Synthesis and Acid-Catalyzed Rearrangement of Iso-*p*-anisylapocamphene[1]

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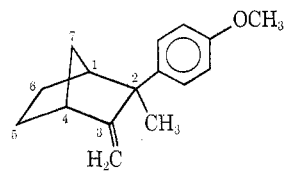
A stereospecific synthesis of iso-*p*-anisylapocamphene (**1**) and its methyl-deuterated analog (**1**-CH_3-*d*) are described. In concentrated sulfuric acid solution **1** generates the long-lived *p*-anisylcamphenilyl cation **5**, which undergoes rapid racemization. It is suggested that racemization involves a 6,2-hydride migration preceded and followed by Wagner–Meerwein rearrangements. Racemization of the cation **5** *via* cyclene formation, in contrast to the results found for the same ion in 98+% formic acid, does not take place in concentrated sulfuric acid. The differences in the nature and velocity of the racemization processes of cation **5** in 98+% formic acid and concentrated sulfuric acid are discussed in terms of the different H_0 values of the two solvents.

One of the more germane questions which remains unresolved in the area of cationic transformations in the norbornyl series is that of the observed exo stereospecificity of 3,2 shifts.[3] It is likely that the same phenomena responsible for predominant exo attack on 2-norbornyl cations during solvolysis are also responsible for the exclusive exo nature of 3,2 shifts in the same cations.[4] A complete understanding of the factors responsible for stereospecific 3,2 shifts is necessary if one hopes to comprehend the larger question of the nature of substituted 2-norbornyl cations.

Several rationalizations have evolved in attempts to explain 3,2 shifts in these cations.[4,5] These rationalizations are extensions of more comprehensive theories dealing with the behavior of 2-norbornyl esters during solvolysis. Schleyer has offered convincing arguments against both the steric and nonclassical theories as providing adequate explanations for the observed 3,2 shifts[4] and, as an alternative, has advanced the torsional strain theory. However, recent data suggest that the influence of torsional strain in reactions of the norbornyl skeleton is minimal.[6] Although much data has been collected regarding the stereochemistry and kinetics of 3,2 shifts[7] (mainly 3,2 hydrogen shifts), presently there is no single theory which adequately accounts for the observed stereospecificity of 3,2 shifts in substituted norbornyl cations while remaining consistent with other known properties of the same ions.[8] The work of Wilder and coworkers[9,10] has produced the first examples of endo 3,2 shifts which constitute a major reaction pathway. The bornyl system is implicated in their work and is in sharp contrast to the analogous norbornyl system, which scrupulously avoids the endo 3,2 shift.[11] Certainly further research on this interesting dichotomy is suggested.

It was felt that the above dilemma was due in part to the lack of experiments designed to probe directly for fundamental phenomena responsible for the stereospecific 3,2 shifts in the norbornyl system. Therefore, this research was initiated in an attempt to begin this probe and at the same time extend the present scope of knowledge of 3,2 carbon shifts in the norbornyl system. As part of this objective it was proposed to prepare precursors which might tend to promote previously unobserved 3,2 shifts in substituted norbornyl cations. Analysis of the behavior of the precursors under cationic conditions would allow conclusions to be drawn regarding the nature of the presumed shifts and possibly the nature of the intermediate ions involved.

The precursor chosen for the present study was *exo*-2-*p*-anisyl-*endo*-2-methyl-3-methylenenorbornane (**1**)



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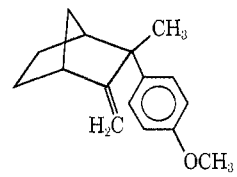


2

(iso-*p*-anisylapocamphene). Since Bartlett, *et al.*,[12] have studied its epimer *p*-anisylapocamphene (**2**) extensively under cationic conditions, one is indirectly aware of much of the chemistry of **1**. Although there is no literature precedent for aryl 3,2-bridging in substituted norbornyl cations,[11-14] it was felt that **4**, produced *via* protonation of **1**, should have a good opportunity for bridging between C-2 and C-3 because (1) the *p*-anisyl group is in the favorable exo position and (2) the bridged ion **3** should benefit from the stabilizing ability of the *p*-methoxy group. Ion **4** also contains features which should serve to promote an endo 3,2-methyl migration. Such a migration will lead to the highly delocalized anisylic ion **5** and the activation energy for migration should be decreased due to partial formation of **5** at the transition state. This lowering of the activation energy could conceivably make endo 3,2-methyl migration competitive with other rearrangement pathways.

(1) Abstracted from the Ph.D. Dissertation of David L. Adams, The University of Connecticut, 1971.

(2) NDEA Fellow, 1967–1970; Texaco Fellow in Organic Chemistry, 1970–1971.

(3) See A. F. Fry and G. Karabatsos in "Carbonium Ions," Vol. II, G. A. Olah and P. von R. Schleyer, Ed., Interscience, New York, N. Y., 1970, Chapter 14, pp 521–571.

(4) P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 699, 701 (1967), and references cited therein.

(5) J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *ibid.*, **89**, 2590 (1967).

(6) S. P. Tindal and T. T. Tidwell, *Tetrahedron Lett.*, 783 (1971), and references cited therein. For a further view see J. W. Mellor and C. F. Webb, *ibid.*, 4025 (1972).

(7) C. J. Collins and C. E. Harding, *Justus Liebigs Ann. Chem.*, **745**, 124 (1971), and references cited therein.

(8) See C. W. David, B. W. Everling, R. J. Killian, J. B. Stothers, and W. R. Vaughan, manuscript submitted for publication, The University of Connecticut and The University of Western Ontario, 1972, for suggestions regarding the possible geometrical control of 3,2 shifts in the norbornyl series and the first example of endo 3,2-methyl shift.

(9) A. W. Bushell and P. Wilder, *J. Amer. Chem. Soc.*, **89**, 5721 (1967).

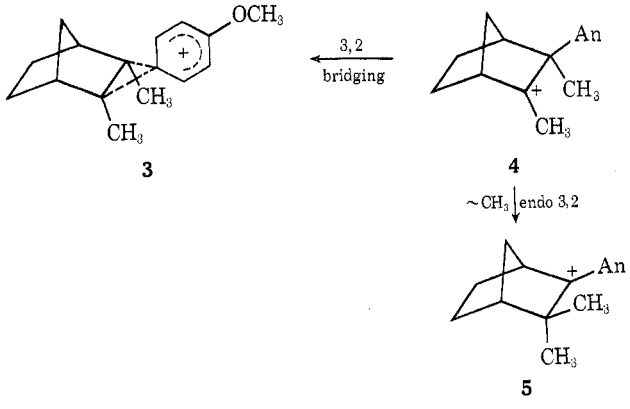
(10) P. Wilder and W.-C. Hsieh, *J. Org. Chem.*, **36**, 2552 (1971).

(11) C. J. Collins, Z. K. Chema, R. G. Werth, and B. M. Benjamin, *J. Amer. Chem. Soc.*, **86**, 4913 (1964).

(12) P. D. Bartlett, E. R. Webster, C. E. Dills, and H. G. Richey, Jr., *Justus Liebigs Ann. Chem.*, **623**, 217 (1959).

(13) D. C. Kleinfelter, E. S. Trent, J. E. Mallory, and T. E. Dye, *J. Amer. Chem. Soc.*, **88**, 5350 (1966).

(14) C. J. Collins, V. F. Raaen, B. M. Benjamin, and I. T. Glover, *ibid.*, **89**, 3940 (1967).



Results and Discussion

Synthesis of Iso-*p*-anisylapocamphene (1).—The key step in the synthesis of **1**, regardless of which route is selected, is that which controls the stereochemistry at C-2. During this step the *p*-anisyl group must assume an exo orientation. The pathway which suggests itself is the Diels–Alder reaction between cyclopentadiene and *p*-anisylmaleic anhydride (**6**). This reaction would serve both to construct the bicyclic framework and, in accord with the Alder endo rule, place the *p*-anisyl group in the exo position.

Since none of the published procedures[15] for *p*-anisylmaleic anhydride gave workable quantities, a new synthesis of **6** was developed. Ethyl anisylglyoxylate (**7**) was prepared from anisole (**8**) according to the procedure of Kindler, *et al.*[16] Keto ester **7** was converted *via* an Emmons[17] reactio nusing triethyl phosphonoacetate to the diester **9**, which was subsequently saponified to the corresponding diacid **10**. The diacid **10** was cyclized by a modification of the procedure of Vaughan, *et al.*,[18] to *p*-anisylmaleic anhydride (**6**) in 29% overall yield from **8**.

Reaction of **10** with cyclopentadiene in benzene–acetone followed by basic hydrolysis gave the unsaturated diacid **11**. Redissolution of **11** into aqueous potassium hydroxide followed by catalytic hydrogenation gave the saturated diacid **12**, and treatment of **12** with acetic anhydride overnight afforded the anhydride **13**.

Reaction of the anhydride **13** with liquid dimethylamine gave the acid salt amide **14**.[19] Attempts to convert **14** to the free acid amide by treatment with acid led to partial (60%) recyclization to the anhydride **13**, a result which is anomalous in the current literature.[19,20] However, direct reduction of the acid salt amide **14** with lithium aluminum hydride in tetrahydrofuran gave the desired amino alcohol **15**. Treatment of **15** with 30% hydrogen peroxide in methanol yielded the amine oxide alcohol **16**, which in turn yielded the unsaturated alcohol **17** upon thermal decomposition at 160°.

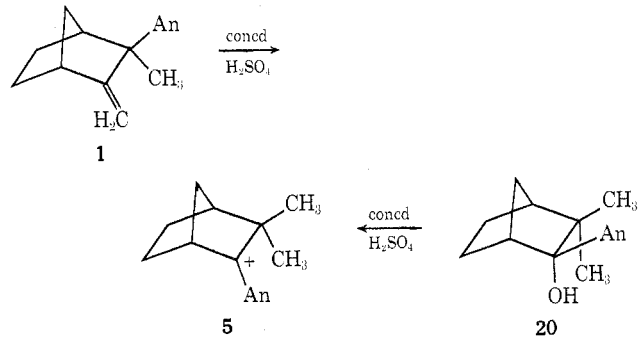
Reaction of **17** with *p*-toluenesulfonyl chloride in pyridine afforded a tosylate which reacted with lithium aluminum hydride under a variety of solvent and temperature conditions to give an unidentified product mixture which exhibits no exocyclic methylene protons in the nmr spectrum. Consequently, an alternative route for replacement of hydroxyl by hydrogen was developed.

Oxidation of alcohol **17** with chromium trioxide and pyridine in methylene chloride according to the procedure of Ratcliff and Rodehorst[21] gave the corresponding unsaturated aldehyde **18**, which was converted to its semicarbazone **19** by the usual method; and decomposition of **19** with powdered potassium hydroxide according to the procedure of Linstead and Cook[22] led to the desired iso-*p*-anisylapocamphene (**1**).

This final modified Wolff–Kishner reaction was particularly useful since it provided a method for deuterium incorporation into the methyl group. Thus, decomposition of **19** with potassium deuteroxide prepared from potassium *tert*-butoxide and deuterium oxide led to **1**-CH_3-*d*. Mass spectral analysis showed the **1**-CH_3-*d* to be a mixture of deuterated species: 22.6% d_0, 47.9% d_1, 27.5% d_2, and 2.0% d_3. The complete synthesis of **1** is illustrated in Scheme I.

The validity for assigning the exo configuration to the *p*-anisyl group in **1** rests on several grounds: (1) comparision of **1** with its known epimer **2**[12,23] *via* nmr spectra and chemical behavior; (2) the demonstrated preference of the phenyl group for the exo configuration during the related Diels–Alder reaction of phenylmaleic anhydride with cyclopentadiene;[24] and (3) the general character of the synthesis, which in principle can only lead either to **1** or **2**, and clearly does not lead to **2**.

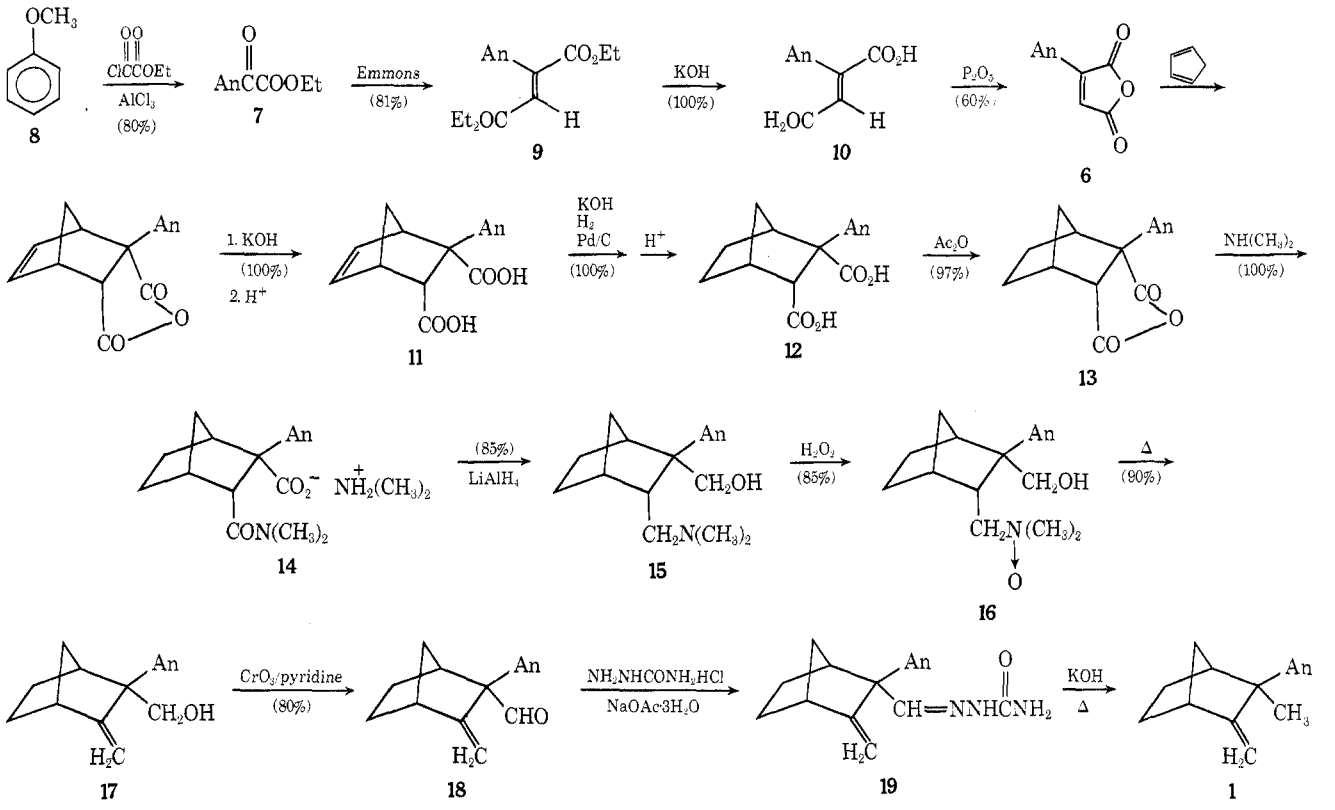
Study of Iso-*p*-anisylapocamphene (1) in Acid Solution.—Iso-*p*-anisylapocamphene (**1**) dissolves in concentrated sulfuric acid with formation of the orange-red, long-lived *p*-anisylcamphenilyl cation (**5**).[12] This is readily demonstrated by comparison of the visible and nmr spectra (see Experimental Section), and aqueous quenching products of a solution of **1** in concentrated sulfuric acid with those of an authentic sample of **5** generated directly from *p*-anisylcamphenilol (**20**).[12]



The possibility that the stable carbonium ion derived from **1** might be the symmetrical bridged species **3**, derived by exo 3,2 *p*-anisyl migration, is excluded by the following observation. The nmr spectrum of the carbonium ion derived from **1** in trifluoroacetic acid

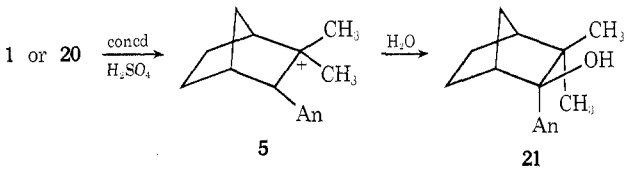
(15) See R. K. Hill, *J. Org. Chem.*, **26**, 4745 (1961).
(16) K. Kindler, W. Metzendorf, and D-y-Kwok, *Chem. Ber.*, **76**, 308 (1943).
(17) W. S. Wadsworth, Jr., and W. E. Emmons, *J. Amer. Chem. Soc.*, **83**, 1733 (1961).
(18) W. R. Vaughan and K. S. Andersen, *ibid.*, **77**, 6702 (1955).
(19) W. R. Vaughan, C. T. Goetschel, M. H. Goodrow, and C. L. Warren, *ibid.*, **85**, 2282 (1963).
(20) A. Foucaud, *Bull. Soc. Chim. Fr.*, 873 (1963).
(21) R. Ratcliff and R. Rodehorst, *J. Org. Chem.*, **35**, 400 (1970).
(22) A. H. Cook and R. P. Linstead, *J. Chem. Soc.*, 956 (1934).
(23) G. B. Herschbach, Ph.D. Thesis, Harvard University, 1968, has isolated **1** in small quantities from rearrangement of **20** in formic acid. Its exo *p*-anisyl nature has been rigorously defined and Herschbach's **1** is identical with that prepared in the present study.
(24) G. I. Poos and M. M. Lehman, *J. Org. Chem.*, **26**, 2575 (1961).

SCHEME I



contains two nonequivalent methyl groups. This nonequivalence is consistent with **5** but inconsistent with formulation **3** where both methyl groups are identical.

Confirmation of **5** as the stable species in concentrated sulfuric acid is deduced from quenching experiments. Rapid addition of the carbonium ion solution to ice water produces iso-*p*-anisylcamphenilol (**21**) as the major product. Similiar quenching of a concentrated sulfuric acid solution of **20** also produces **21**.[12] If **3**, or



any slightly unsymmetrical version thereof, constituted a correct formulation for the stable carbonium ion, a structurally different alcohol would be produced upon quenching.

In an attempt to determine the pathway for the rearrangement **4** → **5**, the decision was made to generate the stable ion **5** from suitable deuterium-labeled precursors in concentrated sulfuric acid and then to trap the carbonium ion as the alcohol **21** by aqueous quenching. Subsequent nmr and mass spectral analysis of **21** would reveal the quantity and location of the original deuterium label.

From ion **4** there are potentially three distinct pathways to **5**, of which one involves exo 3,2-aryl migration. The net result of such a shift is racemization and interconversion of the two methyl groups. Since published evidence in aryl-substituted norbornyl cation systems argues against an exo 3,2-aryl shift,[11-14] it is most reasonable to consider pathways which avoid such a migration. Therefore, although exo 3,2-aryl migration cannot be ruled out by the present work, it will not be considered in the discussion.

Of the remaining two pathways the most direct route for this conversion is an endo 3,2-methyl migration, which predicts that a deuteriomethyl group originally at C-3 would be found as the endo C-2 methyl group of the isolated alcohol **21**. Similarly, a deuteriomethyl group originally at C-2 would be found as the exo C-2 methyl group.

The remaining potential route involves preliminary Wagner–Meerwein rearrangement, 6,2-hydride shift, and Wagner–Meerwein rearrangement again,[11,25] followed by exo 3,2-methyl shift. This pathway predicts that a deuteriomethyl group originally at C-3 will be found as the exo methyl group of the alcohol **21**. Similarly, a deuteriomethyl group at C-2 will be found as the endo C-2 methyl group.

Since deuterium analysis of **21** involves relative integration of the methyl signals, it is critical to establish correct assignments and record accurate integral traces for the three methyl groups. The nmr spectrum of **21** shows three sharp methyl singlets. The methoxy methyl is found at δ 3.79 and is unobscured by other absorptions. The two aliphatic methyl groups appear at δ 0.80 and 1.29, the signal at 0.80 falling at relatively high field when compared with other methyls found in the same series.[26,27] Because of the shielding by the cis *p*-anisyl group, the high-field methyl singlet is un-

(25) E. Huang, R. Ranganayakulu, and T. S. Sorensen, *J. Amer. Chem. Soc.*, **94**, 1780 (1972).

(26) The methyl signals of *endo*-3-*p*-anisyl-*exo*-2,3-dimethyl-*endo*-2-norbornanol appear at δ 1.7 and 1.38,[23] and those for *exo*-3-*p*-anisyl-2,2-dimethylnorbornane appear at δ 0.50 and 1.20.[23]

(27) The methyl signals for methylcamphenilol appear at δ 0.90 and 0.93: R. J. Kilian and W. R. Vaughan, personal communication, The University of Connecticut, 1971.

TABLE I

INTEGRATION[a] AREAS FOR ISO-*p*-ANISYLCAMPHENILOL (21) OBTAINED FROM THE VARIOUS REARRANGEMENT EXPERIMENTS

Source	Acid	Aromatic	C_1 H syn 7-H	OCH_3	OH	exo 3-CH_3	CH_2's	endo 3-CH_3	Run
20	H_2SO_4	3.74	1.78	3.00		2.99	6.21	3.05	1
20	D_2SO_4	3.74	1.97	3.00		2.87	6.04	2.85	2
2	D_2SO_4	3.84	2.00	3.00	0.84	2.37	6.04	2.60	3
1	D_2SO_4	3.69	2.03	3.00	1.14	2.54	6.06	2.52	4
1-CH_3-*d*	H_2SO_4	3.26	1.68	3.00		2.02	6.04	2.14	5

[a] All integrations are the average of four determinations and are relative to the OCH_3 signal (3.00). Error estimated to be ±0.05 ppm based on the results of run 1.

obscured and assigned to the endo 3-methyl group;[28] but the exo 3-methyl signal falls in the absorption region of the methylene protons and cannot be accurately integrated in the normal spectrum. This problem was solved by recording spectra of the alcohol **21** after complexation with tris(dipivalomethanato)europium(III).[29] In accordance with the recent findings[30] of greater induced pseudocontact shift with decreasing distance from the coordinating center, the exo methyl group is shifted 1.89 ppm to lower field and the endo methyl group is shifted 0.88 ppm to lower field, both to unobscured portions of the spectrum.

After the analytical technique for analysis had been established, 1-CH_3-*d* was dissolved in concentrated sulfuric acid and quenched with water to form alcohol **21**, and **21** was purified and analyzed for deuterium content. Similar procedures were followed for **1**, **2**, and **20** in concentrated deuteriosulfuric acid. The results of these experiments are tabulated in Table I.

It is immediately obvious from runs 3, 4, and 5 that deuterium is found in both methyls in approximately equal amounts. In order to explain the labeling results in terms of only the two pathways considered above, one is forced to assume that half of the alcohol **21** is formed *via* one path and half *via* the second path. This would be a highly fortuitous result, requiring two very different pathways to have nearly identical rates, and seems very unlikely.

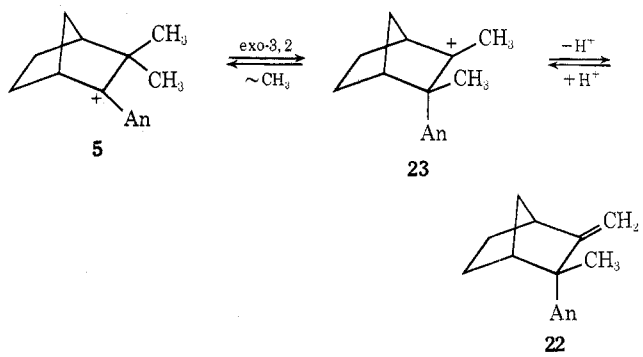
Consequently, the possibility that the *p*-anisylcamphenilyl cation (**5**) might itself be undergoing rearrangement subsequent to its formation must be considered. Run 2 (Tables I and II) shows that when cation **5** is generated directly from **20** in deuteriosulfuric acid only small amounts of deuterium enter the two methyl groups, establishing that equilibration with the neutral olefin **22** is slow. This result is in contrast to the rapid equilibrium between **5** and **22** in 98+% formic acid.

TABLE II

DEUTERIUM ANALYSES[a] OF ISO-*p*-ANISYLCAMPHENILOL (21) OBTAINED FROM THE VARIOUS REARRANGEMENT EXPERIMENTS

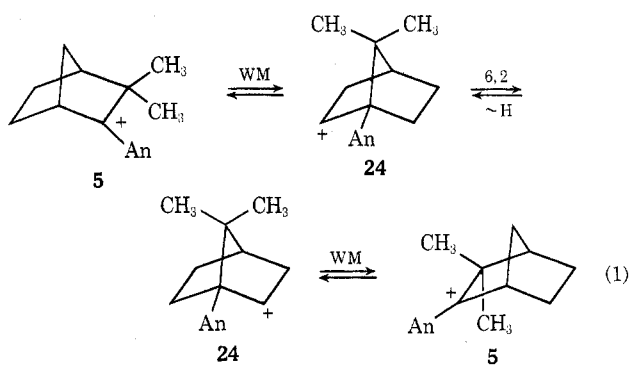
		Percentage				
Source	Acid	d_0	d_1	d_2	d_3	Run
20	D_2SO_4	95.89	3.55	0.55		2
1	D_2SO_4	4.35	88.67	6.89	0.09	4
1-CH_3-*d*	H_2SO_4	20.76	48.00	29.24	1.99	5

[a] Percentages of the deuterated isomers were calculated in the usual fashion from the $(M - 18)^+$ peak.



This loss of a proton with formation of a neutral molecule is strongly inhibited in concentrated sulfuric acid, owing to its highly ionizing nature and the absence of sufficiently basic species to assist in proton removal.

Since Bartlett's[12] original work with ion **5** in 98+% formic acid showed only small amounts of racemization in the ion after 24 min, the possibility of a racemizing process such as path 1 was initially disregarded. It will be noted that the net result of path 1 is racemization of the cation and interconversion of the methyls under equilibrium conditions. In order to test for the



(1)

operation of path 1 in concentrated sulfuric acid, optically active *p*-anisylcamphenilol (**20**), $[\alpha]D$ −24.7° (*c* 6.2, benzene), was subjected to the usual rearrangement conditions in sulfuric acid, and the **21** isolated was found to be racemic within experimental error after 2 min.

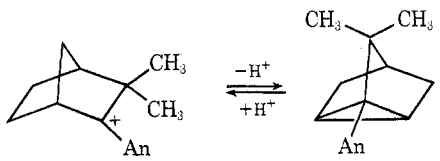
Thus, the equal deuterium distribution in the exo and endo methyl groups of **21** isolated from the rearrangement experiments is explained by the operation of a racemizing process subsequent to the formation of ion **5**. The deuterium studies are inconclusive regarding the actual rearrangement pathway for **4** → **5** since, regardless of which methyl group contains the label after the initial rearrangement, the equilibration reaction will distribute equal quantities of deuterium to both methyls.

(28) See B. L. Shapiro, M. J. Gattuso, H. P. Hepfinger, R. L. Shore, and W. C. White, *Tetrahedron Lett.*, 219, 223 (1971), for further examples of methyl shielding due to aromatic nuclei in constrained ring systems.

(29) J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, **93**, 641 (1971).

(30) P. V. DeMarco, T. K. Elzey, A. F. Fentamin, and R. L. Foltz, *ibid.*, **92**, 5734, 5737 (1970).

A process having identical mechanistic consequences with path 1 involves a rapid equilibrium between the cation **5** and the symmetrical cyclene **25**, which has



5 **25**

been isolated from 98+% formic acid solutions of **20**; and Bartlett, *et al.*, invoke it to explain the partial racemization of **2** in this acid.[31] However, the results of run 2 (Tables I and II) indicate no significant deuterium incorporation into the methylene positions of **5** when the ion is generated in concentrated deuteriosulfuric acid. Since a rapid equilibrium between **5** and **25**, necessary to account for total racemization, would involve significant multiple deuterium incorporation, **25** cannot account for the racemization observed in concentrated sulfuric acid. Accordingly, we propose that the principal mechanism resulting in racemization is path 1, although it is possible that some reacemization occurs *via* **25**, but to an extent undeterminable by the present methods.

Facile formation of the symmetrical cyclene **25** in 98+% formic acid contrasts with its apparently difficult formation in concentrated sulfuric acid. This is explained by an argument similar to that cited to account for the increased formation of olefin **22** from **5** in formic acid relative to concentrated sulfuric acid. In 96.8% formic acid ($H_0 = -0.90$)[31] the concentration of the stable carbonium ion **5** decreases to 58% of its initial concentration after 2 min, and to 18% of its initial concentration after 10 min. The decrease in concentration of **5** is due to the rapid reversible formation of olefin **22**. From a solution of optically active **20** in 98+% formic acid after 9 min the olefin **22**, still containing a substantial portion of the optical activity, can be isolated in 67% yield.[12] This demonstrates that equilibration of **5** with **22** is much faster than conversion of **5** to the cyclene **25**. Some racemization due to the formation of **25** does occur, however, and its observed rate is governed by the concentration of **5**; since this decreases rapidly in formic acid, only minor amounts of racemization take place in this acid.

Under the experimental conditions for these racemization studies in formic acid,[12] alcohol **20** was dissolved completely as the ion **5**, but the olefin **22** separated as it was formed. When a formic acid–petroleum ether (bp 30–60°) mixture was used, shaking was continued throughout the experiment, thereby preserving active equilibrium between the phases and causing the olefin to restore the concentration of **5**, which then yields the cyclene **25**, isolated in 32% yield after a few minutes. Bartlett has accordingly attributed the increased cyclene formation (*i.e.*, racemization) to the higher ion concentration.[31]

In concentrated sulfuric acid ($H_0 = -10.27$)[32] ion **5** is fully formed and its concentration does not decrease for long periods of time, as evidenced by the persistence of the visible absorption due to the ion. This is attributable to the previously discussed inhibited formation of both **22** and **25** in this solvent. The small amount of **22** which forms is rapidly converted to its conjugate acid **23** in the highly acidic medium. Therefore, **5** enjoys a continuously high concentration in concentrated sulfuric acid, and the observed rates of the transformations of path 1 are increased to the point where racemization (*i.e.*, epimerization) is a rapid process, much faster than equilibration with the olefin **22**.

It is difficult to understand the rearrangement of the stable anisylic ion **5** to the secondary ion **24** in terms of classical intermediates. For this reason, in a related sequence during the pinacol rearrangement of *endo*-2-phenylnorbornane-*cis*,*exo*-2,3-diol, Collins chose to represent the ions as nonclassical.[11] In view of the growing body of evidence that 2-aryl-2-norbornyl cations are classical,[33] ion **5** is best represented as an open anisylic cation. However, the partial nonclassical formulation for **24** should be preferable to the classical structure in order to explain the rapid conversion of **5** into **24**.

In summary then, the following facts emerge from the present study. (1) In spite of a structure designed to favor endo 3,2-methyl migration through providing an unusually stable ion as the immediate product of such rearrangement, the present research cannot demonstrate that no endo 3,2-methyl migration occurs. (2) If one agrees that such endo migration is unlikely, the initially formed carbonium ion rapidly achieves epimerization *via* Wagner–Meerwein rearrangement, 6,2-hydride migration, and Wagner–Meerwein rearrangement; and the resultant epimer rapidly affords the very stable anisylic ion *via* exo 3,2-methyl migration. (3) The anisylic ion, in concentrated sulfuric acid, rapidly equilibrates with its enantiomer without involving a cyclene, becoming racemic in ~2 min, incorporating but traces of deuterium in the methyl groups and none in the ring system, when formed from **20** in deuteriosulfuric acid. (4) Equivalence in deuterium distribution between the two alkyl–methyl groups of **21** formed from labeled **1** is explicable in terms of the same mechanism which accounts for racemization. (5) The remaining, though remote, possibility that such equivalence in deuterium labeling of the alkyl–methyl groups may be achieved *via* exo 3,2-*p*-anisyl migration is not presently answerable.

One may infer that in the substituted norbornyl cation there is at least some nonclassical character where the classical formulation requires a secondary carbonium ion in order to account for the facile intervention of such ions in the array of available rearrangement mechanisms.

Experimental Section

Melting points, determined using a Thomas-Hoover or modified Hershberg apparatus, are uncorrected. Infrared data were obtained on a Perkin-Elmer Model 273B grating spectrophotometer. Ultraviolet and visible spectra were obtained on a Beckman Model DB spectrophotometer. The nmr data were obtained at 60 Mc using a Varian Associates Model A-60 nmr spectrometer and are expressed as shift downfield from internal tetramethylsilane in parts per million. The mass spectra were recorded on an Associated Electrical Industries Ltd. Model MS-

(31) P. D. Bartlett, C. E. Dills, and H. G. Richey, Jr., *J. Amer. Chem. Soc.*, **82**, 5414 (1960).

(32) C. H. Rochester in "Acidity Functions," Academic Press, New York, N. Y., 1970.

(33) See D. G. Farnam and G. Mehta, *J. Amer. Chem. Soc.*, **91**, 3256 (1969), and references cited therein.

12 mass spectrometer. Deuterium analyses were obtained from mass spectra recorded on an Associated Electrical Industries Ltd. Model MS-9 mass spectrometer. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Preparation of the Nmr Samples Containing Tris(dipivalomethanato)europium(III).[34]—The sample was prepared in the usual manner by dissolving 80–85 mg (3.3×10^{-4} mol) of **21** in 0.4 ml of deuteriochloroform. To this was added 40–45 mg (0.6×10^{-4} mol) of tris(dipivalomethanato)europium(III). Gentle heating on the steam bath facilitated dissolution of the slightly soluble reagent. The mole ratio of **21** to shift reagent was 0.17. The resulting solution was filtered through a small cotton plug directly into an nmr sample tube. TMS (2 drops) was added and the spectra were recorded. The reported integration areas represent the average of four determinations.

Ethyl Anisylglyoxylate (7).—Into a 1000-ml, three-neck flask equipped with a mechanical stirrer, reflux condenser, and addition funnel was placed dry methylene chloride (160 ml) under nitrogen. To this, with stirring and cooling, was added gradually 36.4 g (0.27 mol) of anhydrous aluminum chloride. To this all at once was added 25 g (0.2 mol) of ethyl oxalyl chloride, and with further stirring and cooling, 19.8 g (19.9 ml, 0.18 mol) of purified anisole in dry methylene chloride (50 ml) over a period of 45 min. This mixture was stirred at room temperature for 1.5 hr.

Ice water (300 ml) was added to the cooled reaction with *caution*. The large chunks of white precipitate which formed initially upon hydrolysis went into solution with stirring, which was continued for 30 min. The reaction mixture was transferred to a 1.0-l. separatory funnel, the organic layer was separated, and the aqueous layer was extracted with 50 ml of methylene chloride. The combined organic extracts were washed with 75 ml of water, 75 ml of 10% sodium carbonate, and 75 ml of water, dried (anhydrous magnesium sulfate), concentrated, and fractionally distilled, giving 30 g (79%) of the keto ester **7**: bp 125–128° (1.0 mm) [lit.[16] bp 178–179° (13 mm)]; ir (thin film) 1730 (ester C=O), 1675 (ketone C=O), 1600, 1215, and 1165 cm^{-1}.

Diethyl 2-Anisyl-2-butenedioate (9).—In a 250-ml flask equipped with a mechanical stirrer, thermometer, reflux condenser, and addition funnel was placed 3.6 g (6.3 g of a 57% mineral oil dispersion, 0.15 mol) of sodium hydride and dry benzene (50 ml) under nitrogen. To this stirred mixture was added dropwise over a 30-min period 33.7 g (0.15 mol) of triethyl phosphonoacetate. During the addition the temperature was maintained below 30° by cooling with an ice bath. The clear solution was then stirred at room temperature for 1 hr. To this was added dropwise over a period of 30 min 30 g (0.14 mol) of the keto ester **7**. Upon addition a yellowish, gummy precipitate formed around the walls of the reaction flask. After all the ketone was added, the flask was heated with a steam bath to 65–70° for 20 min and cooled to 15–20°, and the benzene was decanted. Additional benzene (50 ml) was added to the flask, which was heated to 70–75° with stirring and cooled to 15–20°; then the benzene was decanted. This procedure was repeated five times. (Alternatively, water could be added to dissolve the gummy precipitate and benzene used to extract in the normal fashion.) Concentration of the organic extracts at atmospheric pressure followed by distillation gave 39.5 g (90%) of the diester **9**: bp 145–160; ir (thin film) 1720 and 1735 (C=O), 1600, 1290, and 1176 cm^{-1}; nmr ($CDCl_3$) δ 1.16–1.46 (t, 6, $-CH_2CH_3$), 3.77 (s, 3, $-OCH_3$), 3.98–4.50 (q, 4, $-OCH_2CH_3$), 6.1 (s, 1, =CH), and 7.09 (q, 4, J = 9 Hz, aromatic).

2-Anisyl-2-butenedioic Acid (10).—In a 250-ml flask was placed 32.5 g (0.12 mol) of the diester **9** in 95% ethanol (100 ml). To this with cooling was added 19.8 g (0.35 mol) of potassium hydroxide in water (75 ml). After refluxing for 1 hr, the solution was cooled and added to an equal volume of water. After the ethanol was removed *in vacuo*, the aqueous solution was extracted with 2 × 50 ml of ether, cooled in an ice bath, and acidified by the slow addition of concentrated sulfuric acid. The precipitate was collected and dried (phosphorus pentoxide) to yield 26.1 g (100%) of slightly yellow diacid **10**: mp 215–218°; ir (KBr) 1665 (C=O), 1595, 1225, and 1185 cm^{-1}; nmr (DMSO-d_6) δ 3.80 (s, 3, $-OCH_3$), 6.23 (s, 1, =CH), and 7.25 (q, 4, J = 9 Hz, aromatic).

***p*-Anisylmaleic Anhydride (6).**—The diacid **10** (10.0 g, 0.045 mol) was intimately mixed with 6.82 g (0.05 mol) of phosphorus pentoxide. The mixture was transferred to a large sublimer and the sublimer was evacuated and immersed in an oil bath at 100°. The temperature was increased slowly and yellow crystals began collecting after 15 min. After subliming at 125–135° (0.4 mm) for 5–15 hr, the crystals were collected (sometimes more than one collection was necessary) and recrystallized from petroleum ether (bp 30–60°)–acetone to yield 5.6 g (60%) of the yellow anhydride **6**: mp 142–143.5° (lit.[15] mp 143–144°); ir (KBr) 1840 and 1760 (C=O), 1605, 1512, 1180, and 840 cm^{-1}; nmr ($CDCl_3$) δ 3.9 (s, 3, $-OCH_3$), 6.82 (s, 1, =CH), and 7.49 (q, 4, aromatic).

***exo*-2-*p*-Anisylnorbornane-*cis*,*endo*-2,3-dicarboxylic Acid (12).**—In a 250-ml, three-neck flask equipped with a magnetic stirrer, reflux condenser, and addition funnel was placed 6.9 g (0.03 mol) of the anhydride **6** in dry benzene (70 ml) and reagent acetone (56 ml) under nitrogen. To this all at once was added 5.6 g (6.9 ml, 0.085 mol) of freshly cracked cyclopentadiene. The mixture was stirred at room temperature for 21 hr and at 45–50° for 27 hr. After cooling, the organic solvents were removed *in vacuo* to yield a yellow oil.

The oil was added to a 500-ml flask in 95% ethanol (60 ml), and 12% aqueous potassium hydroxide (70 ml) was added. This mixture was refluxed for 12 hr and cooled, and the ethanol was removed *in vacuo*. The remaining aqueous layer was extracted with 2 × 50 ml of ether, treated with charcoal, and filtered to yield a slightly yellow solution.

The yellow solution was added to a 500-ml Parr hydrogenation bottle with 100 mg of 5% palladium on charcoal. After 8 min the theoretical amount of hydrogen had been absorbed. Hydrogenation was continued for 0.5 hr to ensure the completeness of the reaction. The mixture from hydrogenation was vacuum filtered through a layer of charcoal on top of a layer of Celite Filter-aid, and subsequently washed with small amounts of water. The resulting filtrate was added dropwise to a cooled (ice bath) solution of concentrated hydrochloric acid (30 ml) over a period of 45 min. After the addition, the precipitate was stirred for an additional 30 min, filtered and dried under vacuum (phosphorus pentoxide) to yield 8.9 g (92%) of the bicyclic diacid **12** as a white solid, mp 151–154°. Recrystallization from acetone gave an analytical sample: mp 155–156.5°; ir (KBr) 1700 (C=O), 1505, 1250, and 860 cm^{-1}; nmr (DMSO-d_6) δ 1.18–3.10 (complex m, bridgehead H and CH_2's), 3.69 (s, 3, $-OCH_3$), 7.20 (q, 4, J = 9 Hz, aromatic), and 11.9 (broad s, 1.5, –COOH).

Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.26. Found: C, 66.16; H, 6.22.

***exo*-2-*p*-Anisylnorborn-5-ene-*cis*,*endo*-2,3-dicarboxylic Acid (11).**—The unsaturated diacid **11** can be isolated by addition of the basic saponification solution from the previous experiment to concentrated hydrochloric acid with cooling and stirring. Further stirring, followed by collection and drying (phosphorus pentoxide) under vacuum, yielded the unsaturated diacid **11** as a white solid, mp 174–179° (lit.[35] mp 182.5–183.5°). Recrystallization from acetone gave an analytical sample: mp 187–188.5; ir (KBr) 1705 (C=O), 1520, 1225, and 850 cm^{-1}; nmr (DMSO-d_6) δ 1.3 (broad, s, 2, bridge CH_2), 2.88–3.68 (complex m, 3, bridgehead H and tertiary H), 3.72 (s, 3, $-OCH_3$), 6.29 (m, 2, =CH), 6.28 (q, 4, J = 9 Hz, aromatic), and 12.7 (broad s, 1.9, –COOH).

Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.51; H, 5.63.

***exo*-2-*p*-Anisylnorbornane-*endo*-2,3-dicarboxylic Anhydride (13).**—In a 500 ml flask was placed 5.0 g (0.02 mol) of the diacid **12** in reagent acetic anhydride (210 ml). The mixture was stirred magnetically for 18 hr at room temperature. The excess acetic anhydride was removed after this time at 40–50° (2.0 mm) to yield a yellow oil. Distillation gave 4.06 g (88%) of the anhydride **13**: bp 172° (0.25 mm); ir (thin film) 1850 and 1775 (C=O), 1610, 1250, and 920 cm^{-1}; nmr ($CDCl_3$) δ 1.62 (m, 6, CH_2's), 2.95 (m, 2, bridgehead H), 3.70 (m, 1, tertiary H), 3.79 (s, 3, $-OCH_3$), and 7.16 (q, 4, J = 9 Hz, aromatic).

Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.65; H, 5.97.

Dimethylammonium *exo*-2-*p*-Anisyl-*endo*-3-(*N*,*N*-dimethylcarbamido)norbornane-*endo*-2-carboxylate (14).—In a 500-ml, three-neck flask equipped with a Dry Ice condenser capped with a drying tube was placed 5.3 g (0.02 mol) of the anhydride **13** in dry benzene (10 ml) and dry ether (30 ml) under nitrogen. To this at −5° was added as quickly as possible 2.6 ml (1.8 g,

(34) Tris(dipivalomethanato)europium(III) purchased as Eu-resolve from Alfa Inorganics, Inc., Beverly, Mass., No. 87898.

(35) H. Ruus, Ph.D. Thesis, University of Illinois, 1957.

0.04 mol) of liquid dimethylamine. The yellow solution turned colorless instantaneously, and after 5 min a voluminous white precipitate filled the reaction vessel. This was stirred magnetically overnight, the Dry Ice condenser being allowed to spend itself naturally. The white precipitate was collected by suction filtration and washed with ether to yield 6.7 g (93%) of the dimethylammonium salt **14**: mp 135–140°; ir (KBr) 1640 (amide C=O), 1575 (carboxylate C=O), 1515, and 1250 cm^{-1}.

Anal. Calcd for $C_{20}H_{30}O_4N_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.34; H, 8.26; N, 7.69.

***exo*-2-*p*-Anisyl-*endo*-2-(hydroxymethyl)-*endo*-(*N*,*N*-dimethylamino)norbornane (15).**—In a 500-ml three-neck flask equipped with a mechanical stirrer, reflux condenser, and addition funnel was placed dry tetrahydrofuran (100 ml) under nitrogen. To this was added 4.4 g (0.12 mol) of lithium aluminum hydride with stirring and cooling. To this at 0° was added dropwise 4.2 g (0.012 mol) of the dimethylammonium salt **14** suspended in dry tetrahydrofuran (150 ml). After the addition was complete the mixture was refluxed for 10 hr and cooled to ice bath temperature, and 4.4 ml of water, 4.4 ml of 25% potassium hydroxide solution, and 13.2 ml of water were added in succession with *caution*. The white suspension was vigorously stirred at room temperature for 10 min and at reflux for 30 min. The solution was then cooled and filtered, the salts being washed several times with ether. The tetrahydrofuran was removed *in vacuo*, and the residue was taken up in ether, washed with water, dried (anhydrous magnesium sulfate), and concentrated to yield 13.2 g (82.5%) of the amino alcohol **15**, mp 75–92°. Recrystallization from heptane (3 g/75 ml) gave a sample with mp 80–85°. An analytical sample (four recrystallizations from heptane) had mp 97.5–99.5°: ir (KBr) 3200 (–OH), 2955, 2880, 1515, 1255, and 1045 cm^{-1}; nmr (CCl_4) δ 1.0–1.6 (complex m, 6.9, CH_2's), 2.3 (s, 6, $-NCH_3$), 2.5–3.8 (complex m, 7, $-CH_2N-$, bridgehead H, and tertiary H), 3.71 (s, 3, $-OCH_3$), and 7.13 (q, 4, J = 9 Hz, aromatic).

Anal. Calcd for $C_{18}H_{27}O_2N$: C, 74.70; H, 9.40; N, 4.84. Found: C, 74.45; H, 9.34; N, 4.67.

***exo*-2-*p*-Anisyl-*endo*-2-(hydroxymethyl)-*endo*-(*N*,*N*-dimethylaminomethyl)norbornane Oxide (16).**—In a 100-ml flask equipped with a magnetic stirrer was placed 5.0 g (0.02 mol) of the amino alcohol **15** in reagent methanol (24 ml). To this at room temperature was added 4.50 ml (0.052 mol) of 30% hydrogen peroxide over a period of 3 min. After the solution was stirred for 60 hr, an additional 2.0 g (0.021 mol) of 30% hydrogen peroxide was added all at once, and stirring was continued. After a total of 120 hr, platinum black was added to destroy the cess hydrogen peroxide. After oxygen evolution had ceased, the mixture was filtered through Celite Filter-aid to remove the platinum black and concentrated *in vacuo* to yield a viscous oil which partially solidified on standing: ir (thin film) 1515, 1250, and 1030 cm^{-1}. At this point the amine oxide **16** was suitable for use in the following reaction. A picrate was prepared by treatment with ethanolic picric acid: mp 168–172°; ir (KBr) 3480 (–OH), 1625, 1560, 1320, and 720 cm^{-1}.

Anal. Calcd for $C_{24}H_{30}O_{10}N_7$: C, 53.93; H, 5.66; N, 10.48. Found: C, 53.58; H, 5.54; N, 10.37.

***exo*-2-*p*-Anisyl-*endo*-2-(hydroxymethyl)-3-methylenenorbornane (17).**—The crude amine oxide **16** from the previous reaction was placed in a 200-ml flask equipped with a distillation head and evacuated to 20 mm with a water aspirator. The flask and contents were immersed in an oil bath at 90° and the temperature was slowly increased. Decomposition and distillation of dimethylhydroxylamine commenced at 158°, and was finished after 15 min at 168°. The flask was maintained at 170° for an additional 10 min and cooled to room temperature, and the residue was taken up in ether. The ether solution was washed with 5% hydrochloric acid, 5% sodium bicarbonate, and water, dried (anhydrous magnesium sulfate), concentrated, and distilled, giving 2.76 g (64%) of the unsaturated alcohol **17**: bp 138° (0.1 mm); ir (thin film) 3400 (–OH), 3050 (=CH), 2950 (–CH), 1650 (C=C), 1510, 1250, 1040, and 830 cm^{-1}; nmr (CCl_4) δ 0.87–2.10 (complex m, 7, CH_2's and –OH), 2.5–2.8 (broad d, 2, bridgehead H), 3.60 (broad s, 2, $-CH_2O$), 3.70 (s, 3, $-OCH_3$), 4.77 and 5.15 (d, s, $=CH_2$), and 7.0 (q, 4, J = 9 Hz, aromatic).

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.69; H, 8.25. Found: C, 78.85; H, 8.41.

***exo*-2-*p*-Anisyl-*endo*-2-formyl-3-methylenenorbornane (18).**—In a 1000-ml flask was placed 19.8 ml (19.4 g, 0.025 mol) of dry pyridine in dry methylene chloride (375 ml) under nitrogen. To this with magnetic stirring and cooling was added 12.3 g (0.123 mol) of chromium trioxide. After the solution was stirred at room temperature for 30 min, most of the chromium trioxide had dissolved and the solution was dark burgundy in color. To this all at once was added 5.0 g (0.021 mol) of unsaturated alcohol **17** in methylene chloride (5 ml). A black, gummy precipitate formed immediately. After stirring for 2 hr at room temperature, the solution was decanted and the residue was triturated with ether. To the combined organic layers was added an additional 500 ml of ether. The organic portion was washed with 3 × 100 ml of 5% sodium hydroxide, 100 ml of 5% hydrochloric acid, 100 ml of 5% sodium bicarbonate, and 100 ml of saturated sodium chloride, dried (anhydrous magnesium sulfate), and concentrated to yield a slightly colored oil which partially crystallized overnight. Distillation gave 4.05 g (81.7%) of the unsaturated aldehyde **18**: bp 127–130° (0.2 mm); ir (thin film) 3055 (=CH), 2950 (–CH), 1720 (C=O), 1650 (C=C), 1515, and 1250 cm^{-1}; nmr (CCl_4) δ 0.98–1.8 (complex m, 6, $-CH_2$'s), 2.66–2.94 (broad d, 2, bridgehead H), 3.70 (s, 3, $-OCH_3$), 4.92 and 5.45 (d, 1.7, $=CH_2$), 7.01 (q, 4, J = 9 Hz, aromatic), and 9.55 (s, 0.75, –CHO).

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.34; H, 7.41.

***exo*-2-*p*-Anisyl-*endo*-2-formyl-3-methylenenorbornane Semicarbazone (19).**—In a 125-ml erlenmeyer flask, 4.05 g (0.017 mol) of the unsaturated aldehyde **18** was dissolved in 95% ethanol (40 ml). Water was added until cloudiness persisted and the ethanol was added to regenerate the clear solution. To this was added 3.54 g (0.032 mol) of semicarbazide hydrochloride and 5.45 g (0.04 mol) of sodium acetate trihydrate. After dissolution by swirling the mixture was heated on a steam bath for 5 min. The solution was cooled, and the white solid which separated was collected and dried (phosphorus pentoxide), giving 4.18 g (84.4%) of the unsaturated semicarbazone **19**: mp 197.5–201.5°; ir (KBr) 3455 (NH), 2955 (CH), 1695 (C=O), 1580 (C=N), 1510, and 1250 cm^{-1}.

Anal. Calcd for $C_{17}H_{21}O_2N_3$: C, 68.20; H, 7.07; N, 14.04. Found: C, 68.17; H, 7.01; N, 14.03.

***exo*-2-*p*-Anisyl-*endo*-2-methyl-3-methylenenorbornane (1) (Iso-*p*-anisylapocamphene).**—In a 15-ml flask was placed an intimate mixture of 1.0 g (0.0034 mol) of the unsaturated semicarbazone **19** and 657 mg (0.012 mol) of potassium hydroxide. The flask was fitted with a semimicro distillation apparatus and evacuated to 0.06 mm. Heating was applied by means of an oil bath and the temperature was increased. At 205–215° decomposition commenced and proceeded vigorously until 230°. Heating was maintained for an additional 10 min at 230° to ensure the completeness of the reaction. The yield of crude collected 1 was 686 mg (90%). This material was redistilled, giving 574 mg (75%) of 1: bp 115–118° (0.08 mm); ir (thin film) 3055 (CH), 1650 (C=C), 1515, 1250, 1180, 1040, and 830 cm^{-1}; nmr (CCl_4) δ 0.85–1.97 (broad m, CH_2's), 1.38 (s, $-CH_3$), 2.32 and 2.75 (broad s, bridgehead H), 3.67 (s, 3, $-OCH_3$), 4.68 and 5.16 (d, 1.7 $=CH_2$), and 6.94 (q, 4, J = 9 Hz, aromatic); nmr (concentrated H_2SO_4) δ 1.04–2.49 (complex m, 7, CH_2's and C_4 H), 1.57 (broad 5, 6, $-CH_3$'s), 4.16 (broad s, 1, CH), 4.19 (broad s, 3, $-OCH_3$), and 7.84 (m, 4, aromatic); nmr (CF_3COOH) δ 0.82–2.40 (complex m, 7, CH_2's and C_4 H), 1.26 (2, 3, $-CH_3$), 1.29 (s, 3, $-CH_3$), 3.61 (broad s, 1, C_1 H), 3.89 (s, 3, $-OCH_3$), and 7.53 (m, 4, aromatic); uv max (concentrated H_2SO_4) 384.9 nm (log ϵ 4.68).

Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.31; H, 8.84.

***exo*-2-*p*-Anisyl-*endo*-2-(deuteriomethyl)-3-methylenenorbornane (1-CH_3-*d*).**—In a 15-ml flask was placed 1.23 g (0.011 mol) of potassium *tert*-butoxide and 0.21 g (0.21 ml, 0.01 mol) of deuterium oxide. These reacted within 15 min to yield a grayish, syrupy liquid. To this was added 1.0 g (0.0034 mol) of the unsaturated semicarbazone **19**. Manual mixing with a spatula ensured the wetness of the solid semicarbazone. The flask was fitted with a semimicro distillation apparatus and the system was evacuated to 0.14 mm. Heating was applied with an oil bath and the temperature was increased. Decomposition began at 215° and continued through 250°. The yield of crude collected 1-CH_3-*d* was 671 mg (88%). Redistillation gave 491 mg (65%) of the colorless 1-CH_3-*d*: bp 115–127° (0.08 mm); ir (thin film) 3055 (CH), 2950 (CH), 1650 (C=C), 1520, 1250, 1180, and 830 cm^{-1}; nmr ($CDCl_3$) δ 0.88–1.96 (complex m, $-CH_2$'s), 1.38 (broad s, $-CH_3$-*d*), 2.35 and 2.79 (broad s, 2, bridgehead H), 3.78 (s, 3, $-OCH_3$), 4.71 and 5.21 (d, 1.8, $=CH_2$),

and 7.09 (q, 4, J = 9 Hz, aromatic). The nmr spectra displayed a considerable reduction of the methyl singlet while other portions of the spectra remained constant.

exo-2-*p*-**Anisyl-3,3-dimethyl-*endo*-2-norbornanol (20)** (*p*-**Anisylcamphenilol**).—Alcohol **20** was prepared by the method of Bartlett, *et al.*, from (−)-camphenilone: mp 138–140° (lit.[12] mp 143.5–144.5°); $[\alpha]_D$ −24.72° (*c* 6.22 benzene) [lit.[12] $[\alpha]_D$ −25.7° (*c* 4.2, benzene)]; nmr (concentrated H_2SO_4) δ 1.3–2.9 (complex m, CH_2's) and C_4H), 1.72 (broad s, 6, $-CH_3$'s), 4.35 (broad s, C_1 H), 4.37 (broad s, $-OCH_3$), and 8.02 (m, aromatic); uv max (concentrated H_2SO_4) 385.2 nm (log ε 4.6).

endo-2-*p*-**Anisyl-*exo*-methyl-3-methylenenorbornane (2)** (*p*-**Anisylapocamphene**).—Olefin **2** was prepared according to the procedure of Bartlett, *et al.*:[12] nmr ($CDCl_3$) δ 0.85–2.00 (complex m, CH_2's), 1.38 (s, 3, $-CH_3$), 2.22 and 2.75 (m, 2, bridgehead H), 3.65 (s, 3, OCH_3), 4.65 and 5.10 (d, 2, $=CH_2$), and 6.99 (q, 4, aromatic).

Carbonium Ion Trapping Experiments. *endo*-2-*p*-**Anisyl-3,3-dimethyl-*exo*-2-norbornanol (21)** (**Iso-*p*-anisylcamphenilol**). **A. General Procedure.**—The starting substrate (450–550 mg) was dissolved in concentrated sulfuric acid or deuteriosulfuric acid by swirling. The resulting orange solution was allowed to stand at room temperature for the specified time. This was then rapidly and with stirring poured into 200 ml of ice water, and the resulting aqueous solution was extracted with 2 × 100 ml of ether. The ether extracts were combined and washed with 100 ml of 5% sodium bicarbonate and 100 ml of saturated sodium chloride, dried (anhydrous magnesium sulfate), and concentrated to yield a yellow oil which crystallized after standing at room temperature for several hours. Two recrystallizations from heptane yielded white needles of **21**. The physical constants found for **21** from the various starting substrates are listed in Table III.

TABLE III
PHYSICAL CONSTANTS FOR 21 ISOLATED FROM VARIOUS STARTING MATERIALS

Substrate	Acid	Time, min	Mp, °C	$\alpha^{26.6}D$
20	H_2SO_4	30	77.4–78.4	
2	D_2SO_4	10	77.0–78.5	
1	D_2SO_4	10	74.5–75.5	
20	D_2SO_4	10	79.0–79.5	
1-CH_3-*d*	H_2SO_4	10	71.0–74.5	
(−)-**20**	H_2SO_4	2	79.0–79.5	−0.10°
(−)-**20**	H_2SO_4	21	79.0–80.5	−0.08°
(−)-**20**	H_2SO_4	30	77.8–79.5	

B. Specific Procedure.—The alcohol **20** (1.0 g, 0.04 mol) was dissolved in 10 ml of concentrated sulfuric acid by swirling. The orange solution, after standing at room temperature for 30 min, was poured into 200 ml of ice water with stirring. The aqueous mixture was extracted with 2 × 100 ml of ether, and the ether extracts were combined and washed with 100 ml of 5% sodium bicarbonate and 100 ml of saturated sodium chloride, dried (anhydrous magnesium sulfate), and concentrated to yield a yellow oil which solidified after standing at room temperature for 2 hr to give 820 mg (82%) of crude **21**, mp 66–76°. Recrystallization from 10 ml of hot heptane gave 478 mg (48%) of **21** as white needles: mp 77.4–78.4° (lit.[12] mp 76–78°); ir (KBr) 3455 (-OH), 2940 (CH), 1515, and 1245 cm^{-1}; nmr ($CDCl_3$) δ 0.80 (s, 3, $-CH_3$), 1.10–1.90 (complex m, CH_2's and -OH), 1.29 (s, $-CH_3$), 2.15–2.63 (complex m, 2, bridgehead H), 3.79 (s, 3, $-OCH_3$), and 7.10 (q, 4, J = 9 Hz, aromatic); nmr [$CDCl_3$ and Eu(DPM)$_3$] δ 1.68 (s, 3, $-CH_3$), 1.76–2.76 (complex m, 6, CH_2's), 3.18 (s, 3, $-CH_3$), 3.50 (s, 1, -OH), 3.88 (s, 3, $-OCH_3$), 4.34–4.98 (m, 2, C_1 H and syn 7-H), and 7.80 (q, 4, aromatic).

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.99; H, 8.94.

Registry No.—**1**, 36004-27-0; 1-CH_3-*d*, 36004-28-1; **9**, 36004-29-2; **10**, 36004-30-5; **11**, 36004-31-6; **12**, 36004-32-7; **13**, 36004-33-8; **14**, 36004-34-9; **15**, 36004-35-0; **16** picrate, 36004-36-1; **17**, 36004-37-2; **18**, 36015-21-1; **19**, 36004-38-3; **21**, 22551-05-9.

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Hydrogenation of 9,10-Dimethylanthracene with Cobalt Hydrocarbonyl

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The hydrogenation of 9,10-dimethylanthracene can be achieved with cobalt hydrocarbonyl at room conditions. Although the product consists of a mixture of *cis*- and *trans*-9,10-dihydro-9,10-dimethylanthracenes, a mechanism consistent with exclusive cis addition is suggested.

The catalytic homogeneous hydrogenation of a variety of polynuclear hydrocarbons is reported[1] to proceed smoothly in the presence of $Co_2(CO)_8$ and synthesis gas (CO + H_2) at elevated temperatures and pressures. The hydrogenation is reported to be quantitative and to lead exclusively to dihydro and tetrahydro products. With anthracene, for example, 9,10-dihydroanthracene is the sole product. Since under these reaction conditions the catalytic species is unquestionably $HCo(CO)_4$, or $HCo(CO)_3$ with which it is in equilibrium, it was of interest to learn whether such aromatic compounds could be reduced at room conditions with stoichiometric quantities of $HCo(CO)_4$. We have now found that such is the case; *e.g.*, 9,10-dimethylanthracene (**1**) is converted essentially completely into the corresponding 9,10-dihydro derivative. This reaction provided a further opportunity to study the stereochemistry of $HCo(CO)_4$ reactions. Although the stereochemistry of the hydroformylation of olefins has not been ascertained conclusively, the hydrogenation[2] and the isomerization[3] of olefins with $HCo(CO)_4$

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