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A NOVEL METHOD FOR SPIRO ANNULATION. REACTION OF CYCLIC SULFONIUM YLIDES WITH KETENE DIMER

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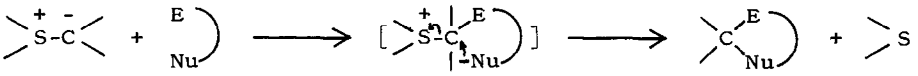
Through our recent research in the area of sulfonium ylide chemistry, we became interested in annulation methods by way of methylene transfer of sulfonium ylides[1,2]. The methylene transfer is considered to proceed through a series of two reactions, i.e., an initial electrophilic addition toward a sulfonium ylide and subsequent intramolecular nucleophilic displacement of the resulting sulfonium betaine accompanied with elimination of the sulfide (eq 1). For example, it was shown in an earlier paper[3] that the reaction between dimethylsulfoniumphenacylide and ketene dimer gave a 3-hydroxyfuran derivative by transfer of substituted methylene in the manner as described in eq 1.

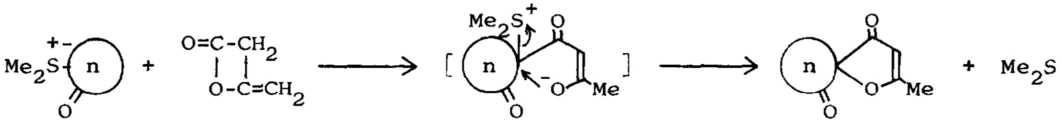


E : Electrophile (eq 1)
Nu: Nucleophile

On the basis of the above fact, it was suggested that the use of cyclic sulfonium ylides would make it possible to form spiro rings directly from two cyclic components. There has been much recent interest in spiro compounds in connection with photochromism[4], pharmacological activities[5] and polymers[6]. Concerning spiro annulations, however, the method of the direct annulation from two cyclic components has not yet been reported[7].

We wish to report in this paper a new and facile annulation method for the synthesis of spiro furan derivatives by way of transfer of substituted methylene of cyclic sulfonium ylides (I) to ketene dimer (II).

When a benzene solution of II (5 mmole) was added dropwise at room temperature to a suspension of dimethylsulfonium-2-oxocyclohexylide[8] (Ia) (5 mmole) in benzene, an exothermic reaction soon took place and the precipitates of Ia gradually disappeared giving a slight yellow solution. After stirring over night followed by an hour's warming at 65°, the solvent was evaporated to give 1-oxa-2-methyl-4,6-dioxospiro[4,5]decene-2 (IIIa) in 94% yield, mp 84.5-86.0° (recrystallized from ether).



(eq 2)

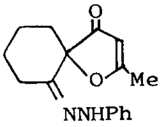
(I) (II) (III)

a, n=6 a, n=6 94%

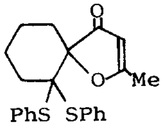
b, n=7 b, n=7 97%

The structural assignment was made on the basis of elemental analysis and spectroscopic data [Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.66; H, 6.70. Infrared spectrum (KBr): 1724 (saturated ketone), 1690 (α,β-unsaturated ketone) and 1610 (conjugated olefin) cm^{-1}. NMR spectrum ($CDCl_3$): δ 1.5-2.65 (6H, m, C_3H_6), 2.29 (3H, s, CH_3), 2.91 (2H, a pair of triplets, CH_2-$C\underline{H}_2$-CO) and 5.27 (1H, s, C=C-H) ppm. Ultraviolet spectrum: λ_{max}^{EtOH} 266 mμ (ϵ 9,500).].

Further proof for the structure IIIa was obtained by the fact that the reaction of IIIa with phenylhydrazine afforded phenylhydrazone (IV)[9], mp 84.0-85.0°. In addition, IIIa was converted to diphenyl mercaptole (V)[9], mp 114.5-115.5°, upon reaction with benzenethiol in the presence of catalytic amount of boron trifluoride etherate.



(IV)



(V)

The photochemical reactions of IIIa and its derivatives are now under investigation.

In a similar manner, a seven-membered cyclic sulfonium ylide, dimethylsulfonium-2-oxocycloheptylide (Ib) afforded the corresponding spiro furan derivative (IIIb), mp 105-106°, in 97% yield by the reaction with II. Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 67.76; H, 7.17. Infrared spectrum (KBr): 1727 (saturated ketone), 1682 (α,β-unsaturated ketone) and 1602 (conjugated olefin) cm^{-1}. NMR spectrum ($CDCl_3$): δ 1.2-2.6 (8H, m, C_4H_8), 2.32 (3H, s, CH_3), 2.98 (2H, a pair of triplets, CH_2-$C\underline{H}_2$-CO), and 5.31 (1H, s, C=C-H) ppm. Ultraviolet spectrum: λ_{max}^{EtOH} 266 mμ (ϵ 9,100).

In conclusion, it is noted that the reaction of I with II afforded spiro furans III in excellent yields under mild conditions by the direct annulation. The process provides a general method for the formation of spiro ring systems from two cyclic components. Further investigation will be made on this point of view.

REFERENCES

1) T. Mukaiyama, M. Higo, and H. Takei, Bull. Chem. Soc. Japan, **43**, 2566 (1970).

2) M. Higo and T. Mukaiyama, Tetrahedron Letters, 2565 (1970).

3) H. Takei, M. Higo, K. Saito, and T. Mukaiyama, Bull. Chem. Soc. Japan, **41**, 1738 (1968).

4) (a) R. Dessaver, J. P. Parvis, "Advance in Photochemistry", Vol. 1, Inter. Pub., N. Y. (1963);

(b) J. B. Flannery, Jr., J. Amer. Chem. Soc., **90**, 5660 (1968).

5) (a) C. H. Grogan, R. Kelley, and L. M. Rice, *J. Med. Chem.*, **9**, 654 (1966);
(b) J. R. Bamburg, W. F. Marasas, N. V. Riggs, E. B. Smalley, and F. M. Strong, *Biotechnol. Bioeng.*, **10**, 445 (1968).

6) A. A. Volpe and W. J. Bailey, AD 641873 (1966).

7) It has been reported recently that a spiro cyclobutanone derivative was obtained by a spiro annulation by means of diphenylsulfoniumcyclopropylide through molecular rearrangement. See, B. M. Trost, R. LaRochelle, and M. J. Bogdanowicz, *Tetrahedron Letters*, 3449 (1970).

8) T. Mukaiyama and M. Higo, *Tetrahedron Letters*, 5297 (1970).

9) Satisfactory elemental analysis and ir and nmr spectra were obtained.