Communications TO THE EDITOR

Rhodium-Catalyzed Nuclear Hydrogenation of α-Substituted Benzyl Alcohols and Esters. A Useful Procedure for Establishing Configurations

Sir:

The catalysts that might be employed in the nuclear hydrogenation of compounds containing the benzyloxy moiety promote hydrogenolysis to such an extent that the method is considered to be of inferior synthetic value.[1]

We now wish to report that the rhodium-catalyzed hydrogenation of several representative α-substituted benzyl alcohols and benzyl ethers proceeded rapidly and smoothly at room temperature and a pressure of 3–4 atm. of hydrogen, to produce the cyclohexyl analogs in satisfactory to excellent yield. The use of 1.5 g. of rhodium catalyst for each 0.05 mole of phenyl led to reaction times of 1–3 hr. with the specific exceptions noted below. A representative procedure employed 7.60 g. (0.05 moles) of DL-mandelic acid, 1.5 g. of 5% rhodium-on-alumina,[2] 40 ml. of absolute methanol, and 0.5 ml. of glacial acetic acid; the mixture absorbed the theoretical amount of hydrogen (Parr low-pressure apparatus) in 1.5 hr. and, following filtration through a Celite mat and concentration on a rotary evaporator, yielded 98.6% of DL-hexahydromandelic acid, m.p. 135–136° without recrystallization. (Lettré et al.[3] have reported 134–135°.) Similar treatment of α-methylbenzyl alcohol, followed by distillation, produced 80% of methylcyclohexylcarbinol, b.p. 83–85° (9 mm.), n^{25}D 1.4630 (lit.[4] b.p. 85–87° (17 mm.), n^{25}D 1.4639). The hydrogenation product from benzhydrol was purified by chromatography on alumina; extended cooling of a petroleum ether solution of the benzene eluate yielded 80% of very large chunky crystals of dicyclohexylcarbinol, m.p. 64–65° (reported[5] m.p. 66°). Dibenzyl ether produced 60% of dicyclohexylmethyl ether,[6,7] b.p. 83° (0.4 mm.), n^{26}D 1.4676. Methyl benzyl ether gave 50% of methyl cyclohexylmethyl ether,[7] ether[7] b.p. 154° (760 mm.),[8] n^{25}D 1.4325. An

additional 14% of somewhat impure product could be obtained from the methanol distillate by the addition of twice its volume of water. Hydrogen take-up usually ceased after a pressure drop equivalent to complete hydrogenation of the phenyl groups. The hydrogenation of methyl benzyl ether was a notable exception in that the pressure continued to drop steadily beyond this point and required more attention.

To establish that no racemization was taking place unobserved, D-mandelic acid[9] was hydrogenated[10] to D-hexahydromandelic acid[9] in 94% yield. Accordingly, the procedure recommends itself as the one of choice in establishing the configurations of the cyclohexyl counterparts of the many ring substituted mandelic and atrolatic acids for which such configurations are known and particularly in the general synthesis of these compounds themselves.[11] It could further be employed in conjunction with the Prelog[12] atrolactic ester synthesis to establish the configuration of the hydrogenated acids thereby derived. It was utilized most profitably in the present study in the hydrogenation of *meso*- and *dl*-2,3-diphenylbutanediol[13] to the corresponding 2,3-dicyclohexyl-2,3-butanediols. (Reaction time, 24 hr.; *meso* form[7] m.p. 127° from hexane, 88% yield; racemic form[7] m.p. 107° from hexane, 94% yield.) Since the configurations of the starting materials utilized here have been established,[14] those of the hydrogenated products automatically follow. The procedure served thereby both to prepare needed materials and to establish their relative configurations. While these compounds might be prepared by the stereoselective addition of organometallic reagents to appropriate diketones, previous work has shown that methods of prediction of the domi-

(9) The starting material was purchased from the Columbia Organic Chemical Co., Columbia, South Carolina, m.p. 134, α^{21}D −151.5° (2% in absolute ethanol). Based on a reported value of α^{20}D −159.7° (ethanol) (Heilbron's "Dictionary of Organic Compounds," Oxford University Press, New York, New York, 1953, Vol. 3, p. 212), it calculates to 95% optical purity. The product had a m.p. of 129°, α^{23}D −23.4° (9% in glacial acid). Assuming an α^{20}D −25.5° (1% in acetic) (ref. 3), the product was of 92% optical purity.

(10) Acetic acid was not employed in this hydrogenation. Its absence approximately doubled the reaction time required for the hydrogenation of the racemic material. Freifelder [*J. Org. Chem.*, **26**, 1835 (1961)] has reported organic acids have an accelerating effect in certain rhodium catalyzed hydrogenations.

(11) It should be noted that platinum-catalyzed ring hydrogenation has been employed to establish the configuration of the cyclohexyl analogs of at least two substituted benzyl alcohols. [See P. A. Levene and P. G. Stevens, *J. Biol. Chem.*, **89**, 473 (1950), also ref. 3.]

(12) V. Prelog and G. Tsatsas, *Helv. Chim. Acta*, **36**, 1178 (1953) and preceding papers.

(13) J. H. Stocker, P. Sidusunthorn, B. M. Benjamin, and C. J. Collins, *J. Am. Chem. Soc.*, **82**, 3913 (1960).

(14) D. J. Cram and K. R. Kopecky, *J. Am. Chem. Soc.*, **81**, 2748 (1959).

(1) W. H. Harting and R. Simonoff, *Org. Reactions*, VII, 447ff (1953); H. Adkins and R. L. Shriner, "Organic Chemistry," Vol. I, H. Gilman, ed., J. Wiley and Sons, Inc., New York, 1943, pp. 817ff.

(2) Available from Engelhard Industries, Inc., Newark 2, N. J.

(3) H. Lettré, H. Barnbeck, and H. Stanau, *Ber.*, **69B**, 1597 (1936).

(4) W. K. Johnson, *J. Org. Chem.*, **24**, 865 (1959).

(5) O. Neunhoffer, *Ann.*, **509**, 123 (1934).

(6) A distillation forerun consisted of 9.6% of cyclohexylcarbinol.

(7) Satisfactory elementary analysis were obtained for all new compounds.

(8) A small forerun was identified by its infrared spectrum and 2,4-dintrophenylhydrazone as cyclohexanecarboxaldehyde.

nant diastereoisomer formed are not always reliable.[15]

Several attempts to hydrogenate benzyl alcohol[16] by this procedure resulted in an uptake of less than 50% of the theoretical amount of hydrogen; 10% of impure product was isolated. Attempted hydrogenation of benzopinacol was very slow and gave intractable products.

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DEPARTMENT OF CHEMISTRY   J. H. STOCKER
LOUISIANA STATE UNIVERSITY OF NEW ORLEANS
NEW ORLEANS 22, LOUISIANA

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(15) See ref. 13. The cyclohexyl glycols were needed for continuing study of such systems; the work to be submitted for publication shortly.

(16) The kinetics of the rhodium catalyzed reduction of benzyl alcohol have been reported by Gilman and Cohn ("Advances in Catalysis," Vol. IX, Academic Press, Inc., New York, New York, 1957, p. 736) without describing products or yields. It appears to be the only benzyl alcohol or ether of which rhodium-catalyzed hydrogenation has been reported.

The Effect of Oxygen in Free Radical Aromatic Alkylation with Diaroyl Peroxides

Sir:

In a previous publication[1] it has been postulated that the arylcyclohexadienyl radicals $ArC_6H_6 \cdot$ which are formed in the decomposition of a diaroyl peroxide, $(ArCOO)_2$, in benzene disproportionate to arylbenzene, ArC_6H_5, and arylcyclohexadiene, ArC_6H_7, and that the latter may then give rise to further arylbenzene through dehydrogenation by benzoyl peroxide which, in turn, is converted to

(1) (a) E. L. Eliel, S. Meyerson, Z. Welvart, and S. H. Wilen, *J. Am. Chem. Soc.*, **82**, 2936 (1960); see also (b) D. F. DeTar and R. A. J. Long, *ibid.*, **80**, 4742 (1958); (c) D. F. DeTar, Abstracts, 17th National Organic Chemistry Symposium Am. Chem. Soc., Bloomington, Ind., 1961, pp. 64-70.

benzoic acid, the latter process being more prevalent in concentrated than in dilute solution. We have since established (see Table I, entries 4, 5, 14, 23, 24) that phenylcyclohexa-1,4-diene is, in fact, dehydrogenated to biphenyl by diaroyl peroxides. The process requires heat and the dehydrogenating species are thus presumably the carboxy radicals $ArCOO \cdot$ rather than the diaroyl peroxides as such.

It occurred to us that if the dehydrogenation could be effected by a reagent other than the benzoate radicals, this would avoid the wastage of half these radicals in the form of benzoic acid and might increase the yield of arylbenzene from a maximum of one mole per mole of peroxide: $C_6H_6 + (ArCOO)_2 \rightarrow ArC_6H_5 + ArCOOH + CO_2$ to a theoretical maximum of two moles per mole of peroxide: $2C_6H_6 + (ArCOO)_2 + Oxidant \rightarrow 2ArC_6H_5 + 2CO_2 + H_2 \cdot Oxidant$. In fact, we have now found that in the presence of oxygen (bubbled through the refluxing benzene solution of the decomposing peroxide) the actual yield of arylbenzene can be increased from 0.47 mole per mole of peroxide to 0.60 mole per mole of peroxide in concentrated solution (runs 1–3, 6) and, more dramatically, from about 0.50 mole per mole of peroxide to 1.26–1.51 moles per mole of peroxide in dilute solution (runs 7–13, 15–21). The pertinent data are shown in Table I.

Although the yield of biphenyl (as well as 1,4-dihydrobiphenyl) in most instances was established gas-chromatographically, the biphenyl was actually isolated by steam distillation in runs 15 and 16, the isolated yield agreeing with the analytical. Recrystallization of the material from these runs gave pure biphenyl, m.p. 70–71° in 50% (1.55 g.) and 55% (1.75 g.) yield, respectively. (These yields are calculated on the basis of two moles of arylbenzene per mole of peroxide and clearly exceed the yield obtainable if one mole of peroxide gave rise to only one mole of biaryl.)

Although the increased yield of biaryl follows

TABLE I

YIELD OF PRODUCTS FROM BENZOYL PEROXIDE AND BENZENE IN PRESENCE AND ABSENCE OF OXYGEN (20–24-HR. REFLUX)

Run	Regents	Moles benzene[a] moles peroxide	Biaryl	1,4-Dihydrobiphenyl	Benzoic acid
			Major products, moles per mole peroxide[b]		
1–3	$(C_6H_5COO)_2$	54.7:1	0.38–0.47	0.025–0.031	0.30–0.33
4	$(C_6H_5COO)_2, C_6H_5C_6H_7{}^d$	54.7:1	.49	.062	c
5	$(C_6H_5COO_2), C_6H_5C_6H_7{}^e$	54.7:1	.54	.124	c
6	$(C_6H_5COO_2), O_2$	54.7:1	.60	0	c
7–13	$(C_6H_5COO)_2$	547:1	.48–0.50	0.17–0.19	0.10–0.15[f]
14	$(C_6H_5COO)_2, C_6H_5C_6H_7{}^d$	547:1	.60	.36	c
15–21	$(C_6H_5COO)_2, O_2$	547:1	1.26–1.51[g]	0	0.10–0.11[h]
22	$(p\text{-}ClC_6H_4COO)_2$	70:1	0.36	...	...
23	$(p\text{-}ClC_6H_4COO)_2, C_6H_5C_6H_7{}^i$	70:1	.28[j](.19[k])	0.0395	...
24	$(p\text{-}ClC_6H_4COO)_2, C_6H_5C_6H_7{}^i$	700:1	c(0.095[k])	.27	...

[a] Peroxide, 25 g., benzene, 50 ml. at low dilution, 500 ml. at high dilution.   [b] In some runs, quaterphenyl was also identified.   [c] Not analyzed.   [d] 1,4-Dihydrobiphenyl, (0.31 mole/mole peroxide) added.   [e] 1,4-Dihydrobiphenyl (0.62 mole/mole peroxide) added.   [f] Also 1.13–1.36 g. high-boiling material, probably tetrahydroquaterphenyls (ref. 1c).   [g] Yield dependent on rate of passing oxygen through solution; see text.   [h] Also 0.19–0.30 g. high-boiling material and, in some runs, up to 0.1 mole of phenol per mole of peroxide.   [i] 1,4-Dihydrobiphenyl, 0.395 mole, added per mole of peroxide.   [j] p-Chlorobiphenyl.   [k] Biphenyl.

prediction, the data (runs 7–13 vs. 15–21) show that it is not in fact obtained at the expense of benzoic acid. Thus in concentrated solution, where abstraction of hydrogen by benzoate radicals is prevalent, the increase in yield in the presence of oxygen is not dramatic. In dilute solution, where the spectacular increase occurs, it is *not* at the expense of benzoic acid, but rather at the expense of dihydrobiphenyl and higher boiling products (runs 7–13 vs. 15–21). In fact, comparison of runs 9–13 with 15–21 indicates a nearly constant yield of benzoic acid but an increase in the material recovery of peroxide-derived aryl groups from 41 to 79%.

The following conclusions may be reached from these and related observations: (1) In dilute solution, oxygen leads to cleaner arylation and triples the yield of biaryl. (2) Since the yield of benzoic acid is nearly unaffected by oxygen and since the increase in yield of biphenyl is much greater than the decrease in yield of dihydrobiphenyl, oxidation of dihydrobiphenyl cannot account for all the extra biphenyl found. Much of the extra biphenyl is evidently formed at the expense of higher boiling material, shown by DeTar[1c,2] to consist mainly of tetrahydroquaterphenyls. The fact that formation of these dimers of phenylcyclohexadienyl radicals is largely suppressed by oxygen indicates that another function of oxygen is to react with phenylcyclohexadienyl radicals, converting them to biphenyl. (3) At the rates at which oxygen was supplied (15–20 mL per minute), its reaction with phenyl radicals is not important. Not more than 0.1 mole of phenol per mole of peroxide was formed (runs 19, 20), and at the optimum rate of passage of oxygen, dihydrobiphenyl formation could be completely suppressed and biphenyl yield maximized with almost no phenol being generated. Evidently, the initial phenyl radicals are relatively short-lived and add to benzene to form the much more stable phenylcyclohexadienyl radicals. (4) Whereas in the absence of oxygen, many of the initially generated aryl radicals end up in products other than biphenyls, in the presence of oxygen nearly all aryl radicals are accounted for as arylbenzene. Thus isomer composition studies in the phenylation of substituted benzenes in the presence of oxygen should give a truer picture of the relative reactivity of the *ortho*, *meta*, and *para* positions than presently available studies in the absence of oxygen. This point is being explored.

DEPARTMENT OF CHEMISTRY MANFRED EBERHARDT
  AND RADIATION LABORATORY[3] ERNEST L. ELIEL
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA

(2) D. F. DeTar, personal communication.
(3) The Radiation Laboratory is operated under Atomic Energy Commission Contract.

The Effect of Remote Substituents in the Addition of Trifluoroacetic Acid to Alkenes[1]

Sir:

During a study of the addition of trifluoroacetic acid to 5-substituted 1-hexenes (I. equation 1)[2]

$$\text{I} \longrightarrow \text{II} \tag{1}$$

X = H, Cl, Br, O_2CCH_3, O_2CCF_3
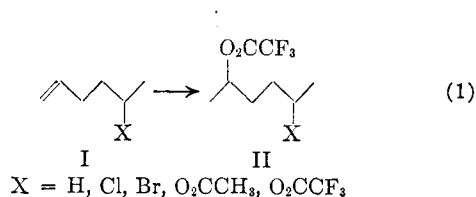
we observe that the trifluoroacetoxy and the acetoxy compounds (I. X $= O_2CCF_3$, O_2CCH_3) react at rates which are decreased by factors of 168 and 38, respectively, compared to the rate for 1-hexene, previously reported (I. X $=$ H).[3] That these rate effects are remarkably large compared to the effects which might have been expected is indicated by the data in Table I, in which our rate constants are compared with those previously observed[4] for the formolysis of 1-substituted 4-bromopentanes. Although both types of reaction may be regarded as carbonium ion reactions in which a substituent is present on the fourth carbon from the potential cationic carbon, only small rate decreases (presumably resulting from inductive effects) were observed in the bromopentane formolyses. Furthermore, in a recent comprehensive survey of the current status of inductive effects it was pointed out that although the magnitude of inductive effects in 4-substituted cyclohexenes and in comparable aromatic systems is similar (rate retardations by factors of approximately 100 are involved), "comparable rate effects in γ- or δ-substituted aliphatic functions simply cannot be realized (even though the substituent is not any further from the reaction site than in the aromatic case)."[5] It may be concluded that if the rate effects reported in Table I are the result of inductive effects, their magnitude represents a novel departure from previous experience.

(2) Addition products of type II were the major products in the cases studied: X = H and X = O₂CCF₃. In the latter case, two diastereomers were shown to be present.
(3) In view of the observed Markownikoff addition, the initial step in the addition of trifluoroacetic acid to alkenes is presumed as usual to be the addition of a proton to give a cationic intermediate or transition state. *Cf.* (a) P. E. Peterson, *J. Am. Chem. Soc.*, **82**, 5834 (1960); (b) P. E. Peterson and G. Allen, Abstracts, St. Louis Meeting of the American Chemical Society, March, 1961, p. 340; (c) P. E. Peterson and G. Allen, *J. Org. Chem.*, **27**, 1505 (1962.).
(4) S. Oae, *J. Am. Chem. Soc.*, **78**, 4032 (1956).
(5) H. Kwart and L. J. Miller, *ibid.*, **83**, 4552 (1961).

In an attempt to find whether the rate of addition of trifluoroacetic acid to alkenes is unusually sensitive to steric hindrance we measured the rate

Table I

RATES OF ADDITION OF TRIFLUOROACETIC ACID TO 5-SUBSTITUTED 1-HEXENES AND RATES OF FORMOLYSIS OF 1-SUBSTITUTED 4-BROMOPENTANES

Substituent	$k \times 10^6$, sec.$^{-1}$ (addition)^a	$k \times 10^5$, sec.$^{-1}$ (formolysis)^b
H	235	6.5
Cl	67	...
Br	83	6.3
O_2CCH_3	6.2	6.4
O_2CCF_3	1.4	...
CN	...	1.4

^{a} For reaction at 35.0° of 0.10 M alkene in trifluoroacetic acid 0.125 M in sodium trifluoroacetate. The procedure described in ref. 3c was used. The substituted hexenes are described in the literature with the exception of the trifluoroacetate. *Anal.* Calcd. for $C_8H_{11}O_2F_3$: C, 48.98; H, 5.65. Found: C, 49.41; H, 6.11. ^{b} Data from ref. 4 for reaction at 85° in 78.5% formic acid.

of reaction of 4,4-dimethyl-1-pentene. Since only a 2.8-fold rate decrease compared to the rate for 1-hexene was observed for this olefin, which should be moderately hindered,[6] it appears that steric hindrance is not likely to be the major factor which accounts for our large rate decelerations.

In Table II evidence is presented which suggests that the rate effects may in fact be the result of surprisingly large inductive effects. Estimated values of Taft's inductive constants, σ_I, are given for the acetoxy and trifluoroacetoxy groups, based on the fluorine NMR frequencies of m-fluorophenyl acetate and m-fluorophenyl trifluoroacetate and the previously observed linear relationship between $meta$-fluorine frequencies and σ_I.[7]

Table II

INDUCTIVE CONSTANTS FROM NMR DATA

Group	σ_I (carbon tetrachloride)	σ_I (trifluoroacetic acid)
O_2CCH_3	0.32	0.60
O_2CCF_3	.67	.72

The large magnitudes of the estimated σ_I values in the second column of Table II and the increased magnitudes observed when the NMR spectra were determined in trifluoroacetic acid support the idea that unusually large inductive rate depressions may be involved in our addition reactions. Trifluoroacetic acid presumably hydrogen bonds to the oxygen containing substituent groups involved

or protonates them to increase their inductive effect.[8]

DEPARTMENT OF CHEMISTRY   P. E. PETERSON
SAINT LOUIS UNIVERSITY   G. ALLEN
SAINT LOUIS, MISSOURI

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(8) It will be shown in a subsequent paper that the magnitude of the rate effect is considerably larger than that which would have been anticipated from the NMR data.

Photoisomerization of Methyl Thujate[1]

Sir:

Methyl thujate (Ia) should photoisomerize smoothly to the bicyclic products IIa and IIIa by analogy with other cycloheptatrienes,[2,3] cycloheptadienes,[2,4] and tropolones.[5-7] Irradiation of methyl thujate in ether, however, gives as the major product (40–50%) the cycloheptatriene IVa in which a methyl migration has taken place and the bicyclic product IIa (25–30%). The Wagner-Meerwein product (IVa) shows ultraviolet ab-
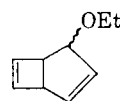

Ia. R = CH₃
b. R = H
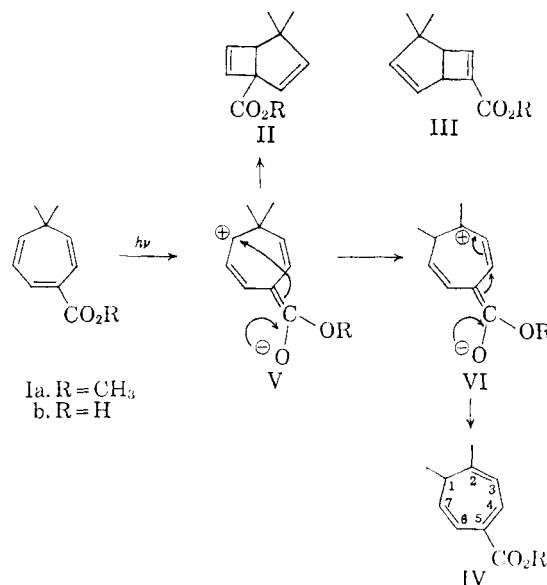
sorption in 95% ethanol [216.5 mμ (15,400) and

(1) Part II of photochemical transformations of troponoid systems (See ref. 5 for Part I).
(2) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).
(3) Unpublished research by G. W. Borden (Iowa State University) has shown that ethyl tropyl ether photoisomerizes to

in good yield.
(4) (a) O. L. Chapman and D. J. Pasto, *Chem. Ind.*, 53 (1961); (b) O. L. Chapman, D. J. Pasto, A. A. Griswold, and G. W. Borden, *J. Am. Chem. Soc.*, **84**, 1220 (1962).
(5) O. L. Chapman and D. J. Pasto, *ibid*, **82**, 3642 (1960).
(6) W. G. Dauben, K. Koch, O. L. Chapman, and S. L. Smith, *ibid.*, **83**, 1768 (1961).
(7) E. J. Forbes, *J. Chem. Soc.*, 3864 (1955).

(6) *Cf.* M. S. Newman in "Steric Effects in Organic Chemistry," John Wiley & Sons, Inc., New York, 1956, p. 205.
(7) R. W. Taft, Jr., *J. Chem. Phys.*, **64**, 1805 (1960), and references given therein. We thank Professor Taft for permission to report these NMR frequencies, determined by one of us (P.E.P.) at Pennsylvania State University as part of Professor Taft's research program in which shifts of fluorine NMR frequencies in trifluoroacetic acid had already been observed.

293 mμ (7000)] and infrared absorption (>C=O, 5.84 μ) very similar to methyl thujate [Ia, 212 mμ (20,000) and 282.5 mμ (5500), 5.84 μ]. The NMR spectrum of IVa unambiguously establishes the structure. The hydrogens at positions 3 and 4 appear as a pair of doublets (J_{34} = 6.6 c.p.s.) at 2.55 and 3.93 τ. The olefinic proton at position 6 appears as a doublet (J_{67} = 9.7 c.p.s.; 3.46 τ) coupled to the proton at position 7 [which appears as a quartet (4.92 τ)].[8] The proton at position 1, which is coupled to H-7 (J_{17} = 6.6 c.p.s.), is partially obscured by the —C=C—CH₃ resonance at 8.02 τ. It has been rigorously established that H-1 and H-7 are coupled by a double resonance experiment in which the 8.02 τ signal was saturated reducing the 4.92 τ quartet to a doublet (J_{67} = 9.7 c.p.s.). The methyl group at position 1 produces a doublet (J = 7.1 c.p.s.) at 8.79 τ. Structure IIa for the bicyclic product from the irradiation of methyl thujate follows from the fact that this product shows an infrared maximum at 5.78 μ, no ultraviolet maxima above 210 mμ and the NMR spectrum. The hydrogens of the cyclopentene double bond produce a pair of doublets (J = 6.0 c.p.s.)[9] at 4.31 and 4.52 τ. The hydrogens of the cyclobutene double bond appear as a pair of doublets (J = 2.8 c.p.s.)[10] at 3.55 and 3.88 τ [the 3.88 τ doublet is also coupled (ca. 1 c.p.s.)[10] to the bridgehead proton (6.80 τ)]. The non-equivalent methyl groups give signals at 8.92 and 8.97 τ.

(8) The resonance locations of the olefinic protons in IVa agree very well with the locations of the corresponding olefinic proton signals in methyl thujate.

(9) These values for the coupling constants accord well with those obtained in closely related bicyclo[3.2.0]heptadiene systems.[5,6]

(10) The coupling between cyclobutene hydrogen in systems of this type is weaker than similar coupling in larger rings.[4b] The coupling between cyclobutene protons and bridgehead protons is also rather weak (ca. 0.5-1 0 c.p.s.; cf. i)[4b] compared to the coupling between a bridgehead hydrogen and a cyclopentene double bond (3.2 c.p.s. in ii).[6]
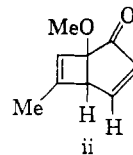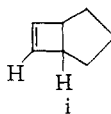
Irradiation of thujic acid [Ib, 214 mμ (18,600) and 282.5 mμ (5700)] for 7 hr. in ether gives IVb [(m.p. 114.5–115.3°; 216 mμ (15,900) and 292 mμ (7100)] in 56% yield. The NMR spectrum of IVb shows two doublets (J_{34} = 6.7 c.p.s.) at 2.31 and 3.80 τ (H-4 and H-3), a doublet J_{67} = 9.9 c.p.s.) at 3.30 τ and a quartet (J_{17} = 6.7 c.p.s.) at 4.81 τ (H-6 and H-7), and a three proton doublet (J = 7.3 c.p.s.) at 8.75 τ (—CH—CH₃). The —C=C—CH₃ resonance at 7.97 τ overlaps the H-1 resonance. Thujic acid was recovered unchanged after 11 hours' reflux in ether in the dark.

Formation of the Wagner-Meerwein product IV can be rationalized on the basis of the polar intermediate V. Methyl migration gives a slightly more stable intermediate VI which gives IV. Redistribution of the electrons in V also leads *specifically* to the bicyclic product II.

Satisfactory analyses have been obtained for all new compounds.

DEPARTMENT OF CHEMISTRY   O. L. CHAPMAN
IOWA STATE UNIVERSITY   S. L. SMITH[11]
AMES, IOWA

(11) National Institutes of Health Predoctoral Fellow, 1960–1961.