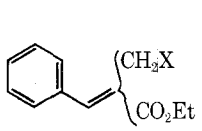
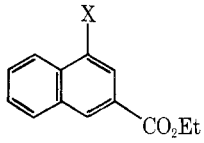
increased yields by 10–20%. Although some cooling is desirable for the mildly exothermic reaction, low temperature (−70°) offered no advantages. Finally, it was noticed that the rigorous exclusion of oxygen afforded a cleaner product.

The question of mechanism has not been studied in detail, and no firm conclusions can be drawn. The formation of **6** from **5** methoxyoxime and lithium 2,2,6,6-tetramethylpiperidide and mechanistic studies of the Neber reaction[6] suggest path B in Scheme II. Nevertheless, it is intriguing that optimum conditions for this reaction are very similar to those found for the closely related Neber conversion. A point which apparently has not been given prior attention is whether naphthylamines are formed from simple tetralone oxime tosylates under Neber conditions.[7] We have found that in fact 5–10% of 1-aminonaphthalene is formed from 1-tetralone oxime tosylate with sodium ethoxide in dimethoxyethane–ethanol. Clearly the carboethoxy group facilitates but does not induce the pathway to naphthylamines. Thus several different mechanisms may be involved in the naphthylamine formation.[9]

Other approaches to the formation of 4-amino-2-naphthoate esters were explored with very limited success. The dimethylenamine[10a] or pyrrolidine enamine[10b] of **5** could be prepared in low yield only with difficulty, and preliminary dehydrogenation experiments were not encouraging. The benzylamine Schiff base of **3** or **5** provided **4** or **6** in moderate yield (40–50%) after treatment with 10% palladium on carbon in refluxing mesitylene;[11] but under similar conditions the benzylamine Schiff base of **7** gave **8** in only 5% yield. Other attempts to aromatize the Schiff base of **3**, as well as **3** itself, failed to provide adequate yields of the corresponding aminonaphthalene or naphthol.[12] Despite a variety of precedents, direct cyclization of **9** to **10**[13] or of **11**–**14** to the corresponding naphthylamine[14,15] failed with one exception. Amide **14** capriciously provided up to 30% of amine **15** after treatment with phosphorus oxychloride.[15]



9, X = CO_2H
11, X = CN
12, X = $CONH_2$
13, X = CONHMe
14, X = $CONMe_2$



10, X = OAc
15, X = NMe_2

Experimental Section

General Procedure.[16] **Ethyl 4-Amino-1-methyl-2-naphthoate (4).** A solution of 0.350 g (1.50 mmol) of 3-carboethoxy-1-tetralone **3**, 0.115 g (1.1 equiv) of hydroxylamine hydrochloride, 0.132 g (1.1 equiv) of sodium acetate, and 10 ml of 80% ethanol was refluxed for 1 hr. The solution was partitioned between ether and water (25 ml each), and the layers separated. The aqueous layer was washed with additional ether (3 × 25 ml). The combined ether layers were then washed with saturated sodium chloride solution, dried over anhydrous sodium sulfate, and condensed to provide a quantitative yield of the oily oxime: ir (film) 3400 and 1730 cm^{-1}. This crude oxime and 0.306 g (1.60 mmol) of *p*-tosyl chloride were dissolved in 20 ml of dry dimethoxyethane and treated with 0.090 g (1.87 mmol) of sodium hydride mineral oil dispersion.[17] The mixture was stirred under nitrogen for 17 hr, cooled to 0°, and treated with 10 ml of 0.6 *N* sodium ethoxide in ethanol.[18] The solution was stirred at 0° under nitrogen for an additional 2 hr and then subjected to the ether–water extractive work-up described above to provide crude oily amine. Purification by elution with 1:9 ethyl acetate–pentane from alumina provided 0.248 g (72%) of **4**: mp 73–74°; ir ($CHCl_3$) 3490, 3400, and 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.34 (t, 3 H), 2.77 (s, 3 H), 4.00 (s, 2 H), 4.37 (q, 2 H), 7.05 (s, 1 H), and 7.1–8.2 ppm (m, 4 H).

The hydrochloride salt was prepared by crystallization of **4** from ethanolic hydrochloric acid: mp 243–246°.

Anal. Calcd for $C_{14}H_{16}NO_2Cl$: C, 63.28; H, 6.07; N, 5.27. Found: C, 63.02; H, 6.08; N, 5.24.

Acknowledgment. Financial support from the National Science Foundation through Research Grant GP 33265X is gratefully acknowledged.

Registry No.—**1**, 22743-00-6; **2**, 54143-46-3; **3**, 54143-47-4; **4**, 54143-48-5; **4** HCl, 54143-49-6; **5**, 54143-50-9; **6**, 54143-51-0; **7**, 54307-68-5; **8**, 54143-53-2.

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(15) See ref 14e.
(16) This procedure is typical of those used for preparation of amines **2**, **4**, **6**, and **8** and provides comparable yields on a 0.1-mol scale. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian T-60 spectrometer at 60 MHz using tetramethylsilane as an internal standard. Infrared (ir) spectra were determined with a Perkin-Elmer 567 spectrometer. Melting points are uncorrected. Analyses were completed by Midwest Microlab, Ltd., Indianapolis, Ind. All new compounds have been adequately characterized. Reagent aluminum oxide for chromatography was purchased from Merck Chemical Division, Rahway, N.J.
(17) The sodium hydride was purchased from Alpha Ventron, Beverly, Mass., and washed with pentane after weighing, immediately prior to use.
(18) The reaction is relatively insensitive to concentration. During 0.1-mol scale reactions the tosylate and ethoxide concentrations were ten times greater. A volume ratio of 2:1 dimethoxyethane to ethanol is optimal.

Electrophilic Addition of $RPX_2/AlCl_3$ to Olefins. The Possibility of Phosphiranes

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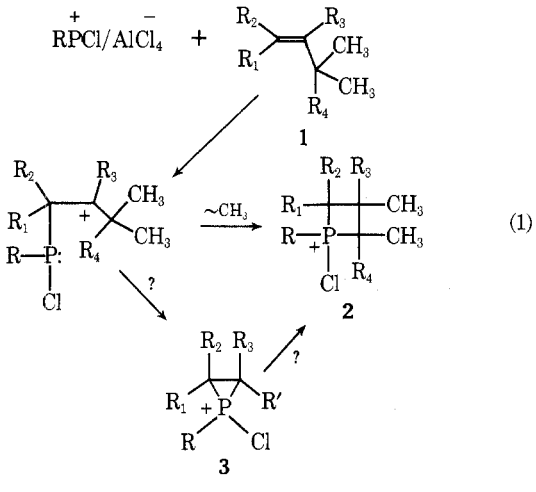
Small-ring heterocycles containing nitrogen, oxygen, or sulfur atom centers are rather common, whereas phosphorous analogs are obtainable only under special or awkward circumstances.[1,2,8] Phosphiranes are usually prepared by coupling vicinal dihalides with phosphides, while an unusual coupling reaction between $RPX_2/AlCl_3$ complexes and branched monoenes yields phosphetanes. Equation 1 summarizes this latter reaction and shows the breadth of ole-

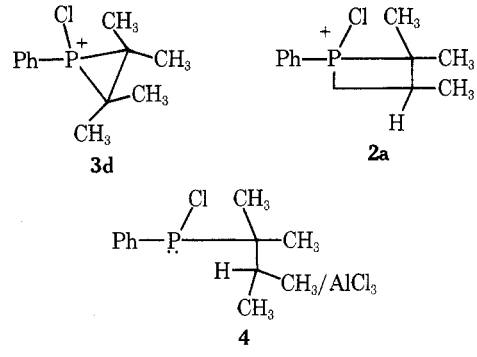
fins which yield phosphetanes (via methyl migration),[2] but curiously, three-membered rings are not formed.[3] Our interest in the synthesis and stability of small phosphorous systems[4] prompted us to evaluate this anomalous feature of that coupling reaction. We envisioned that phosphoranium ions (**3**) might be isolable intermediates in such reactions if suitable modifications were made in the character of the reagents. We report below our results of the reaction of $RPX_2/AlCl_3$ complexes with olefins such as 2,3-dimethyl-2-butene in which the surface to phosphetanes would not be expected to be open.



(1)

a, $R_1 = R_2 = R_3 = H$; $R_4 = CH_3$
a′, $R_1 = R_2 = R_4 = H$; $R_3 = CH_3$
b, $R_1 = R_2 = H$; $R_3 = R_4 = CH_3$
c, $R_1 = R_2 = R_4 = CH_3$; $R_3 = H$

Employing a procedure similar to Cremer's[2d] we are able to isolate an adduct from mixing equal molar amounts of $PhPCl_2/AlCl_3$ with 2,3-dimethyl-2-butene followed by evaporation (at room temperature) of the CH_2Cl_2 solvent ca. 5–12 hr after mixing. The 100-MHz ^1H NMR ($CDCl_3$ solvent) of the residual viscous oil displayed aromatic H's (A = 5, broad multiplet, δ 7.0–8.3 ppm), a multiplet (A = 1, δ 2.4–2.9 ppm), and four single lines (A = 12, δ 1.15, 1.22, 1.57, and 1.90 ppm). Upon ^{31}P irradiation the low-field pair of this latter set collapsed to a single line (δ 1.77 ppm) while the remaining two transitions were unchanged. These spectra along with the ^{13}C NMR data of Table I were not consistent with either expected phosphiranium ion **3d** or known phosphetanium ion **2a** but instead required the acyclic structure **4** (isopropyl group, $^3J_{HH}$ = 7.0 Hz; *gem*-dimethyls, $^3J_{PCCH_3}$ = 33 Hz and $^2J_{PCC}$ = 9.8 Hz; and quaternary C α to P, $^1J_{PC}$ = 26.9 Hz). Additional support for this assignment was afforded by H_2O quench of this salt, which yielded a phosphine oxide[5] **5** (ir P=O at 1205 cm^{-1}), and the mass spectrum, which showed a parent ion at *m/e* 244 (and a P + 2 of relative ⅓ intensity) and principal fragments *m/e* 204, 202; 162, 160; 125; and 85. Our assignment of **5** was confirmed by basic hydrolysis of this material to give known 1,1,2-trimethylpropylphenylphosphinic acid (**6**)[6] (Scheme I).



Close inspection of the ^1H NMR spectra of **4** and **5** and comparison of their respective CCH_3 regions was informative. Structures **4a** and **5** both contain a chiral phosphorous which should impart chemical nonequivalence to both sets of geminal methyls. Interestingly, the δ's for the methyls of each geminal set in the salt **4** were coincident. This can be rationalized either by a preponderance of **4b** (planar phosphorus) or by a rapid equilibration between **4a** and **4b**. That the equivalence in chemical shifts for the geminal

Scheme I

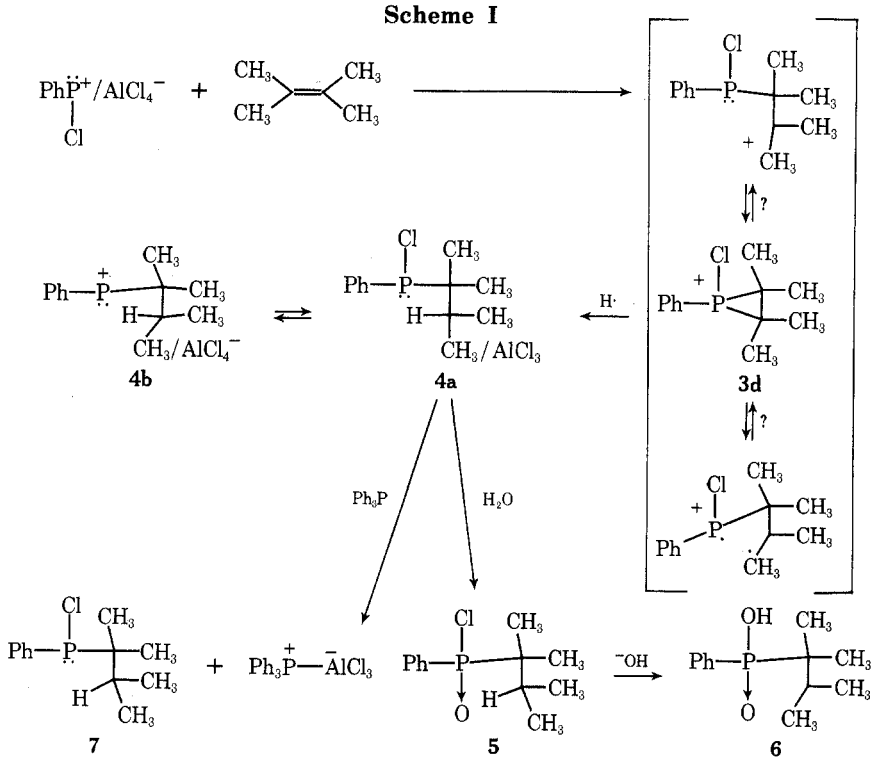
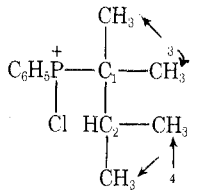


Table I
^{13}C NMR (25.1 MHz) Data for 4



Carbon	δ, ppm[a]	Multiplet pattern: H decoupled	Multiplet pattern: H coupled	$J(^{13}C-{}^{31}P)$[b]	$J(^{13}C-H)$[b]
1	51.9	d	d	26.9	
2	31.3	s	d		127
Me_3	16.9	d	dq	9.8	134
Me_4	17.6	s	q		134

[a] Relative to internal Me_4Si. [b] J value error ±1 Hz.

CH_3's in **4a** ⇄ **4b** is directly due to **4b** could be shown by the conversion of 4 to **7**. Treatment of 4 in CH_2Cl_2 with a equimolar amount of $(Ph)_3P$ followed by addition of pentane caused separation of $(Ph)_3P$–$AlCl_3$ with **7** remaining in solution. The aromatic H's were visible at 7.1–8.1 ppm and the CCH_3 region of the 100-MHz ^{31}P decoupled ^1H NMR of **7** displayed an overlapping six-line multiplet (A = 12) owing to observable nonequivalent δ's for the methyls of each geminal set: singlets at 0.86 and 1.10 ppm; two doublets (J = 7.0 Hz) with transitions at 1.09, 1.16, 1.11, and 1.18 ppm; and $^3J_{PCCH}$ = 9 and 16.5 Hz, could be measured without ^{31}P irradiation. Relative to **4** (but analagously to **7**) the ^1H NMR of **5** was more complex in the CCH_3 region, displaying ($CDCl_3$ solvent) a nine-line multiplet (A = 1.0, δ 1.90–2.40, $^3J_{HH}$ = 7.0, $^3J_{PCCH}$ = 14.0 Hz) and seven single lines (A = 12.3, δ 1.01, 1.06, 1.08, 1.13, 1.16, 1.31, 1.38; relative intensities 1:1:1:1:2:1:1) and aromatic H's (A = 3.1, δ 7.2–7.45; A = 1.8, δ 7.55–7.90). Decoupling at ^{31}P transformed the CCH_3 region into a six-line multiplet composed of two doublets ($^3J_{HH}$ = 7.0 Hz) with transitions at δ 1.01, 1.08, 1.06, and 1.13 ppm and singlets at 1.20 and 1.27 ppm (intensities 1:1:1:1:2:2). Comparison between the ^{31}P decoupled and nondecoupled spectra enabled assignment of $^3J_{PCCH_3}$ = 22 and 23 Hz and identity of a chiral P-carbon skeleton of P^*–$C(CH_3)_2CH(CH_3)_2$ constitution.

In order to pinpoint the proton source in the formation of **4** and **5** the reaction sequence of Scheme I was repeated with several different deuterium sources added. Duplicate runs were carried out under the following conditions: (a) CD_2Cl_2 as solvent, (b) CD_3NO_2 as solvent, (c) $AlCl_3$ doped with D_2O with CH_2Cl_2 as solvent. The ^1H NMR and ^{13}C NMR spectra of intermediate **4** isolated from run c showed deuterium incorporation exclusively at the methine position, whereas runs under conditions a and b gave respectively no D incorporation and nonreproducible D incorporation.

A tentative mechanism which accounts for the formation of products **5–7** is summarized in Scheme I. The two most reasonable precursors to **4**, namely, a diradical phosphonium ion or a phosphine carbonium ion, are in principle distinguishable on the basis of the deuteration experiments reported above. Carbonium ion promoted H^- transfer from protic solvents is a rarity; however, trapping of carbon radicals by hydroxylic species has been observed.[7] Previous work on the addition of $RPX_3/AlCl_3$ to olefins provides a precedent for expecting 2-(phenylchlorophosphine)-1,2-dimethyl-1-butenium ion as an initial adduct in Scheme I.[2] Consequently, we favor the phosphonium diradical of Scheme I as a relay species between this adduct and the isolated species **4**. The apparent lability of the phosphiranium ion suggested by Scheme I is not completely unexpected, because phosphiranes are known to be thermally labile. For example, the phosphirane ring of 9-phenyl-9-phosphabicyclo[6.1.0]nonatriene requires a temperature of 70° to promote ring expansion to a phospholene derivative,[8] while phosphirane itself decomposes completely at room temperature (over 24 hr) to give ethylphosphine and other products.[2b] Phosphiranes with pentasubstituted phosphorus have been prepared but decompose rapidly at −78°, yielding ring-expanded products.[9] Recent theoretical calculations on three-membered phosphorus heterocycles predict decomposition energies consistent with the above trends.[10] Undoubtedly the stability of phosphoranium ions such as **3d** lies somewhere inbetween that of the pentacoordinate and the tricoordinate phosphorus derivatives. It may be possible, however, to stabilize the phosphoranium intermediates to ring opening by manipulation of substituents, especially since Cremer[2d] has noted an enhancement of lability to ring opening for pentamethyl phosphetanium ions vs. pentamethylphosphetanes, and in the former the rate of ring opening increases in the series $>P^+$–$(CH_3)Cl$, $>P^+$–$(Ph)Cl$, $>P^+Cl_2$.

Experimental Section

The NMR spectra were determined on a Jeol PS-100 NMR spectrometer operating on ^1H (continuous wave) at 100 MHz or ^{13}C (Fourier transform) at 25 MHz. The ^{13}C NMR ^1H coupled spectra were obtained via the alternatively pulsed ^1H technique of Ganson.[11] Aldrich Chemical Co. was the supplier of 2,3-dimethyl-2-butene, CD_2Cl_2 (99.5% D) was purchased from Merck Sharp & Dohme, and CD_3NO_2 (56% D) was prepared according to the literature.[12] All reactions were conducted under a nitrogen atmosphere.

2-(Chlorophenylphosphine)-2,3-dimethylbutane–$AlCl_3$ (4). To a chilled suspension of anhydrous aluminium chloride (0.4 g, 3.0 mmol) in CH_2Cl_2 (10 ml) was added dropwise phenylphosphonous dichloride (0.55 g, 0.4 ml, 3.0 mmol). The colorless mixture became homogeneous and clear after 5 min of stirring. While the mixture was still chilled 2,3-dimethyl-2-butene (0.25 g, 3.0 mmol) was added. A slight color developed at the point of contact of the olefin with the reaction mixture but it was quickly dissipated. After 5 hr of stirring at room temperature an aliquot taken for NMR showed essentially complete formation of **4**. Evaporation of the solvent in vacuo gave 0.7 g of a viscous liquid whose ^1H NMR and ^{13}C NMR spectra are reported in the text and Table I.

2-(Chlorophenylphosphine)-2,3-dimethylbutane-*d*–$AlCl_3$ (4-*d*). To anhydrous aluminum chloride (0.4 g, 3.0 mmol) in a chilled flask was added D_2O (40 μl, 2.0 mmol) and evolution of DCl could be observed. The CH_2Cl_2 solvent (10 ml) was added and the suspension had a yellow tinge. While the mixture was still chilled phenylphosphonous dichloride (0.55 g, 3.0 mmol) and 2,3-dimethyl-2-butene (0.25 g, 3.0 mmol) were added as described above. After stirring at room temperature overnight the solvent was evaporated to yield a viscous, colorless liquid. The ^1H NMR was the same as that described for **4** in the text with the exception of a singlet absorption for the $-C(CH_3)_2D$ function visible at 1.19 ppm (% D incorporation 55). The ^{13}C NMR, in which ^1H coupling remained, clearly showed the presence of the tertary C with a D attached (^{13}C NMR of **4** and **4-*d*** exhibited in the ^1H coupled spectra the following absorptions for C_2: **4**, a doublet at 33.7 and 28.6 ppm, J_{CH} = 127 Hz; **4-*d***, a doublet at 33.7 and 28.6 ppm and a broad peak at 32.0 ppm).

2-(Chlorophenylphosphine Oxide)-2,3-dimethylbutane (5). The reaction intermediate **4** prepared as above (in a 3-mmol run) could be converted to **5** by first redissolving the former in 10 ml of CH_2Cl_2 and pouring the mixture onto 50 g of ice. The organic phase was separated and washed with saturated $NaHCO_3$ (2 × 25 ml) and saturated NaCl (25 ml). The organic phase was dried with $MgSO_4$ and evaporated in vacuo, yielding **5** (0.26 g, 36% yield) which displayed a clean NMR as described in the text. Further purification could be effected by Kugelrohr, bp 110° (0.2 mm).

2-(Chlorophenylphosphine)-2,3-dimethylbutane (7). The reaction intermediate **4** (2.8 g, 7.1 mmol) prepared as above could be converted to **7** by first redissolving it in CH_2Cl_2 (20 ml) and

adding Ph_3P (1.9 g, 7.2 mmol) in CH_2Cl_2 (5 ml). The mixture was stirred for 30 min and pentane (50 ml) was added, causing a yellow oil to deposit on the bottom of the flask. The solution was chilled and the organic phase was carefully drawn off. Evaporation of the solvent gave **7**, whose spectral properties are described in the text.

1,1,2-Trimethylpropylphenylphosphinic Acid (6). Compound **5** (200 mg, 0.83 mmol) was suspended in NaOH (10 ml of 5 *N* solution) and refluxed for 2 hr. Upon cooling white crystals of **8** were deposited (140 mg, 75% crude yield) whose ^1H NMR was in agreement with the literature.[6] Recrystallization from water gave needles, mp 94–95° (after drying) (lit. mp 91–93°).

Acknowledgment. I acknowledge support from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No.—**4a**, 54193-52-1; **4a**-*d*, 54193-53-2; **4b**, 54293-23-1; **4b**-*d*, 54293-25-3; **5**, 54193-50-9; **6**, 28660-28-8; **7**, 54193-51-0; aluminum chloride, 7446-70-0; phenylphosphonous dichloride, 644-97-3; 2,3-dimethyl-2-butene, 563-79-1.

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(3) Other olefins, including 2-pentene, 2-methyl-2-butene, and 4-methyl-2-pentene, reportedly gave uncharacterized adducts in low yields.[2a]
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(5) No attempt was made to exclude oxygen during the work-up; hence it is not surprising that the phosphine intermediate (i.e., **7**) is oxidized to **5**. Air oxidation of alkyl phosphines has long been recognized to be a facile process. As an example, Buckler [S. A. Buckler, *J. Am. Chem. Soc.*, **84**, 3093 (1962)] has shown that Bu_3P: can be rapidly air oxidized in organic or aqueous solvent to $Bu_3P \rightarrow O$.
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Polyfluorobenzopinacols

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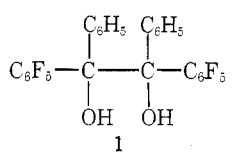
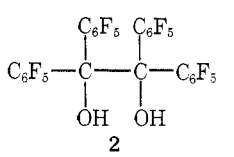
We report the preparation and chemical behavior of decafluorobenzopinacol (**1**)[2] and our attempts to prepare perfluorobenzopinacol (**2**), a compound which is still unknown.



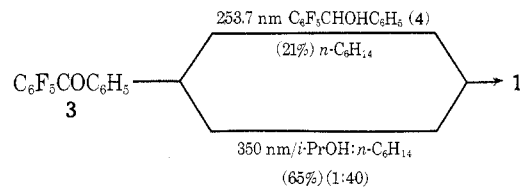
1



2

Decafluorobenzopinacol. Photochemical bimolecular reduction of pentafluorobenzophenone (**3**) by irradiation with 253.7-nm light in the presence of 2-propanol gave only an intractable tar. Under these conditions, benzophenone is converted to benzopinacol in high yield.[3] When 2-propanol was replaced by pentafluorobenzhydrol (**4**), the desired benzopinacol **1** was isolated in 21% yield. This conversion was more readily accomplished (65% yield) by irradiating **3** with 350-nm light in a 2-propanol–*n*-hexane (1:40) system (Scheme I).

Scheme I

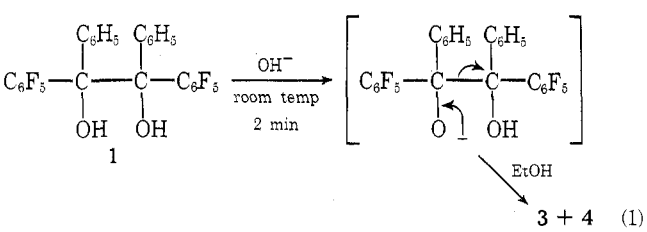


Compound **1** was also prepared by chemical reduction of **3** with zinc and acetic acid.[4] All of the samples of **1** exhibited a melting range of 153–156°. Mixture melting points showed no depression and the infrared spectra were identical. The wide melting range suggested the presence of a mixture of *dl* and meso forms, but attempts to separate components by chromatography on silica gel were unsuccessful.

Decafluorobenzopinacol (**1**) showed a remarkable reluctance to undergo the pinacol–pinacolone rearrangement under conditions in which most benzopinacols react with ease. No evidence of a rearrangement product could be detected on treatment with a wide range of mineral and organic acids. Frequently, fragmentation into **3** and **4** was observed (vide infra).

In considering the participation of **1** in this rearrangement, we must consider both the ease of formation of the electron-deficient carbenium ion center and the intrinsic migratory aptitudes of the phenyl and pentafluorophenyl groups in the subsequent 1,2 shift. From previous studies we would anticipate that phenyl would migrate without difficulty and much more readily than pentafluorophenyl.[5] The failure to observe a rearrangement product strongly suggests the dominance of the electron-withdrawing inductive effect of the pentafluorophenyl group (σ_I 0.25[7]) which so destabilizes the carbenium ion[8] as to preclude any migration. Resistance to rearrangement of 1,1,1,4,4,4-hexafluoro-2,3-diphenyl-2,3-butanediol was also attributed to the destabilizing influence of the trifluoromethyl group (σ_I 0.33–0.41[7]) to development of carbenium ion character.[9] Perfluoropinacol[10a] and the diol derived from octafluoroacetophenone[10b] behaved similarly.

In contrast to its behavior in acidic medium, compound **1** reacted with exceptional facility when treated with 0.1 *N* ethanolic sodium hydroxide solution at room temperature to give an equimolar mixture of pentafluorobenzophenone (**3**) and pentafluorobenzhydrol (**4**) in nearly quantitative yield (eq 1).



(1)

Under the same conditions, benzopinacol failed to react, but, on heating, evidence of a similar cleavage was observed. This unusual reactivity of **1** in undergoing the cleavage is probably a reflection of the role of the C_6F_5 group in (1) enhancing the acidity of the hydroxyl group and (2) stabilizing the resulting anion of the benzhydrol. In