separated by preparative GC (10 ft × $^3/_8$ in. column, 15% UCON 50-HB-2000 on Chromosorb P) and identified by their IR and NMR spectra.[17]

3-Phenyl-1-butene (4) was prepared by the Wittig reaction[16] of 2-phenylpropionaldehyde[18] and methyltriphenylphosphonium iodide and purified by preparative GC (10 ft × $^3/_8$ in. column, 15% UCON 50-HB-2000 on Chromosorb P). The NMR spectrum is in agreement with the published values.[19]

The preparation and purification of other reagents and solvents and the standardization of MeLi have been described earlier.[5]

Alkylation of *cis*- and *trans*-Cinnamyl Acetate (2-OAc) with $LiCuMe_2$. In a typical procedure 1.91 g (10 mmol) of CuI was placed in an oven-dried 100-mL round-bottom flask equipped with a magnetic stirrer. The flask was flushed with nitrogen and capped with a septum. Twenty milliliters of dry ether was introduced and the stirred suspension cooled to 0 °C after which 18.5 mL of 1.08 M MeLi was added and the resulting mixture stirred 10 min (0 °C) to obtain homogeneity. A solution of 0.88 g (5 mmol) of *cis*-2-OAc in 10 mL of dry ether was rapidly added and the mixture stirred 105 min at 0 °C under a positive pressure of dry nitrogen. The reaction was quenched with 10 mL of saturated aqueous NH_4Cl and filtered (washing the precipitate well with ether), and the organic layer was dried ($MgSO_4$). After careful concentration by fractional distillation, the product distribution was determined by capillary GC (94-ft column, UCON LB-550-X). Reaction of *trans*-2-OAc was done in a similar fashion. For reaction of *cis*-2-OAc at −78 °C the $LiCuMe_2$ solution was cooled to −78 °C after attaining homogeneity and a prechilled solution of acetate was added. The reaction mixture was stirred 2 h at −78 °C and then gradually warmed over another 30 min. Reactions with excess acetate were performed the same way, using only 2 mmol of $LiCuMe_2$ for 3 mmol of 2-OAc.

Alkylation of *cis*-Cinnamyl Alcohol with MeLi by the Murahashi Method. To a stirred suspension of 0.76 g (4 mmol) of CuI in 10 mL of dry THF was added a solution of 4 mmol of alkoxide (prepared at 0 °C by adding 3.4 mL of 1.19 M MeLi to 0.54 g (4 mmol) of *cis*-cinnamyl alcohol). The reaction mixture was stirred 30 min at room temperature and cooled to −78 °C, after which 10 mL of 1.19 M MeLi was added. After being stirred 4 min, a solution of 1.75 g (4 mmol) of (methylphenylamino)-triphenylphosphonium iodide[5] in 20 mL of dry DMF was added dropwise over 15 min. The solution was stirred 1 h at −78 °C, warmed to room temperature, and stirred 3 more h. The reaction was quenched by addition of 10 mL of saturated aqueous NH_4Cl and filtered, and the aqueous layer was extracted with pentane (25 mL). The combined organic layers were washed with 5% HCl (10 mL), saturated aqueous $NaHCO_3$ (10 mL), and brine (10 mL), dried ($MgSO_4$), and carefully concentrated by fractional distillation. The product distribution was determined by capillary GC (94-ft column, UCON LB-550-X).

Acknowledgment. This work was supported by the National Science Foudation (Grant CHE 8108535).

Registry No. *cis*-2-OAc, 77134-01-1; *trans*-2-OAc, 21040-45-9; $LiCuMe_2$, 15681-48-8; *cis*-cinnamyl alcohol, 4510-34-3; 1-phenyl-1-propyn-3-ol, 1504-58-1.

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(18) Allen, C. F. H.; Van Allen, J. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 733.
(19) Kawata, N.; Maruya, K.; Mizoroki, T.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 413.

Acetyl Hypofluorite, a New Moderating Carrier of Elemental Flourine and Its Use in Fluorination of 1,3-Dicarbonyl Derivatives

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Elemental fluorine and most of the fluoroxy reagents do not react efficiently or cleanly with 1,3-dicarbonyl derivatives or with their corresponding metal enolates even at −75 °C. It has been found that a suspension of sodium acetate in $CFCl_3$ or in $CFCl_3$–AcOH, when treated with elemental fluorine, forms a new electrophilic fluorinating reagent, CH_3COOF (1), which reacts with substrates without further isolation or purification. This reagent is milder than F_2, CF_3OF, or CF_3COOF and reacts successfully where the other reagents fail. When 1 reacts with 1,3-dicarbonyl compounds, the main product is the 1,3-dioxo-2-fluoro derivative in reasonable yields. When, however, the corresponding sodium enolates were treated with 1, the yields of the monofluoro derivatives were considerably higher. In the case of 1,3-dicarbonyl derivatives with low enol content, only the sodium enolates react with 1 to produce good to very good yields of the corresponding 2-monofluoro derivatives. Thus 1 can be considered as a moderating carrier of the highly reactive F_2.

Very few works have been published in the last decade dealing with perchloryl fluoride ($FClO_3$). The main reasons are its treacherous nature[1] and the introduction of alternative electrophilic fluorinating agents that are more potent, efficient, and easy to handle such as CF_3OF,[2] CF_3CF_2OF and CF_3COOF,[3] F_2,[4] and XeF_2.[5] These reagents, with the exception of elemental fluorine, were also used successfully for synthesis of α-fluoro ketones from the corresponding enol ethers,[2] enol acetates,[2,6,7] or silylenol ethers.[8] Direct fluorination of ketones by F_2 has also been tried, but success was limited to a few pyruvic acid derivatives.[9]

While there are reports of perchloryl fluoride reacting with certain metal enolates of 1,3-dicarbonyl compounds to produce fluorocarbonyl derivatives, no such reactions have been reported with the new generation of the above electrophilic fluorinating agents.[10] It seems to us that the

(1) Perchloryl fluoride tends to form in its reactions chloric acid or its salts, which have been responsible for several serious and sometimes tragic explosions.
(2) Hesse, R. H. *Isr. J. Chem.* **1978**, *17*, 60.
(3) (a) Rozen, S.; Lerman, O. *J. Org. Chem.* **1980**, *45*, 672. (b) Lerman, O.; Rozen, S. *Ibid.* **1980**, *45*, 4122.
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(5) Filler, R. *Isr. J. Chem.* **1978**, *17*, 71.
(6) Rozen, S.; Menahem, Y. *J. Fluorine Chem.* **1980**, *16*, 19.
(7) Zajc, B.; Zupan, M. *J. Org. Chem.* **1982**, *47*, 573.
(8) Middleton, W. J.; Bingham, E. M. *J. Am. Chem. Soc.* **1980**, *102*, 4845.
(9) Tsushima, T.; Kawada, K.; Tsuji, T.; Misaki, S. *J. Org. Chem.* **1982**, *47*, 1107.

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major reason for this gap is the very high reactivity of these reagents. Indeed, in our laboratory we have examined the reaction of some metal-containing organic compounds, other than carboxylic acid salts, with F_2, CF_3OF, and CF_3COOF. Usually, troublesome, low-yield, and sometimes violent reactions took place, even at −78 °C. 2-Carbethoxycyclopentanone can serve as an example for the 1,3-dicarbonyl compounds. When it or its sodium enolate was treated with very dilute fluorine (about 1% in N_2), no monofluoro compound could be detected in the complex reaction products. When this dicarbonyl reacted with CF_3COOF, only 13% of the corresponding 2-fluoro derivative was obtained, together with some starting material and a lot of tar. When the sodium enolate was brought in contact with CF_3COOF, neither monofluoro compound nor starting material could be detected in the complicated reaction mixture. These results are in accord with Barton and Hesses' warning about Lewis bases that may react violently and uncleanly with CF_3OF.[11] Obviously, there is a need for a more gentle electrophilic fluorinating reagent that will readily react either with the enol form or, like $FClO_3$, with the metal enolate of compounds possessing the 1,3-dicarbonyl moiety, but without producing potentially explosive byproducts such as chlorate ion.

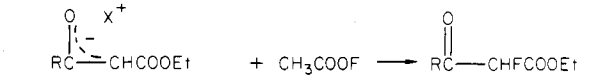
Recently, we have synthesized acetyl hypofluorite (CH_3COOF, 1), a new electrophilic fluorinating agent. We thought, for reasons which will be mentioned below, that this reagent would have the best chance to succeed where the other electrophilic fluorinating agents have failed, especially for the fluorination of 1,3-dicarbonyl derivatives.

The preparation of 1 was outlined in a previous communication.[12a] We noted that it can be prepared by two somewhat different methods. The first involves the action of nitrogen-diluted fluorine on a suspension of NaX (X = OAc, $OCOCF_3$, F) in $CFCl_3$ (Freon 11) and AcOH (10:1) at −78 °C (method A); the second uses a stream of F_2/N_2 passing through a suspension of NaOAc in Freon alone at −78 °C (method B). The main difference between these methods is the efficiency of producing the CH_3COOF (1).[13] In general, we noticed that when a substrate is entirely insoluble in the reaction solvent, as, for example, *trans*-stilbene or a salt of a polymeric organic acid in Freon, no reaction takes place between the nitrogen-diluted fluorine and the substrate at −78 °C. It is also an advantage that the solvent, or at least a large part of it, will consist of $CFCl_3$, since it has a low freezing point, is stable to fluorine, and, probably most importantly, can dissolve small but sufficient amounts of fluorine.[3a] It is likely, then, that every reaction with elemental fluorine, which is not of a radical nature, takes place in the solvent phase and not between the gas bubbles and the solid suspension as believed previously. Consequently, when method A is used for the synthesis of CH_3COOF, the small amount of acetic acid dissolved in $CFCl_3$ helps to bring more salt, or at least more hydrophilic ends of the salt, into the solution which results in relatively quick and efficient production of CH_3COOF. When, however, an acidic media has to be avoided, as in work with organometallic compounds, method B, although slightly less efficient because of solubility problems, was used. In any case, no attempt was made to isolate or purify the acetyl hypofluorite, since it decomposes gradually at elevated temperatures. For practical purposes, however, there is no need for isolation or purification of 1, and its concentration can be easily determined.

While the oxygen-bound fluorine in CH_3COOF exhibits electrophilic properties, as is obvious from its reactions with olefins and aromatic compounds,[12] this O–F bond is less polarizable and hence less reactive in ionic reactions than other perfluoroalkyl fluoroxy compounds, like CF_3OF or CF_3COOF, which frequently suffer from overreactivity. This consideration makes 1 an excellent candidate for reactions with centers of high electron density. It was quite natural, then, to examine the reaction of acetyl hypofluorite with 1,3-dicarbonyl compounds and their metal enolates to see if it would succeed where F_2, CF_3COOF, and CF_3OF have failed.

The 1,3-dicarbonyl compounds were treated in two different ways: (a) a solution of CH_3COOF (1) was prepared, usually by method A, and the dicarbonyl compound was added; (b) a solution of 1 was prepared by method B to exclude any acid from the reaction mixture, and then the corresponding sodium enolate was added. In general, when the contribution of the enol form of the dicarbonyl compound is considerable, the reaction can be accomplished by either method, although with the metal enolates the yields were always higher in comparison to the unmetalated parent compounds.

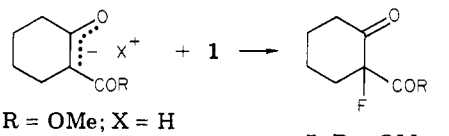
Thus, when diethyl oxaloacetate (2) reacted with 1, diethyl fluoroxaloacetate (3)[14] was obtained in 65% yield.



2, R = COOEt; X = H
2a, X = Na
4, R = CH_3; X = H
4a, X = Na

1

3, R = COOEt
5, R = CH_3



6, R = OMe; X = H
6a, X = Na
8, R = Me; X = H
8a, X = Na

7, R = OMe
9, R = Me
10, R = CH_2F

Reaction of the sodium enolate **2a** with 1 increases the yield to 75%. The same pattern was observed with ethyl acetoacetate 4 and its sodium enolate **4a**, both producing the expected ethyl fluoroacetoacetate (5)[15] in very good yields. Cyclic 1,3-dicarbonyls behave similarly. Thus, 2-carbomethoxy-2-fluorocyclohexanone (7)[16] was obtained when 6 reacted with acetyl hypofluorite, although in only 30% yield. The yield of 7 more than doubled when the

(10) Zupan[7] treated a few 1,3-dicarbonyl compounds with XeF_2 and various catalysts but was unsuccessful in obtaining monofluoro derivatives in reasonable yields, the main products being usually 1,3-dioxo-2,2-difluoro derivatives.

(11) Barton, D. H. R.; Godinho, L. S.; Hesse, R. H.; Pechet, M. M. *J. Chem. Soc., Chem. Commun.* **1968**, 804.

(12) (a) Rozen, S.; Lerman, O.; Kol, M., *J. Chem. Soc., Chem. Commun.* **1981**, 443. (b) Lerman, O.; Tor, Y.; Rozen, S. *J. Org. Chem.* **1981**, *46*, 4629.

(13) In the case of method A, about 80–90 mmol of fluorine were passed through the solution in order to get 25–30 mmol of acetyl hypofluorite. Method B usually requires twice as much. However, in most cases where nitrogen-diluted fluorine is bubbled through a reaction mixture, a considerable amount of the gas leaves the reaction vessel unreacted. The path length of the fluorine–nitrogen bubbles through the reaction mixture, the fine dispersion of the gas, the rate of the reaction, and the rate of the introduction of the bubbles into the reaction vessel all have important roles in the absorbance of the fluorine by the solvent and consequently by the reactant. It is difficult then to standardize, at this point, the relationship between the amount of the fluorine passed through the solution and the amount which actually reacts with the sodium acetate.

(14) Blank, I.; Mager, J.; Bergmann, E. D. *J. Chem. Soc.* **1955**, 2190.

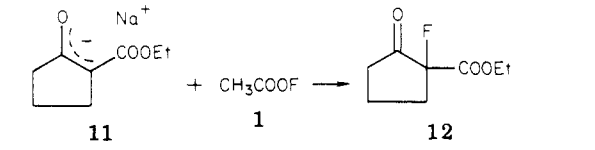
(15) Bergmann, E. D.; Cohen, S.; Shahak, I., J. Chem. Soc. **1959**, 3278.

(16) The corresponding ethyl ester was prepared by use of $FClO_3$. Machleidt, H.; Hartmann, V. *Justus Leibigs Ann. Chem.* **1964**, *679*, 9.

sodium enolate **6a** was used as the substrate. When the diketone **8** was treated with **1**, two products were isolated in equal amounts. The first product proved to be the expected 2-acetyl-2-fluorocyclohexanone (**9**) while the other was identified as 2-(fluoroacetyl)-2-fluorocyclohexanone (**10**), which results from a secondary enolization of the already-formed α-fluoroacetyl moiety. Indeed, when a large excess of **1** reacted with **8**, the ratio of **10**/**9** increased to 2.5:1. However, if the sodium enolate **8a** was treated with **1**, only the monofluoro derivative **9** was obtained in high yield.

When the contribution of the enol form of a 1,3-dicarbonyl derivative is small, no reaction takes place between the substrate and the acetyl hypofluorite. Fortunately, however, the reaction between the corresponding metal enolates and **1** is efficient and generally proceeds in good yields. Thus, 2-carbomethoxycyclopentanone sodium enolate (**11**) was transformed into 2-carbethoxy-2-fluorocyclopentanone (**12**) in greater than 90% yield. It is of interest to point out that the preparation of this compound was attempted by using $FClO_3$ but resulted in ring opening and formation of fluoroglutaric acid.[16]

Dimethyl sodiomalonate (**13**) also reacts with **1** (unlike dimethyl malonate itself) to produce the very poisonous dimethyl fluoromalonate (**14**) in 55% yield. Although **14**



11 **12**

$RC^-(COOR')_2$ Na^+ + **1** → $RCF(COOR')_2$ → →

13, R = H; R′ = Me
15, R = Et

14, R = H; R′ = Me
16, R = R′ = Et

RCHFCOOH

17, R = Et

has been described previously,[17] relatively few reports have dealt with this potentially key chemical because of the lack of a safe and efficient way to prepare it. Malonate derivatives can also be easily fluorinated by this method.

Diethyl ethylsodiomalonate (**15**), for example, was successfully fluorinated to yield 77% of diethyl ethylfluoromalonate (**16**).[17] This compound undergoes hydrolysis and decarboxylation in very high yield to produce α-fluorobutyric acid, thus opening a new route for convenient synthesis of α-fluoro mono- and polyacids.[18]

In conclusion, we have shown that acetyl hypofluorite, a new member of the growing family of fluoroxy reagents, is also the mildest one and is capable of reacting cleanly with metal enolates. In a sense, CH_3COOF serves as a "taming" carrier of the chemically most reactive element, F_2.

Experimental Section

NMR ^1H spectra were recorded with a Bruker WH-90 spectrometer at 90 MHz with $CDCl_3$ as the solvent and Me_4Si as an internal standard, while ^{19}F spectra were measured at 84.67 MHz and are reported in parts per million upfield from $CFCl_3$, which also served as the internal standard. Mass spectra were measured with a Du Pont 21-491B spectrometer. IR spectra were recorded as neat films on a Perkin-Elmer 177 spectrometer.

Only unpublished physical data for the fluorine-containing compounds are given in this section. Microanalyses also confirm the correct composition of the new fluorinated compounds.

General Fluorination Procedure. Caution: Fluorine and acetyl hypofluorite should be treated with care since they are strong oxidizers. The work should be conducted in an efficient hood or in a very well ventilated area. The toxicity of acetyl hypofluorite is not known yet, but some of the oxyfluoro reagents like CF_3OF are known to be strong poisons. If elementary precautions are taken, work with fluorine and its fluoroxy derivatives is safe and relatively simple. In the past, we have never had any explosions or accidents while working with fluorine.

A description of the setup and the procedures for working with fluorine has previously been described.[3a] It should be noted that although premixed mixtures of fluorine in inert gases like N_2, He, or Ar are commercially available, it is easy and always less expensive to prepare the desired mixture in a secondary cylinder attached to the system before starting the reaction. This provides the flexibility of working with any desired concentration and even changing it during the reaction.

Preparation of the Hypofluorite 1. About 10% of fluorine in nitrogen was bubbled slowly through a suspension of 8 g of sodium acetate in 400 mL of solvent [$CFCl_3$/AcOH (10:1) for method A or only $CFCl_3$ for method B) at −75 °C by using an efficient vibromixer.[3] The progress of the reaction was monitored by treating aliquots with KI and titrating the liberated iodine. When the desired concentration of **1** was achieved (usually 25–30 mmol), a cold (−75 °C) solution of a 1,3-dicarbonyl compound in $CHCl_3$ or a metal enolate in dry THF was added in one portion. Unless otherwise stated, the ratio of **1** to substrate was about 1:1. After about 1 min, the reaction mixture was poured into dilute thiosulfate solution, the organic layer washed with $NaHCO_3$ solution and then water until neutral, dried over $MgSO_4$, and evaporated. The crude product was usually purified by chromatography on a short silica gel column and, if needed, also by high-pressure liquid chromatography.

Diethyl fluoroxaloacetate (3)[14] was obtained in 65% yield when diethyl oxaloacetate was the substrate and in 75% yield when the sodium enolate was used. Purification was done by chromatography (30% EtOAc in petroleum ether serving as the eluent): NMR δ 5.20 (1 H, d, J = 50 Hz); ^{19}F NMR ϕ* 202 (d, J = 50 Hz); MS, m/e 206 (M^+, 188 [$(M - CO)^+$], 133 [$(M - COOEt)^+$, base peak].

Ethyl fluoroacetoacetate (5)[15] was obtained in 72% and 81% yields when ethyl acetoacetate or its sodium enolate, respectively, served as substrates. It was purified by chromatography (25% EtOAc in petroleum ether): NMR δ 5.27 (1 H, d, J = 50 Hz); ^{19}F NMR ϕ* 194 (d, J = 50 Hz), MS, m/e 148 (M^+), 105 [$(M - Ac)^+$, base peak].

2-Carbomethoxy-2-fluorocyclohexanone (7) was prepared in 30% yield by using **6** as the starting material and in 75% when the sodium enolate **6a** was employed. Compound **7** was purified by chromatography (20% EtOAc in petroleum ether): NMR δ 3.84 (3 H, s), 2.65 (2 H, m), 2.25 (2 H, m), 1.92 (4 H, m); ^{19}F NMR ϕ* 161.5 (t, J = 18 Hz); MS; m/e 174 (M^+), 115 [$(M - COOMe)^+$, base peak]. Anal. Calcd for $C_8H_{11}FO_3$: C, 55.17; H, 6.32; F, 10.92. Found: C, 54.92; H, 6.51; F, 10.45.

Fluorination of 2-Acetylcyclohexanone (8) and Its Sodium Enolate 8a. When the ratio of **8**/**1** was 1:1, two fluorinated products were obtained. They were separated by HPLC with 10% EtOAc in petroleum ether. One of the compounds proved to be the monofluoro derivative **9**: (30% yield; ^{19}F NMR ϕ* 158 (narrow m); MS; m/e 158 (M^+), 138 [$(M - HF)^+$], 116 [$(M - Ac)^+$]. Anal. Calcd for $C_8H_{11}FO_2$: C, 60.76; H, 6.96; F, 12.06. Found: C, 60.64; H, 7.25; F, 12.43. The second compound was also obtained in 30% yield and proved to be 2-(fluoroacetyl)-2-fluorocyclohexanone (**10**): NMR δ 5.24 (2 H, $J_{HF(gem)}$ = 47 Hz), 2.68–1.95 (8 H, m); ^{19}F NMR ϕ* 237 (1 F, $J_{HF(gem)}$ = 47 Hz), 169.5 ppm (1 F, m); MS; m/e 176 (M^+), 156 [$(M - HF)^+$], 133 [$(M - CH_2F)^+$], 115 [$(M - COCH_2F)^+$], 95 [$(M - COCH_2F - HF)^+$, base peak]; IR 1720, 1735 cm^{-1}. Anal. Calcd for $C_8H_{10}F_2O_2$: C, 54.55; H, 5.68. Found: C, 54.63; H, 5.96. When the ratio of acetyl hypofluorite to substrate was changed to 7:1, the yield of **9** dropped to 20% while the yield of **10** was raised to 50%. When the sodium enolate **8a** was treated with **1** in the usual **1**/substrate ratio of 1:1, the monofluoro derivative **9** was obtained as the sole product in 90% yield.

(17) Pattison, F. L. M.; Buchanan, R. L.; Dean, F. H. *Can. J. Chem.* **1965**, *43*, 1700.

(18) Research involving new syntheses of α-fluoro acids by this and other routes based on fluorination of enolates is underway in our laboratory.

2-Carbethoxy-2-fluorocyclopentanone (12) was obtained in 92% yield when **11** reacted with **1**: NMR δ 4.28 (2 H, q, J = 7.1 Hz), 2.6–2.05 (6 H, m), 1.34 (3 H, t, J = 7.1 Hz); ^{19}F NMR ϕ^* 164 (t, J = 20 Hz); MS; m/e 174 (M^+), 129 (M – OEt, base peak); IR 1780, 1725 cm^{-1}. Anal. Calcd for $C_8H_{11}FO_3$: C, 55.17; H, 6.32; F, 10.92. Found: C, 54.89; H, 6.60; F, 10.91.

Dimethyl fluoromalonate (14)[17] was prepared from dimethyl sodiomalonate (**13**): 52% yield; NMR δ 5.33 (1 H, d, J = 45 Hz), 3.88 (6 H, s); ^{19}F NMR ϕ^* 195.8 (d, J = 48 Hz); MS; m/e 150 (M^+, base peak).

Diethyl ethylfluoromalonate (16)[17] was obtained in 77% yield from diethyl ethylsodiomalonate (**15**): ^{19}F NMR ϕ^* 169.5 (t, J = 7.1 Hz); MS; m/e 177 [(M – Et)$^+$], 133 [(M – COOEt)$^+$], 105 [(CHFCOOEt)$^+$, base peak]. Compound **16** (650 mg) was refluxed in 50 cm^3 of HCl (6 N) for 48 h. The reaction mixture was extracted with ether, the ether layer dried, and the ether removed by distillation. A yield of 310 mg (92%) of α-fluorobutyric acid (**17**) was obtained: ^{19}F NMR ϕ^* 194.6 (dt, J_1 = 48, J_2 = 23 Hz).

Registry No. **1**, 78948-09-1; **2**, 108-56-5; **2a**, 40876-98-0; **3**, 392-58-5; **4**, 141-97-9; **4a**, 19232-39-4; **5**, 1522-41-4; **6**, 41302-34-5; **6a**, 56137-55-4; **7**, 84131-42-0; **8**, 874-23-7; **8a**, 72072-37-8; **9**, 74279-75-7; **10**, 84131-43-1; **11**, 13697-91-1; **12**, 84131-44-2; **13**, 18424-76-5; **14**, 344-14-9; **15**, 18995-13-6; **16**, 1578-75-2; **17**, 433-44-3; F_2, 7782-41-4; NaOAc, 127-09-3.

Thermally Induced Degradation of 2,3,5,6-Tetrachloroterephthalylidenebis(*o*-aminoaniline)

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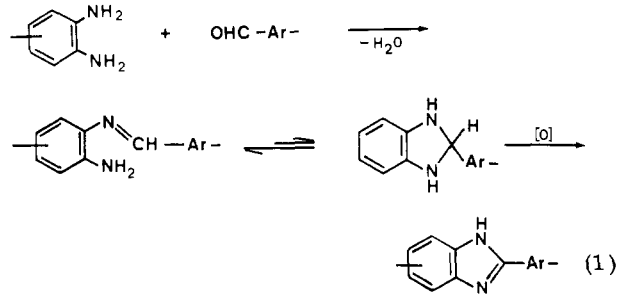
The bis(Schiff base) **1**, 2,3,5,6-tetrachloroterephthalylidenebis(*o*-aminoaniline), obtained by low-temperature solution condensation of *o*-phenylenediamine with 2,3,5,6-tetrachloroterephthalaldehyde, suffers fragmentation at 100 °C in dipolar aprotic solvent media under strictly anaerobic conditions, giving benzimidazole (**3**) and 1,2,4,5-tetrachlorobenzene (**4**). The same fragmentation of **1**, although accompanied by side reactions, is observed in refluxing ethanol or toluene. The reaction involves fission of the C–C bonds connecting the central tetrachlorophenylene segment with the outer two substituent groups and probably proceeds via the ring-tautomeric bis(imidazoline) form of **1**. Neither the bis(benzimidazole) **2**, 1,4-bis(benzimidazol-2-yl)-2,3,5,6-tetrachlorobenzene, in which the outer two substituent groups already exist in the aromatized state, nor the bis(Schiff base) **6**, terephthalylidenebis(*o*-aminoaniline), lacking the four bulky chloro groups at the center unit, undergo such C–C bond cleavage under the conditions indicated. These findings show that it is the combined effect of steric buttressing at the perchlorophenylene segment and imidazolation, i.e., aromatization, of the outer substituent groups which provides the driving force for the fragmentation observed. In a suitable oxidative environment, cyclodehydrogenation of the bis(Schiff base) **1** competes efficaciously enough with the degradative process to suppress the generation of the fragmentation products, and only the bis(benzimidazole) **2** is isolated.

It has been amply demonstrated[1-5] that aromatic Schiff bases possessing an additional amino group in the ortho position to the azomethine nitrogen atom undergo smooth oxidative cyclodehydrogenation, thereby converting to the corresponding benzimidazoles, and use of this aromatization process has been made[6] in polymerization studies aiming at the synthesis of linear polybenzimidazoles from open-chain polyazomethine precursors. The latter reaction, illustrated in eq 1 for a typical azomethine segment



(1)

(Ar = 1,3- or 1,4-phenylene, etc.), is catalytically assisted by certain transition-metal compounds and most likely proceeds via the imidazoline tautomer structure shown, hydrogen peroxide being the byproduct of oxidation.[4] Polyazomethines lending themselves as polybenzimidazole precursors in this type of reaction are generally accessible by anaerobic solution polymerization of aromatic bis *o*-diamines with aromatic dialdehydes in *N*,*N*-dimethylacetamide or related solvents at temperatures up to 100 °C.[6] However, attempts in our laboratory[7] to synthesize a chlorinated poly(Schiff base) in an analogous fashion from 3,3′-diaminobenzidine and 2,3,5,6-tetrachloroterephthalaldehyde over the temperature range –15 to +80 °C revealed grossly anomalous behavior: instead of the expected poly(Schiff base), low-molecular-mass fragments resulting from extensive chain cleavage were the main products isolated.

In an effort to shed some light on the causes underlying this unexpected chain scission, we investigated, and herein describe, the model reaction involving the solution condensation of *o*-phenylenediamine with 2,3,5,6-tetrachloroterephthalaldehyde at various temperatures in both oxidative and anaerobic environments.

Results

The low-temperature condensation behavior of the reactant pair, *o*-phenylenediamine and tetrachloroterephthalaldehyde, was investigated in an initial series of experiments in which the two reactants were allowed to undergo anaerobic condensation in a 2:1 molar ratio at –15 to +25 °C. *N*,*N*-Dimethylacetamide (DMAC), previously

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