

Studies of the Stereochemistry and Mechanism of the Ene Reaction Using Specifically Deuterated Pinenes

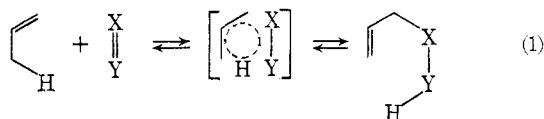
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Abstract: The ene reactions of *cis*- and *trans*-[3-²H]- β -pinenes with methyl phenylglyoxylate and benzyne have been examined. In each case, it has been established that the hydrogen atom of the methylene group at C₃ in β -pinene which is *trans* to the *gem*-dimethyl bridge is involved, overwhelmingly, in this reaction. This remarkable degree of stereoselectivity is presented in support of earlier proposals (ref 3) that these ene reactions occur in a concerted fashion through a single, cyclic transition state. In concert with this view: (1) no difference was observed in the rate of reaction of β -pinene with methyl phenylglyoxylate (at 140°) when polar and nonpolar solvents (*e.g.*, nitrobenzene and *o*-xylene) were used; and (2) no products resulting from the rearrangement of possible carbonium ion intermediates have been observed in ene reactions with β -pinene. We believe these data cannot be rationalized in terms of a two-step mechanism involving a dipolar intermediate.

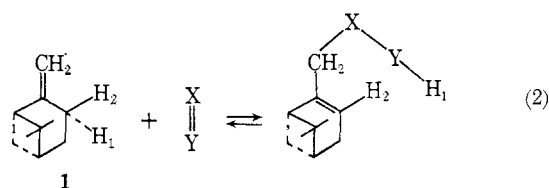
Alder's ene reaction¹ usually involves thermal inter-
action of an electron-rich monoolefin bearing an
allylic hydrogen atom called the ene component and an
electron-deficient enophile (X=Y) to form a 1:1 adduct
as described, schematically, in eq 1.²



In the cases reported, to date, the enophiles used most frequently are identical with the dienophiles (*e.g.*, maleic anhydride, acetylenedicarboxylic ester, etc.) which take part in the classical Diels-Alder reaction. However, many other types including active carbonyl compounds,³⁻⁵ singlet oxygen,⁶ azodicarboxylates,^{1,7} benzyne,⁸⁻¹¹ and nitrosoarenes¹² may also serve as effective enophiles.

When the geometry is such that the enophile (X=Y) can attack the π electrons and the allylic hydrogen atom of the ene component, simultaneously, a facile reaction appears to take place *via* a concerted reaction involving a cyclic transition state.^{2,3,13,14}

This view leads to the prediction that an enophile (X=Y) in reacting with β -pinene (**1**) should easily differentiate between the two allylic hydrogen atoms (*i.e.*, H₁ and H₂) at C₃ (eq 2), and that H₁, which is axial



and *cis* to the methylene bridge, should react preferentially. In addition, this allows for an approach of the enophile (X=Y) from the side of the β -pinene molecule which is least hindered, sterically. This mechanism leads to the further prediction that the reverse ene reaction, represented by the pyrolysis of the 1:1 adduct, should proceed *via* the same cyclic transition state and regenerate **1** in a highly stereoselective manner. The results of the present study, which was designed to test these postulates, have confirmed them.¹⁵ Studies in which benzyne and methyl phenylglyoxylate serve as enophiles will be described.

Benzyne, a powerful enophile, which can be generated, conveniently, at mild temperatures (*ca.* 40°) and under anhydrous conditions by the elegant method of Friedman,¹⁶ proved to be a very useful enophile in the present investigation.

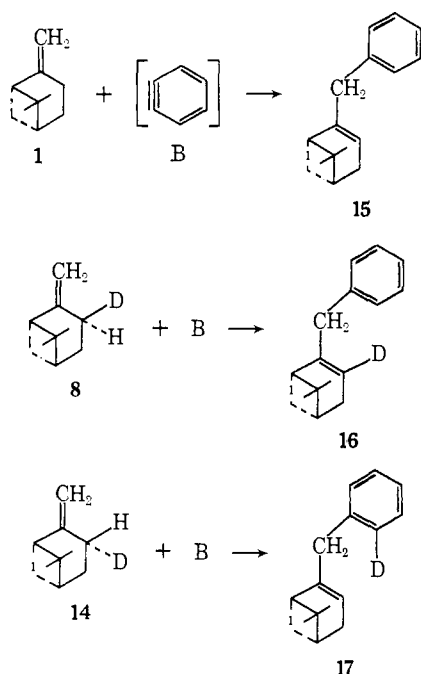
When benzyne is generated in the presence of β -pinene (**1**), a facile reaction occurs to form 10-phenyl- α -pinene (**15**) as shown in Scheme I. Under identical conditions, *cis*- and *trans*-[3-²H]- β -pinene (**8** and **14**, respectively) react in a highly stereoselective manner (>95%) to form the monodeuterated derivatives **16** and **17**, respectively.

Experiments involving the ene reaction in which an active carbonyl group served as the enophile proved to be highly instructive. When, for example, β -pinene (**1**) was allowed to react, thermally, with methyl phenylglyoxylate (**18**), the expected³ adduct (**19**) was formed (Scheme II). The hydroxyl group of **19** underwent a rapid isotopic exchange with deuterium oxide (*ca.* 100%) to form the labeled compound **20**. Upon partial

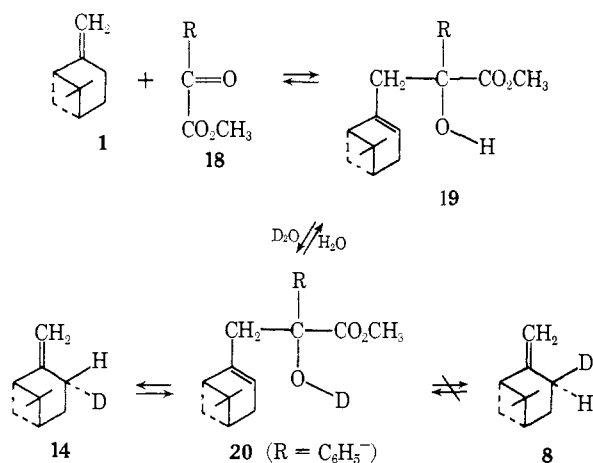
- (1) K. Alder, F. Pascher, and A. Schmitz, *Chem. Ber.*, **76**, 27 (1943).
- (2) For an excellent review of all major facets of the ene reaction, see H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).
- (3) R. T. Arnold and P. Veeravagu, *J. Amer. Chem. Soc.*, **82**, 5411 (1960).
- (4) W. H. Urry, J. H. Y. Niu, and L. G. Lunsted, *J. Org. Chem.*, **33**, 2302 (1968).
- (5) D. R. Taylor and D. Bruce Wright, *J. Chem. Soc., Perkin Trans. 1*, 953 (1973).
- (6) C. S. Foote, T. T. Fujimoto, and Y. C. Chang, *Tetrahedron Lett.*, **45** (1972), and earlier papers.
- (7) R. Huisgen and H. Pohl, *Chem. Ber.*, **93**, 527 (1960).
- (8) E. M. Arnett, *J. Org. Chem.*, **25**, 324 (1960).
- (9) H. E. Simmons, *J. Amer. Chem. Soc.*, **83**, 1657 (1961).
- (10) G. Wittig and H. Dürr, *Justus Liebigs Ann. Chem.*, **672**, 55 (1964).
- (11) J. A. Kampmeier and A. B. Rubin, *Tetrahedron Lett.*, 2853 (1966).
- (12) G. T. Knight and B. Pepper, *Tetrahedron*, **27**, 6201 (1971).
- (13) R. T. Arnold and J. S. Showell, *J. Amer. Chem. Soc.*, **79**, 419 (1957).
- (14) R. K. Hill and M. Rabinovitz, *J. Amer. Chem. Soc.*, **86**, 965 (1964).

- (15) Following publication of the Abstracts of the 165th National Meeting of the American Chemical Society, Dallas, Texas, Apr 8-13, 1973, at which a portion of our results was presented, we learned from Professor R. K. Hill (University of Georgia, Athens, Ga.) that he and his associates had, independently, arrived at the same general conclusions; *cf.* *J. Amer. Chem. Soc.*, **96**, 4201 (1974).
- (16) L. Friedman, *J. Amer. Chem. Soc.*, **89**, 3071 (1967).

Scheme I



Scheme II



pyrolysis (under dry N_2) at a temperature of 275° , **20** regenerated the ester (**18**) and a hydrocarbon mixture consisting of a monodeuterated β -pinene (**14**) and isomers formed from it by thermal rearrangement.¹⁷ Mass spectroscopic measurements on **14** (prepared by glpc) showed it to be 88% monodeuterated. The absolute structure of **14** was readily established by showing that its deuterium nmr spectrum was (within experimental error) identical with that of an authentic sample of *trans*-[3- 2H]- β -pinene.

When **14** was allowed to react with methyl phenylglyoxylate at 165° for 120 hr, compound **20** was regenerated. Its ir spectrum indicated a OD:OH ratio of 70:30. While the latter result (which disregards the isotope effect which favors protium over deuterium) indicates a reasonable degree of stereoselectivity for this ene reaction, we believe that the values reported here are conservative due to some unexpected difficulties encountered in handling these materials. The most

(17) When the pyrolysis of **20** was carried out at lower temperatures the proportion of β -pinene, relative to other terpenic hydrocarbons in the product, increased markedly, which establishes that β pinene is the hydrocarbon formed in the primary reaction. The slow rates at lower temperatures, however, made these conditions impractical.

awkward problem arose from the fact that **20** undergoes an extraordinarily rapid deuterium-hydrogen exchange with extraneous water in the atmosphere, on the surface of glassware, etc. For example, if the entire operation leading to the synthesis and purification of **20** from **19** were carried out in a drybox in an atmosphere of dry N_2 , we were able to obtain an excellent ir (neat) spectrum for **20** with strong OD absorption (*ca.* 2590 cm^{-1}) and no detectable OH band (*ca.* 3500 cm^{-1}). When, however, the ir cell (containing **20**) was removed from the spectrometer and opened, and the sample exposed to the atmosphere for only 15 sec prior to repeating the spectral determination, the OD band disappeared, and was replaced by a strong OH band.¹⁸

Although a number of ene reactions described in the literature¹⁴ have been shown to be stereospecific, we believe that the regeneration of **14** from **20** represents the first reported example of a stereospecific reverse ene reaction.

During the course of this study, it was also demonstrated that the rate of formation of **19** from **1** and **18** appears to be independent of the polarity of the solvent. For example, no difference in rate was observed when nitrobenzene or *o*-xylene was employed as solvent under conditions which were, otherwise, identical. In addition, we have never been able to detect any camphane derivatives which might arise from carbonium ion intermediates. While all of these data are fully consistent with a mechanism for the ene reaction which involves a cyclic transition state, they are not easily rationalized in terms of a mechanism involving dipolar intermediates.⁴

The deuterated pinenes (*i.e.*, **8** and **14**) employed in this study resulted from the development of a highly successful series of stereospecific reactions (Scheme III) all based upon the fact that approach of any reagent from the *gem*-dimethyl side of the pinene ring system is strongly inhibited. Because deuterated pinenes of a wide variety are potentially useful in mechanistic studies, we extended the synthetic method described here to include some additional mono- and dideuterated pinenes (*e.g.*, **4**, **10**, and **11**) not required in the present study of the ene reaction.

Formation of the mesylates **3**, **7**, and **13** (in solution) was followed spectroscopically, but these compounds proved to be much too unstable to isolate. Fortunately, however, it was found that solutions of these intermediates, in ether, could be reduced directly, either with lithium aluminum hydride or deuteride, to give the appropriate hydrocarbons as indicated in Scheme III.

As expected, **3**, for which an S_N2 reaction at C_3 is practically excluded, reacts with deuteride anion (possibly by a S_N2' mechanism,¹⁹ almost exclusively at the exocyclic carbon atom to form [10- 2H]- α -pinene (**4**).

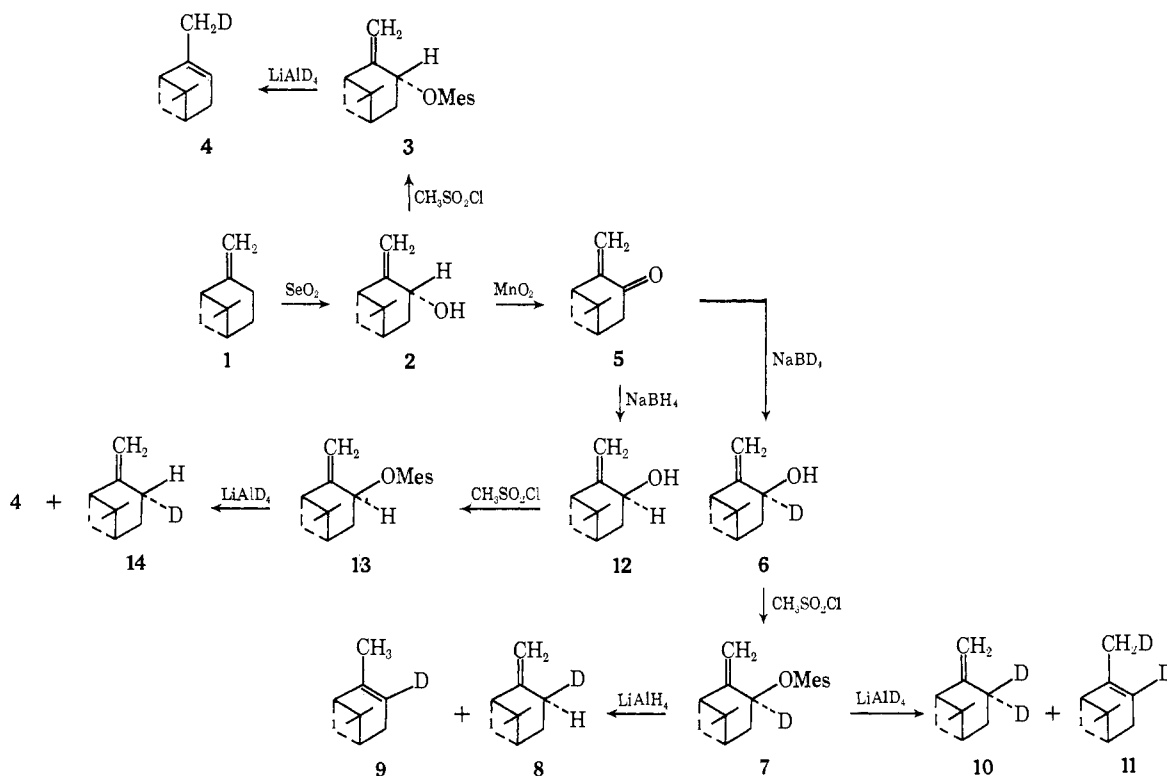
Reduction of **13**, which can undergo a S_N2 reaction, with lithium aluminum deuteride gives a mixture of **4** and **14** in approximately equal amounts, and these were readily separated by preparative glpc. Mass spectra²⁰

(18) We acknowledge the aid of Professor James Tyrrell who assisted us in taking these measurements with a Perkin-Elmer (Model 226) infrared spectrophotometer.

(19) F. G. Bordwell, *Accounts Chem. Res.*, **3**, 281 (1970), has shown that S_N2' mechanisms are not as common as earlier believed. A few authentic cases, however, appear to have been established [*cf.* J. A. Hemmingson and B. D. England, *J. Chem. Soc. B*, 1347 (1971)]

(20) We are indebted to Professor G. V. Smith of this Department for assistance with these measurements.

Scheme III



showed a minimum incorporation of 95% deuterium into **4** and **14**. Proton and deuterium nmr spectra,²¹ independently, confirmed the structures assigned to these products.

Similarly, reduction of a solution of **7** with lithium aluminum hydride gave essentially equal quantities of **8** and **9**. Comparable experiments, using lithium aluminum deuteride, gave **10** and **11**.

Experimental Section

(-)-*trans*-Pinocarveol (**2**). This alcohol was prepared by the oxidation of β -pinene (1450 g) with a solution of selenious acid prepared from selenium dioxide (480 g), absolute ethanol (1070 ml), and water (66 ml). The reaction conditions and method of isolation were those employed by Quinn.²² The product (680 g; 58%) was isolated by fractional distillation, bp 67–68° (2.5 mm). When cooled, the bulk product solidified (mp 3°). Recrystallization from the melt gave pure (-)-*trans*-pinocarveol, mp 5°.²³ The ir and nmr spectra agreed fully with those in the literature.^{22,24}

(-)-Pinocarvone (**5**). To a well-stirred suspension of active manganese dioxide²⁵ (390 g) in low-boiling petroleum ether (1500 ml) was added (-)-*trans*-pinocarveol (55 g) over a period of 10 min. The mixture was stirred, vigorously, for 1 hr at 25°. After separation of the solids by filtration, the solvent was removed by vacuum distillation, and the residue was fractionated to give (-)-pinocarvone (37 g; 68%): bp 36–37° (0.15 mm) (lit.²⁶ 48–49° (1.5 mm)); ir (neat) 1710 cm⁻¹; nmr (CCl₄) δ 5.8 (d, 1 H, $J = 2$ Hz, vinylic), 4.9 (d, 1 H, $J = 2$ Hz, vinylic), 2.9–2.0 (m, 5 H), 1.4 (s, 3 H, CH₃), 1.3 (m, 1 H), 0.80 (s, 3 H, CH₃).²⁴

(+)-*cis*-Pinocarveol (**12**). A solution of sodium borohydride (7 g) in ethanol (500 ml, 95%) was added, dropwise and with good stirring, to a cooled (0–5°) solution of (-)-pinocarvone (15 g) in ethanol (500 ml, 95%) over a period of 30 min. After the mixture had been stirred at 0–5° for 10 hr, water (500 ml) was added and the ethanol removed by vacuum distillation at 25°. The aqueous mix-

ture was extracted with two separate portions of low-boiling petroleum ether. The latter were combined, dried (MgSO₄), and evaporated to give a pale yellow oil (12 g) which was subjected to liquid-phase chromatography on neutral activated alumina. Low-boiling petroleum ether was used to introduce the sample to the column (5 × 50 cm). Elution with ethyl ether readily removed unreacted ketone (3 g). Further elution with methanol-ether (4:96) gave (+)-*cis*-pinocarveol (6.5 g; 43%) as a white crystalline solid: mp 49–50° (lit.²³ 50–50.3°); ir (neat) 3400 cm⁻¹ (OH); nmr (CCl₄) δ 5.2 (m, 1 H, vinylic), 4.7 (m, 1 H, vinylic), 4.5 (d, 1 H, $J = 10$ Hz, CHOH), 4.1 (s, 1 H, OH), 2.7–1.3 (m, 6 H), 1.3 (s, 3 H, CH₃), 0.7 (s, 3 H, CH₃).

Preparation of *trans*-[3-²H]- β -Pinene (**14**) and [10-²H]- α -Pinene (**4**). To a cooled (0–5°) solution of (+)-*cis*-pinocarveol (5.7 g) in pyridine (50 ml) was added methanesulfonyl chloride (4.5 g). After the mixture had stirred for 1.5 hr at 0–5°, cold ether (80 ml) and 6 *N* hydrochloric acid (80 ml) were added. The aqueous layer was extracted twice with ether and the combined ether layer was extracted once with 6 *N* hydrochloric acid and once with cadmium chloride solution (40 ml, 10%). The ether solution was dried (MgSO₄) for 2 hr and partially evaporated (under vacuum) to a volume of 20 ml. All efforts to isolate the intermediate mesylate (**13**) failed. Consequently, the ethereal solution of **13** was added, dropwise, to a cold (0°) suspension of lithium aluminum deuteride (0.8 g) in ether (50 ml), and stirred for 3 hr at 25°. The reaction mixture was poured, slowly and with cooling, into ether (80 ml) which had been acidified with sulfuric acid (30 ml, 20%) so as to ensure that the temperature remained below 10°. The aqueous layer was extracted with ether (50 ml) and the combined ethereal layer washed with sodium bicarbonate (50 ml, 10%), dried (MgSO₄), and evaporated under reduced pressure to a crude product (ca. 5 g) containing equal quantities of **4** and **14**. Separation was effected on a 30-ft 30% Apiezon-L Chromosorb W chromatographic column (140°, helium pressure 20 lb). Analysis of the β -pinene (**14**) component (1.2 g, 23%) by proton and deuterium nmr and mass spectra indicated monodeuteration to the extent of, at least, 95%; ²H nmr (**14**), δ 4.80 (m, 1 D), upfield from benzene-*d*₆.

Examination of the α -pinene (**4**) component also indicated monodeuteration ($\geq 95\%$); ²H nmr (**4**), δ 5.7 (t, 1 D, CH₂D), upfield from benzene-*d*₆.

Preparation of *cis*-[3-²H]- β -Pinene (**8**) and [3-²H]- α -Pinene (**9**). (-)-Pinocarvone (**5**) (23 g), dissolved in ethanol (1700 ml, 95%), was reduced with a solution of sodium borodeuteride (9.3 g) in ethanol (700 ml, 95%) to give *cis*-[3-²H]pinocarveol (**6**) (13.2 g, 56%), using the procedure described above for the preparation of

(21) Nmr spectra were taken on a Varian (HA-100-15) spectrometer. Deuterium nmr spectra were determined at 15.3 MHz.

(22) J. M. Quinn, *J. Chem. Eng. Data*, **9**, 389 (1964).

(23) H. Schmidt, *Ber.*, **77**, 167 (1944).

(24) J. K. Crandall and L. H. Chang, *J. Org. Chem.*, **32**, 435 (1967).

(25) I. M. Goldman, *J. Org. Chem.*, **34**, 1979 (1969).

(26) M. P. Hartshorn and A. F. A. Wallis, *J. Chem. Soc.*, 5254 (1964).

12. The proton nmr of **6** was identical with that for **12** except for the absence of an absorption at δ 4.5 (d, 1 H, CHOH); ^2H nmr (**6**) δ 2.9 (s, 1 D, CDOH) upfield from benzene- d_6 . To an ethereal solution of the intermediate mesylate (**7**) [prepared from **6** (2.85 g), methanesulfonyl chloride (2.25 g), and pyridine (25 ml)] was added lithium aluminum hydride (1 g) over a period of 2 min. The solution was stirred for 1.5 hr at 25° and worked up as described above to yield a 50:50 mixture of monodeuterated α - and β -pinenes (**9** and **8**, respectively). Separation by glc gave [3- ^2H]- α -pinene (**9**) (0.7 g, 27%) and *cis*-[3- ^2H]- β -pinene (**8**) (0.7 g, 27%): ^2H nmr (**9**) δ 3.27 (s, 1 D, vinylic), downfield from acetone- d_6 ; ^2H nmr (**8**) δ 5.10 (d, 1 D, $J_{\text{HD}} = 2$ Hz), upfield from benzene- d_6 .

Preparation of [3,10- $^2\text{H}_2$]- α -Pinene (11**) and [3,3- $^2\text{H}_2$]- β -Pinene (**10**).** These dideuterated pinenes were prepared by the method described above for **8** and **9** except that the intermediate ethereal solution of the mesylate (**7**) was reduced with lithium aluminum deuteride (1 g) to give **11** (0.7 g, 27%) and **10** (0.7 g, 27%): ^2H nmr (**11**) δ 5.3 (s, 1 D, vinylic), 5.7 (t, 1 D, CH_2D), upfield from benzene- d_6 ; ^2H nmr (**10**) δ 4.83 (s, 1 D, trans), 5.1 (s, 1 D, cis), upfield from benzene- d_6 .

[10- ^2H]- α -Pinene (4**) from *trans*-Pinocarveol (**2**).** An ethereal solution of the mesylate (**3**), prepared from *trans*-pinocarveol (1.9 g), was reduced with lithium aluminum deuteride (0.47 g) as previously described to give a terpenic product (*ca.* 0.85 g, 50%). Analysis (glc) of an aliquot showed this material to consist of **4** to the extent of 95%. Deuterium nmr and mass spectrum of the purified sample were (within experimental error) identical with those of **4** obtained from the reduction of **13**.

Thermal Condensation of β -Pinene with Methyl Phenylglyoxylate (18**).** A solution composed of methyl phenylglyoxylate (16.5 g), hydroquinone (0.1 g), and β -pinene (250 g) was maintained under reflux for 96 hr. The excess β -pinene was removed under reduced pressure. Fractionation of the viscous reaction product gave the 1:1 adduct (**19**), methyl 2'-hydroxy-2'-phenyl-3'-[6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]propionate (18.7 g, 62.4%): bp 127–128° (0.2 mm); ir (neat) 3500 cm^{-1} (OH) and 1735 cm^{-1} (C=O); ^1H nmr (CCl_4) δ 7.6–7.0 (m, 5 H, ArH), 5.3 (m, 1 H, vinylic), 3.7 (s, 1 H, OH), 3.6 (s, 3 H, CH_3), 3.1–1.5 (m, 7 H), 1.2 (s, 3 H, CH_3), 1.2–0.9 (m, 1 H), 0.8 (d, 3 H, CH_3 , $J = 2$ Hz).

Anal. Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_3$: C, 75.95; H, 8.07. Found: C, 75.59; H, 8.18.

Solvent Effects in the Formation of **19.** Into two separate tubes was added β -pinene (1.36 g, 0.01 mol) and methyl phenylglyoxylate (1.64 g, 0.01 mol). To one of the tubes was added *o*-xylene (1.06 g, 0.01 mol) and to the other nitrobenzene (1.23 g, 0.01 mol). Both tubes were sealed under an atmosphere of nitrogen and heated (140°). Several samples were withdrawn over a period of 140 hr and their ir spectra recorded. Examination of the hydroxyl region indicated that there was no noticeable difference in the rate of 1:1 adduct formed in the two media.

Pyrolysis of Methyl 2'-Hydroxy-2'-phenyl-3'-[6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]propionate (20**).** The undeuterated hydroxy ester (**19**) (18.7 g) was dissolved in dry ether (20 ml) and shaken, successively, with three portions (13 g each) of pure deuterium oxide. The ethereal solution was dried (Na_2SO_4) and distilled to give a quantitative yield of **20**. This material, when prepared under conditions which rigorously excluded ordinary water,

showed no hydroxyl absorption (ir) but absorbed strongly at 2590 cm^{-1} (–OD). A portion (3 g) of this sample was pyrolyzed (275°) in a semimicro distilling apparatus, under N_2 , to give methyl phenylglyoxylate (**18**) (0.41 g, 25%) and a hydrocarbon fraction. From the latter, *trans*-[3- ^2H]- β -pinene (**14**) (0.34 g, 25%) was separated on a 15-ft 30% Apiezon-L Chromosorb W chromatographic column (160°, helium pressure 19 lb). A deuterium nmr spectrum of **14** showed it to be identical with an authentic sample. Its mass spectrum indicated 88% deuterium incorporation. As expected the recovered **18** showed no deuterium incorporation.

Thermal Condensation of *trans*-[3- ^2H]- β -Pinene (14**) with Methyl Phenylglyoxylate.** A solution consisting of methyl phenylglyoxylate (3.7 g), hydroquinone (0.05 g), and *trans*-[3- ^2H]- β -pinene (2.7 g, >95% monodeuterated) was heated in a sealed tube at 165° for 120 hr. Direct vacuum distillation yielded the ester (**20**) (1.0 g, 16.6%). Comparison of the ir spectrum of this sample with those of pure **19** and **20** gave OD:OH equal to 70:30.

10-Phenyl- α -pinene (15**).** To a slurry of benzenediazonium-2-carboxylate (prepared from anthranilic acid (3 g) by the method of L. Friedman¹⁶) in methylene chloride (30 ml) was added β -pinene (1.36 g) in methylene chloride (15 ml). The resulting slurry was heated under reflux (40–45°) for 3 hr, at which time the diazonium salt was completely decomposed. Removal of the solvent, under vacuum, gave a dark oil most of which readily dissolved in low-boiling petroleum ether (100 ml). The filtered petroleum ether solution was evaporated to give a limpid yellow oil (2.0 g) which was chromatographed on neutral activated alumina using petroleum ether as the liquid phase. Evaporation of the product fractions yielded pure 10-phenyl- α -pinene (**15**) (1.3 g, 62%): bp 76° (0.05 mm); nmr (CCl_4) δ 7.4 (s, 5 H, ArH), 5.4 (m, 1 H, vinylic), 3.3 (m, 2 H, CH_2), 2.6–1.9 (m, 5 H), 1.3–1.1 (m, 4 H), 0.8 (s, 3 H, CH_3).

Anal. Calcd for $\text{C}_{16}\text{H}_{26}$: C, 90.49; H, 9.51. Found: C, 90.10; H, 9.22.

Reaction of Benzene with *cis*- and *trans*-[3- ^2H]- β -Pinenes (8** and **14**).** (a) Compound **8** (1.0 g; >99% monodeuterio) was allowed to react with benzene as described in the preceding experiment. Careful examination of the proton and deuterium nmr of the product (1.2 g, 77%) showed it to consist overwhelmingly (>95%) of 10-phenyl[3- ^2H]- α -pinene (**16**). Deuterium nmr δ 3.3 (s, 1 D, vinylic), downfield from acetone- d_6 . (b) When compound **14** (1.1 g, >99% monodeuterio) was allowed to react with benzene as described above, the product (0.9 g, 53%) proved to be 10-[2'- ^2H]phenyl- α -pinene (**17**). Its deuterium nmr, δ 5.2 (s, 1 D, ArD), downfield from acetone- d_6 , showed that the deuterium was attached overwhelmingly (>95%) to the phenyl ring.

Reaction of Benzene with α -Pinene. To a solution of α -pinene (60 g, 0.44 mol) in methylene chloride (70 ml) was added benzenediazonium-2-carboxylate (prepared from 9 g, 0.066 mol, of anthranilic acid¹⁶). After the slurry had been stirred at 45–50° for 6 hr, the diazonium salt had completely decomposed. The dark brown oil, which remained after removal of solvent and excess α -pinene under reduced pressure, was chromatographed on a column of neutral alumina (5 × 13 cm) with low-boiling petroleum ether to give 3,10-diphenyl- α -pinene (3.0 g, 32%): bp 133° (0.1 mm); nmr (CCl_4) δ 7.2 (m, 10, Ar), 3.40 (m, 2 H, CH_2Ar), 2.4 (m, 5 H), 1.3 (m, 4 H), 0.9 (s, 3 H, CH_3).

Anal. Calcd for $\text{C}_{22}\text{H}_{24}$: C, 91.60; H, 8.40. Found: C, 91.53; H, 8.29.