Table I. Isomerization–Hydrolysis[a] of Imines 3a–d

starting amine[b]	carbonyl product[c]	distilled yield[d] (%) of 7a–d
n-undecylamine	undecanal (7a)[e]	94
benzylamine	benzaldehyde (7b)	81
cyclooctylamine	cyclooctanone (7c)	28
dl-α-methylbenzylamine (2d)	acetophenone (7d)[f]	58

[a] All reactions were run by using the general procedure listed in the Experimental Section. [b] Available from Aldrich Chemical Co., Milwaukee, WI. [c] The IR and NMR spectral properties of each product were identical with those exhibited by the authentic compounds sold by Aldrich Chemical Co. [d] Based on starting imine (3a–d). [e] VPC analysis (6 ft × 1/8 in. SE-30 column, 173 °C, flow rate 15 mL/min, retention time 8.3 min) indicated the product [bp 64–82 °C (bath temperature, 0.15 mm)] to be >99% pure. [f] VPC analysis (6 ft × 1/8 in. 2.5% Carbowax 20M column, 138 °C, flow rate 15 mL/min, retention time 8.2 min) indicated the product to be >98% pure.

As the results in Table I indicate, this process is equally successful for converting benzylic amines to the corresponding aromatic aldehydes. Less satisfactory were the yields of ketones obtained from primary amines containing *secondary* alkyl groups (Table I, entries 3 and 4). These results may be a reflection of the diminished kinetic acidity of the corresponding Schiff base (i.e., **3c** vs. **3a**; **3d** vs. **3b**), resulting in a smaller extent of anion formation[7] (**4c** and **4d** vs. **4a** and **4b**, respectively).

In view of the overall facility with which this process can be effected, it offers a convenient method for the preparation of aldehydes from an appropriate primary amine. Furthermore it complements earlier synthetic methodology by which ketones (but not aldehydes) could be obtained from primary amine precursors.

Experimental Section

General Procedures. Reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran was purified prior to use by distillation from lithium aluminum hydride. Products were recovered from the ether extracts after the organic layer was dried over anhydrous magnesium sulfate and the solvent was removed by using a rotary evaporator under reduced pressure. Evaporative distillation refers to bulb-to-bulb (Kugelrohr) short-path distillation. The NMR spectra were recorded with a Varian EM-360 spectrometer, and infrared spectra were obtained by using a Beckman Acculab 1 spectrophotometer. Vapor-phase chromatography (VPC) was performed on a Hewlett-Packard 5750 chromatograph. The microanalysis was performed by Micro-Tech Laboratories, Skokie, IL.

***N*-Undecyl-2-picolinimine (3a).** A solution of 0.50 mL (5.25 mmol) of 2-pyridinecarboxaldehyde (1)[6] and 897 mg (5.24 mmol) of *n*-undecylamine (**2a**)[6] in 2.0 mL of anhydrous ether was stirred at room temperature for 40 min. The product was isolated by drying the mixture over anhydrous magnesium sulfate and removal of the ether in the usual manner. Subsequent evaporative distillation afforded 1.34 g (98%) of imine **3a**:[8] bp 125–150 °C (bath temperature, 0.20 mm); IR ν_{max} (film) 1640 (C=N), 1580, 1562, 1455, 1430, 1365, 1328, 1037, 985, 965, 765, 735 cm^{-1}; NMR (CCl_4, Me_4Si) δ 8.59 (m, $J_{5,6} = 5$, $J_{3,6} = 1$ Hz, aromatic H-6), 8.32 (br s, $CH{=}NCH_2$), 8.05 (m, $J_{3,4} = 7.5$, $J_{3,6} = 1$ Hz, aromatic H-3), 7.68 (td, $J_{4,6} = 1.7$, $J_{3,4} = J_{4,5} = 7.5$ Hz, aromatic H-4), 7.23 (m, aromatic H-5), 3.63 (t, $J = 6$ Hz, NCH_2), 0.88 (br t, $J = 5$ Hz, CH_3). Anal. Calcd for $C_{17}H_{28}N_2$: C, 78.41; H, 10.84; N, 10.76. Found: C, 78.40; H, 11.03; N, 10.64.

Isomerization–Hydrolysis of Imines 3a–d. A solution of 1.5 mmol of imine (**3a–d**) in 3.0 mL of anhydrous tetrahydrofuran (THF) was added dropwise to a solution of 4.8 mmol of lithium diisopropylamide[9] in 5.0 mL of THF and 3.0 mL of hexane. After this mixture was stirred at -70 °C for 1 h,[7] the reaction was quenched by quickly pouring the solution into a well-stirred mixture of 1.9 g of oxalic acid dihydrate and 3.0 mL of water in 12 mL of methyl alcohol and 12 mL of THF. The mixture was stirred at room temperature for 2 h, and the product was subsequently isolated by dilution of this mixture with 125 mL of 4:1 (v/v) 2 M aqueous hydrochloric acid–saturated brine and extraction with ether. The organic layer was washed with 3:1 (v/v) 2 M aqueous hydrochloric acid–saturated brine, 1:1 (v/v) 1 M aqueous sodium hydroxide–saturated brine, and saturated brine in successive order. The product was isolated from the organic extract in the usual manner and purified by evaporative distillation.

Registry No. 1, 1121-60-4; **2a**, 7307-55-3; **2b**, 100-46-9; **2c**, 5452-37-9; **2d**, 618-36-0; **3a**, 76684-24-7; **3b**, 19198-87-9; **3c**, 57707-72-9; **3d**, 76739-45-2; **7a**, 112-44-7; **7b**, 100-52-7; **7c**, 502-49-8; **7d**, 98-86-2.

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(7) Increasing the reaction time to 4 h for imine **3c** failed to alter significantly the yield of cyclooctanone isolated after the standard hydrolysis procedure.

(8) Imines **3b–d** were prepared in a similar manner from benzylamine, cyclooctylamine, and *dl*-α-methylbenzylamine, respectively. For a previous synthesis of these imines (**3b–d**) using 2-pyridinecarboxaldehyde and the appropriate amine, see: Dinizo, S. E.; Watt, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 6900.

(9) This base was prepared by the addition of a 1.6 M solution of *n*-butyllithium in hexane (3.0 mL) to a solution of diisopropylamine (0.75 mL, 5.35 mmol) in 5.0 mL of anhydrous tetrahydrofuran at -10 °C. For more details, see: Cregge, R. J.; Herrmann, J. L.; Lee, C. S.; Richman, J. E.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 2425, 2429.

Reaction of Perfluoroalkyl Carbanions with Thiocyanates. Synthesis of Fluorinated Sulfides and Sulfenyl Chlorides

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Nucleophilic attack on thiocyanates can occur either on the sulfur atom or on the cyanide group.[1] An old report shows that the condensation of an arylmagnesium halide with an alkyl thiocyanate yields chiefly a nitrile or a ketone.[2] The behavior of perfluoroalkylmagnesium bromides is not always similar to that of usual Grignard reagents.[3] Our initial goal was to examine the reaction of alkyl or aryl thiocyanates with the Grignard reagent $CF_3(CF_2)_3MgBr$ (**1**). We extended this study to the more stable perfluorobutylcopper[4] (C_4F_9Cu, **2**) and to the perfluoroalkyl carbanion **3** formed by addition of potassium fluoride to perfluoroalkenes $CF_2{=}CFX$ (X = Cl, CF_3).[5] These condensations could lead to the formation of sulfides **5** or nitriles **6**.

The results obtained are summarized in Table I. With the perfluoro Grignard reagent we obtained a sulfide. The only side product was a 1*H*-perfluoroalkane which arose from hydrogen abstraction. The copper derivative, easier to handle than the Grignard reagent, behaved similarly.

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(4) McLoughlin, V. C. R.; Thrower, J. *Tetrahedron* **1969**, *25*, 5921.

(5) Young, J. A. *Fluorine Chem. Rev.* **1967**, *1*, 1967.

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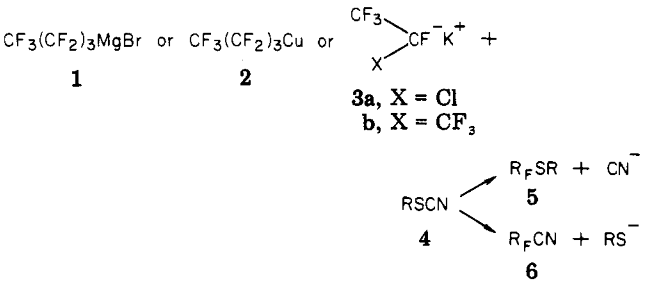

3a, X = Cl
b, X = CF_3

$R_F = CF_3(CF_2)_3, CF_3CFCl, CF_3CFCF_3$

A sulfide was formed, albeit in much lower yield. Reaction with perfluoroisopropyl carbanion also gave a sulfide, showing that steric effects do not prevent attack on the sulfur atom. We considered the possibility of a reverse reaction between nitrile and thiolate anion, which could account for the absence of nitrile (eq 1).

$$R_FCN + RS^- \rightarrow R_FSR + CN^- \qquad (1)$$

According to Brown and Wetzel[6] such a reaction is improbable and would lead to a perfluoroacyl thioimidate ($R_FC(SR){=}NH$) instead of a sulfide. Moreover, we carried out a reaction between perfluorobutyl cyanide and sodium *p*-chlorothiophenate and showed that no sulfide was formed.

It therefore appears that attack of a perfluoroalkyl anion on the thiocyanate group occurs on the sulfur atom with elimination of the cyanide group.[11] In order to determine whether this course of the reaction results from the structure of the thiocyanate or from the nature of the perfluoroalkyl anion, we carried out the following two experiments. First, we used an aryl thiocyanate to examine the stabilizing effect of the aryl group on the thiolate anion. Second, we used chlorotetrafluoroethyl anion. In both cases only a sulfide was formed. We have not observed attack of a perfluoroalkyl anion on the nitrile part of a thiocyanate, as is observed with an arylmagnesium halide.[2] *The course of the reaction with thiocyanate groups is a striking example of the difference in behavior between a perfluoroalkylmagnesium halide and its hydrocarbon analogue.*

This reaction is a useful method for preparing perfluoroalkyl sulfides. It is simple to carry out and gives only monosulfide to the exclusion of di- and polysulfides. Compared with known methods for preparing perfluoroalkyl sulfides, it is particularly useful for making those with branched perfluoroalkyl groups.[7]

Benzyl perfluoroalkyl sulfides **7** are converted to perfluoroalkylsulfenyl chlorides **8** by chlorinolysis (eq 2).

$$R_F^- + C_6H_5CH_2SCN \xrightarrow{-CN^-} \underset{\mathbf{7}}{R_FSCH_2C_6H_5} \xrightarrow{Cl_2} \underset{\mathbf{8}}{R_FSCl} + C_6H_5CH_2Cl \qquad (2)$$

Thus, reaction of a perfluoroalkyl anion with benzyl thiocyanate followed by chlorinolysis can be a useful two-step route to sulfenyl chloride.[8] It avoids the toxicity hazard associated with handling the disulfides.[9]

Experimental Section

^1H NMR determinations were carried out on a 60-MHz Perkin-Elmer R24 spectrometer. Approximately 20% solutions in $CDCl_3$ were employed with Me_4Si as the internal standard. ^{19}F NMR were carried out with the same solutions on a JEOL C60 HL spectrometer at 56.4 MHz. A $CFCl_3$ external standard was used on the ϕ scale. Microanalyses were performed by the Service Central de Microanalyses du CNRS, Lyon.

The benzyl and methyl thiocyanates were purchased from Aldrich Chemical Co., the fluoroolefins from Fluorochem Co. The perfluoroalkyl iodides were graciously donated by the Pechiney Ugine Kuhlman Co. to whom we are grateful. KF and CsF were purchased from Alfa Ventron.

Reaction of Perfluorobutyl Grignard Reagent with Benzyl Thiocyanate. A Grignard solution was prepared under a nitrogen atmosphere from 0.8 g of Mg (33 mmol), 3.5 g of ethyl bromide (32 mmol), and 30 mL of anhydrous diethyl ether. To this solution was added dropwise with mechanical stirring a solution of 9 g (26 mmol) of C_4F_9I in 10 mL of ether. The temperature was maintained at ca. −40 °C. An exchange reaction took place and C_4F_9MgBr was formed. The temperature was then allowed to rise to −15 °C then a solution of 4 g (26.8 mmol) of benzyl thiocyanate in 15 mL of diethyl ether was added dropwise. Hydrolysis was carried out at 0–5 °C by dilute hydrochloric acid. The organic layer was separated, washed with water three times, and dried over Na_2SO_4. After removal of the ether, the oily residue was distilled under 15-mm pressure. Two main fractions were obtained, boiling at 100–130 °C and at 130–160 °C. The first fraction contained chiefly the sulfide and the second the unreacted benzyl thiocyanate. The benzyl perfluorobutyl sulfide was purified by redistillation and preparative-scale GLC (SE-30, 160 °C): yield 4.5 g (50%); bp 130–135 °C (15 mm); ^{19}F NMR ϕ 78.4 (CF_3), 84.6 (CF_2S), 117.9 and 122.6 (CF_2CF_2); ^1H NMR δ 7.38 (C_6H_5, s), 4.2 (CH_2, s). Anal. Calcd for $C_{11}H_7F_9S$: C, 38.58; H, 2.06; F, 49.99. Found: C, 38.61; H, 2.06; F, 49.97. The residue of the distillation was untractable material.

Reaction of Perfluorobutylcopper with Benzyl Thiocyanate. A mixture of 7 g (20 mmol) of perfluorobutyl iodide, 3 g (20 mmol) of benzyl thiocyanate, 3.4 g of copper bronze, and 40 mL of dimethyl sulfoxide was heated on an oil bath at 100 °C under a nitrogen atmosphere. After 1 h a green color began to develop and the copper bronze appeared more brilliant. The evolved gaz was led through a trap cooled by a mixture of dry ice and acetone. 1*H*-Perfluorobutane was condensed in it. After 4 h, hydrolysis was carried out with dilute sulfuric acid. The mixture was filtered on a Büchner funnel. Workup of the filtrate as above afforded 1.7 g (5 mmol) of benzyl perfluorobutyl sulfide; yield 25%.

Reaction of Perfluoropropene with Potassium Fluoride and Benzyl Thiocyanate. A mixture of 15 g (100 mmol) of benzyl thiocyanate, 12 g (206 mmol) of potassium fluoride, 1 g (6.5 mmol) of cesium fluoride, and 100 mL of sulfolane was introduced into a stainless-steel autoclave with 15 g (100 mmol) of perfluoropropene. The autoclave was then closed and heated at 100 °C overnight. After being cooled to ambient temperature the autoclave was opened. The evolved gas was led through a trap where unreacted perfluoropropene and 2*H*-perfluoropropane were condensed. The residue in the autoclave was poured into 200 mL of water and extracted with ether. The extract was washed with water and dried. After removal of ether, distillation under reduced pressure afforded benzyl perfluoroisopropyl sulfide (11 g, 37 mmol, yield 37%): *m/e* 292 (M^+), bp 85 °C (20 mm); ^{19}F NMR ϕ 71 (CF_3, d), 153 (CF, sept, $^3J_{FF}$ = 9 Hz); ^1H NMR δ 7.2 (C_6H_5, s), 4.1 (CH_2, s). Anal. Calcd for $C_{10}H_7F_7S$: C, 41.11; H, 2.41; F, 45.52. Found: C, 41.11; H, 2.57; F, 44.22.

Reaction of Perfluoropropene with Potassium Fluoride and Methyl Thiocyanate. The same procedure was used with

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Table I

reagent	thiocyanate	solvent	temp, °C	sulfide	% yield
$CF_3(CF_2)_3MgI$	$C_6H_5CH_2SCN$	diethyl ether	−15	$C_6H_5CH_2S(CF_2)_3CF_3$	50
$CF_3(CF_2)_3Cu$	$C_6H_5CH_2SCN$	dimethyl sulfoxide	100	$C_6H_5CH_2S(CF_2)_3CF_3$	25
$(CF_3)_2CFK$	$C_6H_5CH_2SCN$	sulfolane	100	$C_6H_5CH_2SCF(CF_3)_2$	37
$(CF_3)_2CFK$	CH_3SCN	sulfolane	100	$CH_3SCF(CF_3)_2$	51
$(CF_3)_2CFK$	C_6H_5SCN	sulfolane	100	$C_6H_5SCF(CF_3)_2$	56
$(CF_3)_2CFK$	*p*-$NO_2C_6H_4SCN$	sulfolane	100	*p*-$NO_2C_6H_4SCF(CF_3)_2$	57
$CF_3(CF_2)_3MgI$	*p*-ClC_6H_4SCN	diethyl ether	−15	*p*-$ClC_6H_4S(CF_2)_3CF_3$	45
CF_3CFClK	$C_6H_5CH_2SCN$	sulfolane	100	$C_6H_5CH_2SCFClCF_3$	50

a mixture of 7.3 g (100 mmol) of methyl thiocyanate, 15 g (100 mmol) of perfluoropropene, 12 g of potassium fluoride, 1 g of cesium fluoride, and 100 mL of sulfolane. Because of the low boiling point of methyl perfluoroisopropyl sulfide, bp 53–55 °C, the contents of the autoclave were distilled directly to afford 11.2 g of the sulfide (51.8 mmol): yield 51%; ^{19}F NMR ϕ 70.5 (CF_3, d), 155 (CF, sept, $^3J_{FF} = 4.5$ Hz); ^{1}H NMR δ 2.5.

Reaction of Perfluoropropene with Potassium Fluoride and Phenyl Thiocyanate. The phenyl thiocyanate was prepared from diphenyl disulfide according to the method described by Harpp et al.[10] Starting from 13.5 g of the cyanate (100 mmol), 15 g of perfluoropropene (100 mmol), 12 g of potassium fluoride, 1 g of cesium fluoride, and 75 mL of sulfolane, 15.6 g of phenyl perfluoroisopropyl sulfide was isolated (56 mmol): yield 56%; *m/e* 278 (M^+); bp 67–69 °C (20 mm); ^{19}F NMR ϕ 73 (CF_3, d), 155.5 (CF, sept, $^3J_{FF} = 7.5$ Hz); ^{1}H NMR δ 7.15 (m). Anal. Calcd for $C_9H_5F_7S$: C, 38.86; H, 1.81; F, 47.81. Found: C, 38.79; H, 1.83; F, 46.35.

Reaction of Perfluoropropene with Potassium Fluoride and *p*-Nitrophenyl Thiocyanate. Starting from 3.4 g (18.8 mmol) of *p*-nitrophenyl thiocyanate,[10] 5 g of perfluoropropene, 2 g of potassium fluoride, 0.2 g of cesium fluoride, and 20 mL of sulfolane, 3.5 g (10.8 mmol) of *p*-nitrophenyl perfluoroisopropyl sulfide was isolated: yield 57%; bp 120 °C (3 mm); *m/e* 323–325 (M^+); ^{19}F NMR ϕ 72.5 (CF_3), 150 (CF); ^{1}H NMR δ 7.9 (CH, d, $^3J_{HH} = 8$ Hz), 8.25 (CH, d). Anal. Calcd for $C_9H_4F_7NO_2S$: C, 33.43; H, 1.23; F, 41.17. Found: C, 33.36; H, 1.23; F, 41.69.

Reaction of Perfluorobutylmagnesium Bromide with *p*-Chlorophenyl Thiocyanate. The Grignard reagent was prepared from 5.4 g (50 mmol) of ethyl bromide, 1.4 g of Mg, 50 mL of diethyl ether, and 13.8 g (40 mmol) of perfluorobutyl iodide. To this solution kept at −15 °C was added a solution of 6.5 g (40 mmol) of *p*-chlorophenyl thiocyanate[10] in 20 mL of diethyl ether. Hydrolysis was carried out with dilute hydrochloric acid at 0 °C. After workup as above, 6.7 g (18 mmol) of *p*-chlorophenyl perfluorobutyl sulfide was isolated: yield 45%; bp 70–75 °C (1 mm); *m/e* 376–378 (M^+); ^{19}F NMR ϕ 82.9 (CF_3), 89 (CF_2S), 122 and 127.4 (CF_2CF_2); ^{1}H NMR δ 7.41 and 7.58 ($^3J_{HH} = 9$ Hz). Anal. Calcd for $C_{10}H_4ClF_9S$: C, 35.08; H, 1.60; F, 45.40. Found: C, 34.92; H, 1.62; F, 45.10.

Reaction of Chlorotrifluoroethylene with Potassium Fluoride and Benzyl Thiocyanate. Starting from 12 g (100 mmol) of chlorotrifluoroethylene, 15 g (100 mmol) of benzyl thiocyanate, 12 g of potassium fluoride, 1 g of cesium fluoride, and 75 mL of tetramethylenesulfone, 13 g (50 mmol) of benzyl 1-chloro tetrafluoroethyl sulfide was isolated: bp 75–80 °C (1 mm); Yield 50%; *m/e* 258–260 (M^+); ^{19}F NMR ϕ 76.3 (CF_3, d), 95 (CF, 9, $^3J_{FF} = 8$ Hz); ^{1}H NMR δ 7.15 (phenyl, s), 4.1 (CH_2, s). Anal. Calcd for $C_9H_7ClF_4S$: C, 41.77; H, 2.7; F, 29.4. Found: C, 41.87; H, 2.76; F, 29.41.

Chlorinolysis of Benzyl Perfluoroisopropyl Sulfide. Benzyl perfluoroisopropyl sulfide (4.5 g, 15.4 mmol) was dissolved in 10 mL of tetrachloroethane. Chlorine was bubbled into this solution until the formation of a persistent yellow color over it. The evolved gas was led to a condenser surrounded by a mixture of dry ice and carbon tetrachloride where part of the perfluoroisopropylsulfenyl chloride was trapped. The remaining chloride was distilled from the reaction mixture under a nitrogen atmosphere: yield 2.7 g (11.4 mmol, 77%); bp 52 °C; mass spectrum, *m/e* 236–238 (M^+), 217–219 ($(M - F)^+$), 201 ($(M - Cl)^+$), 167–169 ($(M - CF_3)^+$); ^{19}F NMR ϕ 78.3 (CF_3, d), 163 (CF, sept, $^3J_{FF} = 6$ Hz). Benzyl chloride was separated from the residue and identified by comparison with an authentic sample.

Chlorinolysis of Benzyl 1-Chlorotetrafluoroethyl Sulfide. The sulfide 5.2 g (20 mmol) was dissolved in 10 mL of tetrachloroethane. Chlorine was bubbled into this solution. After 0.5 h, the solution was distilled under reduced pressure, and the fraction boiling in the range 30–50 °C (15 mm) was collected. It contained (1-chlorotetrafluoroethyl)sulfenyl chloride and a small amount of tetrachloroethane (insoluble). The sulfenyl chloride was separated and purified by redistillation: 1.6 g (39%); bp 95–97 °C; ^{19}F NMR ϕ 90.6 (CF_3, d), 124.3 (CFCl, q, $^3J_{FF} = 9$ Hz). Anal. Calcd for $C_2Cl_2F_4S$: C, 11.82. Found: C, 12.12.

Registry No. 4 (R = $CH_2C_6H_5$), 3012-37-1; 4 (R = CH_3), 556-64-9; 4 (R = C_6H_5), 5285-87-0; 4 (R = *p*-$NO_2C_6H_4$), 2137-92-0; 4 (R = *p*-ClC_6H_4), 3226-37-7; **5** (R = $CH_2C_6H_5$; R_F = $(CF_2)_3CF_3$), 76665-91-3; **5** (R = $CH_2C_6H_5$; R_F = $CF(CF_3)_2$), 68409-03-0; **5** (R= CH_3; R_F = $CF(CF_3)_2$), 34968-41-7; **5** (R = C_6H_5; R_F = $CF(CF_3)_2$), 65799-63-5; **5** (R = *p*-$NO_2C_6H_4$; R_F = $CF(CF_3)_2$), 76665-92-4; **5** (R = *p*-ClC_6H_4; R_F = $(CF_2)_3CF_3$), 76665-93-5; **5** (R = $CH_2C_6H_5$; R_F = $CFClCF_3$), 76684-17-8; 8 (R_F = $CF(CF_3)_2$, 51031-50-6; 8 (R_F = $CFClCF_3$), 57160-01-7; perfluorobutyl iodide, 423-39-2; perfluoropropene, 116-15-4; chlorotrifluoroethylene, 79-38-9.

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[10] Harpp, D. N.; Friedlander, B. T.; Smith, R. A. *Synthesis* **1979**, 181.

[11] Reaction of organic thiocyanates with carbanions generated from chloroform in aqueous medium leads to trichloromethyl sulfides. Makosza, M.; Fedorynski, M. *Synthesis* **1974**, 274.

Cycloaddition Reactions of Indenes. 4. 1:2 Adducts from 1-(1*H*-Inden-2- and -3-yl)pyrrolidines with Dimethyl Acetylenedicarboxylate[1]

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Discussion

1-(1*H*-Inden-3-yl)pyrrolidine[3] (**1a**) in 1:2 molar ratio reacted with dimethyl acetylenedicarboxylate (DMAD) in refluxing benzene to give a 1:2 adduct (**4**, 25%; Scheme I) as a white crystalline solid. The product is different in type from the previously described[1b] 1:2 adducts (**7** formed via intermediate 1:1 adducts (**6**) from 3-substituted indenes (**5**, Scheme II). Its NMR spectrum (in $CDCl_3$) shows four aromatic protons and no vinyl protons. In addition, there are a methylene doublet at δ 2.98 and a methine triplet at δ 4.33 which appear to be coupled (J = 3.5 Hz). No other aliphatic protons are present except those in the

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[2] Taken in part from the Ph.D. thesis of Venkataraman Kameswaran, University of Minnesota, Minneapolis, MN, June 1971; *Diss. Abstr. B.* **1972**, *32*, 6918–6919.

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