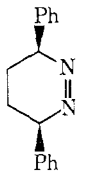

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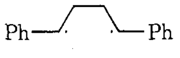

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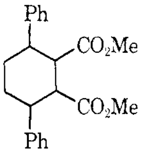

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surface with a secondary minimum (~10 kcal/mol deep) may be estimated. Despite the reasonably long lifetime (10^{-8} sec at 200°) indicated for a diradical on this surface, trapping by good "diylophiles" such as dimethyl maleate[22] and dodecanethiol[23] in pyrolysis (trapping agent used as solvent) and photolysis experiments is not observed. Expected products **5** and 1,4-diphenylbutane were obtained independently and shown to survive the decomposition conditions. The diradical dichotomy which persists involves a species which on the one hand may have a lifetime of a bond rotational period (for stereochemical loss *via* an intermediate) but which eludes direct detection ($\tau < 10^{-11}$ sec?). The latter elusiveness is predicted by theoretical calculation of the surfaces for small ring reorganizations.[24]

References and Notes

(1) (a) This work was presented in part at the Northeast Regional Meeting of the American Chemical Society, Rochester, N. Y., 1973, abstract no. 137. (b) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(6) *Traces of styrene and* **2** *were produced in these sensitization runs,* and benzophenone was the most effective energy transfer agent (ϕ_{styrene} = 0.004). This parallels behavior reported earlier by Brown.[7] It would appear that use of these and other low energy sensitizers (E_T < 74 kcal/mol) is effective through chemical or nonvertical energy transfer[8] (perhaps to an available low energy "diradical" triplet as with the 1,2-diphenylcyclopropanes[8b,9]) *rather* than through the conventional mechanism.

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(15) For comparison see the values for stereoretention[2d] which range over three orders of magnitude depending on substitution for several types of reaction involving in principle 1,4 diradicals. The comparison of photochemical stereoretention in **1** and **2** will be discussed in the full paper.

(16) The effect of phenyl substitution on the activation energy for thermal cracking of **1** (lower than that for cyclobutane[17] by 15 kcal/mol/phenyl) is more consistent with the diradical mechanism than with a concerted process in which the effect of phenyl is expected to be much smaller (3-5 kcal/mol).[18]

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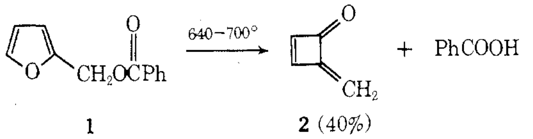
On the Mechanism of the Formation of Methylenecyclobutenone from the Pyrolysis of Furfuryl Benzoate

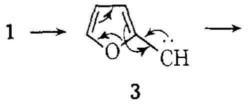
Summary: Aspects of the mechanism of the formation of methylenecyclobutenone by the pyrolysis of furfuryl benzoate are defined by the findings that pyrolysis of furfuryl-α,α-d_2 benzoate gives methylenecyclobutenone-*5,5*-d_2 and pyrolysis of 5-methylfurfuryl benzoate gives a good yield of 2,5-dimethylene-2,5-dihydrofuran.

Sir: Recently we reported that the low pressure (~10^{-4} Torr) gas phase pyrolysis of furfuryl benzoate (**1**) gives methylenecyclobutenone (**2**) in fair yield.[1]



1 **2** (40%)

A likely mechanism for this interesting reaction involves the initial formation of furfurylidene (**3**) by α elimination followed by rearrangement of this carbene to *cis*-pent-2-en-4-ynal (*cis*-**4**), rearrangement of *cis*-**4** to allenylketene (**5**), and rearrangement of **5** to **2**. This mechanism is supported by the fact that **3** is known to rearrange to **4**[2] and by the detection by ir and nmr spectroscopy of small amounts of *trans*-**4** in the pyrolysis product mixture from **1**.



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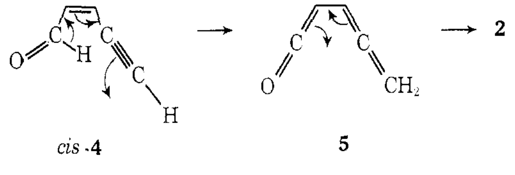
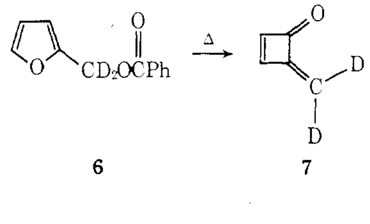


cis-**4** **5**

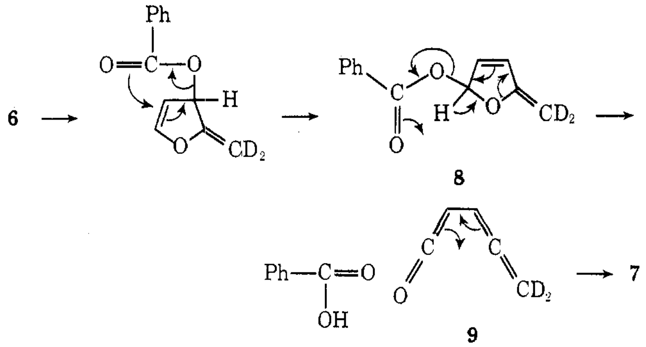
This mechanism predicts that pyrolysis of the α,α-dideuterio ester (**6**) would give **2** that contains only one deuterium atom. We wish to report that the pyrolysis of **6**[3] gives a 40% yield of **2** which has both methylene protons



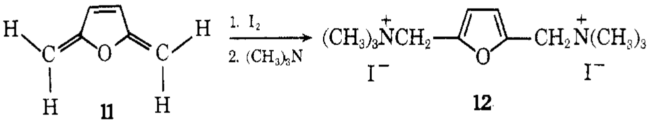
6 **7**

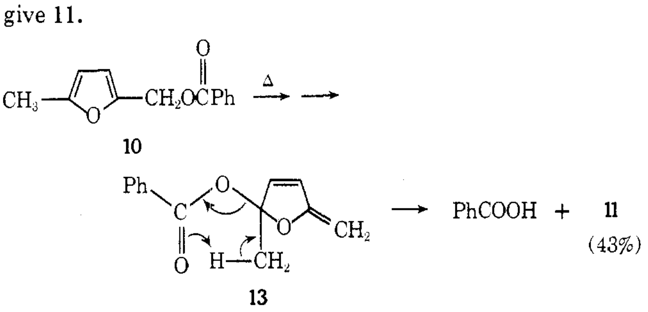
replaced with deuterium atoms (**7**). The nmr ($CDCl_3$) spectrum of the product shows only two strong peaks, a doublet (J = 2.75 Hz) at δ 8.65 and a doublet (J = 2.75 Hz) at 6.98. These peaks have been assigned to the ring protons of **2**[1] and their different splitting pattern (compared to **2**) is accounted for by the replacement of the two methylene protons with deuterium atoms. Integration of the *four* signals of **2** showed that each methylene position contained >96% deuterium.

These results clearly rule out the mechanism presented above which involves α elimination and indicate that both α substituents of the ester end up on the methylene carbon of the product, an observation that could be useful in attempting to prepare substituted methylenecyclobutenones. A mechanism which accounts for these results is the following one which involves initial migration of the benzoate group into the furan ring.[4]



Support for this mechanism was gained by the study of the pyrolysis of 5-methylfurfuryl benzoate (**10**). Pyrolysis of **10**[5,6] at 640° gave a 43% yield of 2,5-dimethylene-2,5-dihydrofuran (**11**). Compound **11** was identified by its nmr spectrum [δ 6.41 (s, 2), 4.50 (d, J = 1.5 Hz, 2), 4.21 (d, J = 1.5 Hz, 2)] and conversion to the known[7] bis(quaternary ammonium iodide) **12**: nmr δ 7.06 (m, 2), 4.77 (m, 4), 3.27 (s, 18); dec pt 227–229° (lit.[7] dec pt 227–229°). Production of **11** is consistent with the above mechanism since the expected intermediate **13** should undergo β elimination to give **11**.





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(3) Ester **6** was prepared by reducing methyl 2-furoate with lithium aluminum deuteride (Ventron Co., Alfa Products, 97.5% D) and esterifying the alcohol with benzoyl chloride in the presence of triethylamine. The nmr spectrum of **6** showed no α protons and mass spectral analysis indicated that the ester was 94% d_2, 5% d_1, and 1% d_0.
(4) The conversion of **8** to **9** could be a one-step process or a two-step process involving α elimination of benzoic acid to form a carbene which then rearranges to **9**.
(5) Ester **10** was prepared by reducing 5-methyl-2-furfural (Aldrich) with sodium borohydride in water and esterifying the alcohol with benzoyl chloride in the presence of pyridine: nmr ($CDCl_3$) δ 8.00–7.12 (m, 5), 6.35 (d, J = 3.2 Hz, 1, H_3), 5.91 (m, 1, H_4), 5.22 (s, 2, CH_2), 2.28 (s, 3, CH_3); ir ($CDCl_3$) 1715 (vs), 1265 (vs), 1100 (m), 1089 (m) cm^{-1}; mass spectrum calcd for $C_{13}H_{12}O_3$ 216.07865, found 216.07846.
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Alkylation of α-Bromosulfonyl Compounds with Trialkylboranes

Summary: α-Alkylated sulfonyl derivatives have been prepared in good yields by treatment of the corresponding α-bromosulfonyl compounds with trialkylboranes in the presence of potassium *tert*-butoxide.

Sir: One general method for the preparation of sulfonyl derivatives[1] involves alkylation of α-sulfonyl carbanions. This method is likely to suffer in those systems where alkyl halides other than primary are employed, or for unsymmetrical sulfones when there is little if any difference in the relative acidities of the hydrogens α to the sulfonyl grouping. Trialkylboranes have been shown to serve as excellent alkylating agents for α-haloalkanoic esters, α-halo ketones, and α-halonitriles.[2] We wish to report the facile reaction of α-bromomethanesulfonyl compounds[3] with trialkylboranes under the influence of potassium *tert*-butoxide to produce the alkylated derivatives in good to excellent yields (eq 1).

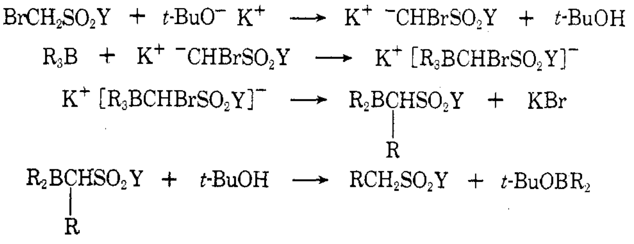
$$R_3B + BrCH_2SO_2Y \xrightarrow[tert\text{-BuOH}]{tert\text{-BuOK}} RCH_2SO_2Y \qquad (1)$$

$$Y = C_6H_5,\ C_2H_5,\ OCH_2C(CH_3)_3,\ N(C_2H_5)_2$$

The reaction is easily performed and appears to be complete within a relatively short period of time under mild conditions. The trialkylborane is prepared by treating the appropriate olefin with a calculated amount of diborane in tetrahydrofuran according to the standard procedure.[4] The bromosulfonyl derivative is then added, followed by dropwise addition of potassium *tert*-butoxide in *tert*-butyl alcohol at either 0 or −40°. The results of this study are summarized in Table I. The reaction appears to be general, although somewhat lower isolated yields are realized employing cyclic secondary boranes.

Presumably the reaction involves the steps indicated in Scheme I.[2]

Scheme I



$$BrCH_2SO_2Y + t\text{-BuO}^- K^+ \longrightarrow K^+\ {}^-CHBrSO_2Y + t\text{-BuOH}$$
$$R_3B + K^+\ {}^-CHBrSO_2Y \longrightarrow K^+[R_3BCHBrSO_2Y]^-$$
$$K^+[R_3BCHBrSO_2Y]^- \longrightarrow R_2\underset{\underset{\displaystyle R}{|}}{B}CHSO_2Y + KBr$$
$$R_2\underset{\underset{\displaystyle R}{|}}{B}CHSO_2Y + t\text{-BuOH} \longrightarrow RCH_2SO_2Y + t\text{-BuOBR}_2$$

The following procedure for the preparation of cyclopentylmethyl phenyl sulfone is representative.

A dry 50-ml round-bottomed flask equipped with a septum inlet, a magnetic stirring bar, and a nitrogen inlet was flushed with nitrogen and maintained under a constant pressure of nitro-