

aqueous  $\text{Na}_2\text{CO}_3$ , and saturated  $\text{NaCl}$  and finally dried with  $\text{MgSO}_4$ . The crude product was recrystallized from 1-propanol after treatment with charcoal to yield bis(pentamethylphenyl)acetonitrile (3.84 g, 74%) as large needle-like crystals: mp 185–188 °C;  $\delta$  ( $\text{CDCl}_3$ ) 2.13 (s, 24 H), 2.18 (s, 6 H), 5.71 (s, 1 H);  $\nu_{\text{max}}$  (KBr) 2922 (CH), 2223 ( $\text{C}\equiv\text{N}$ )  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{31}\text{N}$ : C, 86.43; H, 9.37; N, 4.20. Found: C, 86.24; H, 9.50; N, 4.36.

**Bis(pentamethylphenyl)cyanomethyl.** Method 1. *N*-(Diphenylmethyl)bis(pentamethylphenyl)ketene imine (0.2 g, 0.4 mmol) was dissolved in 5 mL of carbon tetrachloride. This colorless solution was then heated to 50 °C for 30 min, and the resulting dark purple solution was analyzed: TLC (1:9 ether/petroleum (40–60 °C))  $R_f$  0.38 (purple spot fading within 30 min), none of the starting material was present;  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 2120  $\text{cm}^{-1}$ ;  $g(\text{CCl}_4) = 2.0037$ . Quinol (0.22 g, 2 mmol) was added to the reaction vessel with the immediate change in the solution to the yellow color of quinone. Analysis of this quenched solution confirmed that no starting *N*-benzhydrylketene imine remained. Bis(pentamethylphenyl)acetonitrile, however, was present: TLC (1:9 ether/petroleum (40–60 °C))  $R_f$  0.36 which is the same as the  $R_f$  value for an authentic sample of bis(pentamethylphenyl)acetonitrile;  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 2230  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CCl}_4$ ) 2.16 (s, 24 H), 2.18 (s, 6 H), 5.74 (s, 1 H). Therefore, the thermal decomposition of *N*-(diphenylmethyl)bis(pentamethylphenyl)ketene imine yielded  $\alpha$ -cyanobis(pentamethylphenyl)methyl and presumably diphenylmethane and/or 1,1,2,2-tetraphenylethane (which were not isolated).

**Method 2.** Bis(pentamethylphenyl)acetonitrile (0.24 g, 0.72 mmol) in 3 mL of dry THF was sealed by a rubber septum in a round-bottom flask and flushed with anhydrous oxygen-free nitrogen. This was followed by the addition of tetramethylene diamine (0.32 mL, 2.16 mmol) and *n*-butyllithium (1.38 mL, 2.16 mmol) at ambient temperature. The resulting solution went from yellow to orange as it was left stirring for 1 h. A further 5 mL of THF was added to the vessel, and its contents were then exposed to the atmosphere. For the first 5–10 min there was no color change, and then a permanent purple color quickly developed throughout the mixture. After being stirred for a further 10–15

min the solution was poured into 24 mL of water and vigorously stirred until a solid precipitated. This dark crimson powder was collected by filtration, washed with water followed by a little methanol, and dried at 50 °C overnight: TLC (1:9 ether/petroleum (40–60 °C));  $R_f$  0.34 (purple), 0.45 and a baseline spot;  $\nu_{\text{max}}$  (KBr) 2229, 2189 ( $\text{C}\equiv\text{N}$ ), 2116 ( $\text{C}-\text{C}\equiv\text{N}$ ), 2008 ( $\text{C}=\text{C}\equiv\text{N}$ )  $\text{cm}^{-1}$ ;  $g(\text{CCl}_4) 2.0036$ . The identified constituents of the crude product were therefore bis(pentamethylphenyl)acetonitrile and  $\alpha$ -cyanobis(pentamethylphenyl)methyl, and the third product had a spectrum consistent with that of the dimer *N*-(bis(pentamethylphenyl)cyanomethyl)bis(pentamethylphenyl)ketene imine.

**Reductions of  $\alpha$ -Cyanobis(pentamethylphenyl)methyl by Quinol and by *n*-Butyllithium.** A solution of  $\alpha$ -cyanobis(pentamethylphenyl)methyl radical (0.6 g, ~2 mmol) in THF (5 mL) was stirred at ambient temperature. To this red/purple solution was slowly added quinol (1.1 g, 10 mmol). The dark color of the solution was quickly replaced by the yellow color of quinone: TLC (1:9 ether/petroleum (40–60 °C))  $R_f = 0.32$ , identified as the corresponding diarylacetonitrile (together with other spots none of which were purple in color (indicating residual radical)).

$\alpha$ -Cyanobis(pentamethylphenyl)methyl (0.6 g, ~2 mmol) was dissolved in 5 mL of dry THF. This solution was deoxygenated and cooled to -16 °C. *n*-Butyllithium (1.6 mL, 2.5 mmol) in hexane was slowly added by syringe. The red-purple color of the radical solution was replaced by the orange color of  $\alpha$ -cyanobis(pentamethylphenyl)methyl lithium as the solution was allowed to reach ambient temperature. After 15 min, acetic acid (0.16 g, 2.6 mmol) in dry THF (1 mL) was added and the reaction mixture was analyzed: TLC (1:9 ether/petroleum (40–60 °C))  $R_f$  0.28; this spot which appeared to be the main component of the reaction mixture was identified as bis(pentamethylphenyl)acetonitrile by comparison with an authentic sample.

**Registry No.** 3, 700-12-9; 4, 563-96-2; 5, 107846-81-1; 6, 112752-37-1; 7a, 137122-88-4; 7b, 137122-89-5; 8a, 137122-90-8; 8b, 137122-91-9; 9, 137122-92-0; 10, 137122-93-1; 13, 137122-94-2; benzenemethanamine, 100-46-9;  $\alpha$ -phenylbenzenemethanamine, 91-00-9.

## Nuclear Spin-Spin Coupling via Nonbonded Interactions. 7. Effects of Molecular Structure on N-F Coupling<sup>1</sup>

Frank B. Mallory,<sup>\*2a</sup> Eddie D. Luzik, Jr.,<sup>2a</sup> Clelia W. Mallory,<sup>2b</sup> and Patrick J. Carroll<sup>2b</sup>

Department of Chemistry, Bryn Mawr College, Bryn Mawr, Pennsylvania 19010, and Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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To test whether the recently discovered phenomenon of through-space nuclear spin-spin coupling between intramolecularly crowded  $^{15}\text{N}$  and  $^{19}\text{F}$  nuclei shows the same sort of striking dependence on molecular structure as the long-known phenomenon of through-space nuclear spin-spin coupling between pairs of intramolecularly crowded  $^{19}\text{F}$  nuclei, several  $^{15}\text{N}$ -enriched oximes and some simple derivatives thereof were synthesized and their  $J_{\text{NF}}$  values were determined by  $^{19}\text{F}$  NMR spectroscopy. The experimental  $J_{\text{NF}}$  values ranged from 8.6 to 43.5 Hz. The molecular structures of these compounds were determined by single-crystal X-ray diffraction. The observed dependence of the  $^{15}\text{N}$ - $^{19}\text{F}$  coupling constants on molecular structure was qualitatively consistent with the predictions of the lone-pair orbital overlap theory that was developed earlier to account for through-space coupling involving fluorine nuclei.

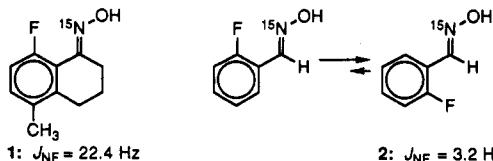
In part 5 of this series,<sup>3</sup> we reported the first example of "through-space" spin-spin coupling between  $^{15}\text{N}$  and  $^{19}\text{F}$  nuclei. In that earlier work, we found that oxime 1 has

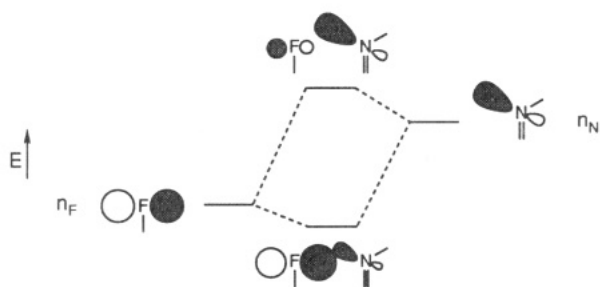
the exceptionally large  $J_{\text{NF}}$  value of 22.4 Hz, whereas oxime 2, which possesses the same bond connectivity as 1 but lacks the close spatial proximity between the nitrogen and fluorine atoms that is enforced in 1 by tethering, has a  $J_{\text{NF}}$  value of only 3.2 Hz.

(1) (a) For part 6, see: Mallory, F. B.; Mallory, C. W.; Baker, M. B. *J. Am. Chem. Soc.* 1990, 112, 2577. (b) Presented in part at the 194th National Meeting of the American Chemical Society, New Orleans, LA, Aug 31, 1987, ORGN-121 and the 23rd Middle Atlantic Regional Meeting of the American Chemical Society, Cherry Hill, NJ, May 25, 1989. (c) Taken from the Ph.D. dissertation of Eddie D. Luzik, Jr., Bryn Mawr College, 1991.

(2) (a) Bryn Mawr College. (b) University of Pennsylvania.

(3) Mallory, F. B.; Mallory, C. W. *J. Am. Chem. Soc.* 1985, 107, 4816.





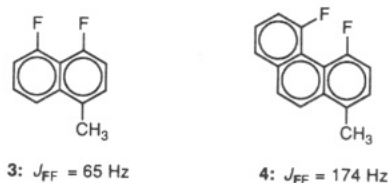
**Figure 1.** Illustration of the overlap interactions of the two lone-pair atomic basis orbitals ( $n_F$ , a 2p orbital on a fluorine atom, and  $n_N$ , a  $2sp^2$  orbital on a nitrogen atom) that generate the filled bonding and antibonding molecular orbitals thought to be involved in through-space  $^{15}\text{N}$ - $^{19}\text{F}$  nuclear spin-spin coupling. As a first approximation, these bonding and antibonding molecular orbitals are of the form  $n_F + \lambda n_N$  and  $n_N - \lambda n_F$ , respectively, where  $\lambda$  is a constant ( $\lambda < 1$ ).

As a corollary of the lone-pair overlap theory<sup>4</sup> that one of us developed some time ago to account for the long-known phenomenon of through-space F-F coupling, we had predicted in advance that overlap of a  $2sp^2$  lone-pair orbital on the nitrogen atom with a 2p lone-pair orbital on the fluorine atom would give rise to through-space N-F coupling in oxime 1.<sup>3</sup> As illustrated in Figure 1 for a structural array similar to that found in oxime 1, the overlap interactions of these nominally *one-center* atomic basis orbitals would generate a pair of *two-center* molecular orbitals, one bonding and one antibonding. These two filled two-center orbitals would not give rise to any net chemical bonding between the nitrogen and the fluorine atoms; the orbitals would cancel each other in this regard. We hypothesized, however, that these two-center orbitals *both* would be effective in transmitting nuclear spin information. Our observation<sup>3</sup> of such a large value for  $J_{\text{NF}}$  in oxime 1 provided experimental support for the validity of that hypothesis. We now report our further experimental investigations of this new phenomenon of through-space N-F coupling in a series of oximes and related molecules.

### Results and Discussion

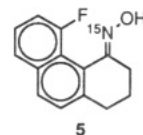
A key feature of our lone-pair orbital overlap theory of through-space coupling is the concept that the *magnitude* of the coupling between intramolecularly crowded atoms that each bear a lone-pair depends on the *effectiveness* of the overlap interactions between the two lone-pair basis orbitals.<sup>1a,4</sup> This leads to the expectation that for a given type of through-space coupling, e.g., F-F or N-F, the coupling constants should increase with increasing overlap of the appropriate lone-pair orbitals.

A benchmark in our thinking about the phenomenon of through-space F-F coupling is the comparison of  $J_{\text{FF}}$  values for related members of the 1,8-difluoronaphthalene<sup>5</sup> and the 4,5-difluorophenanthrene<sup>6,7</sup> families, such as 4-methyl-1,8-difluoronaphthalene (3) and 1-methyl-4,5-difluorophenanthrene (4). The contribution to the overall F-F coupling from the traditional through-bond mechanism is expected to be small<sup>5</sup> in naphthalene 3, where the shortest path is over four bonds, and even smaller in phenanthrene 4, where the shortest path is over five bonds.



The experimental observation that  $J_{\text{FF}}$  is so much higher for 4 (174 Hz)<sup>6,7</sup> than it is for 3 (65 Hz)<sup>5</sup> has been attributed to more effective overlap between the fluorine lone-pair orbitals in the 4,5-difluorophenanthrene system.<sup>4</sup>

The first experimental objective in the present study was to test the prediction of our lone-pair overlap theory that through-space N-F coupling should show a similar benchmark dependence on molecular structure. Accordingly, we synthesized oxime 5 in order to evaluate our initial expectation that it would exhibit a much larger N-F coupling constant than oxime 1, just as difluoro compound 4 exhibits a much larger F-F coupling constant than difluoro compound 3.



To our surprise, we found that the value of  $J_{\text{NF}}$  for oxime 5 (19.7 Hz) is *smaller* than that for oxime 1 (22.4 Hz)! The reason for this anomalously small value of  $J_{\text{NF}}$  became apparent, however, when we determined the structures of oximes 1 and 5 by single-crystal X-ray diffraction. Whereas 1 has a nearly coplanar arrangement for all of its atoms (for example, the F-C---C=N dihedral angle is only 11.0°), the NOH group of 5 is greatly tipped out of the mean plane of the aromatic portion of the molecule (for example, the F-C---C=N dihedral angle is 66.3°). In fact, the measured N-F distance in oxime 5 (2.642 Å) is about 0.05 Å longer than the measured N-F distance in oxime 1 (2.595 Å)! We now realize that the partly saturated six-membered ring of 5 is too flexible for our purposes. In particular, out-of-plane puckering of the C-3 methylene carbon atom in 5 permits marked out-of-plane tipping of the oxime group in the opposite sense, which allows the molecule to avoid the severe van der Waals crowding that we had naively hoped would exist between its nitrogen and fluorine atoms.

In order to carry out our benchmark comparison of N-F and F-F coupling without interference from the noncoplanarity problem that we encountered with the six-membered ring oxime 5, we synthesized the pair of oximes 6 and 7 in which the desired tethering is accomplished by



structurally more rigid five-membered rings. From our single-crystal X-ray diffraction studies, we know that the F-C---C=N dihedral angles in oximes 6 and 7 are 2.6 and 24.3°, respectively. The deviation from coplanarity for oxime 7 is thus much less severe than for oxime 5. Gratifyingly, our  $^{19}\text{F}$  measurements reveal that  $J_{\text{NF}}$  is strikingly larger for oxime 7 (39.5 Hz) than for oxime 6 (8.8 Hz), which confirms our prediction that through-space N-F coupling and through-space F-F coupling should exhibit a similar dependence on molecular structure. All of our NMR and X-ray results are listed in Table I.

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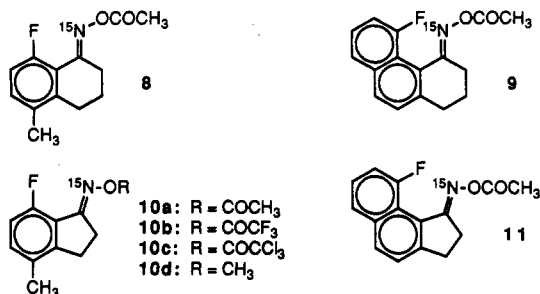
Table I.  $^{19}\text{F}$  NMR Spectroscopic<sup>a</sup> and X-ray Crystallographic<sup>b</sup> Results

cpd	$J_{\text{NF}}$ (Hz)	$\delta_{\text{F}}^{\text{c}}$ (ppm)	N-F distance (Å)	F-C...C=N dihedral angle (deg)
1	22.3, 22.1 <sup>d</sup>	-0.11, -0.06 <sup>d</sup>	2.595 (4)	11.0
5	19.4 <sup>d</sup>	12.36 <sup>d</sup>	2.642 (2)	66.3
6	8.8, 8.8 <sup>d</sup>	-4.81, -5.18 <sup>d</sup>	2.897 (4)	2.6
7	39.5 <sup>d</sup>	11.02 <sup>d</sup>	2.627 (7)	24.3
8	23.3	3.41	<i>e</i>	<i>e</i>
9	19.0	6.36	<i>e</i>	<i>e</i>
10a	9.3 <sup>f</sup>	0.26	<i>e</i>	<i>e</i>
10b	9.2	2.28	<i>e</i>	<i>e</i>
10c	8.9	1.36	<i>e</i>	<i>e</i>
10d	8.7	-3.68	<i>e</i>	<i>e</i>
11	43.5, <sup>g</sup> 42.0 <sup>d</sup>	10.80, 10.76 <sup>d</sup>	<i>e</i>	<i>e</i>

<sup>a</sup>  $^{19}\text{F}$  NMR measurements were carried out with the  $^{15}\text{N}$  isotope of the indicated oxime or oxime derivative; except as noted, these studies were done in  $\text{CDCl}_3$  solution. <sup>b</sup> X-ray determinations were carried out with the  $^{14}\text{N}$  isotope of the indicated oxime or oxime derivative. <sup>c</sup> Measured relative to 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane. <sup>d</sup> Measured in  $\text{CD}_3\text{SOCD}_3$  solution. <sup>e</sup> X-ray determinations were not carried out for compounds 8–11. <sup>f</sup> An extensive study of 10a revealed only a slight solvent dependence for  $J_{\text{NF}}$ : 9.3 Hz in  $\text{CDCl}_3$ , 9.2 Hz in  $\text{C}_6\text{D}_6$  and  $\text{CCl}_4$ , 9.1 Hz in  $\text{CD}_2\text{COCD}_3$  and  $\text{CHBr}_2\text{CHBr}_2$ , 9.0 Hz in  $\text{CH}_3\text{OH}$ , and 8.9 Hz in  $\text{CH}_2\text{I}_2$ ,  $\text{CH}_3\text{NO}_2$ , and  $\text{CD}_3\text{SOCD}_3$ . On diluting 10a in  $\text{CDCl}_3$  from 0.8 to 0.02 M the  $^{19}\text{F}$  chemical shift changed from  $\delta$  0.49 to 0.23 but  $J_{\text{NF}}$  stayed constant at 9.3 Hz. <sup>g</sup> This value represents the current world's record magnitude for through-space N-F coupling.

Our lone-pair theory identifies orbital overlap as the governing factor for through-space coupling and therefore predicts that the magnitudes of the coupling constants should depend on both distance and orientation factors. *Qualitatively*, the results in Table I are consistent with these expectations. For example, we suggest that for oximes 1 and 6, which have rather similar intramolecular orientations of their C—F and C=N bonds, the fact that  $J_{\text{NF}}$  is larger for 1 (22 Hz) than for 6 (9 Hz) can be attributed *primarily* to the shorter N—F distance in 1 (2.60 Å) than in 6 (2.90 Å). Furthermore, we suggest that for oximes 1, 5, and 7, which have rather similar N—F distances (2.60, 2.64, and 2.63 Å, respectively), the fact that  $J_{\text{NF}}$  ranges rather widely (from 20 to 40 Hz) can be attributed *primarily* to the considerable variations these three oximes exhibit in the orientations of their C—F and C=N bonds, although we do not yet fully grasp the *precise* relationship between these spatial orientations and the magnitudes of the coupling constants. Using the detailed structural knowledge of oximes 1, 5, 6, and 7 that we have in hand from our X-ray studies, we plan to carry out *ab initio* molecular orbital calculations<sup>8</sup> of the actual overlap interactions between the lone-pair orbitals in these four oximes in an attempt to provide a *quantitative* rationale for the relative magnitudes of the N—F coupling constants that we have measured experimentally (Table I).

Also listed in Table I are the N—F coupling constants for compounds 8, 9, 10a–d, and 11, which are simple derivatives of oximes 1, 5, 6, and 7, respectively. From these results we conclude that  $J_{\text{NF}}$  is essentially independent of the nature of the substituent on the oxime oxygen atom. This conclusion is in accord with the lone-pair overlap theory: the orbital overlap interactions that result from van der Waals contact between the nitrogen and fluorine atoms in these systems should not depend markedly on whether the substituent on the remotely oriented oxygen atom of the oxime is a hydrogen atom, an acyl group, or an alkyl group.



The intramolecular crowding between nitrogen and fluorine atoms that we believe causes the “through-space” NF coupling in these systems also should cause a downfield shift in the  $\delta_{\text{F}}$  values. Excluding from consideration the structurally anomalous oxime 5 and its acetyl derivative 9, one does indeed find such a trend in the data given in Table I. That is, in the series of three oximes 6, 1, and 7 there is a roughly linear relationship between  $\delta_{\text{F}}$  and  $J_{\text{NF}}$  in which  $\delta_{\text{F}}$  moves downfield by 16.20 ppm while  $J_{\text{NF}}$  increases by 30.7 Hz. The analogous series of three acetyl derivatives 10a, 8, and 11, in which  $\delta_{\text{F}}$  moves downfield by 10.54 ppm while  $J_{\text{NF}}$  increases by 34.2 Hz, shows a similar relationship with a smaller slope.

## Experimental Section

**General Procedures.** Unless otherwise noted,  $^{19}\text{F}$  NMR spectra were obtained at 282.4 MHz in  $\text{CDCl}_3$  solution at 17 °C.  $^{19}\text{F}$  chemical shifts were measured in ppm downfield from 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane. X-ray data were collected on an Enraf-Nonius CAD4 automated diffractometer, and the structures were solved and refined using the VAXSDP package. Sublimations at reduced pressure (0.005–0.05 mm) were carried out as described previously.<sup>9</sup> High-resolution mass spectra were obtained with a VG Micromass 70-70 double-focusing spectrometer by John Dykins of the Mass Spectrometry Facility of the Department of Chemistry at the University of Pennsylvania. Other general procedures of ours are specified in part 6.<sup>1a</sup>

**[ $^{15}\text{N}$ ]-5-Fluoro-4-oxo-1,2,3,4-tetrahydrophenanthrene Oxime (5).** The procedure of Fieser<sup>10</sup> for the preparation of 3-(4'-bromobenzoyl)propanoic acid by the Friedel-Crafts succinylation of bromobenzene was modified by the use of boiling cyclohexane as a solvent in order to minimize the troublesome formation of debrominated 3-benzoylpropanoic acid. To a mixture of 108.9 g (0.82 mol) of anhydrous  $\text{AlCl}_3$  and 41.1 g (0.41 mol) of succinic anhydride in 200 mL of boiling cyclohexane in a 1-L Erlenmeyer flask was added, in one portion with manual stirring, 150 mL (1.4 mol) of bromobenzene. After about 15 min of further heating, the vigorous evolution of HCl had ceased. The viscous red reaction mixture was cooled, diluted with 200 mL of toluene, and treated with ice and aqueous HCl. The keto acid was extracted from this mixture with hot toluene. The toluene extract was washed with water and then extracted with 2 M aqueous NaOH solution. The basic extract was acidified with aqueous HCl, and the keto acid was extracted with toluene. Rotary evaporation of the toluene extract yielded 86.8 g (84%) of material shown by GC/MS to consist of about 96% 3-(4'-bromobenzoyl)propanoic acid contaminated with about 3% of 3-benzoylpropanoic acid. Recrystallization from a mixture of 50% cyclohexane, 35% toluene, and 15% 2-propanol yielded 72.1 g (69%) of material with mp 149.5–150.2 °C (lit.<sup>10</sup> mp 149–149 °C).

A Clemmensen procedure<sup>11</sup> was used to convert 5.5 g of the preceding keto acid to 4-(4'-bromophenyl)butanoic acid (94% yield), mp 71.5–71.9 °C (lit.<sup>11</sup> mp 71–72 °C).

Treatment of 10.0 g (0.044 mol) of the preceding carboxylic acid with 60 g of stirred PPA at 90 °C for 15 min gave, after workup, 9.3 g (100%) of 7-bromo-1-tetralone. Fractional dis-

(8) These computational investigations are being carried out in collaboration with Professor Michelle M. Francl at Bryn Mawr College.

(9) Mallory, F. B. *J. Chem. Educ.* 1962, 39, 261.

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tillation at 0.8 mm of pressure followed by recrystallization from cyclohexane and then from methanol gave material with mp 76.6–77.4 °C (lit.<sup>10</sup> mp 76–77 °C).

The preceding tetralone was treated with an excess of hydroxylamine hydrochloride and NaOH in refluxing 95% ethanol. Workup gave an oil from which the crystalline oxime was obtained by sublimation<sup>9</sup> at 95 °C (0.05 mm). Recrystallization from methanol and then from hexane gave material with mp 119.2–119.8 °C (lit.<sup>12</sup> mp 116–118 °C).

The preceding oxime (17 g, 0.071 mol) was subjected to a Semmler–Wolff reaction with 20 mL of acetic anhydride, 100 mL of acetic acid, and 20 mL of concentrated H<sub>2</sub>SO<sub>4</sub> at 60–95 °C for 30 min. After ice and water were added, the solution was made basic with aqueous NaOH and extracted with ether. Treatment of the dried ether extract with gaseous HCl yielded 11 g (60%) of 7-bromo-1-naphthylamine hydrochloride, mp 245 °C (lit.<sup>13</sup> mp 250 °C). Treatment with aqueous NaOH followed by acetic anhydride gave the *N*-acetyl derivative, mp 194.5–195.5 °C (lit.<sup>14</sup> mp 195.5–196.5 °C).

Treatment of 2.2 g (8.5 mmol) of the preceding amine hydrochloride in aqueous HCl with excess NaNO<sub>2</sub> followed by excess NaBF<sub>4</sub> yielded 2.4 g (87%) of the diazonium fluoroborate, mp 111–113.5 °C dec. This salt was decomposed by adding it slowly to boiling xylene. The xylene was removed by distillation through a fractionating column, and the residue (to which a small amount of K<sub>2</sub>CO<sub>3</sub> had been added) was vacuum distilled to give 7-bromo-1-fluoronaphthalene, bp 90–100 °C (1 mm) (lit.<sup>15</sup> bp 95–100 °C (0.5 mm)). Sublimation to a dry ice cold finger at 0.5 mm gave material with mp 25.6–26.1 °C.

The Grignard reagent prepared from 13.1 g (0.058 mol) of the preceding bromo compound and magnesium was transformed to the corresponding organocadmium reagent by treatment with 7.2 g (0.039 mol) of CdCl<sub>2</sub>. Addition of 12.0 g (0.080 mol) of 3-carbomethoxypropionyl chloride followed by workup yielded 13.7 g (91%) of crude methyl 3-(8'-fluoro-2'-naphthoyl)propanoate as an oil that eventually crystallized. Recrystallization from methanol and then from cyclohexane gave material with mp 60.2–60.6 °C: HRMS *m/e* calcd for C<sub>15</sub>H<sub>14</sub>FO<sub>3</sub> (M<sup>+</sup> + H) 261.0927, obsd 261.0920. Anal. Calcd for C<sub>15</sub>H<sub>13</sub>FO<sub>3</sub>: C, 69.22; H, 5.04. Found: C, 69.15; H, 5.22.

Treatment of the preceding ester with aqueous 2 M NaOH gave, after acidification, 7.0 g (50% yield overall from 7-bromo-1-fluoronaphthalene) of 3-(8'-fluoro-2'-naphthoyl)propanoic acid. Recrystallization from ethanol gave material with mp 141.5–142.3 °C. Anal. Calcd for C<sub>14</sub>H<sub>11</sub>FO<sub>3</sub>: C, 68.29; H, 4.50. Found: C, 68.37; H, 4.64.

The preceding keto acid (3.34 g, 13.6 mmol) was subjected to Clemmensen reduction as above<sup>10</sup> to yield 3.08 g (98%) of crude 4-(8'-fluoro-2'-naphthyl)butanoic acid. Sublimation<sup>9</sup> followed by recrystallization from a mixture of cyclohexane and 2-propanol (19:1, v/v) gave material with mp 89.0–89.5 °C. Anal. Calcd for C<sub>14</sub>H<sub>13</sub>FO<sub>2</sub>: C, 72.40; H, 5.64. Found: C, 72.26; H, 5.89.

Treatment of 2.2 g (9.5 mmol) of the preceding carboxylic acid with 30 g of PPA as described above yielded 1.9 g (93%) of 5-fluoro-4-oxo-1,2,3,4-tetrahydrophenanthrene as an oil. This crude product was purified by chromatography on silica gel with a mixture of pentane and acetone (4:1, v/v) as eluent and then by recrystallization from a mixture of cyclohexane and 2-propanol (19:1, v/v) to give material with mp 85.4–85.8 °C. Anal. Calcd for C<sub>14</sub>H<sub>11</sub>FO: C, 78.49; H, 5.18. Found: C, 78.42; H, 5.28.

Treatment of the preceding ketone with hydroxylamine hydrochloride and NaOH in ethanol gave 5-fluoro-4-oxo-1,2,3,4-tetrahydrophenanthrene oxime, mp 235 °C dec. Anal. Calcd for C<sub>14</sub>H<sub>12</sub>FNO: C, 73.35; H, 5.28. Found: C, 73.12; H, 5.43.

Analogous treatment of the preceding ketone using hydroxylamine hydrochloride 95% enriched in <sup>15</sup>N (Cambridge Isotope Laboratories) gave the corresponding <sup>15</sup>N oxime 5: <sup>19</sup>F NMR (CD<sub>3</sub>SOCD<sub>3</sub>, <sup>1</sup>H decoupled) δ 12.39 (d, *J*<sub>NF</sub> = 19.7 Hz).

Treatment of oxime 5 with acetic anhydride and acetic acid gave the *O*-acetyl derivative 9, mp 118.9–119.5 °C: <sup>19</sup>F NMR (<sup>1</sup>H decoupled) δ 11.39 (d, *J*<sub>NF</sub> = 19.0 Hz); MS *m/e* (relative intensity)

272 (M<sup>+</sup>, 22), 230 (82), 210 (54), 175 (100).

[<sup>15</sup>N]-7-Fluoro-4-methyl-1-indanone Oxime (6). 2-Bromo-4-fluorotoluene was prepared as reported earlier.<sup>3</sup> A mixture of 8.21 g (0.0434 mol) of this bromo compound, 60 mL of diethyl ether, and 1.5 g (0.062 mol) of magnesium was heated and stirred under nitrogen for 2 h. In a modified version of a previously described general method,<sup>16</sup> the mixture was then cooled to -17 °C and 100 mg of finely powdered CuCl was added, after which a solution of 2.21 g (0.022 mol) of ethyl acrylate in 10 mL of diethyl ether was added slowly over a period of 25 min from a syringe through a septum. The amount of unreacted Grignard reagent was estimated by a GC analysis of the product obtained by the treatment of an aliquot of the reaction mixture with acetophenone. On this basis, an additional 1.20 g (0.012 mol) of ethyl acrylate in 10 mL of diethyl ether was added slowly as before. The reaction mixture was then treated with dilute aqueous HCl and extracted with diethyl ether. Workup gave 6.39 g (76% yield) of a brown oil (95% pure as shown by GC). Purification by distillation at 85–95 °C (0.5 mm) followed by chromatography on silica gel with a 19:1 (v/v) mixture of pentane and ethyl acetate as the eluent gave, after evaporation of the eluate, ethyl 3-(5'-fluoro-2'-methylphenyl)propanoate as a pure colorless oil: HRMS *m/e* calcd for C<sub>12</sub>H<sub>15</sub>FO<sub>2</sub> (M<sup>+</sup>) 210.1056, obsd 210.1062.

Saponification of the preceding ester with aqueous 2 M NaOH gave, after workup and recrystallization from a 1:1 (v/v) mixture of cyclohexane and hexane, 3-(5'-fluoro-2'-methylphenyl)propanoic acid, mp 44.0–44.5 °C. Anal. Calcd for C<sub>10</sub>H<sub>11</sub>FO<sub>2</sub>: C, 65.92; H, 6.09. Found: C, 65.67; H, 6.06.

Treatment of a 5-g sample of the preceding carboxylic acid with 30 g of PPA at 95 °C for 8 min as described above gave, after workup, a brown oil. Purification by chromatography on silica gel with a 70:30 (v/v) mixture of pentane and acetone as the eluent followed by recrystallization from methanol and then from a 10:1 (v/v) mixture of cyclohexane and 2-propanol gave 7-fluoro-4-methyl-1-indanone, mp 89.8–90.5 °C. Anal. Calcd for C<sub>10</sub>H<sub>9</sub>FO: C, 73.16; H, 5.53. Found: C, 73.20; H, 5.34.

Treatment of 1 g of the preceding indanone with hydroxylamine hydrochloride and NaOH in ethanol followed by recrystallization of the crude product from 2-propanol yielded 0.43 g (40%) of 7-fluoro-4-methyl-1-indanone oxime, mp 254–259 °C dec. Anal. Calcd for C<sub>10</sub>H<sub>10</sub>FNO: C, 67.03; H, 5.62. Found: C, 67.05; H, 5.53.

Analogous treatment of 100 mg of the preceding indanone with NaOH and hydroxylamine hydrochloride 95% enriched in <sup>15</sup>N (Cambridge Isotope Laboratories) yielded 47 mg (43%) of the corresponding <sup>15</sup>N oxime 6: <sup>19</sup>F NMR (<sup>1</sup>H decoupled) δ -4.81 (d, *J*<sub>NF</sub> = 8.8 Hz); <sup>19</sup>F NMR (CD<sub>3</sub>SOCD<sub>3</sub>, <sup>1</sup>H decoupled) δ -5.16 (d, *J*<sub>NF</sub> = 8.8 Hz).

Treatment of 6 with acetic anhydride and acetic acid followed by rotary evaporation and recrystallization from methanol gave the *O*-acetyl derivative 10a, mp 146.6–147.4 °C: <sup>19</sup>F NMR (<sup>1</sup>H decoupled) δ 0.49 (d, *J*<sub>NF</sub> = 9.3 Hz); MS *m/e* (relative intensity) 222 (M<sup>+</sup>, 9), 180 (100). Treatment of 6 with trifluoroacetyl chloride, prepared in situ from sodium trifluoroacetate and PCl<sub>5</sub>, gave the *O*-trifluoroacetyl derivative 10b: <sup>19</sup>F NMR δ 2.26 (t of dq, F-7, *J*<sub>N,7</sub> = *J*<sub>6,7</sub> = 9.2 Hz, *J*<sub>5,7</sub> = 4.8 Hz, *J*<sub>Me,7</sub> = 1.2 Hz); <sup>19</sup>F NMR (<sup>1</sup>H decoupled) δ 2.28 (d, F-7, *J*<sub>N,7</sub> = 9.2 Hz); MS *m/e* (relative intensity) 276 (M<sup>+</sup>, 100). An analogous treatment of 6 starting with sodium trichloroacetate gave the *O*-trichloroacetyl derivative 10c: <sup>19</sup>F NMR (<sup>1</sup>H decoupled) δ 1.36 (d, *J*<sub>NF</sub> = 8.9 Hz); MS *m/e* (relative intensity) 330 (M<sup>+</sup>, 2), 328 (M<sup>+</sup>, 22), 326 (M<sup>+</sup>, 76), 324 (M<sup>+</sup>, 76), 163 (100). Treatment of 6 with a mixture of methyl iodide, methanol, and KOH gave the *O*-methyl derivative 10d: <sup>19</sup>F NMR (<sup>1</sup>H decoupled) δ -3.68 (*J*<sub>NF</sub> = 8.7 Hz); MS *m/e* (relative intensity) 194 (M<sup>+</sup>, 100).

[<sup>15</sup>N]-9-Fluoro-2,3-dihydro-1*H*-benz[*f*]inden-1-one Oxime (7). A mixture of 2.65 g (11.8 mmol) of 7-bromo-1-fluoronaphthalene (prepared as described above in connection with the synthesis of oxime 5) and 5 g (20.6 mmol) of magnesium in 20 mL of diethyl ether was heated and stirred under nitrogen for 2 h. The mixture was then cooled to -17 °C, after which 33 mg of finely powdered CuCl was added. This was followed by the slow addition over 45 min (with monitoring as described above

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for the sequence leading to oxime 6) of a total of 1.08 g (10.8 mmol) of ethyl acrylate in 10 mL of diethyl ether. Workup gave 2.64 g (68%) of an oil (about 75% pure as shown by GC) that was purified by distillation to give ethyl 3-(8'-fluoro-2'-naphthyl)propanoate as a colorless liquid: HRMS *m/e* calcd for C<sub>15</sub>H<sub>15</sub>F<sub>2</sub>O<sub>2</sub> (M<sup>+</sup>) 246.1056, obsd 246.1050.

Saponification of 1.95 g of the preceding ester with aqueous 2 M NaOH yielded, after workup, 1.5 g (87%) of 3-(8'-fluoro-2'-naphthyl)propanoic acid. Recrystallization from a 19:1 (v/v) mixture of cyclohexane and 2-propanol gave white needles, mp 102.4–102.8 °C. Anal. Calcd for C<sub>13</sub>H<sub>11</sub>F<sub>2</sub>O<sub>2</sub>: C, 71.55; H, 5.08. Found: C, 71.48; H, 4.96.

Treatment of 1.13 g of the preceding carboxylic acid with about 20 g of polyphosphoric acid at 90 °C for 8 min, followed by workup, yielded 0.54 g (52%) of 9-fluoro-2,3-dihydro-1*H*-benz[*f*]inden-1-one. Recrystallization from a 19:1 (v/v) mixture of cyclohexane and 2-propanol gave material with mp 105.5–106.2 °C: <sup>19</sup>F NMR δ 11.23 (ddd, *J*<sub>8,9</sub> = 11.7 Hz, *J*<sub>7,9</sub> = 4.7 Hz, *J*<sub>5,9</sub> = 2.0 Hz). Anal. Calcd for C<sub>13</sub>H<sub>9</sub>FO: C, 77.99; H, 4.53. Found: C, 78.16; H, 4.66.

Treatment of 1.46 g of the preceding ketone with hydroxylamine hydrochloride and NaOH in ethanol yielded 0.85 g (54%) of 9-fluoro-2,3-dihydro-1*H*-benz[*f*]inden-1-one oxime. Sublimation<sup>9</sup> followed by low-temperature recrystallization from a 4:1 (v/v) mixture of ethanol and dimethyl sulfoxide gave fine white crystals, mp 235 °C dec: <sup>19</sup>F NMR (CD<sub>3</sub>SOCD<sub>3</sub>) δ 11.07 (ddd, *J*<sub>8,9</sub> = 12.3 Hz, *J*<sub>7,9</sub> = 4.6 Hz, *J*<sub>5,9</sub> = 1.9 Hz); <sup>1</sup>H NMR (CD<sub>3</sub>SOCD<sub>3</sub>, <sup>1</sup>H decoupled) δ 11.09 (s). Anal. Calcd for C<sub>13</sub>H<sub>10</sub>NOF: C, 72.55; H, 4.68. Found: C, 72.56; H, 4.74.

Analogous treatment of 96 mg of the preceding ketone with NaOH and hydroxylamine hydrochloride 95% enriched in <sup>15</sup>N (Cambridge Isotope Laboratories) yielded 60 mg (58%) of the corresponding <sup>15</sup>N oxime 7: <sup>19</sup>F NMR (CD<sub>3</sub>SOCD<sub>3</sub>) δ 11.07 (dddd, *J*<sub>NF</sub> = 39.5 Hz, *J*<sub>8,9</sub> = 12.3 Hz, *J*<sub>7,9</sub> = 4.6 Hz, *J*<sub>5,9</sub> = 1.7 Hz); <sup>15</sup>N NMR (CD<sub>3</sub>SOCD<sub>3</sub>, <sup>1</sup>H decoupled) δ 11.10 (d, *J*<sub>NF</sub> = 39.5 Hz).

Treatment of oxime 7 with acetic anhydride and acetic acid followed by rotary evaporation and recrystallization of the residue from a mixture of cyclohexane and toluene gave the *O*-acetyl derivative 11, mp 134.2–135.8 °C: <sup>19</sup>F NMR δ 10.83 (dddd, *J*<sub>N,9</sub> = 43.6 Hz, *J*<sub>8,9</sub> = 12.0 Hz, *J*<sub>7,9</sub> = 4.6 Hz, *J*<sub>5,9</sub> = 1.7 Hz); <sup>1</sup>H NMR (<sup>1</sup>H decoupled) δ 10.89 (d, *J*<sub>NF</sub> = 43.5 Hz); MS *m/e* (relative intensity) 258 (M<sup>+</sup>, 46), 216 (100).

[<sup>15</sup>N]-*O*-Acetyl-3,4-dihydro-8-fluoro-5-methyl-1(2*H*)-naphthalenone Oxime (8). Treatment of oxime 1<sup>3</sup> with acetic anhydride and acetic acid gave the *O*-acetyl derivative 8, mp

94.6–95.6 °C: <sup>19</sup>F NMR δ 3.45 (ddd of q, *J*<sub>N,8</sub> = 23.3 Hz, *J*<sub>7,8</sub> = 11.0 Hz, *J*<sub>6,8</sub> = 5.1 Hz, *J*<sub>Me,8</sub> = 1.2 Hz); <sup>1</sup>H NMR (<sup>1</sup>H decoupled) δ 3.48 (d, *J*<sub>NF</sub> = 23.3 Hz); MS *m/e* (relative intensity) 236 (M<sup>+</sup>, 13), 194 (100).

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**Supplementary Material Available:** <sup>1</sup>H NMR characterizations (δ and *J* values at 300 MHz) for 30 compounds and 300-MHz <sup>1</sup>H NMR spectra for compounds 8–11 (14 pages). Ordering information is given on any current masthead page.

## Reaction of Chiral Cyclopropyl Halides with SmI<sub>2</sub>

H. M. Walborsky\* and Marek Topolski

*Dittmer Laboratories of Chemistry, Florida State University, Tallahassee, Florida 32306-3006*

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Reductions of (*S*)-(+)-1-bromo-1-methyl-2,2-diphenylcyclopropane (7), (*S*)-(+)-1-bromo-1-(methoxymethyl)-2,2-diphenylcyclopropane (19), and (*R*)-(–)-1-fluoro-1-iodo-2,2-diphenylcyclopropane (11) with samarium(II) iodide is reported. Evidence for a samarium(III) intermediate in the reaction is presented.

### Introduction

The seminal work by Kagan<sup>1</sup> on the use of samarium(II) iodide as a reagent for organic synthesis has generated a great deal of activity in this area.<sup>2</sup> In general, the reactivity of Sm(II) iodide is characterized by single electron transfer (SET) from the samarium(II) to a suitable sub-

strate to yield an anion radical intermediate and samarium(III) ( $E_{\text{aq}}^{\circ} \text{Sm}^{2+} = -1.55 \text{ V}$ ). The anion radical intermediate

can dissociate into a radical and an anion or collapse to a molecular radical anion (i.e., ketyl formation from a carbonyl radical anion). The radical intermediates may undergo reaction, either in an inter- or intramolecular mode, or they may be converted to anions by electron transfer from another equivalent of samarium(II) iodide. It is in this manner that samarium(II) has been used to

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