hexane and in perfluorohexane (provided by Professor S. Lipsky, Department of Chemistry, University of Minnesota) were prepared by the thermal depolymerization of pure dry trioxymethylene as described by Cohen and Reid.[31] Since the rate of polymerization of formaldehyde in these solvents was relatively rapid, the optimum concentrations and scan speeds required for the necessary band resolution had to be determined by trial and error. Absorption and MCD measurements were carried out simultaneously using aliquots from the same solution. The spectra were measured at room temperature in cells of 1-cm path length. Cell blanks were obtained immediately following each sample measurement by replacing the solution with the appropriate solvent. The gelatinous polymer which was deposited on the cell windows during the time required for the measurement resulted in a decrease in the signal-to-noise but did not otherwise contribute significantly to the solution spectrum. Vibrational bands were more highly resolved in perfluorohexane than in hexane.

The MCD spectrum of dideuterioformaldehyde in perfluorohexane was also obtained. Although the vibrational bands were not as highly resolved as those of formaldehyde, the essential features observed in the MCD spectra of the two compounds are the same.

**Acknowledgment.** We wish to express our appreciation to Dr. F. S. Johnson and to Professors R. B. Woodward, B. Rickborn, N. L. Allinger, M. Hanack, and R. H. Eastman for their generosity in providing us with the conformationally well-defined ketones required for this study. In addition we are grateful to Mrs. R. Records and Mr. G. H. Scott for their outstanding technical assistance and to Dr. D. L. Elder who carried out the MCD measurements on formaldehyde.

(31) A. D. Cohen and C. Reid, *J. Chem. Phys.*, **24**, 85 (1956).

# The Acid-Catalyzed Rearrangement of Camphor to 3,4-Dimethylacetophenone[1]

**Oscar R. Rodig* and Robert J. Sysko[2]**

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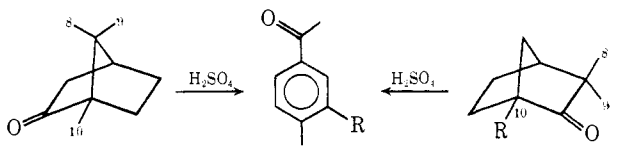
**Abstract:** The long known rearrangement of camphor to 3,4-dimethylacetophenone in concentrated sulfuric acid has been investigated using camphor-*8*-$^{14}C$ and camphor-*9*-$^{14}C$. The results indicate that four interrelated rearrangement processes occur simultaneously, the two main pathways leading to 3,4-dimethylacetophenone (88–92 and 8–12%, respectively), *via* protonated fenchone as an intermediate. The other two processes occur within these main pathways, consisting of the internal racemizations of camphor (16%) and of a rearranged fenchone intermediate (2%).

The reaction of camphor (**1**) with concentrated sulfuric acid was first investigated in 1839, but it was not until 1893 that one of the reaction products was identified as 3,4-dimethylacetophenone (**2**),[3a] and not until 1901 that the other major product was shown to be carvenone.[3b] Fenchone (**3**) also gives 3,4-dimethylacetophenone (**2**) when treated with concentrated sulfuric acid,[4] and in 1950, Noyce[5] suggested a mechanism for this rearrangement, using as supportive evidence the fact that camphenilone (**4**) yields *p*-methylacetophenone (**5**) under similar conditions. The Noyce mechanism received further support from later work by Lutz and Roberts,[6] who studied the fenchone rearrangement using $^{14}C$ labeling in the *gem*-dimethyl groups. Noyce further proposed that fenchone is a likely intermediate in the conversion of camphor (**1**) to 3,4-dimethylacetophenone (**2**), a supposition also supported by Lutz and Roberts, who showed that under the reaction conditions fenchone and camphor are interconvertible. The latter authors further suggested a mechanism for this interconversion. By combining the proposed pathways one arrives at the mechanism shown in Chart I for the rearrangement of camphor to 3,4-dimethylacetophenone.[7]




**1** **2**, R = $CH_3$; **5**, R = H **3**, R = $CH_3$; **4**, R = H

Lutz and Roberts comment on most of the steps in the mechanism, and their labeling experiments with fenchone-*8*,*9*-$^{14}C$ support the suggested pathway from the intermediate **6** (protonated fenchone) to the final product **2**. In order to test further the proposed mechanism for the conversion of camphor to 3,4-dimethylacetophenone, we carried out the rearrangement of camphor-*8*-$^{14}C$ and camphor-*9*-$^{14}C$ by heating these compounds in concentrated sulfuric acid at 110° for 45 min. Under these conditions, very little camphor remained unreacted and the 3,4-dimethylacetophenone

(1) Presented in part at the Southeast–Southwest Regional Meeting of the American Chemical Society, New Orleans, La., Dec 2–4, 1970. Taken from the dissertation of Robert J. Sysko submitted for the Doctor of Philosophy degree, University of Virginia, 1971.

(2) Recipient of a National Science Foundation Traineeship, 1967–1971.

(3) (a) H. E. Armstrong and F. S. Kipping, *J. Chem. Soc., London*, **63**, 75 (1893); (b) J. Bredt, F. Rochussen, and J. Monheim, *Justus Liebigs Ann. Chem.*, **314**, 369 (1901). A summary of the early investigations of the reaction of camphor with sulfuric acid can be found in these two papers.

(4) J. E. Marsh, *J. Chem. Soc., London*, **75**, 1058 (1899); H. E. Zaugg, *J. Amer. Chem. Soc.*, **67**, 1861 (1945).

(5) D. S. Noyce, *ibid.*, **72**, 924 (1950).

(6) R. P. Lutz and J. D. Roberts, *ibid.*, **84**, 3715 (1962).

(7) For greater clarity classical carbonium ions, rather than their nonclassical counterparts, are used throughout this paper.

Chart I. Proposed Mechanism for the Rearrangement of Camphor to 3,4-Dimethylacetophenone (Path 1)

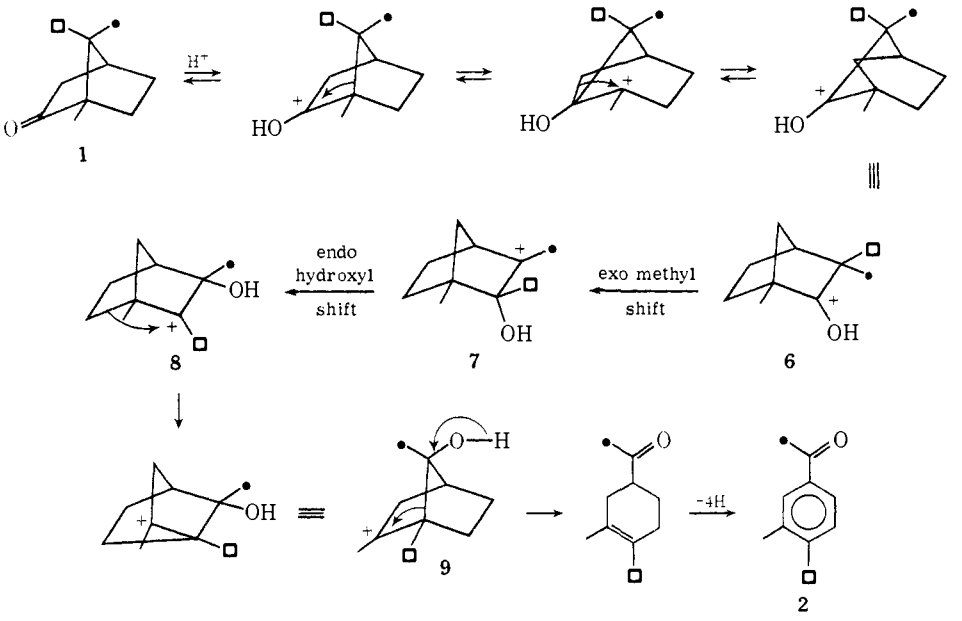
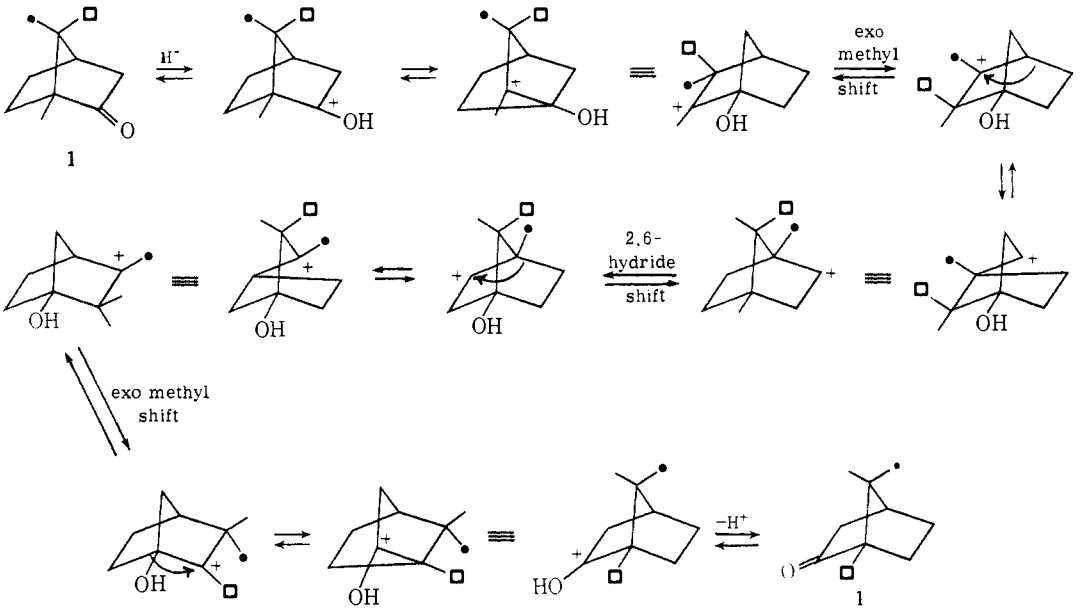
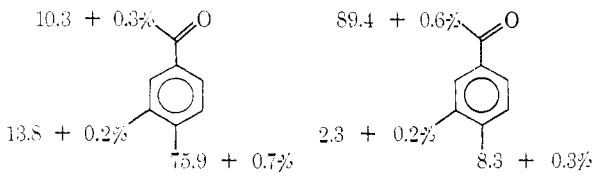



Chart II. The Acid-Catalyzed Racemization of Camphor (Path 2)




from camphor-8-$^{14}C$ from camphor-9-$^{14}C$

Figure 1. The relative distributions of radioactivity in 3,4-dimethylacetophenone isolated from the rearrangement of camphor-8-$^{14}C$ and camphor-9-$^{14}C$.

was readily isolated by preparative tlc. Degradation of the radioactive 3,4-dimethylactophenone was carried out as previously described,[6] and the observed distributions of radioactivity are shown in Figure 1.

## Discussion

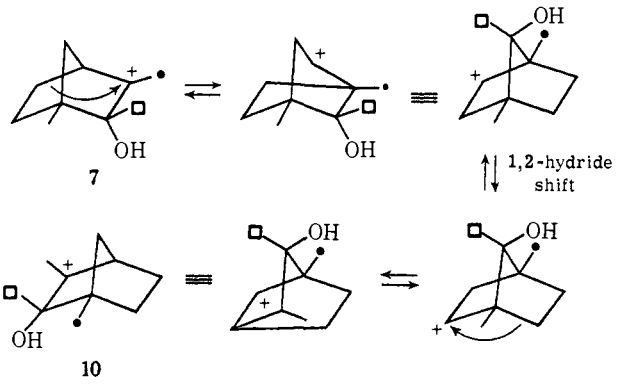
In addition to the pathway (path 1) shown in Chart I. under the reaction conditions camphor should follow two other known rearrangement routes. The first of these (path 2) entails the racemization of camphor, known to occur in concentrated sulfuric acid. The mechanism proposed for this change (Chart II) involves two exo methyl migrations and a 2,6-hydride shift which effects an interchange of the C-8 and C-10 methyl groups, but leaves C-9 unaffected.[8,9]

The second is a modification of path 1, which involves the racemization of the intermediate **7** *via* a 2,3-hydride shift, leading to its mirror image **10** (Chart III). Lutz

(8) A. M. T. Finch, Jr., and W. R. Vaughan, *J. Amer. Chem. Soc.*, **91**, 1416 (1969); T. Miki, M. Nishikawa, and P. H. Hagiwara, *Proc. Jap. Acad.*, 31, 718 (1955).

(9) The same result would obtain if an alternate mechanism proposed by Noyce[5] for the rearrangement of fenchone were operating in the rearrangement of camphor. This route proceeds from the intermediate **8** (Chart I) and leads to **9** in the proposed mechanism, with the C-8 and C-10 methyl groups interchanged. However, Lutz and Roberts[6] failed to detect any evidence of this pathway operating in the rearrangement of fenchone, and since protonated fenchone (6) is a proposed intermediate in the major rearrangement pathway of camphor (Chart I), it appears highly unlikely that this alternate pathway is operating in the present case.

**Chart III.** A Modification of Path 1 to 3,4-Dimethylacetophenone (Path 3)




and Roberts had found it necessary to postulate this variation, operating to the extent of only a few per cent, in the rearrangement of fenchone, to account for the radioactivity distribution in their 3,4-dimethylacetophenone product. This route (path 3) interchanges the positions of the C-9 and C-10 methyl groups, while C-8 remains unaffected.

The rate processes involved in these transformations are summarized by the solid arrows in Figure 2. If one permits the step **6** → **7** (Chart I) to be reversible, then path 3 (Chart III) becomes a racemization process for fenchone, and the interconnections between the pathways shown in Figure 2 allow the positioning of radioactivity at all three methyl locations from either camphor-*8*-$^{14}C$ or camphor-*9*-$^{14}C$. In that case, the solid arrow scheme in Figure 2 would require that in the rearrangement of camphor-*9*-$^{14}C$ the C-3 methyl group of the product contain at least as much radioactivity as that at C-4. However, the C-4 methyl group was found to harbor more than *three times* the radioactivity as the one at C-3. Therefore, a fourth route to the 3,4-dimethylacetophenone isolated from the camphor-*9*-$^{14}C$ rearrangement must exist, one which will increase the radioactivity at the C-4 methyl position. Such a course takes origin if intermediate **6** (Chart I) undergoes an endo methyl shift, followed by an exo hydroxyl shift. However, because most of the published evidence in substituted norbornyl cation systems argues against 3,2-*endo*-alkyl[10] or hydride[11,12] shifts, it is perhaps also desirous to consider a mechanism which avoids such a migration. Such a route (path 4) is shown in Chart IV, also originating from intermediate **6** (Chart I). The mechanism is an adaptation of that proposed by Berson and coworkers[12] to circumvent the need to use pathways involving endo shifts in rearrangements of similar bicyclic systems.[13,14]

(10) For example, see A. M. T. Finch, Jr., and W. R. Vaughan, *J. Amer. Chem. Soc.*, 87, 5520 (1965); G. E. Gream and D. Wege, *Tetrahedron*, 22, 2583 (1966).

(11) R. N. McDonald and R. N. Steppel, *J. Amer. Chem. Soc.*, 92, 5664 (1970); C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Franklin, *ibid.*, 86, 4913 (1964).

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

(13) Recently, several examples of endo 2,3-hydride or methyl shifts in a bicyclo[2.2.1] system have been reported; see A. W. Bushell and P. Wilder, Jr., *ibid.*, 89, 5721 (1967); P. Wilder, Jr., and W. Hsieh, *J. Org. Chem.*, 36, 2552 (1971); S. Rengaraju and K. D. Berlin, *Tetrahedron*, 27, 2399 (1971).

(14) While the validity of proposing an endo hydroxyl shift in a bicyclo[2.2.1] system remains obscure, other workers have postulated such a shift in the past (*cf.* ref 6 and Chart I). However, such oxygen rearrangements have been well documented in aliphatic systems; for example, see K. Bhatia and A. Fry, *J. Org. Chem.*, 34, 806 (1969).

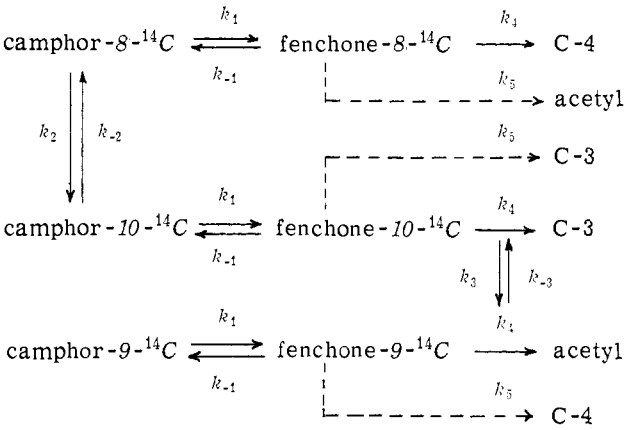



Figure 2. The interrelation of pathways by which camphor-*8*-$^{14}C$ and camphor-*9*-$^{14}C$ rearrange to 3,4-dimethylacetophenone and the termini of the radioactive methyl groups.

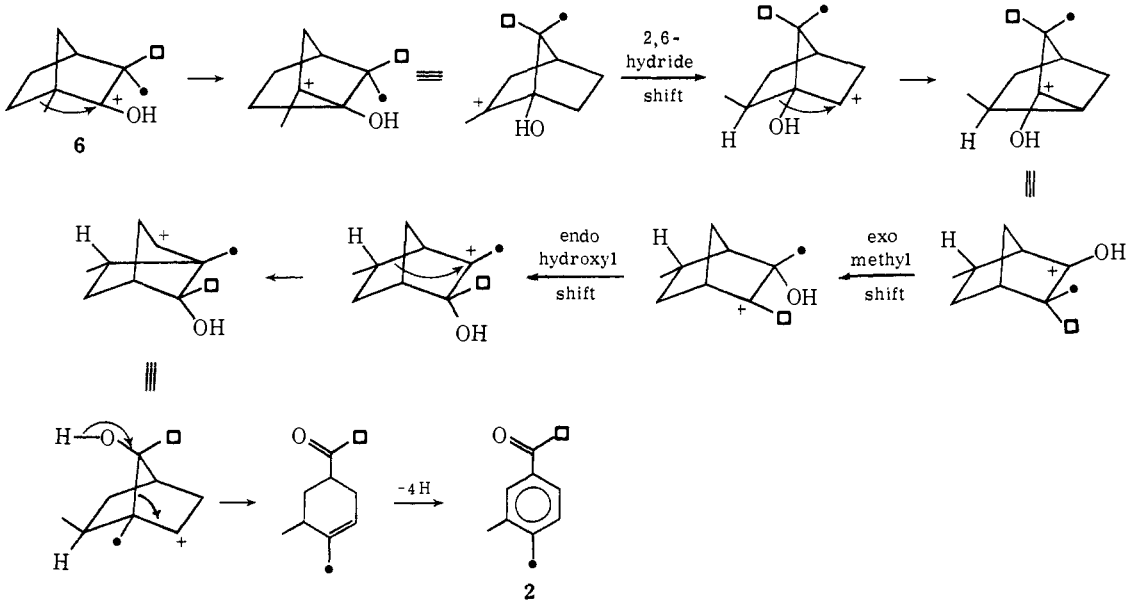
Since the route shown in Chart IV and the endo methyl shift pathway both yield identically labeled products, it was not possible to determine in this study which of these mechanisms was operating in the rearrangement of camphor. The positions where radioactivity is placed in the product by either pathway are shown by the dashed arrows ($k_5$) in Figure 2.

From Figures 1 and 2 the following may now be educed. The major route of rearrangement of both camphor-*8*-$^{14}C$ and camphor-*9*-$^{14}C$ is by path 1 ($k_1$ and $k_4$) because the C-4 and acetyl methyl groups of the product in each case contain the highest radioactivity. Path 3 ($k_3$) plays but a minor role since only about 2% of the radioactivity from camphor-*9*-$^{14}C$ terminates at the C-3 methyl position, a fact which correlates well with the findings of Lutz and Roberts in the rearrangement of fenchone under similar conditions.[6] Furthermore, since $k_2$ is relatively small (see below), the percentage of camphor-*9*-$^{14}C$ rearranging by paths 1 and 4 should be closely reflected in the ratios of the radioactivities observed at the acetyl and C-4 methyl groups, respectively, namely about 89 and 8%.

The camphor-*8*-$^{14}C$ experiment reveals that about 14% of the rearrangement occurs *via* camphor-*10*-$^{14}C$, while the percentage of camphor-*8*-$^{14}C$ undergoing rearrangement by paths 1 and 4 is now mirrored in the radioactivities at the C-4 and acetyl methyl groups, respectively. Further, the C-3 methyl radioactivity arises from the rearrangement of protonated fenchone-*10*-$^{14}C$ by both routes $k_4$ and $k_5$. Since $k_4/k_5$ should be essentially the same in this sequence as that observed for fenchone-*8*-$^{14}C$, it is readily inferred that about 12% of the fenchone-*10*-$^{14}C$ rearranges by way of $k_1$. Thus, the *total* rearrangement of camphor-*8*-$^{14}C$ and camphor-*10*-$^{14}C$ by path 1 ($k_1$ and $k_4$) is about 88%, and by path 4 ($k_1$ and $k_5$) about 12%.[15] In addition, approximately 0.3% (0.138 × 0.023) of the camphor-*8*-$^{14}C$ follows the $k_2 \rightarrow k_1 \rightarrow (k_4)k_3$ route, while about 2% (roughly 0.138 × 0.138) of the camphor-*10*-$^{14}C$ rearranges back to camphor-*8*-$^{14}C$ ($k_{-2}$).

(15) The scheme in Figure 2 predicts that $k_4/k_5$ from fenchone-*8*-$^{14}C$ and fenchone-*9*-$^{14}C$ should be about the same. The fact that the ratios are slightly different may be the result of small unwitting variances in the reaction conditions of the two conducted rearrangements, possible leakage *via* $k_{-3}$ in the case of camphor-*9*-$^{14}C$, and/or due to an isotope effect.

Chart IV. Fourth Route to 3,4-Dimethylacetophenone (Path 4)




In summary, then, these results are in agreement with 88–92% of the camphor rearranging to 3,4-dimethylacetophenone by path 1 (Chart I) and 8–12% by path 4 (Chart IV), with about 16% of the camphor and 2% of the intermediate **7** undergoing internal racemization (Charts II and III, respectively).

## Experimental Section

**General Procedures.** The melting points are uncorrected and were determined with a Thomas-Hoover melting point apparatus. The infrared spectra were recorded on a Perkin-Elmer Model 257 Grating Infrared spectrophotometer, nmr spectra were carried out on a Perkin-Elmer Hitachi R-20 spectrometer using tetramethylsilane as an internal standard, mass spectra were obtained using a Perkin-Elmer RMU-6E low resolution mass spectrometer, and vapor phase chromatograms were carried out on a Varian Aerograph Series 200 instrument using a 5% SE-30 on Chromosorb W column at 130°.

**Rearrangement of Camphor. Camphor-*8*-$^{14}C$.** A 1.00 g (0.0066 mol) sample of camphor-*8*-$^{14}C$[15] was added all at once to 6.0 ml of concentrated sulfuric acid maintained at 110° and magnetically stirred at this temperature for 45 min. The dark brown reaction mixture was cooled to room temperature, poured into cold water, and extracted with pentane. The combined pentane extracts were washed with 1 *N* aqueous sodium hydroxide and dried, and the solvent was removed under reduced pressure. There remained 0.577 g of a yellow oil which consisted of 1.5% fenchone (**3**), 1% camphor (**1**), 65% carvenone, and 32.5% 3,4-dimethylacetophenone (**2**), as determined by vpc analysis.

The crude rearrangement products were chromatographed in 0.145-g portions on 20 × 20 cm plates of Merck silica gel PF-254 (pH 7)[17] using benzene (two developments). The band of $R_f$ 0.32 was eluted with ether to yield pure carvenone: ir (neat) 1665 cm$^{-1}$ (C=O); mass spectrum (70 eV) *m/e* (rel intensity, fragment ion) 152 (49, $M^-$) 111 (9), 110 (100, $M^+ - C_3H_6$), 109 (10), 95 (66, 110 − $CH_3$), 82 (9), 81 (10), 67 (24). The band of $R_f$ 0.54 was similarly eluted to give 96% pure 3,4-dimethylacetophenone (**2**) as determined by vpc analysis: ir (neat) 1680 cm$^{-1}$ (C=O); nmr ($CDCl_3$) δ 7.60 (br m, 3, Ar*H*), 2.59 (s, 3, $COCH_3$), and 2.35 ppm (s, 6, $ArCH_3$).

The isolated, radioactive 3,4-dimethylacetophenone was diluted with inactive ketone[18] and the whole was distilled with a molecular still. Additional inactive ketone was distilled until a total of 1.98 g of diluted, labeled 3,4-dimethylacetophenone had been collected, which was found to be >99.9% pure by vpc analysis.

**Camphor-*9*-$^{14}C$.** Camphor-*9*-$^{14}C$[16] (0.495 g, 0.0033 mol) was rearranged under the same conditions (3.0 ml of concentrated sulfuric acid, 110°, 45 min) as camphor-*8*-$^{14}C$. Work-up yielded 0.289 g of a yellow liquid which was found by vpc analysis to consist of 1% fenchone (**3**), 1% camphor (**1**), 65% carvenone, and 33% 3,4-dimethylacetophenone (**2**).

The crude rearrangement products were separated by preparative tlc as described above to yield pure carvenone and 96% pure 3,4-dimethylacetophenone. The radioactive aromatic ketone was diluted with inactive 3,4-dimethylacetophenone and distilled with a molecular still until a total of 1.10 g of diluted, labeled product had been collected, which was determined to be >99.9% pure by vpc analysis.

**Degradation of 3,4-Dimethylacetophenone.** The procedures used were essentially those reported by Lutz and Roberts,[6] with some minor modifications mentioned below.

**Haloform Reaction of 3,4-Dimethylacetophenone.** From 200 mg (1.35 mmol) of 3,4-dimethylacetophenone was obtained 0.244 mg (46%) of iodoform which was recrystallized three times from ethanol, mp 118–120° (lit.[19] 119°).

The aqueous filtrate was evaporated to near dryness and the residue was redissolved in 8 ml of water. After acidification with 10% hydrochloric acid, solid sodium thiosulfate was added until the iodine color disappeared, and the resulting white precipitate was suction-filtered and air-dried to give 105 mg (52%) of 3,4-dimethylbenzoic acid. The acid was recrystallized three times from benzene and vacuum-dried: mp 165.5–166.5° (lit.[6] mp 165–166°); ir (KBr) 1680 cm$^{-1}$ (C=O); nmr ($CDCl_3$ + DMSO-$d_6$) δ 10.97 [s (exchanged with $D_2O$), 1, $CO_2H$], 7.45 (br m, 3, Ar*H*), and 2.28 ppm (s, 6, Ar-$CH_3$).

**Baeyer–Villiger Rearrangement of 3,4-Dimethylacetophenone. 3,4-Dimethylphenyl Acetate.** The following quantities were used: freshly distilled trifluoroacetic anhydride, 10.00 g (0.048 mol); ~84% hydrogen peroxide, 1.62 g (0.040 mol) in 10 ml of methylene chloride; 3,4-dimethylacetophenone, 2.96 g (0.020 mol) in 20 ml of methylene chloride containing 14.2 g (0.100 mol) of finely powdered anhydrous disodium hydrogen phosphate. The water-clear peroxytrifluoroacetic acid solution was allowed to stir at room temperature for 30 min before being added to the 3,4-dimethylacetophenone–disodium hydrogen phosphate mixture.[20] The crude yield of 3,4-dimethylphenyl acetate obtained as a yellow liquid, 3.01 g (92%), was distilled, bp 55° (2 mm) [lit.[6] bp 62–65° (0.6–0.7 mm)], to give the desired ester as a clear yellow liquid which was >99.9% pure as determined by vpc: ir (neat) 1760 cm$^{-1}$ (C=O); nmr ($CDCl_3$) δ 6.90 (br m, 3, Ar*H*), 2.22 and 2.20 ppm (s, 9, $ArCH_3$ and $OCOCH_3$).

**Reduction of 3,4-Dimethylphenyl Acetate. 3,4-Dimethylphenol.** Distilled 3,4-dimethylphenyl acetate, 2.57 g (0.016 mol), in 20 ml of

(16) O. R. Rodig and R. J. Sysko, *J. Org. Chem.*, **36**, 2324 (1971).
(17) EM Reagents Division, Brinkmann Instruments, Inc., Westbury, N. Y. 11590.
(18) Eastman Organic Chemicals, Rochester, N. Y.; distilled prior to use.
(19) Heilbron's "Dictionary of Organic Compounds," 4th ed, Vol. 3, Oxford University Press, New York, N. Y., 1965, p 1865.
(20) A. S. Pagano and W. D. Emmons, *Org. Syn.*, **49**, 47 (1969).

dry ether was added to a stirred slurry of 0.595 g (0.016 mol) of lithium aluminum hydride in 5.0 ml of dry ether. Work-up was as previously described[6] except that chloroform was used in the extraction, which made a continuous extraction unnecessary, and yielded 1.83 g (96%) of 3,4-dimethylphenol as a pale yellow solid. Recrystallization of the product thrice from hexane gave colorless needles, mp 63.5–64.5° (lit.[21] mp 62–65°); ir (KBr) 3180 $cm^{-1}$ (br, OH); nmr ($CDCl_3$) δ 6.75 (br m, 3, Ar*H*), 5.35 [br s (exchanged with $D_2O$), 1, O*H*], and 2.16 ppm (s, 6, $ArCH_3$).

**Methylation of 3,4-Dimethylphenol. 3,4-Dimethylanisole.** 3,4-Dimethylphenol, 1.69 g (0.014 mol), and dimethyl sulfate, 2.65 ml (3.53 g, 0.028 mol), yielded 1.73 g (92%) of crude 3,4-dimethylanisole by the reported procedure.[6] The product was distilled to give a colorless liquid, bp 43–45° (1 mm) [lit.[6] bp 68.5–69° (5 mm)], which was found to be >99.9% pure by vpc analysis: nmr ($CDCl_3$) δ 6.85 (br m, 3, Ar*H*), 3.73 (s, 3, $OCH_3$), 2.21 (s, 3, $ArCH_3$), and 2.17 ppm (s, 3, $ArCH_3$).

**Oxidation of 3,4-Dimethylanisole. 4-Methoxybenzene-1,2-dicarboxylic Acid.** A 1.48-g (0.011 mol) sample of 3,4-dimethylanisole was oxidized as reported previously except that the addition period of the potassium permanganate solution was shortened to 40 min due to the smaller quantities used. Work-up as described yielded 31 mg (2%) of 2-methyl-4-methoxybenzoic acid: ir (KBr) 1680 $cm^{-1}$ (C=O); mass spectrum (70 eV) *m/e* (rel intensity, fragment ion) 166 (100, $M^+$), 149 (86, $M^+ - OH$), 148 (73, $M^+ - H_2O$), 121 (38, $M^+ - CO_2H$), 120 (31, 121 − H), 91 (35, $C_6H_3O^+$), 77 (38).

The aqueous filtrate from above was evaporated to near dryness, water was added, and the mixture was heated until the solids had completely dissolved. The desired diacid was allowed to crystallize slowly to yield 1.45 g of a white solid. The filtrate was recycled using the procedure described above to yield an additional 0.15 g of product; the combined weights of the two crystallizations represent a yield of 75% of crude 4-methoxybenzene-1,2-dicarboxylic acid. The diacid was recrystallized once from water, twice from 4:1 benzene–acetone, and vacuum-dried; no melting point was determined since the acid readily forms the anhydride on heating:[6] ir (KBr) 1730 ($C_2$=O) and 1680 $cm^{-1}$ ($C_1$=O); nmr [$(CD_3)_2CO$] δ 7.51 (br m, 3, Ar*H*), 7.84 [s (exchanged with $D_2O$), 2, $CO_2H$], and 3.91 ppm (s, 3, $OCH_3$); mass spectrum (70 eV) *m/e* (rel intensity, fragment ion) 196 (22, $M^+$), 179 (15, $M^+ - OH$), 178 (52, $M^+ - H_2O$), 152 (37, $M^+ - CO_2$), 135 (41, 179 − $CO_2$), 134 (100, 178 − $CO_2$), 106 (69, $M^+ - 2CO_2H$).

**Brominative Decarboxylation of 4-Methoxybenzene-1,2-dicarboxylic Acid. 2,4-Dibromo-5-methoxybenzoic Acid.** A 0.86-g (0.0044 mol) sample of 4-methoxybenzene-1,2-dicarboxylic acid in 10.5 ml of 10% aqueous sodium hydroxide and 17.5 ml of water was treated with 1.41 g (0.0088 mol) of bromine using the prescribed procedure.[6] The desired 2,4-dibromo-5-methoxybenzoic acid, 0.414 g (30%), was obtained as a cream-colored solid which, on recrystallization once from 50% aqueous ethanol and twice from benzene, yielded white needles: mp 202.5–203.5° (lit.[22] mp 203°); ir (KBr) 1700 $cm^{-1}$ (C=O); nmr [$(CD_3)_2CO$] δ 7.82 (s, 1, Ar*H*), 7.48 (s, 1, Ar*H*), 5.34 [br s (exchanged with $D_2O$), 1, $CO_2H$], and 3.94 ppm (s, 3, $OCH_3$).

The original filtrate from above was cooled to room temperature and refrigerated to precipitate 4-bromo-5-methoxybenzene-1,2-dicarboxylic acid, 0.288 g (24%), which was obtained as a pale yellow solid. The product was purified by recrystallization from water and ethyl acetate to give a white solid; no melting point was determined because the acid forms the anhydride on heating:[6] ir (KBr) 1730 ($C_1$=O) and 1700 $cm^{-1}$ ($C_2$=O).

**Liquid Scintillation Counting.** Radioactive samples (0.47–7.23 mmol) from the degradation of 3,4-dimethylacetophenone formed from camphor-8-$^{14}C$ and camphor-9-$^{14}C$ were dissolved in 10 ml of scintillation grade toluene[23] containing 4.00 g/l. of 2,5-diphenyloxazole (PPO)[24] and 50 mg/l. of *p*-bis-2-(5-phenyloxazoyl)benzene (POPOP)[24] in a counting vial and counted for 20 min with a Nuclear Chicago Counter Model 723. In the case of 4-methoxybenzene-1,2-dicarboxylic acid it was necessary to first dissolve the sample in 200 μl of reagent grade acetone before adding the scintillation cocktail to effect complete solution of the diacid. The counting efficiencies of all samples were determined from quenching curves obtained by diluting samples of known radioactivities (disintegrations per minute) with increasing amounts of chloroform and of acetone.[25]

(21) Reference 19, Vol. 2, p 1209.

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# Proton Magnetic Resonance Studies of the Conformations and Conformational Equilibrations of *cis*- and *trans*-1,5-Diacetoxycyclooctane

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**Abstract:** The pmr spectra of partially deuterated *cis*- and *trans*-1,5-diacetoxycyclooctane were studied at variable temperature. Both molecules showed a spectral change at different temperatures such that the low-temperature spectra defined the stable conformations to be boat–chair forms (**3** and **4**) containing the substituents at different positions for each isomer. The spectral change for the cis isomer was interpreted in terms of a pseudorotation while that of the trans isomer was explained in terms of an inversion process.

While the conformational analysis of cyclohexane and its derivatives is rather well understood, the conformational possibilities for derivatives of cyclooctane are not as easily envisaged because of the greater complexity of the ring system and the relative paucity of experimental results. Several publications have recently been concerned with experimental[1–3] and theoretical[4] studies on cyclooctane. From this work it has emerged that cyclooctane exists in the boat–chair

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