23445-15-0; **26**, 23417-00-7; **27**, 59938-61-3; **28**, 59938-62-4; **29**-OH, 59938-63-5; **29**-Cl, 59938-64-6; **30**, 59938-65-7; anthracene, 120-12-7; *trans*-1,3-dichloropropene, 10061-02-6; *cis*-1,3-dichloropropene, 10061-01-5; acetic acid, 64-19-7; *cis*-1-propenyl acetate, 3102-47-4; *trans*-1-propenyl acetate, 1528-10-5; *p*-bromobenzenesulfonyl chloride, 98-58-8; *syn*-8-methyl-2-dibenzobicyclo[3.2.1]octadienone, 59938-66-8; *anti*-8-methyl-2-dibenzobicyclo[3.2.1]octadienone, 59981-12-3; lithium aluminum hydride, 16853-85-3; 3,6-dibenzo-2-bicyclo[3.2.2]nonadienone, 24330-03-8; ethyl propiolate-*3-d*, 59938-67-9.

References and Notes

(1) Part 83: S. J. Cristol, H. W. Mueller, W. M. Macintyre, and R. C. Haltiwanger, *J. Org. Chem.*, **41**, 1919 (1976).
(2) See S. J. Cristol, A. A. Roberts, and T. E. McEntee, *J. Org. Chem.*, **39**, 829 (1974), and references cited therein.
(3) R. Gindig and A. D. Cross, *J. Am. Chem. Soc.*, **87**, 4629 (1965).
(4) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **80**, 5323 (1958); **81**, 4256 (1959).
(5) It has previously[6] been shown that the normal stereochemistry required for cyclopropane formation from 1,3-dihalides with zinc is not required with heavily coppered zinc.
(6) S. J. Cristol, A. R. Dahl, and W. Y. Lim, *J. Am. Chem. Soc.*, **92**, 5670 (1970).
(7) (a) S. J. Cristol, R. J. Bopp, and A. E. Johnson, *J. Org. Chem.*, **34**, 3574 (1969); (b) S. J. Cristol and R. J. Bopp, *ibid.*, **39**, 1336 (1974).
(8) J. P. Kochansky, Ph.D. Thesis, University of Colorado, 1971.
(9) (a) S. J. Cristol, F. P. Parungo, and D. E. Plorde, *J. Am. Chem. Soc.*, **87**, 2870 (1965); (b) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *ibid.*, **87**, 2879 (1965).
(10) See ref 6 for discussion of plausible intermediates and appropriate references.
(11) S. J. Cristol and M. C. Kochansky, *J. Org. Chem.*, **40**, 2171 (1975).
(12) We have no information regarding the question of equilibrating vs. mesomeric cations in this system and use classical ions in our discussion for convenience.
(13) (a) P. K. Sheenoy, Ph.D. Thesis, University of Arizona, 1966; (b) S. J. Cristol, G. C. Schloemer, D. R. James, and L. A. Paquette, *J. Org. Chem.*, **37**, 3852 (1972).
(14) Details on the undeuterated compounds were developed by G. C. Schloemer, Ph.D. Thesis, University of Colorado, 1972.
(15) It has previously been noted[16] in acetolysis experiments that **24**-OAc epimers (endo–exo mixture) are principal products of kinetic control, and that these rearrange more or less completely to **7** (along with some elimination products) under acid conditions.
(16) (a) E. Cioranescu, M. Banciu, R. Jelescu, M. Rentzea, M. Elian, and C. D. Nenitzescu, *Tetrahedron Lett.*, 1871 (1969); (b) *Rev. Roum. Chim.*, **14**, 911 (1969).
(17) Footnote 15 in ref 9b.
(18) J. A. Berson, R. T. Luibrand, N. G. Kunder, and D. G. Morris, *J. Am. Chem. Soc.*, **93**, 3075 (1971).
(19) E. Cioranescu, A. Bucur, F. Badea, M. Rentzea, and C. D. Nenitzescu, *Tetrahedron Lett.*, 1867 (1969).
(20) This compound has been previously prepared in the laboratory by Dr. G. O. Mayo by another route.
(21) D. Y. Curtin and M. Hurwitz, *J. Am. Chem. Soc.*, **74**, 5381 (1952).
(22) The ^{1}H NMR spectrum of this acetate indicated a 40:60 cis–trans ratio.
(23) (a) R. J. Bopp, private communication; (b) J. P. Kochansky, Ph.D. Thesis, University of Colorado, 1971.
(24) For details, see A. L. Noreen, Ph.D. Thesis, University of Colorado, 1970.
(25) H. G. Kuivila and O. F. Boemel, *J. Am. Chem. Soc.*, **83**, 1246 (1961).
(26) An alternative that only two isomers are formed also fits the data, but has no mechanistic support.

Ionic Reactions in Bicyclic Systems. 9. Preparation of Optically Active 1,2-Dimethyl-*exo*-2-norbornyl, 1,2-Dimethyl-*exo*-2-benzonorbornenyl, and 6,7-Dimethoxy-1,2-dimethyl-*exo*-2-benzonorbornenyl Chloride

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Hydrochlorination of optically active 1-methyl-2-methylenenorbornane (1) in pentane at −78 °C gives active 1,2-dimethyl-*exo*-2-norbornyl chloride (2) with ~27% retention of optical configuration. Under similar conditions active 1-methyl-2-methylenebenzonorbornene (3) gives active 1,2-dimethyl-*exo*-2-benzonorbornenyl chloride (4) (~80% retention) and active 6,7-dimethoxy-1-methyl-2-methylenebenzonorbornene (5) gives 6,7-dimethoxy-1,2-dimethyl-*exo*-2-benzonorbornenyl chloride (6) with about 13% retention of optical configuration.

Recently we reported results of solvolytic studies of optically active 1,2-dimethyl-*exo*-2-norbornyl chloride (**2**)[1] and 1,2-dimethyl-*exo*-2-benzonorbornenyl chloride (**4**).[2] We have also investigated the 6,7-dimethoxy-1,2-dimethyl-*exo*-2-benzonorbornenyl system[3] including the optically active tertiary chloride (**6**). We now present details of the preparation of these optically active tertiary chlorides.

A possible route to the optically active tertiary chlorides was suggested by the work of Brown and Liu,[4] who observed that under carefully controlled conditions, hydrochlorination of deuterium labeled 1-methyl-2-methylenenorbornane (**1**) gives **2** with only partial scrambling of the methyl groups. Exposure of the product to hydrogen chloride at 0 or −78 °C results in randomization of the methyl groups (hydrogen chloride catalyzed isomeric Wagner–Meerwein rearrangement[5]). A corollary of that work is that optically active **1** should lead to active **2**; however, **2** racemizes under the conditions of the hydrochlorination.

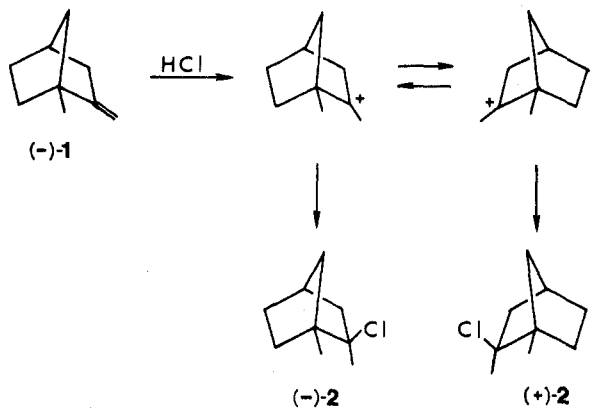
The preparation and determination of absolute configurations and rotations of optically active 1-methyl-2-methylenenorbornane (**1**),[6] 1-methyl-2-methylenebenzonorbornene (**3**),[7] and 6,7-dimethoxy-1-methyl-2-methylenebenzonorbornene (**5**)[8] have been reported elsewhere.[9] Attempts to prepare optically active **2** from active **1** under conditions reported[4] to give minimum scrambling of the methyl groups (hydrochlorination of neat **1**, 0 °C, 1–2 min) were unsuccessful. Hydrogen chloride uptake ceased at about 60% reaction—the remaining liquid **1** was encapsulated by the solid adduct (**2**)—and active chloride could not be separated from the mixture. Evidently, in the earlier work[4b] unreacted **1** in the product did not interfere with NMR analysis of the tertiary chloride. In the present work the additional handling required for separation of pure **2** resulted in racemization.

Hydrochlorination of (−)-**1** in pentane at −78 °C is complete in a few minutes—the reaction is somewhat slower at 0 °C. Removal of the pentane and excess hydrogen chloride under high vacuum at <0 °C gave homogeneous (−)-**2**. The purity of racemic and optically active **2** obtained by this procedure was established by the NMR spectrum, solvolysis equivalent, elemental analysis, and mass spectrum. Efficient

Table I. Retention of Configuration for Hydrochlorination of 1-Methyl-2-methylenenorbornane (1)

(−)-1 $[\alpha]^{30}D$[a]	→ (−)-2 →	(−)-1 $[\alpha]^{30}D$[a]	% retention
−42.1°		−11.5°	27[b]
−35.7°		−9.2°	26[c]
−34.6°		−2.1°	6[b]
−34.6°		−2.9°	8[c]

[a] Rotations for chloroform solutions. [b] Elimination with 0.1 M 2,6-lutidine in chloroform at 30 °C. [c] Elimination with 0.7 M potassium *tert*-butoxide in dimethyl sulfoxide at 45 °C.



stirring during hydrochlorination, chilling (liquid nitrogen) the reaction container during attachment to a vacuum transfer apparatus, and rapid workup are necessary to avoid extensive racemization.

The tertiary chloride (2) racemizes spontaneously in chloroform at room temperature ($k \sim 4 \times 10^{-3}$ min^{-1}, 30 °C) and reliable rotations could not be determined. The most active samples of (−)-2 had rotations about 3% as large as those of the starting olefin. That the chloride was not contaminated with unreacted (−)-1 was clear from the NMR spectrum, rotary dispersion curves for the two compounds, and complete loss of optical activity during first-order racemization under conditions where active 1 is optically stable.

The optical purity of (−)-2 was determined by reconversion to (−)-1 with either potassium *tert*-butoxide in dimethyl sulfoxide at 45 °C or 2,6-lutidine in chloroform at 30 °C. Results of these experiments are shown in Table I which shows rotations of starting olefin and olefin derived from (−)-2. Both methods for converting (−)-2 to (−)-1 give similar results which suggests that optical configuration is not lost in this transformation. The first two experiments are for the best conditions for obtaining active 2. In these cases (−)-2 was obtained which gave (−)-1 with ~27% of the original optical activity. We believe that the loss of configuration occurs during hydrochlorination. In any case the (−)-2 → (−)-1 correlation gives a lower limit of the optical purity of 2. In the last two experiments in the table less efficient stirring during hydrochlorination led to less active 2 (6–8% retention of configuration).

Hydrochlorination of 1-methyl-2-methylenebenzonorbornene (3) in pentane at −78 °C is complete in 3–7 min (depending on sample size) and (+)-3[7] gives (+)-1,2-dimethyl-*exo*-2-benzonorbornenyl chloride [(+)-4]. The purity of racemic and active samples of 4 was established by the NMR spectrum, solvolysis equivalent, elemental analysis, and mass spectrum. The optical purity of active 4 was determined by reconversion to 3 with potassium *tert*-butoxide in dimethyl sulfoxide at 45 °C. Evidently this is an E2 elimination and

Table II. Rates and Relative Rates of Methanolysis of 2, 4, and 6 at 0 °C

Compd	$10^4 k_t$, min^{-1}	Rel rate
2	85.1[a]	254
4	0.335[b]	1
6	60.8[c]	184

[a] Reference 1. [b] Extrapolated from data at higher temperatures reported in ref 2. [c] Reference 3.

proceeds without loss of optical configuration; independent experiments gave the same ratio of rotations for product and reactant and no loss of optical activity occurs in the absence of base.

The (+)-3 → (+)-4 → (+)-3 sequence resulted in only 20% loss of configuration as compared to >70% loss for the dimethylnorbornyl system (1 → 2 → 1). The tertiary benzonorbornenyl chloride (4) is noticeably more optically stable than the tertiary norbornyl chloride (2) as would be expected from relative rates of ionization. Relative rates of methanolysis of 2, 4, and 6 are shown in Table II.

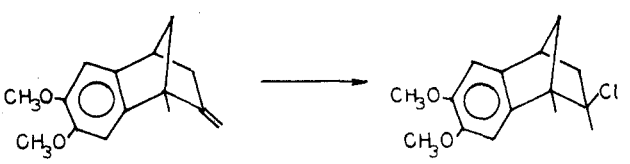
Hydrochlorination of 3 in pentane shows a more pronounced negative temperature coefficient than hydrochlorination of 1. In contrast to the rapid rate at −78 °C (reaction

(−)-3 (−)-4

complete in about 4 min), the reaction is <80% complete in 34 min at 25 °C. Hydrogen chloride uptake is pseudo-first-order and $k = 4.4 \times 10^{-2}$ min^{-1}, 25 °C. Evidently the inverse temperature effect results from a change in medium with change in temperature. For 1,2-dimethylcyclopentene in pentane saturated with hydrogen chloride, the hydrogen chloride/olefin molar ratio increases from 1.3 to 0 °C to 6.3 at −78 °C.[10] This suggests that in the present work the medium changes from essentially pentane at 25 °C to largely hydrogen chloride at −78 °C. The large increase in solvent polarity with decrease in temperature is probably the cause of the increase in rate. Also, hydrochlorination may be second or higher order in hydrogen chloride[11] and the increase in hydrogen chloride concentration could also contribute to the temperature effect.

Hydrochlorination of 6,7-dimethoxy-1-methyl-2-methylenebenzonorbornane (5) was complicated by the low solubility of this olefin in pentane at −78 °C. Thus, optimum conditions for maximum retention of configuration for hydrochlorination of 1 and 3 could not be used in this case. Instead, methylene chloride was used—this solvent gives poorer results for the (−)-1 → (−)-2 conversion.

Hydrochlorination of 5 in methylene chloride at −78 °C is complete in about 2 min and (−)-5[8] gives (−)-6 with varying



(−)-5 (−)-6

amounts of retention. As shown in Table II, 6 is more reactive than 4 and nearly as reactive as 2 in methanol at 0 °C. Moreover, the activation energy for methanolysis is lower for 6 (18.5 kcal) than for 2 (21.2 kcal) which indicates that for the tem-

perature range of the hydrochlorination and workup (−78 → 0 °C) the rate of ionization (racemization) is probably at least as high for **6** as for **2**. In the most successful experiment **(−)-5** gave **(−)-6** with 14% retention of optical configuration [established by reconversion to **(−)-5** with potassium *tert*-butoxide in dimethyl sulfoxide]. Recrystallization of **(−)-6** from pentane (<0 °C) resulted in 25% loss of optical activity. Thus, active **6** racemizes spontaneously in nonpolar solvents. The purity of **6** was established by the NMR spectrum, solvolysis equivalent, and elemental analysis.

Experimental Section

Racemic and Optically Active 1,2-Dimethyl-*exo*-2-norbornyl Chloride (2). The tertiary chloride (**2**) was prepared by hydrochlorination of 1-methyl-2-methylenenorbornane (**1**)[6] with an automatic hydrochlorination apparatus described earlier.[4,12] In a typical experiment the apparatus was flushed with nitrogen through the rubber septum in the generator valve and the reaction vessel was cooled to −78 °C (dry ice–acetone). About 2 ml of concentrated hydrogen chloride was added to the concentrated sulfuric acid (100 ml) and the system was flushed and filled with hydrogen chloride. A solution of 1.01 g of **1** in 4.5 ml of pentane was chilled to −78 °C and then injected into the reaction vessel while maintaining vigorous stirring. Hydrogen chloride uptake ceased in 5.5 min. The reaction vessel was removed, rapidly attached to a vacuum transfer apparatus, and chilled with liquid nitrogen. After evacuation to 0.1 mm, the liquid nitrogen was replaced with an ice bath and the hydrogen chloride and pentane vacuum transferred and then the apparatus was filled with dry nitrogen. *dl*-1,2-Dimethyl-*exo*-2-norbornyl chloride (**2**) has mp 120–122 °C; NMR ($CDCl_3$) δ 1.28 (s, 3 H), 1.63 (s, 3 H), 0.83–2.75 (m, 9 H); mass spectrum parent peaks *m/e* 160 and 158.

Anal. Calcd for $C_9H_{15}Cl$: C, 68.13; H, 9.53; Cl, 22.34; solvolysis equivalent, 159. Found: C, 68.43; H, 9.70; Cl, 22.06; solvolysis equivalent (60% aqueous methanol), 158.

Optically active **2** was obtained by the same procedure. In a typical experiment 1.01 g of **(−)-1**,[6] $[\alpha]^{30}D$ −42° (*c* 3.5, $CHCl_3$), gave 1.0 g (77%) of (−)-1,2-dimethyl-*exo*-2-norbornyl chloride [**(−)-2**], $[\alpha]^{30}D$ −0.197° (*c* 7.63, $CHCl_3$). Optically active chloride was prepared shortly before use[1] and stored under nitrogen at −25 °C. All spectral properties of active **2** were indistinguishable from those of racemic material.

Racemic and Optically Active 1,2-Dimethyl-*exo*-2-benzonorbornenyl Chloride (4). This tertiary chloride was prepared from 1-methyl-2-methylenebenzonorbornene (**3**)[7] by the procedure described above for the **1** → **2** transformation except that during the vacuum transfer the temperature rose from −78 °C to room temperature instead of from −78 to 0 °C. *dl*-1,2-Dimethyl-*exo*-2-benzonorbornenyl chloride (**4**) has mp 48–50 °C; NMR ($CDCl_3$) δ 1.13 (s, 3 H), 1.58 (s, 3 H), 1.67–1.95 (m, 2 H), 2.30–2.92 (m, 2 H), 3.10–3.27 (m, 1 H), 7.02 (s, 4 H); mass spectrum parent peaks *m/e* 206 and 208.

Anal. Calcd for $C_{13}H_{15}Cl$: C, 75.54; H, 7.31; Cl, 17.15. Found: C, 75.63; H, 7.36; Cl, 17.25.

Hydrochlorination of a 0.4-g sample of **3** in 1.6 ml of pentane at −78 °C was complete in 3 min. At 25 °C the hydrogen chloride uptake is pseudo first order and only 78% complete in 34 min. The amount of reaction was determined by NMR analysis ($CDCl_3$) of the reaction mixture using the methylene proton signals in **3** (δ 4.70 and 4.90) and the 2-methyl signal in **4** (δ 1.58).

Hydrochlorination of (+)-1-methyl-2-methylenebenzonorbornene [**(+)-3**],[7] $[\alpha]^{30}D$ 198° (*c* 2.72, $CHCl_3$), by the above method (−78 °C) gave (+)-1,2-dimethyl-*exo*-2-benzonorbornenyl chloride [**(+)-4**], $[\alpha]^{30}D$ 42.9° (*c* 3.74, $CHCl_3$). Spectral properties were the same as for racemic material.

Racemic and Optically Active 6,7-Dimethoxy-1,2-dimethyl-*exo*-2-benzonorbornenyl Chloride (6). 6,7-Dimethoxy-1-methyl-2-methylenebenzonorbornene (**5**)[8] was converted to **6** by hydrochlorination by the method described above for the **1** → **2** conversion except that the solvent was methylene chloride instead of pentane. Hydrochlorination of a 1.15-g sample of **5** at −78 °C was complete in 2 min. *dl*-6,7-Dimethoxy-1,2-dimethyl-*exo*-2-benzonorbornenyl chloride (**6**) has mp 47–49 °C; NMR ($CDCl_3$) δ 1.14 (s, 3 H), 1.65 (s, 3 H), 1.69–2.15 (m, 2 H), 2.39–2.80 (m, 2 H), 3.05–3.20 (m, 1 H), 3.79 (s, 6 H), 6.62 (d, 2 H).

Anal. Calcd for $C_{15}H_{19}O_2Cl$: C, 67.54; H, 7.18. Found: C, 67.73; H, 7.20.

Hydrochlorination of **(−)-5**,[8] $[\alpha]^{25}D$ −143° (*c* 1.5, $CHCl_3$), gave **(−)-6**, $[\alpha]^{25}D$ −3.03° (*c* 1.1, $CHCl_3$). Spectral properties of **(−)-6** were the same as for racemic **6**. In the experiment which gave the most active **(−)-6** the above **(−)-5** gave **(−)-6**, $[\alpha]^{25}D$ −4.04°. From absolute rotations for **5** and **6** (see below) it can be determined that this corresponds to about 14% retention of configuration.

Dehydrochlorination of (+)-1,2-Dimethyl-*exo*-2-benzonorbornenyl Chloride [(+)-4]. In a typical experiment 0.25 g (1.21 mmol) of **(+)-4**, $[\alpha]^{30}D$ 42.9° (*c* 2.7, $CHCl_3$), derived from **(+)-3**, $[\alpha]^{30}D$ 198.2° (*c* 2.7, $CHCl_3$), was dissolved in 80 ml of dimethyl sulfoxide containing 5.2 g (4.6 mmol) of potassium *tert*-butoxide. The solution was held at 45 °C for 1 h and then poured into 300 ml of water. The resulting solution was extracted with pentane, the extract dried ($MgSO_4$), and the solvent removed with a rotary evaporator. Purification by preparative GC (20 ft, 30% Carbowax 20M on Chromosorb P at 200 °C) gave **(+)-3**, $[\alpha]^{30}D$ 159.3° (*c* 4.01, $CHCl_3$). This is 80% retention of configuration for the **(+)-3** → **(+)-4** → **(+)-3** sequence. The absolute rotation for **3** is 315° ($CHCl_3$).[7] From these data a lower limit of 42.9° × (315/159) = 85° can be determined for the absolute rotation of **4**.

In a duplicate experiment similar results were obtained, i.e., 80% retention for **(+)-3** → **(+)-4** → **(+)-3**.

A solution of **(+)-4** in dimethyl sulfoxide was placed in a 1-dm polarimeter tube thermostated at 45 °C. During 40 min α_{365} changed from −3.081° to −3.140°. This shows that the chloride does not racemize under these conditions. The small increase in rotation may be due to slight elimination to form more active **3**.

A solution of 406 mg (0.239 mmol) of **(+)-3**, $[\alpha]^{30}D$ 198.2° (*c* 2.72, $CHCl_3$), in dimethyl sulfoxide containing 52 mg (0.46 mmol) of potassium *tert*-butoxide was placed in a 1-dm polarimeter tube thermostated at 45 °C. There was no change in the observed rotation of 8.691° over a period of 65 min. This shows that **3** is optically stable under the conditions of the **(+)-4** → **(+)-3** conversion.

Dehydrochlorination of (−)-1,2-Dimethyl-*exo*-2-norbornyl Chloride [(−)-2]. To determine the minimum value for retention of optical configuration for the **(−)-1** → **(−)-2** transformation the active tertiary chloride [**(−)-2**] was reconverted to **(−)-1** as described above for the **(+)-4** → **(+)-3** conversion. In a typical experiment 0.25 g (1.58 mmol) of **(−)-2**, derived from **(−)-1**, $[\alpha]^{30}D$ −35.7° (*c* 1.64, $CHCl_3$), was dissolved in 30 ml of dimethyl sulfoxide that contained 2.50 g (22 mmol) of potassium *tert*-butoxide. The solution was warmed to 45 °C for 15 min and then poured into 200 ml of ice water. Workup and isolation by preparative GC as described in the preceding section gave **(−)-1**, $[\alpha]^{30}D$ −9.18° (*c* 2.06, $CHCl_3$). Thus, hydrochlorination of **1** proceeds with at least 26% retention of configuration.

In another experiment 0.46 g (3 mmol) of **(−)-2**, $[\alpha]^{30}D$ 0.197° (*c* 3.50, $CHCl_3$), derived from **(−)-1**, $[\alpha]^{30}D$ −34.6°, was dissolved in 25 ml of chloroform containing 2.52 g (24 mmol) of 2,6-lutidine. The resulting solution was kept at 30 °C for 11 h. The change in rotation in a 1-dm tube was $\alpha_{365}{}^{30}$ 0.030° → 0.610° and the final rotation was constant. The solution was treated with 8.0 g (56 mmol) of methyl iodide for 24 h at 30 °C to quaternize the lutidine and then the solution was extracted with water, dried ($MgSO_4$), and concentrated with a fractionating column. Analytical GC showed the product to be 71% **1** and 29% 1,2-dimethyl-2-norbornene. Preparative GC (20% Ucon Polar IB-550-X on Chromosorb W at 120 °C) gave **(−)-1**, $[\alpha]^{30}D$ −11.5°. This corresponds to 27% retention for the **(−)-1** → **(−)-2** → **(−)-1** sequence.

Dehydrochlorination of (−)-6,7-Dimethoxy-1,2-dimethyl-*exo*-2-benzonorbornyl Chloride [(−)-6]. Dehydrochlorination of **(−)-6**, $[\alpha]^{25}D$ −1.48° (*c* 1.0, $CHCl_3$), in dimethyl sulfoxide as described above for the **4** → **3** transformation gave **(−)-5**, $[\alpha]^{25}D$ −7.3°. Control experiments showed that **5** is optically stable under these conditions. From the absolute rotation for **5**, $[\alpha]^{25}D$ 291°, it can be determined that the absolute rotation for **6** is about 1.48° × 291/7.3 = 59°.

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Registry No.—(±)-**1**, 60338-54-7; (−)-**1**, 18366-95-5; (±)-**2**, 60338-55-8; (−)-**2**, 35733-52-9; (±)-**3**, 35001-33-3; (+)-**3**, 34993-32-3; (±)-**4**, 60383-65-5; (+)-**4**, 60383-66-6; (±)-**5**, 54576-25-9; (−)-**5**, 54630-87-4; (±)-**6**, 60338-56-9; (−)-**6**, 60383-67-7.

References and Notes

(1) H. L. Goering and J. V. Clevenger, *J. Am. Chem. Soc.*, **94**, 1010 (1972).
(2) H. L. Goering, C.-S. Chang, and J. V. Clevenger, *J. Am. Chem. Soc.*, **96**, 7602 (1974).
(3) H. L. Goering, C.-S. Chang, and D. Masilamani, *J. Am. Chem. Soc.*, to be submitted.

(4) (a) H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **97**, 600 (1975); (b) H. C. Brown and K.-T. Liu, *Ibid.*, **89**, 466 (1967).
(5) P. D. Bartlett and I. Pöckel, *J. Am. Chem. Soc.*, **60**, 1585 (1938).
(6) H. L. Goering, C. Brown, S. Chang, J. V. Clevenger, and K. Humski, *J. Org. Chem.*, **34**, 624 (1969).
(7) H. L. Goering, J. V. Clevenger and K. Humski, *J. Org. Chem.*, **37**, 3019 (1972).
(8) H. L. Goering, A. C. Backus, C.-S. Chang and D. Masilamani, *J. Org. Chem.*, **40**, 1533 (1975).
(9) Absolute configurations are shown in all structural illustrations.
(10) G. S. Hammond and C. H. Collins, *J. Am. Chem. Soc.*, **82**, 4328 (1960).
(11) R. C. Fahey and M. W. Monahen, *J. Am. Chem. Soc.*, **92**, 2816 (1970). F. R. Mayo and J. J. Katz, *Ibid.*, **69**, 1339 (1947).
(12) H. C. Brown and M.-H. Rei, *J. Org. Chem.*, **31**, 1090 (1966).

Structure of the *o*-Aminophenol–Adipoin Condensation Product

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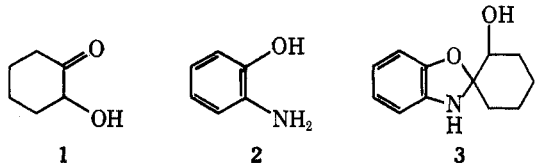
The thermal condensation product from adipoin and *o*-aminophenol is found to be 1,2,3,4,4a,10a-hexahydro-4a-hydroxyphenoxazine (**8**). This structure, which corrects an assignment in the earlier literature, is based on spectral data, chemical transformations, and a single crystal x-ray crystallographic study of 8 HI.

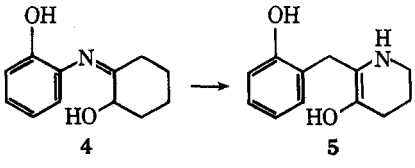
While studying the reactions of adipoin (**1**) with aromatic amines, Cummins and Tomlinson[1] found that heating **1** with *o*-aminophenol (**2**) at 135 °C produced a condensation product, $C_{12}H_{15}O_2N$, mp 171 °C, in unspecified yield. The spirocyclic structure **3** was tentatively assigned to this substance based largely on its infrared spectrum which displayed O–H



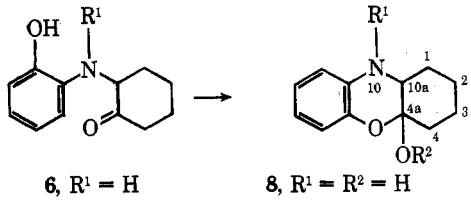
1 **2** **3**

and N–H but no C=O absorption. Our interest in spirocyclic systems prompted us to repeat this preparation so that the properties of the product might be explored. In our hands, heating an intimate mixture of **1** (as the dimer[2]) and **2** under nitrogen for 5 min gave the expected product in 57% yield. Its melting point and infrared spectrum were compatible with the reported data and it could be recrystallized unchanged from aqueous alkali in further agreement with the observations of Cummins and Tomlinson. However the NMR spectrum (in Me_2SO-d_6) of this condensation product ruled out the assigned structure **3** by failing to show a signal in the δ 3.5–4.0 region for the carbinol proton of a secondary alcohol.

At this point, an alternative formulation for the condensation product came to mind by very simple mechanistic



4 **5**



6, R^1 = H
7, R^1 = Ac

8, $R^1 = R^2$ = H
9, R^1 = Ac; R^2 = H
10, R^1 = Ac; R^2 = Ac
11, $R^1 = CH_2C_6H_5$; R^2 = H

reasoning. Initial reaction between **1** and **2** to give the Schiff base **4**, followed by successive proton shifts, would lead via enol **5** to the phenolic ketone **6**; the corresponding hemiketal structure **8** is compatible with all reported properties of Cummins and Tomlinson's condensation product and explains our failure to find a signal for a carbinol proton in its NMR spectrum. The formulation of this product as 1,2,3,4,4a,10a-hexahydro-4a-hydroxyphenoxazine (**8**) accounts for the observation of a 1 H multiplet at δ 3.0 ($-NCHCH_2-$) and the absence of any other signals (excluding exchangeable protons) in the region δ 2.5–6.8. The revised structure is further supported by the properties of several transformation products.

Brief heating with acetic anhydride at its boiling point (137 °C) converted **8** to the *N*-acetyl derivative **9**, mp 162–163.5 °C, whose infrared spectrum showed distinct hydroxyl and amide absorption as well as a weak carbonyl band at 1705 cm^{-1} reflecting a small fraction of the open form **7** in equilibrium with **9**. The 10a proton of **9** appeared as a four-line signal (X part of an ABC system) centered at δ 5.2. This 2 δ downfield shift on acetylation presumably reflects the diamagnetic anisotropy as well as the inductive effect of the acetyl substituent. Treatment of **9** with acetic anhydride at 90 °C in the presence of *p*-toluenesulfonic acid as catalyst provided the *O,N*-diacetyl derivative **10**, mp 126–127.5 °C, which showed bands in the infrared at both the amide and ester carbonyl stretching frequencies. Formation of the tertiary acetate presumably occurred by an alkyl–oxygen cleavage mechanism.

Alkylation of **8** with benzyl bromide yielded the noncrystalline 10-benzylhexahydrophenoxazine **11** which showed appropriate spectral characteristics; its NMR spectrum exhibited the nonequivalent benzylic protons as a widely separated (Δδ 0.36 ppm) AB quartet reflecting the proximity of nearby chiral centers.

The *o*-aminophenol–adipoin condensation product **8** was partly converted to a trideuterio derivative (46.5% d_3, 26.6% d_2) by heating a sample under reflux with NaOD in D_2O followed by H_2O washing of the product. Incorporation of one deuterium at C-10a and two at C-4, expected if **8** is in rapid equilibrium with fb6, is supported by the disappearance of appropriate proton signals in the NMR spectrum of 8-d_3 and its *N*-acetyl derivative.

Final support for the assigned structures was obtained by single-crystal x-ray crystallographic methods. Compound **8**