= 8 G). A popular theory of how conduction occurs in conductive polymers formulates the carrier species for a polymer such as I in terms of polarons (radical cations) and bipolarons (spinless dications).[19,21] These species are charged-localized lattice deformations with electronic states in the band gap. Our ESR studies suggest that bipolarons and/or singly charged cations are initially formed, and at high dopant levels polarons and/or neutral radicals are also present.

Our results demonstrate a new route to a conducting composition by oxidative treatment of a novel cross-conjugated polymer. Others have also obtained conducting compositions by oxidation of precursor polymers lacking extensive delocalization.[22] We are currently investigating the extent of the modification of I with doping and the properties of derivatives of I.

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Registry No. I (homopolymer), 104584-99-8; (I)(norbornene) (copolymer), 105502-58-7; I_2, 7553-56-2.

Supplementary Material Available: UV–vis spectra, ESR spectra, ESR line-shape analysis, and temperature dependence of the total magnetic susceptibility (4 pages). Ordering information is given on any current masthead page.

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A Novel Transformation of a Carbonyl to a CF_2 Group

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The construction of the CF_2 moiety is of importance to organic chemistry from several aspects, including some of considerable biological interest.[1] This has led to the development of a few general, but somewhat limited, methods for its construction. Thus the incorporation of the CF_2 unit into a target molecule can be accomplished by using ethylbromodifluoro acetate[2] or CF_2 containing Freons.[3] Another method, limited to the construction of a benzylic CF_2 group, was developed by reacting some diazo derivatives, or compounds which generate this moiety in situ, with fluorine.[4] Recently we have demonstrated a new transformation of an acetylenic bond into derivatives containing the CF_2 group.[5]

The most widely used method, however, is the general transformation of a carbonyl group into the CF_2 moiety by using SF_4[6] or its most important derivative (diethylamino)sulfur trifluoride (DAST) developed mainly by Middleton.[7] This method although quite popular, has its own limitations, including harsh reaction conditions, toxicity, and some stability problems. Similar fluorides such as MoF_6 have also been used.[6]

We present here a new method for the CO → CF_2 conversion using easily available reagents and starting materials. Recently, as a part of our goal to introduce elemental fluorine to organic chemistry methodology,[8] we have synthesized in situ iodine monofluoride, IF, and demonstrated some of its unique chemistry.[9] One of the most noticeable features of this reagent is the nucleophilic power of its fluoride which is not heavily solvated as in most other sources. This fact, combined with Barton's reaction of unsubstituted hydrazones with elemental iodine,[10] encouraged us to react IF with various hydrazone derivatives under very mild reaction conditions, yielding eventually the desired CF_2 group.

Thus the hydrazones of benzophenone (**1**), deoxybenzoin (**2**), and acetophenone (**3**) when treated with an excess of IF produced, correspondingly, diphenyl difluoromethane (**4**) in 65% yield, 1,1-difluoro-1,2-diphenylethane (**5**) in 75% yield, and (1,1-difluoroethyl)benzene (**6**) in 45% yield.[11]

$$\begin{array}{ccc} \mathrm{PhC({=}NNH_2)R} & \xrightarrow{\mathrm{IF}} & \mathrm{PhCF_2R} \\ \mathbf{1}{:}\ \mathrm{R = Ph} & & \mathbf{4}{:}\ \mathrm{R = Ph} \\ \mathbf{2}{:}\ \mathrm{R = CH_2Ph} & & \mathbf{5}{:}\ \mathrm{R = CH_2Ph} \\ \mathbf{3}{:}\ \mathrm{R = Me} & & \mathbf{6}{:}\ \mathrm{R = Me} \end{array}$$

While F_2 reacts with hydrazones derived from some aryl ketones to produce the CF_2 group, only tars result in other cases.[4b] However, the much milder IF was found to react satisfactory with every hydrazone that we have tried. Thus, for example, hydrazones derived from the cyclic 4-*tert*-butylcyclohexanone (**7**), the steroidal 3-cholestanone (**8**), and the straight-chain 2-decanone (**9**) were all converted in yields of about 70% to the corresponding difluoroalkanes (**10**–**12**).

In both iodination[10] and fluorination[4] of hydrazones with the respective elements, it was necessary to work with an unsubstituted hydrazone. The reaction involves the elimination of HX (X = I or F), an essential step toward the formation of the diazo moiety, which then extrudes N_2, supplying the main driving force of the reaction. In order to find out if this is also the mechanism with IF and since unsubstituted hydrazones are not very stable, we started experiments with substituted ones. Thus *N*-methyl- and *N,N*-dimethylhydrazones of 2-decanone (**13** and **14**) were prepared and reacted with IF. In the case of **13** the yield of **12** was similar to that of the unsubstituted **9**, although a higher final temperature (raising to 25 °C) and a longer reaction time of up to an hour were needed. Even a longer reaction time of 4 h was required with the *N,N*-dimethylhydrazone **14** and then only a 50% yield of the difluoro product **12** was obtained. The substituted *N*-alkylhydrazones, however, are also not always very stable so we

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(1) See, for example: *Biomedical Aspects of Fluorine Chemistry*; Filler, R., Kobayashi, Y., Eds.; Elsevier Biomedical: Amsterdam, 1982. Fried, J.; Halinan, E. A.; Szwedo, M. J., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 3871 and references therein. Middleton, W. J.; Bingham, E. M. *J. Org. Chem.* **1980**, *45*, 2883. Cross, B. E.; Erasmunson, A.; Filippone, P. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1293. Weigert, F. J. *J. Org. Chem.* **1980**, *45*, 3476.

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(11) A typical reaction was performed by pouring a solution of the appropriate hydrazone, usually about 2 g in 20–30 mL of chloroform into a 3–4-fold molar excess of IF suspended in $CFCl_3$ at –78 °C. The latter was prepared from I_2 and F_2 according to ref 5 and 9. In some cases (see text) the temperature was then gradually allowed to raise to 25 °C. The reaction was monitored by GC on 5% SE-30 column. Apart from **12**, all the *gem*-difluoro products are described in the literature and their physical and spectral properties are identical with those published. The spectral properties as well as the microanalysis of **12** are also in excellent agreement with the proposed structure. In some cases the low boiling point of the products presents some difficulties in the isolation process. The products are usually accompanied by 10–15% of the corresponding α-iododifluoro compounds of type $-CHICF_2-$. Present experiments are aimed at reducing these minor quantities of iodo derivatives to the difluoro compounds themselves.

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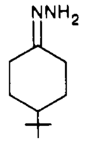

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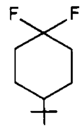

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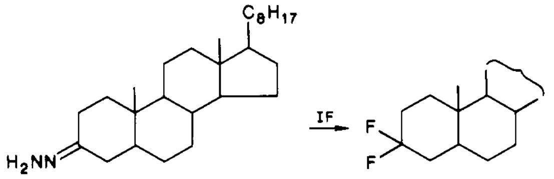
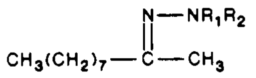


8 **11**



$$CH_3(CH_2)_7-\overset{\overset{\displaystyle N-NR_1R_2}{\|}}{C}-CH_3$$

9: $R_1 = R_2 = H$
13: $R_1 = H$; $R_2 = Me$
14: $R_1 = R_2 = Me$

$CH_3(CH_2)_7CF_2CH_3$
12

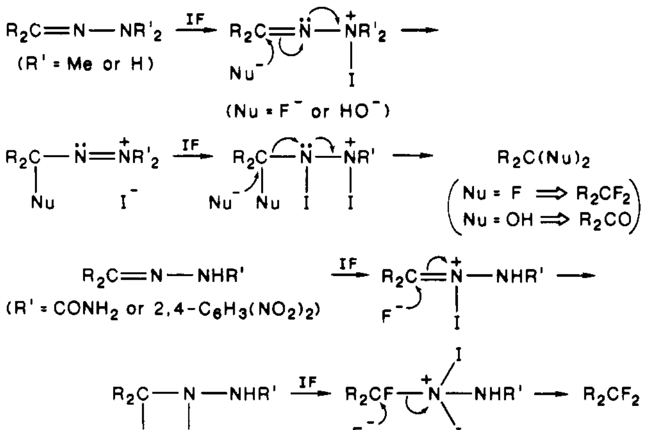
turned our attention to some stable crystalline derivatives such as semicarbazones and (2,4-dinitrophenyl)hydrazones (DNP). These derivatives of acetophenone (**15** and **16**) and of 2-decanone (**17** and **18**) were prepared in practically quantitative yields and

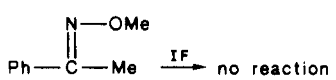
PhC(=NNHR)Me
15: R = $CONH_2$
16: R = 2,4-$C_6H_3(NO_2)_2$

$CH_3(CH_2)_7C(=NNHR)CH_3$
17: R = $CONH_2$
18: R = 2,4-$C_6H_3(NO_2)_2$

reacted with IF. No difluoro derivatives were detected at −78 °C, but after gradual warming and additional stirring for 3–4 h at room temperature the expected *gem*-difluoro products **6** and **12** were obtained, although in yields about 20% lower than the ones obtained with the corresponding unsubstituted hydrazones.

Unlike the mechanisms for the iodination[10] or fluorination[4b] of hydrazones which call for an attack on the NH_2 end of the hydrazone, such an attack would be unfavorable in the case of semicarbazones or DNP's and much slower for the *N*-alkyl ones. We propose the two following schemes for the two different types of hydrazones, based on the differences of the nitrogens' basicity. The key starting step should be the attack of the positive iodine on the more basic nitrogen.





19

In agreement with this mechanism, when a competing nucleophile such as water or alcohols is present, considerable amounts of the corresponding ketone are also formed. This scheme is also in agreement with the fact that when the second nitrogen is either more hindered (R′ = Me) or less basic (NHCOR′) than the imine one, the reaction is slower compared to the unsubstituted hydrazones. The initial reaction must be at low temperatures, at least −40 °C, since above this IF disproportionates mainly to IF_3 and IF_5. These reagents do not possess easily available electrophilic iodine as in IF, giving further support for the initial intervention of electrophilic iodine. Since, however, the slowest step should be the C–N bond cleavage assisted by the nucleophilic fluorine, the subsequent raising of the temperature can only facilitate the reaction. It is also worth noting that when the basicity is low as in the case of the oxime ether **19**, no reaction takes place even after 24 h at room temperature.

In conclusion, this general method can be a very good alternative to the conventional one based on SF_4, eliminating the need for the drastic reaction conditions which this expensive and toxic reagent requires.

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Registry No. 1, 5350-57-2; **2**, 5171-96-0; **3**, 13466-30-3; **4**, 360-11-2; **5**, 350-62-9; **6**, 657-35-2; **7**, 62082-37-5; **8**, 106094-56-8; **9**, 105232-57-3; **10**, 19422-34-5; **11**, 16319-73-6; **12**, 106094-57-9; **13**, 106094-58-0; **14**, 106094-59-1; **15**, 2492-30-0; **16**, 1677-87-8; **17**, 3622-72-8; **18**, 2675-17-4; **19**, 3376-33-8; IF, 13873-84-2.

First Absolute Rate Constants for Some Hydrogen Atom Abstractions and Addition Reactions of an Aroyloxyl Radical: 4-Methoxybenzoyloxyl[1]

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Aroyloxyl radicals are the last major class of reactive organic free radicals for which there are no absolute rate data.[2] We were unsuccessful in a recent attempt to measure absolute rate constants for benzoyloxyl radicals by laser flash photolysis (LFP).[3] After our work was complete, an exciting report appeared[4] that LFP (308 nm) of certain diaroyl peroxides in CCl_4 solution yielded the corresponding aroyloxyl radicals which were detected by time-resolved EPR spectroscopy. Since 4-methoxybenzoyloxyl had the longest lifetime (1.6 μs) we decided to apply LFP (308 nm) to a 10^{-2} M solution of bis(4-methoxybenzoyl) peroxide in CCl_4 at 24 °C using optical detection. Three distinct transient species were observed (see Figure 1). The transient that possesses a broad, structureless absorption in the visible region with the intensity steadily increasing from 500 to 800 nm (monitored at 720 nm throughout this work) we identify as $4\text{-}CH_3OC_6H_4CO_2^\bullet$ for the following reasons:

(i) The 720-nm absorption is produced "instantaneously" (≤4 ns, the full width at half-height of the laser pulse); i.e., there is no observable "grow-in" of this signal.

(ii) The 720-nm absorption decays with (pseudo)-first-order kinetics, $k_{exp} = 6.8 \pm 0.2 \times 10^5\ s^{-1}$, and the lifetime of this transient ($\tau \approx 1.4$ μs) is the same in N_2-, air-, and O_2-saturated solutions.

(iii) The 720-nm absorption can be "quenched", i.e., decays more rapidly, in the presence of H-atom donors and compounds to which $4\text{-}CH_3OC_6H_4CO_2^\bullet$ might be expected to add. Bimolecular rate constants, *k*, for the overall reaction (i.e., abstraction and addition) of this radical with the added substrate (see Table I) can be calculated from these pseudo-first-order decays, i.e., k_{exp}

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(1) Issued as NRCC No. 26599.

(2) For a comprehensive survey of absolute kinetic data for organic radicals in solution, see: *Landolt-Börnstein. New Series. Radical Reaction Rates in Liquids*; Fischer, H., Ed.; Springer-Verlag: Berlin, 1984; Vol. 13, Parts a–e. See, in particular: Scaiano, J. C.; Howard, J. A., Part d, pp 127–141.

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