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THE RING EXPANSION OF A CYCLIC SULFONIUM YLIDE THROUGH A 1,3-ACYL REARRANGEMENT

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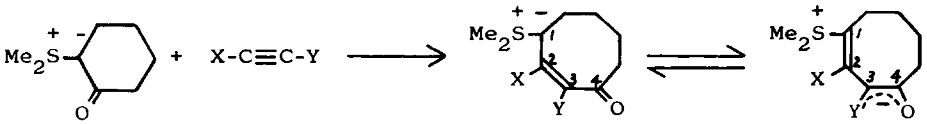
In the preceding paper¹⁾, it was shown that 3,4-furandicarboxylic acid derivatives were produced by the reactions of sulfonium ylides with dimethyl acetylenedicarboxylate (IIa) through a 1,3-acyl rearrangement.

In the present experiment, a new ring expansion of a cyclic sulfonium ylide through an intramolecular 1,3-acyl rearrangement by the reaction with acetylenic compounds was investigated. When dimethylsulfonium-2-oxo-cyclohexylide (I)²⁾ was treated with dimethyl acetylenedicarboxylate (IIa) in dimethyl sulfoxide (DMSO) at 18°C under an atmosphere of nitrogen, an exothermic reaction soon took place and, from the resulting dark brown solution, yellow precipitates were immediately deposited. The precipitates, dimethylsulfonium-2,3-dicarbomethoxy-4-oxo-2-cyclooctenylide (IIIa), were filtered and washed well with benzene, mp 166.5-167.5°C(dec). The yield of IIIa was quantitative. The structural assignment was made on the basis of spectral data [IR(KBr): 1726, 1627(CO_2Me), 1575(C=C) and 1528(C=O) cm^{-1}. NMR(DMSO-d_6): δ=1.3-2.3(8H, m, C_4H_8), 2.94(6H, s, $Me_2\overset{+}{S}$), 3.33(3H, s, CO_2Me) and 3.64(3H, s, CO_2Me) ppm] and of the quantitative formation of a sulfonium salt (IVa)³⁾ with 2,4,6-trinitrobenzenesulfonic acid(TNBS-H).



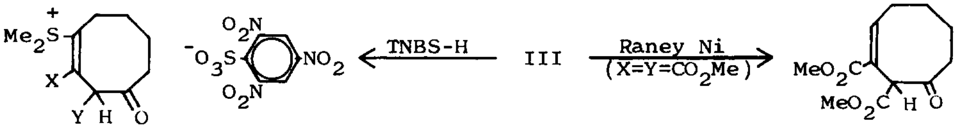
(I) (II) (III)

Table 1. The Reactions of I with II

	X	Y	III Yield (%)	mp* (°C)	IV mp* (°C)
a	CO_2Me	CO_2Me	100	166.5-167.5	202.0
b	COPh	COPh	52	136.0-138.0	196.5
c	Ph	CO_2Et	55	137.0-139.0	201.0
d	Ph	COPh	82	165.0-166.0	211.0

* Decomposing point.

The NMR spectrum(DMSO-d_6) of IVa showed a low field peak at δ=12.80 attributable to a partially enolated α-proton in the β-keto ester system. It is thus obvious that IVa exists in the form of a vinylsulfonium salt rather than that of an allylsulfonium salt.

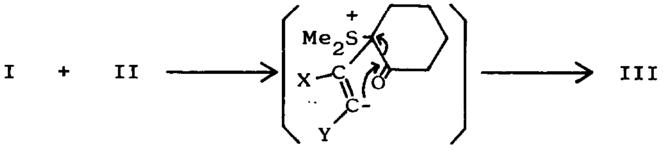


(IV) (V)

The structure of IIIa, the ring expansion product, was firmly supported by the fact that IIIa was desulfurized by Raney nickel to afford dimethyl 8-oxo-2-cyclooctene-1,2-dicarboxylate (V)[3] in a 50% yield, identical with an authentic sample[4].

In a similar manner, when dibenzoylacetylene (IIb), ethyl phenylpropiolate (IIc) and benzoylphenylacetylene (IId) were treated with I, the corresponding ring expansion compounds (IIIb-d) were obtained in good yields. Similarly, IIIb-d afforded TNBS salts (IVb-d)[3]. In the cases of asymmetric acetylenes, IIc and IId, the NMR spectra of IVc and IVd indicate that electron attracting groups, i.e. carboethoxy and benzoyl groups, are attached to C_3 of III. The reaction of I with phenylacetylene, however, did not occur even after the prolonged stirring for several days at room temperature. These results are summarized in Table 1.

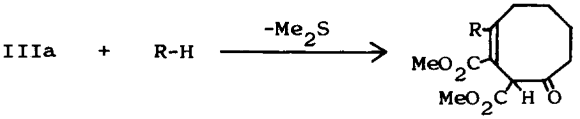
It is reasonable to consider that the reaction of I with II proceeds through an intermediate betaine (VI), which is transformed into III accompanied with the intramolecular 1,3-migration of the acyl group. The chemical driving force of the reaction is probably due to the enhanced stability of III over I gained from the extended conjugation formed by the acyl migration.



(VI)

Concerning the ring expansion reactions involving the direct addition of two carbon atoms, it has been reported by Brannock et al.[5)] that n-membered cyclic enamines (n=5,6,7,8 and 12) afforded (n+2)-membered ones by treatment with IIa in good yields with the exception of n=6. In this case, cyclooctanone enamine was formed only in ca. 8% yield.

Next, the reactions of IIIa with nucleophilic reagents were investigated. When IIIa was allowed to react with nucleophiles as methanol, thiols and hydrogen cyanide, cyclooctenone derivatives (VII)[3)] were obtained in high yields with elimination of dimethyl sulfide. These results are listed in Table 2.



(VII)

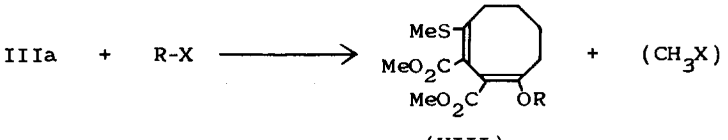
Table 2. The Reactions of IIIa with Nucleophiles

Nucleophile	Reaction Condn.			VII	
	Solvent	Temp.	Time (hr)	R	Yield (%)
MeOH	MeOH	65°C	9	MeO	90
EtSH	Benzene	RT	19	EtS	95
PhSH	Benzene	RT	33	PhS	80
HCN*	Benzene	RT	48	NC	60

* The reaction was carried out with twofold excess of hydrogen cyanide generated in situ from potassium cyanide and acetic acid.

On the other hand, the reactions of IIIa with several active methylene compounds in various solvents resulted only in the formation of dimethyl 3-methylthio-8-oxo-2-cyclooctenedicarboxylate (VII, R=MeS)[3] in 23-74% yield.

In addition, it was established that the reactions of IIIa with acyl and alkyl halides gave vinyl esters (VIII, R=acyl)[3] and vinyl ethers (VIII, R=alkyl)[3], respectively. These results are listed in Table 3.



(VIII)

Table 3. The Reactions of IIIa with Acyl and Alkyl Halides

Halide	Reaction Condn.			VIII	
	Solvent	Temp.	Time (day)	R	Yield (%)
CH_3COCl	Benzene	RT	2	CH_3CO	59
PhCOCl	Benzene	RT	1	PhCO	68
MeJ	MeJ	50°C	0.4	Me	74
$PhCH_2Br$	DMSO	RT	1.5	$PhCH_2$	23

In conclusion, it is noted that the reactions of I with II in DMSO afforded the ring expansion (six membered to eight membered) compounds III through the 1,3-acyl rearrangement in high yields under mild conditions. The cyclic sulfonium ylide III, having a reactive sulfonium group, was found to be an important intermediate for the syntheses of various cyclooctane derivatives with cyclohexanone as a starting material.

REFERENCES

1. M. Higo and T. Mukaiyama, Tetrahedron Letters, 2565 (1970).
2. The ylide I was prepared from the corresponding sulfonium fluoborate by the action of sodium hydroxide.
3. Satisfactory elemental analyses and IR and NMR spectra were obtained.
4. An authentic sample of V was prepared by the method of Brannock *et al.*[5].
5. K. C. Brannock, R. D. Burpitt, V. W. Goodlett, and J. G. Thweatt, J. Org. Chem., **28**, 1464 (1963).