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# OXASPIROPENTANES

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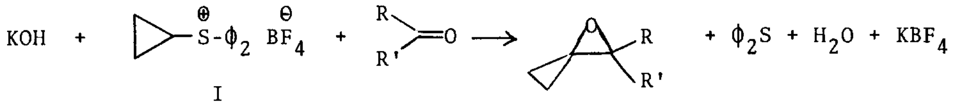
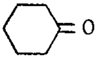
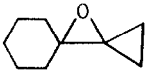
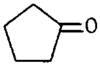
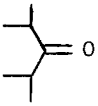
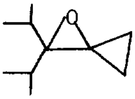
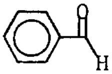
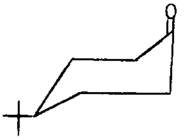
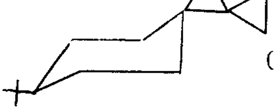
Recently, we reported a useful spiroannelation procedure including a novel cyclobutanone synthesis that employed diphenylsulfoniumcyclopropylide as a new synthetic intermediate.[1,2] The proposed pathway of the cyclobutanone formation involved the intermediacy of an oxaspiropentane;[1-5] however, their detection as intermediates was unsuccessful. In view of recent communications dealing with these previously elusive and highly reactive compounds,[3,4] we wish to report their isolation in good yield by the sulfoniumcyclopropylide one-step method and to discuss their possible mode of formation.

Treatment of an equimolar solution of cyclopropyldiphenylsulfonium fluoroborate(I) and a carbonyl partner with solid potassium hydroxide at 25°C in dimethylsulfoxide followed by flash distillation of the crude extract *in vacuo* resulted in the isolation of the pure oxaspiropentanes. Table I summarizes the results. Spectral data and their further chemical transformation to cyclobutanones establish their structures. Although monoaryl substituted carbonyls allowed isolation of the oxaspiropentane, only rearranged cyclobutanones were detected with benzophenone and cyclopropylmethyl ketone.



I

Table I. Preparation of Oxaspiropentanes

| Ketone or aldehyde | Oxaspiropentane | | % Yield[a] |
|---|---|---|---|
|  |  | (II) | 81[b] |
|  |  | (III) | 72 |
|  |  | (IV) | 59 |
|  |  | (V) | 87 |
|  |  | (VI) | 70[c] |

a) Yield of isolated pure product based on 1 eq of sulfonium salt.
b) 1.25 equivalents of sulfonium salt results in 97% yield.
c) Crystalline solid, mp 26.5-27.0°.

Table II. Spectroscopic Properties

I. UV (EtOH): nm (ε); 231(3840); 261(515); 267(654); 274(522).
Nmr: ($CDCl_3$): 1.3-1.7δ, mult, 4H; 3.5-3.9δ, mult, 1H; 7.5-8.1δ, mult, 10H.
Ir ($CHCl_3$): 3.23, 6.32, 14.74, strong 9-10 due to $BF_4^{\ominus}$.

II. Nmr ($CCl_4$): 0.58-1.02δ, mult, 4H; 1.60δ, bs, 10H.
Ir ($CCl_4$): 3.26, 9.28, 9.55, 9.99, 11.04, 11.58.

III. Nmr ($CCl_4$): 0.59-1.08δ, mult, 4H; 1.80δ, bs, 8H.
Ir ($CCl_4$): 3.25, 9.28, 9.79, 10.01, 10.58, 10.78, 11.09.

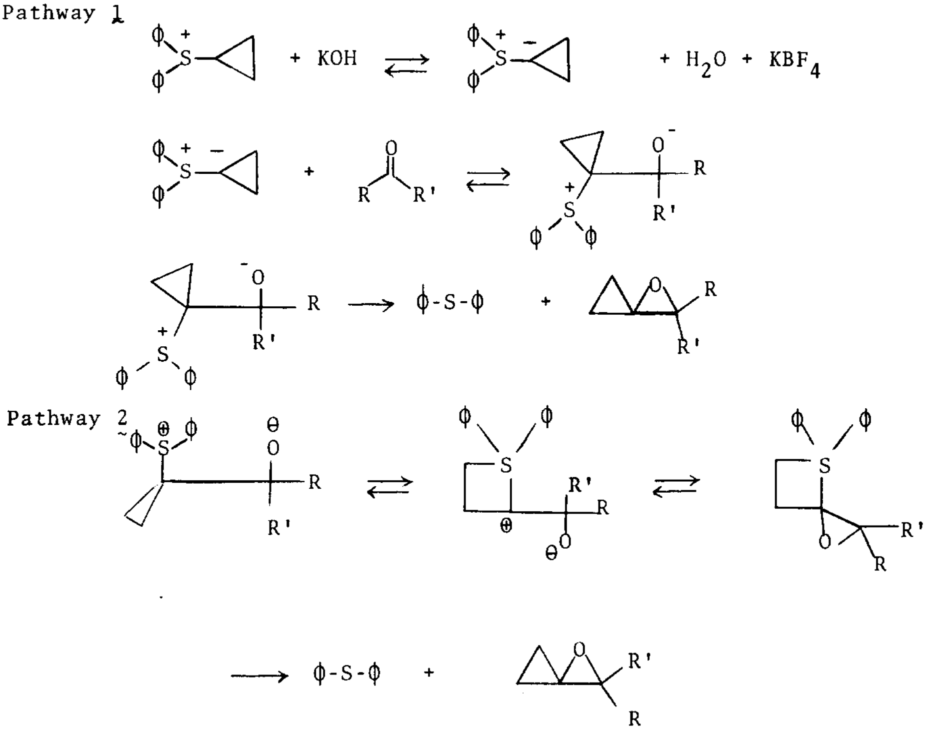
IV. Nmr ($CCl_4$): 0.70-1.10δ, mult, 16H; 2.07δ, sept. J = 6.5 Hz, 2H.
Ir ($CCl_4$): 3.25, 9.28, 9.39, 9.80, 10.21, 10.87, 11.42, 11.93.

V. Nmr ($CCl_4$): 0.8-1.2δ, mult, 4H; 4.14δ, s, 1H; 7.20δ, bs, 5H.
Ir ($CCl_4$): 3.25, 9.28, 9.38, 9.80, 9.98, 10.28, 10.99, 11.25, 11.60, 14.5.

VI. Nmr ($CCl_4$): 0.7-0.9δ, mult, 4H; 0.92δ, s, 9H; 1.1-1.9δ, mult, 9H.
Ir ($CCl_4$): 3.24, 9.28, 10.05, 10.58, 11.02, 11.85.

Scheme I presents a rationalization for the formation of oxaspiropentane.

Scheme I. Rationalization of the Reaction Courses



In this reaction, the unusual elimination of diphenylsulfide from a cyclopropyl ring is a facile process occurring even at -40°. On the other hand, treatment of the sulfonium salt with sodium deuteroxide in $D_2O$ at 75° for 2 hr, yields no decomposition; only complete deuterium incorporation α to sulfur is observed. Thus, an Sn2 displacement, even intramolecular, must be suspect (pathway **1**). Alternatively (pathway **2**), a sulfurane intermediate would be consistent with present results.[6]

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## References

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