lymer must, therefore, predominate.

$$-OCF_2 \wr CF_2O- \xrightarrow{2F\cdot} 2(-OCF_3)$$

Chain cleavage at carbon–oxygen bonds must also occur in order to account for the CF_3CF_2O- end groups. The result of backbone cleavage at the carbon–oxygen bond would be one CF_3CF_2O- end group, one CF_3O- end group, and one molecule of carbonyl fluoride as follows:

$$-OCF_2CF_2 \wr OCF_2CF_2O- \rightarrow -OCF_2CF_2\cdot + \cdot OCF_2CF_2O-$$

$$-OCF_2CF_2\cdot \xrightarrow{F\cdot} -OCF_2CF_3$$

$$-OCF_2CF_2O\cdot \xrightarrow{-COF_2} -OCF_2\cdot \xrightarrow{F\cdot} -OCF_3$$

Chain cleavage occurring predominately at the carbon–carbon bonds is consistent with the calculated bond strengths in perfluoro ethers: C–C = 80–90 kcal, C–O = >100 kcal.

Acyl fluoride terminated compounds did not constitute a significant fraction of the reaction products. At temperatures above 100 °C in a fluorine atmosphere perfluoro ether acyl fluorides are relatively unstable. Functionalized perfluoro ethers are also desirable compounds due to the chemical versatility of the acyl fluoride terminus of the otherwise unreactive structure. Further experimentation in the direct fluorination of polyether polymers is underway with acyl fluoride terminated perfluoro polyethers as target compounds.

Acknowledgment. Fluorine chemistry at the University of Texas is supported by the Air Force Office of Scientific Research (Grant No. AFOSR-76-3031A and AFOSR-78-3658).

Registry No.—α-Trifluoromethyl-ω-trifluoromethoxypoly[oxy(1,1,2,2-tetrafluoro-1,2-ethanediyl)], 67584-21-8; α-hydro-ω-hydroxypoly[oxy(1,1,2,2-tetrafluoro-1,2-ethanediyl)], 67584-22-9; poly(ethylene oxide) polymer, 25322-68-3.

Supplementary Material Available: Infrared spectrum of perfluorotriglyme (Figure 1); boiling point vs. compound mass graph for all perfluoropolyethers produced (Figure 2); and range of boiling temperatures for distillation of product vs. the relative amount of each compound in the fraction (Table V) (3 pages). Ordering information can be found on any current masthead page.

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Reactions of 5-Halogeno-2*H*,3*H*-benzo[*b*]thiophene-2,3-diones with Nucleophiles. An Electron Spin Resonance Investigation on Carbon–Halogen Bond Reactivity

Francesco Ciminale* and Giovanni Bruno

Istituto di Chimica Organica, Università, via Amendola, 173, 70126 BARI, Italy

Lorenzo Testaferri and Marcello Tiecco

Istituto di Chimica Organica Facoltà di Farmacia, Università di Perugia, Italy

Giorgio Martelli

Laboratorio C.N.R. dei Composti del Carbonio contenenti Eteroatomi e loro Applicazioni—Ozzano Emilia, Italy

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The reactions of the 5-halogeno-2*H*,3*H*-benzo[*b*]thiophene-2,3-diones (5-X-BTD: X = F, Cl, Br, I) with several nucleophiles (t-BuO$^-$, MeO$^-$, OH$^-$, PhO$^-$, MeS$^-$, PhS$^-$) have been studied by ESR spectroscopy. The observed halogenated radical anions 5-X-BTD$^{-\cdot}$ are intermediates of a nucleophilic substitution in the presence of PhS$^-$ and of a reductive dehalogenation with the other nucleophiles.

Many examples of reactions of aryl halides with nucleophiles proceeding through a radical pathway have been reported[1] in the last 10 years. A general feature of these processes is an electron transfer to the aromatic substrates to give radical anions which decompose by loss of halide ions thus generating aryl radicals. The fate of the last species determines the overall process which may be a nucleophilic substitution and/or a reductive dehalogenation. The first occurs in Bunnett's $S_{RN}1$ mechanism[1b] characterized by coupling of the aryl radical with a nucleophile; in the second the neutral radical abstracts a hydrogen atom from a suitable donor.[1a]

In these reactions, however, there is no direct physical ev-

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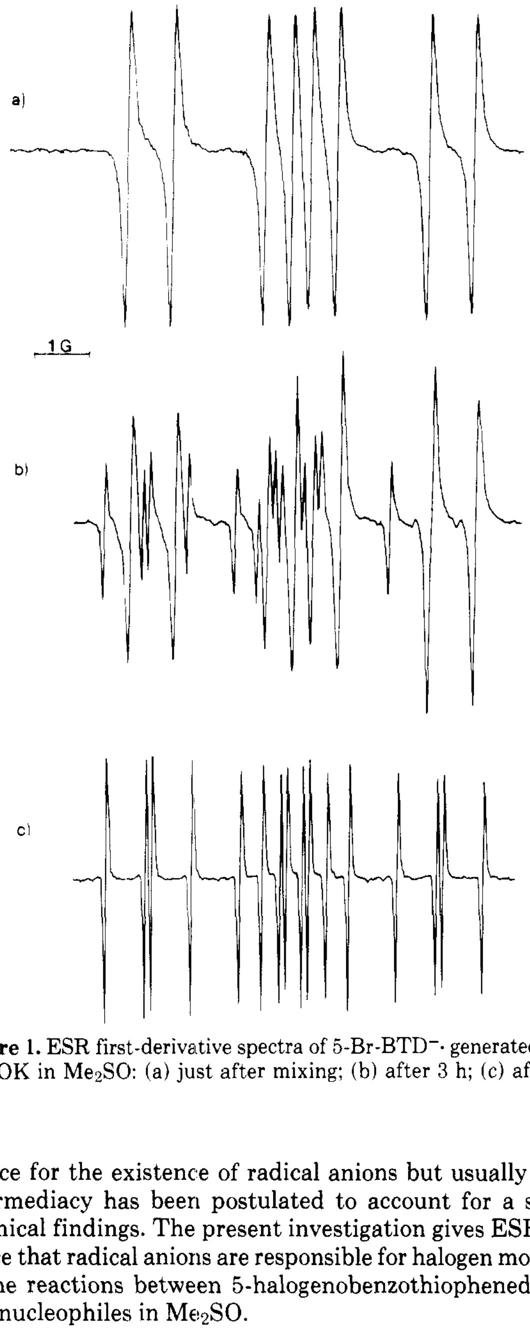
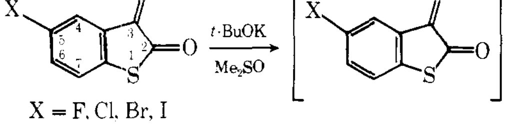


Figure 1. ESR first-derivative spectra of 5-Br-BTD$^{-}\cdot$ generated with t-BuOK in Me$_2$SO: (a) just after mixing; (b) after 3 h; (c) after 24 h.

idence for the existence of radical anions but usually their intermediacy has been postulated to account for a set of chemical findings. The present investigation gives ESR evidence that radical anions are responsible for halogen mobility in the reactions between 5-halogenobenzothiophenediones and nucleophiles in Me$_2$SO.

Results

α-Diketones are known to be easily reduced to remarkably stable semidiones in basic Me$_2$SO.[2] Thus treating the 5-halogeno-2*H*,3*H*-benzo[*b*]thiophene-2,3-diones (5-X-BTD) with an excess of potassium *tert*-butoxide in Me$_2$SO at room temperature we recorded ESR spectra which can be straightforwardly attributed to the corresponding radical anions[3] (5-X-BTD$^{-}\cdot$).



X = F, Cl, Br, I

The observed hyperfine splitting constants listed in Table I were assigned to the various positions by referring to those previously reported by Russell[4] for the unsubstituted term (BTD$^{-}\cdot$). Of particular interest in connection with the stability of these semidiones is the possibility of detecting 5-I-BTD$^{-}\cdot$; radical anions containing iodine in fact usually fragment as soon as they form.[5,9]

The spectrum of the 5-F-BTD$^{-}\cdot$ remained unchanged also after several days, whereas those of the other three 5-X-BTD$^{-}\cdot$ gradually vanished in a few hours; at the same time another paramagnetic resonance, which corresponds to the parent BTD$^{-}\cdot$, grew up.

As an example the spectral modifications for the 5-Br-BTD$^{-}\cdot$ are reported in Figure 1; the final spectrum (c) is identical to that observed by Russell and to the one obtained by us from authentic BTD. Clearly a reductive dehalogenation of the 5-Cl, 5-Br, and 5-I-BTD takes place in these conditions.

The spectrum recorded at the end of the transformation in deuteriated Me$_2$SO showed quite clearly triplets due to deuterium nuclear moment suggesting that the paramagnetic species observed is the radical anion of 5-D-BTD. On the other hand deuterium-labeled semidione was absent when BTD$^{-}\cdot$ was generated by treatment of authentic BTD with t-BuO^{-} in Me$_2$SO-d_6.

Several other nucleophiles were also able to reduce 5-X-BTD to the corresponding anions. Under conditions similar to those described for t-BuO^{-}, the reactions of 5-X-BTD with methoxide, hydroxide, phenoxide, and thiomethoxide anions showed identical spectroscopic transformations; the reductive dehalogenation process is therefore occurring also in these cases.

Quite different were the spectral modifications observed for the 5-Cl- and 5-Br-BTD$^{-}\cdot$ when thiophenoxide was used as the nucleophile.

As reported in Figure 2 for the 5-Br-BTD$^{-}\cdot$, the replacing hyperfine structure was now qualitatively similar to that of the starting paramagnetic species; only the three coupling constants relative to hydrogen atoms at C-4, C-6, and C-7 were in fact observed. The final spectrum (c) agrees with the radical anion of a substitution product which has been unambigously identified as the 5-SPh-BTD$^{-}\cdot$ by comparison of its coupling constants and "g" factor with those of an authentic sample independently prepared.

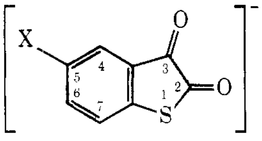
For the fluoro derivative we again observed that no other signals different from the initial 5-F-BTD$^{-}\cdot$ resonance appeared with time. Also the spectrum of 5-I-BTD$^{-}\cdot$ did not display any change in sharp contrast with every expectation. This result is at the moment unaccountable and deserves further investigations but, in our opinion, it does not discredit the explanation of the other spectroscopic evidences we will give later on.

Discussion

The spectral modifications observed, of course, do not by themselves indicate that the halogenated semidiones are the intermediates through whom the reductive dehalogenation or the nucleophilic substitution occurs. Mechanisms not involving radical anions therefore have to be supposed as possible, although they require the unlikely presence of significant amounts of diamagnetic parent substrates in the reaction mixtures.

The reductive dehalogenation could be in fact the result of a nucleophilic attack on halogen followed by protonation of the resulting carbanion.[6] This hypothesis however seems rather unlikely on the basis of the negative outcome of the hydrogen–deuterium exchange experiment carried out on BTD; that is, if the carbanion in C-5 is not formed by abstraction of a proton under the strongly basic conditions employed, it is reasonable to believe that, under the same conditions, the abstraction of a positive halogen should be very difficult, if possible at all. On the other hand for the nucleophilic substitution, the hypothesis of an S$_N$Ar mechanism can be rejected because it would imply that the order of halogen mobility[7] should be the reverse of the one observed, i.e., the 5-F-BTD should be more reactive than the other 5-X-BTD.

Table I. Hyperfine Splitting Constants in Gauss of I in Me_2SO



I

X	registry no.	a_4	a_5	a_6	a_7
H[a]	67632-54-6	2.42	0.71	2.84	0.83
D	67632-55-7	2.42	0.11	2.84	0.83
F	67632-56-8	2.54	2.15	2.90	0.84
Cl	67632-57-9	2.54		3.03	0.84
Br	67632-58-0	2.54		3.04	0.84
I	67632-59-1	2.51		3.00	0.83
SPh	67632-60-4	2.45		2.97	0.82

[a] Russell and co-workers[4] reported the following constants: 2.43, 0.70, 2.86, 0.82.

Having ruled out the possible mechanisms not involving radical anions, we suggest that the observed spectral modifications can be rationalized by the reaction sequence in Scheme I.

In the first step, the initially observed radical anions 5-X-BTD$^{-}\cdot$ are quickly generated by an electron transfer to 5-X-BTD; the electron is most likely provided by the nucleophile itself as it was substantiated, in the case of *t*-BuO$^-$, generating the 5-X-BTD$^{-}\cdot$ in the *t*-BuO$^-$/*t*-BuOH system. It must be taken into account however that in Me_2SO, at least with the more basic anions (*t*-BuO$^-$, MeO$^-$, OH$^-$), another possible electron donor could be the methylsulfinyl carbanion present in the medium.[8]

The next step (2) involves the fragmentation of the carbon–halogen bond; as it has been shown previously by electrochemical studies on the decomposition of halogenated radical anions of nitrobenzenes,[9] benzophenones,[10] and some heterocyclic compounds,[11] this process is dominated by the bond strength and it is therefore consistent with the observed persistence of 5-F-BTD$^{-}\cdot$ resonance.

From the cleavage of the halogenated radical anions indicated in reaction 2 the aryl radical 5-BTD· is formed and this, in our opinion, is consistent with the dichotomy of behavior observed on passing from the other nucleophiles to PhS$^-$.

Thus, the 5-BTD· radical can abstract (step 3a) a hydrogen atom[12] from the solvent leading to diamagnetic BTD, which is then reduced (eq 4) to the detectable semidione by the excess of the nucleophile, or alternatively it may couple (eq 3b) with the nucleophile to give the radical anion of the substitution product.

Scheme I

$$\text{5-X-BTD} + \text{N}^- \longrightarrow \text{5-X-BTD}^{-}\cdot + \text{N}\cdot \qquad (1)$$

$$\text{5-X-BTD}^{-}\cdot \longrightarrow \text{5-BTD}\cdot^{a} + \text{X}^- \qquad (2)$$

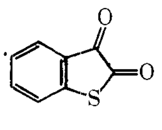
$$\text{5-BTD}\cdot + (\text{CH}_3)_2\text{SO} \longrightarrow \text{BTD} + \cdot\text{CH}_2\text{SOCH}_3 \qquad (3a)$$

$$\text{BTD} + \text{N}^- \longrightarrow \text{BTD}^{-}\cdot + \text{N}\cdot \qquad (4)$$

or

$$\text{5-BTD}\cdot + \text{N}^- \longrightarrow \text{5-N-BTD}^{-}\cdot \qquad (3b)$$

[a] 5-BTD· =



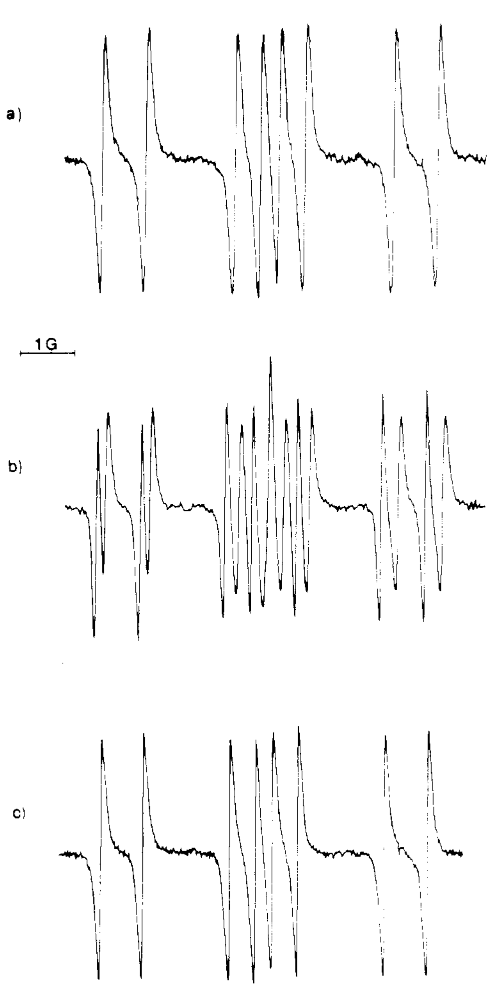


Figure 2. ESR first-derivative spectra of 5-Br-BTD$^{-}\cdot$ generated with PhSK in Me_2SO: (a) just after mixing; (b) after 5 h; (c) after 30 h.

The sequence of eq 1–3b, defined by the latter reaction when N$^-$ is PhS$^-$, corresponds to an $S_{RN}1$ mechanism[1b] in which the character of a chain process is missing as a consequence of the very fast electron transfer (eq 1) and of the excess of the electron donor. Finally, as far as the nature of nucleophile is concerned, our results confirm the special ability of the PhS$^-$ ion in trapping aryl radicals[1e,13] in respect to other nucleophiles.[1f]

Experimental Section

Materials. All substituted benzothiophenediones were prepared following the method described by El Shanta et al.[14] for the 5-chloro derivative: 5-F mp 144–146 °C; 5-Cl mp 148–150 °C; 5-Br mp 175–177 °C; 5-I mp 192–194 °C; 5-SPh mp 107–113 °C. The unsubstituted term was synthesized as described by Papa et al.[15] Satisfactory elemental analyses were obtained for all new compounds; carbonyl absorptions were recorded at 1725 cm^{-1} (CS_2). Solid potassium *tert*-butoxide and hydroxide were commercial materials while methoxide,[16] phenoxide,[17] thiomethoxide,[18] and thiophenoxide[19] were prepared as described in the literature. Dimethyl sulfoxide reagent grade was distilled under reduced pressure from calcium hydride and stored over molecular sieves.

Preparation of Semidiones and Measurements. ESR spectra were recorded with a Varian E-109 spectrometer. Radical anions were simply generated in capillary glass tubes by adding the solvent to solid substrate and an excess of base. Degassing of the solutions resulted neither in any improvement of the quality of the ESR spectra nor in any change of the observed reactivity of the radical anions.

Acknowledgment. Financial support from C.N.R. Rome is gratefully acknowledged.

Registry No.—BTD, 493-57-2; 5-D-BTD, 67632-61-5; 5-F-BTD, 67632-62-6; 5-Cl-BTD, 16807-22-0; 5-Br-BTD, 50891-90-2; 5-I-BTD, 67632-63-7; 5-SPh-BTD, 67632-64-8.

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A Unique Reversal of Regioselectivity in the Photoaddition of 2-Fluorocyclohexenone to Isobutylene

Mark L. Greenlee,[1a] Edward L. Fritzen, Jr., and John S. Swenton*[1b,c]

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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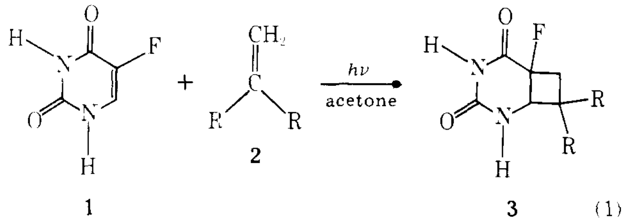
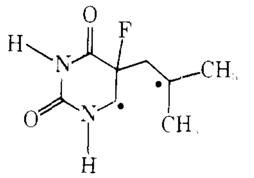
The preparation of 2-fluorocyclohex-2-enone (**13**) via the chlorofluorocarbene adduct of the morpholine enamine of cyclopentanone is described. The photocycloaddition reactions of **13** and isobutylene have been studied. In contrast to the highly regioselective additions of its pyrimidinone analogue (5-fluorouracil), **13** exhibits products from predominantly the head-to-head orientation. The mechanistic implications of these results are briefly discussed.

While photochemical cycloaddition reactions of α,β-unsaturated carbonyl compounds have been extensively utilized in organic synthesis,[2] the low regioselectivity of the reaction with simple olefins detracts from the synthetic method.[2d,3] We recently reported that substitution of the 5 hydrogen of uracil for fluorine remarkably enhances the regioselectivity of the photoaddition reaction with simple olefins[4] (eq 1). Since the photoaddition reactions of uracil and cyclohexenone to isobutylene afford similiar regioselectivity,[5] the photoadditions of 2-fluorocyclohex-2-enone (**13**) to olefins were of interest as a potential method of regiospecific four-ring annulation.



A second impetus for a study of the photochemistry of **13** relates to a possible origin for the highly regioselective additions of fluorouracil. Thus, in the fluorouracil system this high selectivity could be rationalized if biradical **4** had had an enhanced efficiency of ring closure relative to biradical **5**.[6] This possibility was made especially attractive by the work of Wagner and Thomas,[9] who showed that the ratio of fragmentation to closure in the biradical derived from butyrophenone was markedly altered by substitution of fluorine for



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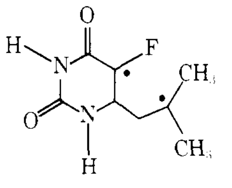

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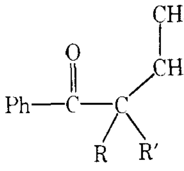

6a, R = R′ = H
b, R = H; R′ = F