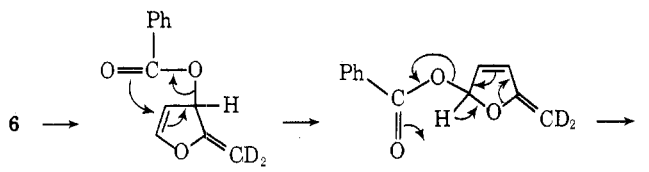
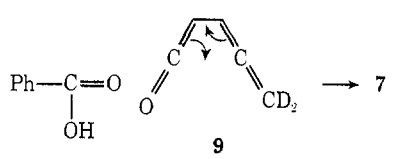
replaced with deuterium atoms (7). The nmr ($CDCl_3$) spectrum of the product shows only two strong peaks, a doublet ($J$ = 2.75 Hz) at $\delta$ 8.65 and a doublet ($J$ = 2.75 Hz) at 6.98. These peaks have been assigned to the ring protons of 2[1] and their different splitting pattern (compared to 2) 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 $\alpha$ elimination and indicate that both $\alpha$ 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]

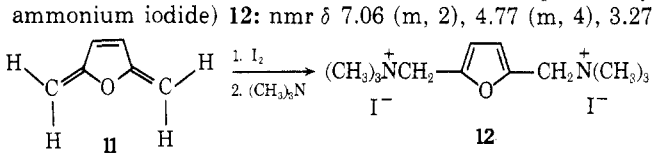


8

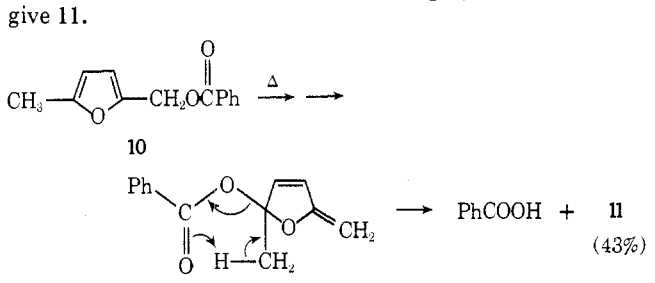


9

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 [$\delta$ 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 $\delta$ 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 $\beta$ elimination to give 11.



13

(43%)

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(2) R. V. Hoffman and H. Shechter, *J. Amer. Chem. Soc.*, **93**, 5940 (1971).

(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 $\alpha$ 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 $\alpha$ 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 ($CDCl_3$) $\delta$ 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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*Received January 29, 1974*

## Alkylation of $\alpha$-Bromosulfonyl Compounds with Trialkylboranes

*Summary:* $\alpha$-Alkylated sulfonyl derivatives have been prepared in good yields by treatment of the corresponding $\alpha$-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 $\alpha$-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 $\alpha$ to the sulfonyl grouping. Trialkylboranes have been shown to serve as excellent alkylating agents for $\alpha$-haloalkanoic esters, $\alpha$-halo ketones, and $\alpha$-halonitriles.[2] We wish to report the facile reaction of $\alpha$-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**

$$BrCH_2SO_2Y + t\text{-}BuO^- K^+ \longrightarrow K^+ {}^-CHBrSO_2Y + t\text{-}BuOH$$

$$R_3B + K^+ {}^-CHBrSO_2Y \longrightarrow K^+ [R_3BCHBrSO_2Y]^-$$

$$K^+ [R_3BCHBrSO_2Y]^- \longrightarrow R_2BCHSO_2Y + KBr \quad (R = \text{alkyl})$$

$$R_2BCHSO_2Y + t\text{-}BuOH \longrightarrow RCH_2SO_2Y + t\text{-}BuOBR_2$$

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-

**Table I**

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

**1**, R = *n*-$C_4H_9$ **a**, Y = $C_6H_5$ **1a–6d**
**2**, R = *i*-$C_4H_9$ **b**, Y = $C_2H_5$
**3**, R = *n*-$C_6H_{13}$ **c**, Y = $OCH_2C(CH_3)_3$
**4**, R = *n*-$C_8H_{17}$ **d**, Y = $N(C_2H_5)_2$
**5**, R = c-$C_5H_9$
**6**, R = c-$C_6H_{11}$

| Borane | a[a] % yield[b] | a[a] Mp, °C | b[a] % yield[b] | b[a] Mp [bp (mm)], °C | c[a] % yield[b] | c[a] Bp, °C (mm) | d[a] % yield[b] | d[a] Bp, °C (mm) |
|---|---|---|---|---|---|---|---|---|
| **1** | 99 | 31.5–32.5[c] | 78 | 57.5–60[d] | 76 | 77 (0.1) | 84 | 87 (0.1) |
| **2** | 92 | 35–36.5[e] | 81 | [74 (0.1)][f] | 59 | 87 (0.3) | 82 | 74 (0.1) |
| **3** | 96 | 37–38 | 91 | 67–69 | 76 | 97 (0.05) | 85 | 110 (0.6) |
| **4** | 79 | 42–43 | 81 | 75–77 | 75 | 123 (0.15) | 77 | 120 (0.35) |
| **5** | 82 | 37–38 | 78 | [101 (0.1)] | 73 | 106 (0.15) | 68 | 102 (0.35) |
| **6** | 87 | 52–53[g] | 65 | [110 (0.1)] | 60 | 111 (0.5) | 72 | 111 (0.5) |

[a] The nmr and ir spectral data of the products were consistent with the assigned structures. [b] Isolated yields. [c] Lit. mp 28.7–31.6°,[5] 31–32°.[6] [d] Lit.[5] mp 56–57°. [e] Lit.[6] mp 35.5–36.5°. [f] Lit.[7] mp 15°. [g] Lit.[8] mp 53–54°.

gen. The flask was charged with 4.25 ml of a 2.35 *M* solution of borane (30 mmol of hydride) in tetrahydrofuran and diluted with an additional 8 ml of tetrahydrofuran. The solution was cooled to 0° with stirring and cyclopentene (2.65 ml, 30 mmol) was added dropwise *via* a syringe over a 3-min period; then the clear solution was stirred at room temperature for 1 hr. The mixture was cooled to 0° and a solution of bromomethyl phenyl sulfone (2.35 g, 10 mmol, in 10 ml of tetrahydrofuran) was added *via* Cannula. Potassium *tert*-butoxide (9.1 ml of a 1.10 *M* solution in *tert*-butyl alcohol, 10 mmol) was added dropwise *via* a syringe over a 20-min period while the reaction stirred at 0°.[9] The addition of the first few drops of base to the clear solution immediately produced a white precipitate and the reaction remained heterogeneous until work-up.

After the reaction mixture had been stirred an additional 30 min at 0°,[10] sodium hydroxide (5.0 ml, 3 *N* aqueous solution, 15 mmol) was added followed by *slow*, dropwise addition of hydrogen peroxide (5.0 ml, 30% aqueous solution, 48 mmol); both solutions were added *via* a syringe. The mixture was stirred at 55° for 2 hr and cooled to room temperature, diethyl ether added, and the aqueous layer removed. The organic layer was washed with two 10-ml portions of water and one 10-ml portion of brine, dried over $MgSO_4$, and filtered. Concentration *in vacuo* yielded a residue, which was recrystallized from an ether–pentane mixture to yield 1.85 g of cyclopentylmethyl phenyl sulfone, mp 37–38°, 82%.

## References and Notes


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(9) The addition of base in the bromomethyl ethyl sulfone series was done at −40°, maintained at −40° for 30 min, then slowly warmed to 0°.
(10) For the sulfonamides, initial addition of base was done at 0°; then the reaction was allowed to proceed overnight at ambient temperature before work-up. Dichlormethane was used rather than ether for extractions in this series.


(11) Financial support to L. A. M. by the Colgate-Palmolive Co. during the course of this work is hereby gratefully acknowledged.



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*Received January 16, 1974*