysis indicated a 12-hr minimum time for reaction), the excess hydride was decomposed by the careful addition of water at 0–5°. The inorganic salts were dissolved by addition of 5% sulfuric acid. The homogeneous, aqueous DME solution was evaporated and the residue was taken up in ether. The ether solution was washed with 5% sulfuric acid, water, 10% sodium carbonate, and water, and then dried over sodium sulfate. Removal of the ether left an oil which was passed through alumina (50 g) with hexane. The hexane was evaporated to yield **13** (360 mg, 83%, mp 74–75° from methanol).[4]

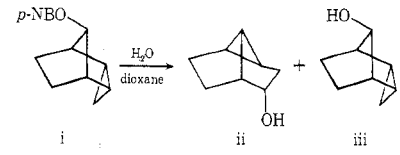
Reaction of 7-Cl in benzene with tri-*n*-butyltin hydride in the presence of azobisisobutyronitrile initiator under relux (nitrogen atmosphere) for 48 hr gave a tarry product that possessed no vinyl protons in the NMR spectrum.

Registry No.—**1**, 54120-24-0; **2**, 54163-78-9; **3**, 54163-79-0; **4**, 54163-80-3; **5**, 54120-31-9; **6**, 54120-25-1; 6-OH, 54120-26-2; 6-OAc, 54120-27-3; **7**, 54163-81-4; 7-OH, 54163-82-5; 7-OAc, 54163-83-6; 7-OMe, 54120-28-4; 7-Cl, 54120-29-5; 7-O-*p*-NB, 54120-30-8; **8**, 54163-84-7; **9**, 54163-85-8; **10**, 54120-32-0; **11**, 29266-06-6; **12n**, 54120-33-1; **12e**, 54163-86-9; **13**, 54163-87-0; diphenyldiazomethane, 883-40-9; 7-*tert*-butoxynorbornadiene, 877-06-5.

Supplementary Material Available. Melting points, combustion analytical data (asterisked compounds), and significant ir and complete NMR data for **1***, **2***, **3***, **4**, **5***, **6***, **7***, **8***, **9***, **10**, 6-OAc*, 7-OAc*, 6-OH*, 7-OH*, 7-*p*-NB, 7-Cl, 7-OMe, **13*** (uv also), **12e*** (uv also), and **12n** (uv also) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JOC-75-1036.

References and Notes

(1) Studies on 3,3-Diaryltricyclo[3.2.1.0^{2,4}]octanes. IV. Part III: J. W. Wilt and J. R. Flanyak, *J. Org. Chem.*, **39**, 716 (1974).
(2) Taken from the Dissertation of D.R.S., 1973. Portions of this material were delivered at the 6th Great Lakes Regional Meeting of the American Chemical Society, Houghton, Mich., June 1972, Abstracts, p 64.
(3) J. W. Wilt, T. P. Malloy, P. K. Mookerjee, and D. R. Sullivan, *J. Org. Chem.*, **39**, 1327 (1974).
(4) See paragraph at end of paper regarding supplementary material.
(5) Bis adduct **5** was assigned its sturcture because the bridgehead protons possessed the same chemical shift. The alternative structure resulting from identical exo additions of the diphenyldiazomethane should have given a bis adduct possessing two different chemical shifts for the bridgehead protons.
(6) Suprafacial, concerted elimination of nitrogen from these pyrazolines should require photochemical conditions. Because these eliminations did succeed thermally, the concerted loss of nitrogen under these conditions may be more difficult (and therefore require high temperatures) or, more likely, the loss may be stepwise.
(7) It is customary[5] in such compounds to name the orientation of the *added* moiety first and the orientation of the *bridge substituent* with respect to the added moiety second. Some confusion is inevitable, but it must be stressed that syn and anti refer to the orientation of the substituent with respect to the pyrazolino (or later, cyclopropyl) ring and *not* the norbornene double bond.
(8) J. Haywood-Farmer, *Chem. Rev.*, **74**, 315 (1974).
(9) The norbornene vinyl triplet is deceptively simple. The vinyl and bridgehead protons actually comprise an AA′XX′ system.
(10) The reduction of a norbornene double bond syn to an oxygen function (–OH, –OR) by lithium aluminum hydride is well documented. Cf. B. Franzus and E. J. Snyder, *J. Am. Chem. Soc.*, **87**, 3423 (1965), and P. R. Story, *J. Org. Chem.*, **26**, 287 (1961). The reduction of an anti norbornene double bond in such compounds does not occur with this reagent.
(11) Because ester i solvolyzed principally (84.3%) to alcohol ii with only 0.1% skeletally retained product iii,[12] it is likely that such gross rearrangement occurred with **8** as well.



(12) Reference 8, pp 328–330, and references cited therein.
(13) J. W. Wilt and T. P. Malloy, *J. Org. Chem.*, **38**, 277 (1973).
(14) H. Bell and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 1473 (1966).
(15) C. W. Jefford, D. Kirkpatrick, and F. Daley, *J. Am. Chem. Soc.*, **94**, 8905 (1972).
(16) K. Alder and G. Stein, *Justus Liebigs Ann. Chem.*, **515**, 185 (1935); K. Alder, G. Stein, and H. Rickert, ibid., **525**, 221 (1936).
(17) D. Findlay, M. Roy, and S. McLean, *Can. J. Chem.*, **50**, 3186 (1972).
(18) J. DeMember and N. Filipescu, *J. Am. Chem. Soc.*, **90**, 6425 (1968); N. Filipescu and J. DeMember, *Tetrahedron*, **24**, 5181 (1968).
(19) K. Alder, H. Ache, and F. Flock, *Chem. Ber.*, **93**, 1888 (1960).
(20) W. Klumpp, A. Veefkind, W. deGraaf, and F. Bickelhaupt, *Justus Liebigs Ann. Chem.*, **706**, 47 (1967).
(21) Such steric hindrance may be the reason why diphenyldiazomethane additions have less favorable $\Delta S^{\ddagger}$ parameters compared to phenyl azide additions.[22]
(22) R. Huisgen, H. Stangl, H. J. Sturm, and H. Wagenhofer, *Angew. Chem.*, **73**, 170 (9161); R. Huisgen, G. Szeimies, and L. Möbius, *Chem. Ber.*, **100**, 2494 (1967).
(23) After submission of this manuscript, a paper by M. Franck-Neumann and M. Sedrati, *Angew. Chem., Int. Ed. Engl.*, **3**, 606 (1974), was noticed by us and subsequently impressed upon us by a referee. These workers observed only endo-anti addition of diazomethane and diazoethane to 7-halonorbornadienes and considerable endo-anti additon of diazoethane to 7-norbornadienol. The aforementioned referee asked that we comment on these results in the light of the results we report in the present paper. First of all, Franck-Neumann and Sedrati report only exo and "probably" syn addition of diazoethane to 7-*tert*-butoxynorbornadiene, the dipolarophile germane to our work. So the frontier orbital considerations that they adduce to explain the endo-anti additions to the 7-halo compound and the 7-alcohol clearly are not applicable to the 7-*tert*-butoxy substance. Moreover, Franck-Neumann and Sedrati comment neither on their own result with the 7-*tert*-butoxy case nor on Klumpp's,[18] a situation that makes a comment from us gratuitous and premature. We prefer to await the result of a study of diphenyldiazomethane additions to the 7-halonorbornadienes before making such a comment.
(24) This argument has been used in the acetolysis of the saturated analog of **6** as well.[3]
(25) N. LeBel and R. Maxwell, *J. Am. Chem. Soc.*, **91**, 2307 (1969).
(26) Melting points were taken on a calibrated Fisher-Johns block. Infrared spectra (ir) were determined on a Beckman IR-5A instrument as 1–3% mixtures in potassium bromide disks. Ultraviolet spectra (uv) were measured on a Cary 14 spectrophotometer. Nuclear magnetic resonance spectra (NMR) were obtained on a Varian A-60A instrument using tetramethylsilane as an internal standard. Integration of signals was within 10% of the theoretical value. The usual splitting abbreviations are used. Chemical shifts are for deuteriochloroform solutions. Homonuclear decoupling experiments were performed with a Varian V-6058A spin decoupler. Complete ir, uv, and NMR spectra are available in the dissertation of D.R.S.
(27) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. I, Wiley, New York, N.Y., 1967, p 338.
(28) P. Story, *J. Org. Chem.*, **26**, 287 (1961).
(29) The (at times complicated) names of these compounds, along with other details, are given in the supplementary tables.[4]