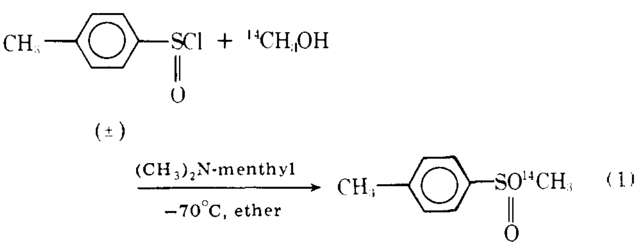
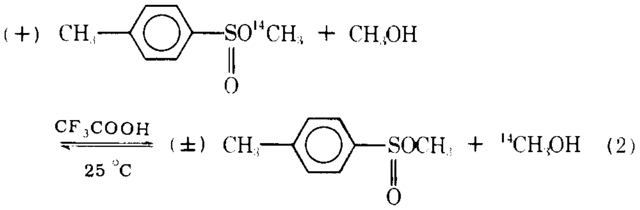
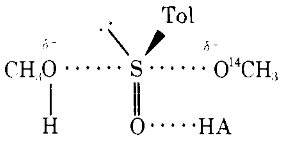


3, $[\alpha]_{589}$ +60.6° (ee, 27.3%)



$k_{rac} = (6.25 \pm 0.01)\ 10^{-5}\ s^{-1}$
$k_{ex} = (2.94 \pm 0.04)\ 10^{-5}\ s^{-1}$

The fact that **3** loses its optical rotation practically twice as fast as it loses the radioactive methoxy group proves unequivocally that the methoxy-methoxy exchange at sulfinyl sulfur proceeds stereospecifically with net inversion of configuration. This result is compatible with the simple bimolecular S_N2-S substitution for exchange involving a transition state (**7**) or with the mechanism involving a transient sulfurane intermediate (**8**).[13] If the latter mechanism is true, the postulated dialkoxysulfurane (**8**) would have a high barrier for the Berry-type pseudorotation since positions of all substituents at sulfur in trigonal bipyramid are most convenient from the point of view of apicophilicity. Therefore, **8** should undergo decomposition much faster than pseudorotation to give nucleophilic substitution product in a stereospecific manner.



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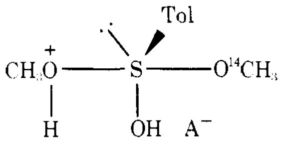

8

Full kinetics of the acid-catalyzed transesterification of sulfinates is being investigated.

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(6) The chirality at sulfur and optical purity of *n*-butyl *p*-toluenesulfinate (**2**) has been estimated as follows: (−)-*S*-menthyl *p*-toluenesulfinate, $[\alpha]_{589}$ −202°, was treated with *N,N*-diethylaminomagnesium bromide to give (+)-(*S*)-*N,N*-diethyl *p*-toluenesulfinamide, $[\alpha]_{589}$ +100°, which on treatment with 1-butanol in the presence of benzenesulfonic acid gave (−)-(*S*)-*n*-butyl *p*-toluenesulfinate (**2**), $[\alpha]_{589}$ −130° (ee, 70.4%). The ee value has been estimated chemically by means of the conversion of (−)-(*S*)-**2** into methyl *p*-tolyl sulfoxide, $[\alpha]_{589}$ +104.3° (ee, 70.4%).
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(12) The rate of racemization of **3** was measured with a Perkin-Elmer 241 MC photopolarimeter. The pseudo-first-order rate constant was calculated from the equation $\log(\alpha_0/\alpha_t) = kt/2.303$. The isotopic exchange experiments were carried out in sealed ampules which contained 0.5 mL of the solution. The samples were frozen at −78 °C before and after reaction. The reactants were separated by extraction in the system toluene (3 mL) and water (10 mL). The radioactivity of the organic phase was measured by the liquid scintilation method. The rate constant for the exchange was determined from the equation $\log[(I - I_\infty)/(I_0 - I_\infty)] = k_{ex}t/2.303$ where I_0, I, and I_∞ are the count rates of the sample at times 0, t, and $t = \infty$, respectively. The value of I_∞ was obtained experimentally for $t_\infty = 10\tau_{1/2}$.
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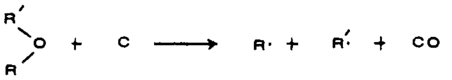
A Novel Rearrangement in the Reaction of Carbon Atoms with Furan

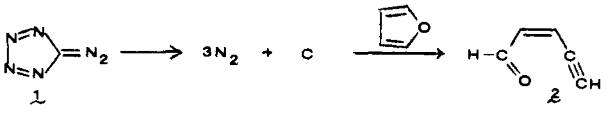
Sir:

The reactions of atomic carbon with substrates containing heteroatoms are generally thought to involve initial attack of the electron-dificient carbon at the most electronegative atom.[1] Thus simple ethers are attacked on oxygen to effect deoxygenation with the concurrent formation of a pair of radicals (eq 1).[2] We report here that the reaction of carbon atoms with the aromatic ether furan takes an entirely different course which is apparently dictated by the electron distribution in the highest occupied molecular orbital (HOMO).

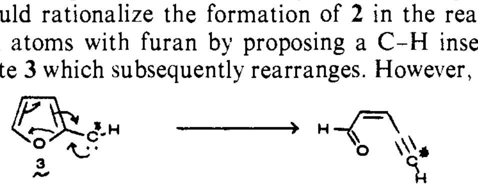


(1)

When atomic carbon was generated by the pyrolysis of 5-diazotetrazole[3,4] (**1**, 9.8 × 10^{-2} mmol) in the presence of gaseous furan (1.17 mmol), the major volatile organic product was *cis*-2-penten-4-ynal (**2**, 1.3 × 10^{-2} mmol). The fact that only trace amounts of carbon monoxide and acetylene are formed in this system indicates that deoxygenation is not an important pathway.



The unsaturated aldehyde **2** has previously been obtained in the rearrangement of the 2-furfurylcarbene, **3** (eq 2).[5] Thus one could rationalize the formation of **2** in the reaction of carbon atoms with furan by proposing a C–H insertion to generate **3** which subsequently rearranges. However, we have reported that atomic carbon is selective in its C–H insertions and invariably prefers the weakest C–H bond.[4] Since vinylic C–H bonds are rather strong and other sites are available for reaction, it does not seem likely that a C–H insertion by atomic



(2)

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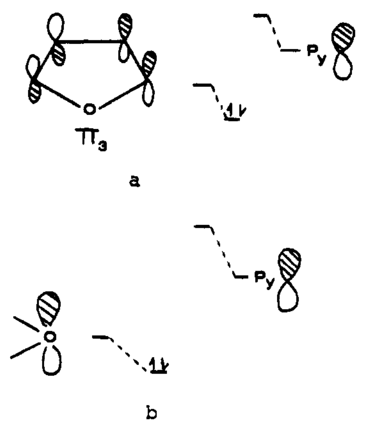
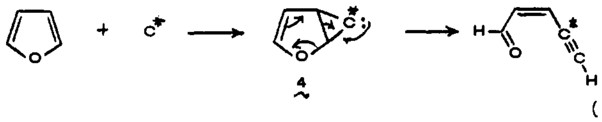


Figure 1.

carbon could be the major pathway in this system.

An alternate mode of attack is initial addition of carbon to one of the double bonds of furan to generate a cyclopropylidene intermediate **4**. The intermediacy of cyclopropylidenes has been well documented in the reaction of carbon with simple alkenes.[6-8] The cyclopropylidene, precluded in this system from normal rearangement to a cumulene, could ring open as shown in eq 3.

As indicated in both eq 2 and 3, the two mechanisms for the formation of **2** may be differentiated through the use of labeled carbon atoms. In order to do this, we synthesized **1**-^{13}C. The synthesis of the carbon-13-labeled diazo compound was accomplished using our previously reported procedure for the carbon-14-containing compound.[4] Authentic **2** was prepared according to the procedure of Schechter and Hoffmann[5] and its ^{13}C NMR measured.



(3)

Although the spectrum of **2** prepared by tosylhydrozone–lithium salt pyrolysis is complicated by the presence of a small amount of the trans isomer, we were able to assign the spectrum of *cis*-**2** as follows: C_1, 191.2; C_2, 139.6; C_3, 127.0; C_4, 88.9; C_5, 77.5 ppm. The assignmemt of the C_5 resonance was confirmed by an observed $J(^{13}C\text{-}H)$ of 254.8 Hz, a typical value for terminal alkyne carbons.[9] When carbon-13 atoms were allowed to react with furan, the spectrum of the product showed only peaks corresponding to carbons 4 and 5. Since the yield of **2** is small, carbons which are not labeled do not appear in the spectrum. Hence, we conclude that ^{13}C atoms react with furan to generate **2** which is labeled at carbons 4 and 5. The ratio of peak height of $C_4{:}C_5 = 1.33$ in the labeled sample as compared to $C_4{:}C_5 = 0.262$ in the unlabeled sample allows us to calculate that **2** is 83.5% labeled at C_4. Thus only a small amount of **2** arises by a C–H insertion, while the remainder probably results from addition to the double bond followed by the rearrangement shown in eq 3.

The fact that carbon atoms do not deoxygenate furan is not surprising when one considers that the furan HOMO (π_3) has no electron density on oxygen.[10] However, π_3 is of the proper symmetry to interact with the empty π orbital of atomic carbon to lower the energy of the transition state for addition to the double bond as shown in Figure 1a.

Attack of atomic carbon on an ether in which the HOMO is the nonbonding orbital on oxygen involves the HOMO–LUMO interaction in Figure 1b which favors attack on oxygen. Thus THF and other simple ethers are attacked by carbon atoms on oxygen.[2]

Reaction of carbenes, which also have an empty π orbital, with ethers appears to follow the same pattern. Thus methylene reacts with THF to give significant quantities of products resulting from attack on oxygen.[11] Furan, however, gives only products of addition to the double bond and of C–H insertion.[12] The rearrangement shown in eq 2 may be compared with that observed when substituted carbenes are added to furans to produce, either directly[13] or upon heating[14] substituted 2,4-pentadienals.

It is anticipated that the use of ^{13}C atoms in conjunction with ^{13}C NMR will allow the detection of other rearrangements of energetic species similar to that reported here.

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(3) Compound **1** was prepared by diazotization of 5-aminotetrazole in HCl and subsequent ether extraction as previously described.[4] Although **1** is extremely difficult to characterize owing to its explosive nature, we have previously formulated it as the diazonium chloride. However in the course of the present investigation, a mass spectrometric study of the thermolysis of **1** showed no HCl as a product. This result leads to the conclusion that 1 is a diazo compound.

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Ferricenyl(III)tris(ferrocenyl(II))borate. Synthesis, Electrochemistry, and Molecular Structure of an Unusual Mixed-Valence Zwitterion

Sir:

We report here our discovery of a novel mixed-valence ferrocene compound, namely, ferricenyl(III)tris(ferrocenyl(II))borate zwitterion (I) and our studies on its electrochemical, spectral, and structural characteristics. An X-ray crystallographic investigation of I has revealed its unique molecular structural features and furnishes valuable information about its electron-transfer processes. Compound I consists of three ferrocenyl(II) and one ferricenyl(III) moieties covalently attached to a tetravalent boron atom, hence the formal description of the complex as a zwitterion. In contrast to mixed-valence biferrocenes with π-bonding bridges[1] through which intervalence charge transfer takes place, it was anticipated that there would be little or no charge transfer through a coordinatively saturated[2a] boron atom. However, data presented below suggest that I acts as a mixed-valence system.

The reaction of an excess ferrocenyllithium, FcLi where Fc = dicyclopentadienyliron, with tri-*n*-butylborane or BF_3 af-

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