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Ring Expansion through a 1,3-Acyl Rearrangement. Reactions of Cyclic Sulfonium Ylides with Acetylenic Compounds[1]

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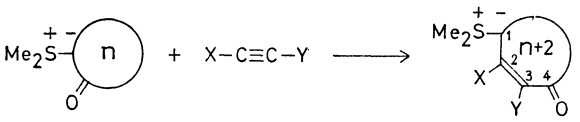
Ring expansion of cyclic sulfonium ylides with acetylenic compounds was investigated. It was found that a six-membered cyclic sulfonium ylide (I) gave eight-membered ring expansion products (IIIa—e) in high yields under mild conditions on treatment with acetylenic compounds (IIa—e) in dimethyl sulfoxide. In a similar manner, the reactions of five- and seven-membered cyclic sulfonium ylides with II afforded ring expansion products (XIa) and (IXa—c). The ring expansion was considered to proceed through an intramolecular 1,3-acylrearrangement. It was found that, when the reaction of I and IIa was carried out in benzene, an intermediate bicyclic sulfonium betaine (VIIa) was obtained as yellow precipitates. The properties and reactions of VIIa were investigated. It was shown that the ring expansion product IIIa gave cyclooctenone derivatives (XIIa—c) by the reaction with some nucleophiles. IIIa was found to give diene esters (XIII, R=acyl) and diene ethers (XIII, R=alkyl) upon reaction with acyl and alkyl halides.

It was found[2] that 3,4-furandicarboxylic acid derivatives were produced by the reactions of sulfonium ylides with dimethyl acetylenedicarboxylate through a 1,3-acyl rearrangement.

This paper deals with a new ring expansion of cyclic sulfonium ylides by two carbon atoms[3] by the reactions with acetylenic compounds through an intramolecular 1,3-acyl rearrangement.



(I) (n=6) (II) (III) (n=6)
(VIII) (n=7) (IX) (n=7)
(X) (n=5) (XI) (n=5)

When a six-membered cyclic sulfonium ylide, *i.e.*, dimethylsulfonium-2-oxocyclohexylide (I) was treated with dimethyl acetylenedicarboxylate (IIa) in dimethyl sulfoxide (DMSO), an exothermic reaction soon took place and a ring expansion product, dimethylsulfonium-2,3-dicarbomethoxy-4-oxo-2-cyclooctenylide (IIIa) was obtained in quantitative yield. The IR spectrum of IIIa showed strong absorptions at 1726, 1627, and 1528 cm^{-1}. The absorption at 1726 cm^{-1} can be attributed to the unsaturated ester carbonyl and those at 1627 and 1528 cm^{-1} to the ester and ketone carbonyl, respectively, both conjugated with the ylide carbanion.[2,4,5] Based upon IR, NMR, and UV spectra, IIIa was found to have the structure of a sulfonium ylide stabilized by a conjugated system.[2,4] The ylide IIIa gave a sulfonium salt (IVa) with 2,4,6-trinitrobenzenesulfonic acid (TNBS-H) in quantitative yield.

The NMR spectrum of IVa showed a low field peak

1) Preliminary report, T. Mukaiyama, and M. Higo, *Tetrahedron Lett.*, **1970**, 5297.

2) M. Higo and T. Mukaiyama, *ibid.*, **1970**, 2565.

3) C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York and London, (1968), p. 161.

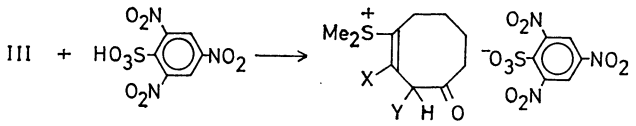
4) (a) C. Kaiser, B. M. Trost, J. Beeson, and J. Weinstock, *J. Org. Chem.*, **30**, 3972 (1965); (b) J. Ide and Y. Kishida, *Tetrahedron Lett.*, **1966**, 1787.

5) (a) B. M. Trost, *J. Amer. Chem. Soc.*, **89**, 138 (1967); (b) G. B. Payne, *J. Org. Chem.*, **33**, 3517 (1968).

TABLE 1. RING EXPANSION OF THE SIX-MEMBERED CYCLIC SULFONIUM YLIDE (I) WITH ACETYLENIC COMPOUNDS (II)

	X	Y	III			III·TNBS-H (IV)					
			Yield (%)	Mp (°C)[a]	IR, $\nu_{C=O}$ (cm^{-1})	Mp (°C)[a]	NMR δ (ppm)[b]	*Anal.* (%)			
									C	H	N	S
a	CO_2Me	CO_2Me	100	166.5—167.5	1726, 1627, 1528	202.0	12.80	Found	40.40	4.21	7.13	10.66
								Calcd	40.47	3.92	7.08	10.78
b	Ph	CO_2Et	55	137.0—139.0	1655, 1500,	201.0	13.02	Found	48.06	4.61	6.91	10.48
								Calcd	48.00	4.35	6.72	10.23
c	Ph	COPh	82	165.0—166.0	1534, 1512,	211.0	16.25	Found	53.16	4.23	6.42	9.70
								Calcd	52.97	4.14	6.39	9.73
d	COPh	COPh	52	136.0—138.0	1652, 1528, 1500	196.5	9.16	Found	52.49	4.19	6.39	9.56
								Calcd	52.55	3.94	6.13	9.34
e	H	CO_2Me	33[c]	c)	c)	183.0	13.00	Found	40.65	4.04	8.00	12.11
								Calcd	40.38	3.95	7.85	11.95

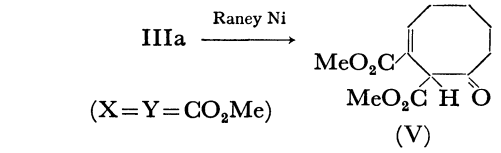
a) Decomposition point.
b) Chemical shift of an enolated proton[6] (in DMSO-d_6).
c) Isolated as 2,4,6-trinitrobenzenesulfonate.



TNBS-H (IV)

at δ=12.80 attributable to a partially enolated α-proton[6] 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.

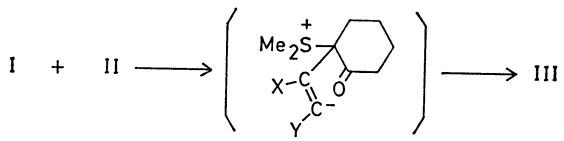
The structure of IIIa, the ring expansion product, was firmly supported by the fact that IIIa was desulfurized by Raney nickel to afford 2,3-dicarbomethoxy-4-oxocyclooctene (V) in 50% yield, identical with an authentic sample.[7]



(V)

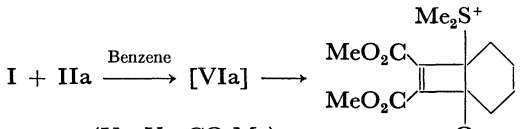
In a similar manner, when ethyl phenylpropiolate (IIb), benzoylphenylacetylene (IIc), dibenzoylacetylene (IId), and methyl propiolate (IIe) were treated with I, the corresponding ring expansion compounds (IIIb—e) were obtained in good yields. Similarly, IIIb—e afforded TNBS salts (IVb—e). In the cases of asymmetric acetylenes IIb,c,e, the NMR spectra of IVb,c,e, indicate that more electron attracting groups, *i.e.*, carboalkoxy and benzoyl groups, are attached to C_3 of III. The reaction of I with phenylacetylene, however, did not occur even after prolonged stirring for several days at room temperature. The 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 by way of the intramolecular 1,3-migration of the acyl group.[8] 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 acyl migration. Perhaps severe steric interaction prevented further cyclization of III to a bicyclofuran ring by means of intramolecular nucleophilic displacement accompanied with elimination of dimethyl sulfide.



(VI)

In order to elucidate acyl migration mechanism, the effect of the solvents in the reaction of I with IIa was investigated. Solvents such as *N,N*-dimethylformamide (DMF), acetonitrile and tetrahydrofuran (THF) also afforded IIIa in 24, 55, and 25% yields, respectively. The results indicate that DMSO is the most suitable as solvent for the reaction. On the other hand, when the reaction of I and IIa was carried out in benzene, IIIa was not formed and yellow precipitates were obtained. The precipitates melted at 90—100°C, resolidified above this temperature and decomposed at 165°C. It was also found that the precipitates were easily transformed into IIIa by heating at 90°C for several minutes or merely dissolving into polar solvents, even into chloroform. Their limited solubility in benzene and facile



(VIIa)

6) L. A. Paquette and R. W. Begland, *J. Amer. Chem. Soc.*, **88**, 4685 (1966).
7) K. C. Brannock, R. D. Burpitt, V. W. Goodlett, and J. G. Thweatt, *J. Org. Chem.*, **28**, 1464 (1963).
8) For reports on 1,3-acyl migrations from carbon to carbon, see a) N. Inamoto, N. Iwata, and O. Shimamura, *Chem. & Ind.*, **1959**, 47 ; b) N. H. Bromham, *ibid.*, **1959**, 258; c) H. Nozaki, M. Takaku, and Y. Hayashi, *Tetrahedron Lett.*, **1967**, 2303; d) E. Baggiolini, K. Schaffner, and O. Jeger, *Chem. Commun.*, **1969**, 1103.

TABLE 2. RING EXPANSION OF THE SEVEN-MEMBERED CYCLIC SULFONIUM YLIDE (VIII) WITH ACETYLENIC COMPOUNDS (II)

	X	Y	IX			IX·TNBS–H						
			Yield (%)	Mp (°C)[a]	IR, $\nu_{C=O}$ (cm^{-1})	Mp (°C)[a]	NMR δ (ppm)[b]		*Anal.* (%) C	H	N	S
a	CO_2Me	CO_2Me	87	100	1710, 1657, 1510	209.0	12.60	Found	41.23	4.04	6.80	10.81
								Calcd	41.52	4.15	6.92	10.54
b	Ph	CO_2Et	35	132	1650, 1515,	211.5	12.68	Found	49.13	4.78	6.71	9.72
								Calcd	48.83	4.57	6.57	10.01
c	Ph	COPh	53	105	1546, 1490	213.5	c)	Found	53.79	4.59	6.22	9.42
								Calcd	53.65	4.35	6.26	9.53

a) Decomposition point.
b) Chemical shift of an enolated proton[6] (in DMSO-d_6).
c) Not observed.

conversion into IIIa in polar solvents precluded measurements of NMR and UV spectra. In view of the above facts, however, it seems most reasonable to assume that the precipitates are a bicyclic sulfonium betaine having [4.2.0]bicyclooctene structure (VIIa), a valence isomer of IIIa.

VIIa ⟶ IIIa

In order to have further proof for the structure VIIa, prevention of a facile ring opening of VIIa, which might be caused by electron migration from the oxygen anion to the bicyclo ring system, was attempted by means of alkylation[9] of the anion. However, alkylation of VIIa with triethyloxonium fluoborate resulted in the ring opening and the product was the same as that formed from IIIa and the alkylating reagent.

It was established that the ring expansion of a seven-membered cyclic sulfonium ylide, dimethylsulfonium-2-oxocycloheptylide (VIII) also occurred upon reaction with IIa giving dimethylsulfonium-2,3-dicarbomethoxy-4-oxo-2-cyclononenylide (IXa) in 87% yield.

Similarly, the reactions of VIII with IIb,c afforded the ring expansion products (IXb,c) in good yields under mild conditions. The results are listed in Table 2.

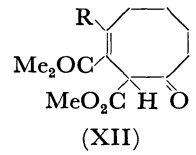
In the case of a five-membered cyclic sulfonium ylide (X), X was prepared *in situ* from the corresponding sulfonium salt on treatment with *n*-butyllithium because of an unsuccessful isolation of X. X was immediately allowed to react with IIa to afford a ring expansion product (XIa) in 52% yield.

The ring expansion of eight- and twelve-membered cyclic sulfonium ylides, however, has not yet been successful.

The reactions of the ring expansion product IIIa were investigated with the expectation that IIIa, being a reactive sulfonium ylide, would become a potential synthetic intermediate.

It was shown that IIIa gave cyclooctenone derivatives (XIIa—c) by displacement reactions with some nucleophiles accompanied with elimination of dimethyl sulfide. When IIIa was allowed to react with benzenethiol, 1-phenylthio-2,3-dicarbomethoxy-4-oxocyclooctene (XIIa) was obtained in 80% yield with evolution of dimethyl sulfide. The structural assignment was made on the basis of elemental analysis and IR and NMR[6] spectra.

In a similar manner, cyclooctenone derivatives (XIIb—d) were obtained in excellent yields when IIIa was allowed to react with ethanethiol, hydrogen cyanide or methanol. The results are shown in Table 3.

IIIa + R–H $\xrightarrow{-Me_2S}$ 

(XII)

On the other hand, the reactions of IIIa with several

TABLE 3. REACTIONS OF THE RING EXPANSION PRODUCT (IIIa) WITH NUCLEOPHILES

	Nucleophile	Reaction conditions			Product, XII					*Anal.* (%)			
		Solvent	Temp.	Time (hr)	R	Yield (%)	Mp (°C)	NMR δ (ppm)[a]		C	H	N	S
a	PhSH	Benzene	RT	33	PhS	80	118.5—119.5	12.66	Found	62.07	5.99		9.46
									Calcd	62.06	5.79		9.19
b	EtSH	Benzene	RT	19	EtS	95	68.3—69.8	b)	Found	56.03	6.88		10.47
									Calcd	55.99	6.71		10.66
c	HCN	Benzene	RT	48	NC	60	154.5—155.5	12.87	Found	59.13	5.97	5.24	
									Calcd	58.86	5.70	5.28	
d	MeOH	MeOH	65°C	9	MeO	90	105.0	12.68	Found	58.04	6.87		
									Calcd	57.77	6.71		

a) Chemical shift of an enolated proton[6] (in $CDCl_3$).
b) Not measured.

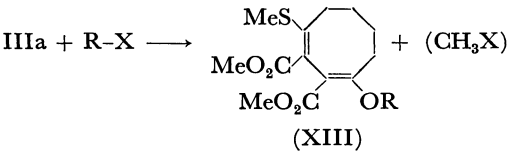
9) S. H. Smallcombe, R. J. Holland, R. H. Fish, and M. C. Caserio, *Tetrahedron Lett.*, **1968**, 5987.

TABLE 4. REACTIONS OF THE RING EXPANSION PRODUCT (IIIa) WITH ELECTROPHILES

	Electrophile	Reaction conditions			Product, XIII					
		Solvent	Temp.	Time (day)	R	Yield (%)	Mp (°C)		*Anal.* (%) C	H	S
a	PhCOCl	Benzene	RT	1	PhCO	68	138.5—139.5	Found	61.53	5.84	8.43
								Calcd	61.53	5.68	8.20
b	MeCOCl	Benzene	RT	2	MeCO	59	96.5—98.0	Found	54.99	6.19	9.80
								Calcd	54.87	6.14	9.75
c	MeI	MeI	50°C	0.4	Me	74	118.0—119.0	Found	55.87	6.96	10.62
								Calcd	55.99	6.71	10.66
d	$PhCH_2Br$	DMSO	RT	1.5	$PhCH_2$	23	127.5—128.5	Found	64.10	6.71	8.36
								Calcd	63.82	6.43	8.50

active methylene compounds, such as acetylacetone and ethyl malonate, in various solvents resulted only in the formation of 1-methylthio-2,3-dicarbomethoxy-4-oxocyclooctene (XII, R=MeS) in 23—74% yields.

The reactions of IIIa with electrophilic reagents were also investigated. It was found that IIIa gave diene esters (XIII, R=acyl) and diene ethers (XIII, R=alkyl) on treatment with acyl and alkyl halides. Acylation and alkylation were found to occur exclusively on the oxygen atom.[10] The results are recorded in Table 4.



(XIII)

It should be noted that the reactions of cyclic sulfonium ylides I, VIII and X with II in DMSO afforded the ring expansion (by two carbon atoms) products III, IX, and XI through the 1,3-acyl rearrangement in high yields under extremely 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.

Experimental

All the experiments were carried out in atmosphere of nitrogen. Melting points are uncorrected. NMR spectra were measured in $CDCl_3$ unless otherwise stated with tetramethylsilane as internal standard.

Preparation of Cyclic Stable Sulfonium Ylides. Dimethylsulfonium-2-oxocyclohexylide (I) was newly prepared from dimethyl-2-oxocyclohexylsulfonium fluoborate in 80% yield by the action of aqueous sodium hydroxide in a mixture of chloroform and saturated aqueous potassium carbonate.

In a similar manner, seven-, eight-, and twelve-membered cyclic stable sulfonium ylides were obtained in good yields from the corresponding fluoborate or methylsulfate. The cyclic ylides gave sulfonium salts with 2,4,6-trinitrobenzenesulfonic acid (TNBS-H)[11] in quantitative yields. The results are listed in Table 5.

Reaction of Dimethylsulfonium-2-oxocyclohexylide (I) with Dimethyl Acetylenedicarboxylate (IIa)[12] *in Dimethyl Sulfoxide (DMSO).* When a solution of IIa (1.42 g, 10 mmol) in 15 m*l* of dry DMSO was added dropwise to a solution of I (1.58 g, 10 mmol) in DMSO with stirring at 18°C, an exothermic reaction soon took place and yellow precipitates of dimethylsulfonium-2,3-dicarbomethoxy-4-oxo-2-cyclooctenylide (IIIa) were deposited. After being stirred for an hour, IIIa was filtered and washed well with dry benzene. Dilution of the filtrate with 1 *l* of dry ether gave additional 0.99 g of IIIa. The total yield was 2.99 g (100%). Mp 166.5—167.5°C (dec). IR (KBr): 1726, 1627, 1528 (C=O) and 1575 (C=C) 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, MeOCO) and 3.64 (3H, s, MeOCO) ppm. UV: λ_{max}^{EtOH} 280 (ε 9,800) and 368 (ε 4,900) mμ.

In a similar manner, reactions of I with ethyl phenylpropiolate (IIb),[13] benzoylphenylacetylene (IIc),[14] dibenzoylacetylene (IId),[15] and methyl propiolate (IIe)[16] afforded the corresponding ring expansion compounds (IIIb—e). The yields and the properties are summarized in Table 1.

Reaction of IIIa with 2,4,6-Trinitrobenzenesulfonic Acid (TNBS-H). An equimolar amount of TNBS-H was added to a solution of IIIa in methanol at room temperature and dimethyl-2,3-dicarbomethoxy-4-oxo-1-cyclooctenylsulfonium 2,4,6-trinitrobenzenesulfonate (IVa) was obtained instantly in quantitative yield. Mp 202.0°C (dec) (recrystallized from methanol).

Similarly, reactions of IIIb—e with TNBS-H afforded the corresponding 2,4,6-trinitrobenzenesulfonates (IVb—e) quantitatively. The results are also shown in Table 1.

Desulfurization of IIIa with Raney Nickel. A mixture of IIIa (0.87 g, 2.9 mmol) and large excess of Raney nickel (W-4)[17] in 20 m*l* of water and 15 m*l* of ethanol was heated at 90—100°C for 8.5 hr. After removal of precipitates from the hot reaction mixture by centrifugal separation, the solution was evaporated to give 2,3-dicarbomethoxy-4-oxocyclooctene (V), 0.35 g (50%), mp 75.0—76.0°C (purified by sublimation). Found: C, 59.69; H, 6.90%. Calcd for $C_{12}H_{16}O_3$: C, 59.99; H, 6.71%. The melting point was not depressed by admixture with an authentic sample prepared by the method of Brannock *et al.*[7] The IR spectra of both samples are identical.

10) E. Winterfeldt and H. J. Dillinger, *Chem. Ber.*, **99**, 1558 (1966).
11) D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, **29**, 2702 (1964).
12) E. H. Huntress, T. E. Lesslie, and J. Bornstein, "Organic Syntheses," Coll. Vol. 4, p. 329 (1963).
13) T. W. Abbott, *ibid.*, Vol. 12, 60 (1932).
14) J. V. Nef, *Ann.*, **308**, 276 (1899).
15) R. E. Lutz and W. R. Smithey, Jr., *J. Org. Chem.*, **16**, 51 (1951).
16) V. Wolf, *Chem. Ber.*, **86**, 735 (1953).
17) G. R. Pettit and E. E. van Tamelen, "Organic Reactions," Vol. 12, p. 406 (1962).

TABLE 5. PROPERTIES OF DIMETHYLSULFONIUM-2-OXOCYCLOALKYLIDES AND 2,4,6-TRINITROBENZENESULFONATES

n	X[a]	Cyclic Ylide		TNBS–H Salt[c]					
		Mp (°C)	IR, $\nu_{C=O}$ (cm^{-1})	Mp (°C)[b]		*Anal.* (%) C	H	N	S
5	TNBS[c]	d)	d)	180	Found	35.52	3.72	9.90	14.63
					Calcd	35.70	3.43	9.61	14.64
6	BF_4	107	1535	198	Found	37.28	3.90	9.16	14.43
					Calcd	37.26	3.80	9.31	14.19
7	BF_4	106	1530	203	Found	38.57	3.95	9.18	13.98
					Calcd	38.73	4.11	9.03	13.75
8	$MeSO_4$	82	1516	195	Found	40.25	4.69	9.03	13.43
					Calcd	40.09	4.41	8.77	13.14
12[e]	$MeSO_4$	80	1505	182	Found	46.07	5.60	7.52	11.48
					Calcd	45.89	5.69	7.65	11.65

a) Anion of starting salt. b) Decomposition point. c) 2,4,6-Trinitrobenzenesulfonate.
d) Not isolated. e) Methylethylsulfonium-2-oxocyclododecylide.

Reaction of I with IIa in Benzene. *1) Isolation of Bicyclic Sulfonium Betaine (VIIa):* A solution of IIa (0.71 g, 5 mmol) in 15 m*l* of dry benzene was added over a period of 25 min at 10°C to a suspension of I (0.79 g, 5 mmol) in 30 m*l* of dry benzene. After stirring for 2 hr, the resulting bright yellow precipitates (VIIa), 0.93 g (62%), were filtered, washed and dried at reduced pressure. IR (KBr): 1710, 1677, and 1532 cm^{-1}. VIIa melted at 90—100°C, resolidified above this temperature and decomposed at 165°C. When VIIa was heated at 90°C for several minutes, its IR spectrum became identical with that of IIIa.

2) Alkylation of VIIa with Triethyloxonium Fluoborate.[18] When VIIa was allowed to react with triethyloxonium fluoborate at room temperature for 6 hr, dimethyl-2,3-dicarbomethoxy-4-ethoxy-1,3-cyclooctadienylsulfonium fluoborate was produced in quantitative yield. Mp 147—148°C (Methanol). Found: C, 45.92; H, 5.88; S, 7.94%. Calcd for $C_{16}H_{25}BF_4O_5S$: C, 46.17; H, 6.06: S, 7.69%. IR (KBr): 1727, 1709, 1681, and 1590 cm^{-1}. NMR: δ 1.43 (3H, t, Me–CH_2, J=4.5 Hz), 1.9—2.8 (8H, m, C_4H_8), 3.13 (6H, s, $Me_2\overset{+}{S}$), 3.65 (3H, s, MeOCO), 3.78 (3H, s, MeOCO), and 6.20 (2H, q, Me–CH_2–O, J=4.5 Hz) ppm.

The same sulfonium fluoborate was obtained by the reaction of IIIa with triethyloxonium fluoborate.

Reaction of Dimethylsulfonium-2-oxocycloheptylide (VIII) with II. When VIII was treated with IIa—c in DMSO in the same manner as described above for the reaction between I and II, the corresponding ring expansion products (IXa—c) were obtained. Reactions of IXa—c with TNBS-H gave 2,4,6-trinitrobenzenesulfonates (IXa—c·TNBS-H) in quantitative yields. The results are listed in Table 2.

Reaction of Dimethylsulfonium-2-oxocyclopentylide (X) with IIa. To a solution of dimethyl-2-oxocyclopentylsulfonium 2,4,6-trinitrobenzenesulfonate[19] (2.19 g, 5 mmol) and IIa (0.71 g, 5 mmol) in 10 m*l* of dry DMSO, a solution of *n*-butyllithium (5 mmol) in 6 m*l* of *n*-hexane was added *via* hypodermic syringe over a period of an hour with occasional cooling. After stirring for 2 hr, TNBS-H (5 mmol) was added to the reaction mixture. Addition of methanol gave crystalline dimethyl-2,3-dicarbomethoxy-4-oxo-1-cycloheptenylsulfonium 2,4,6-trinitrobenzenesulfonate (XIa·TNBS-H), mp 194°C (dec) (methanol), in 52% yield. Found: C, 39.34; H, 3.80; N, 7.44; S, 10.79%. Calcd for $C_{19}H_{21}N_3O_{14}S_2$: C, 39.38; H, 3.63; N, 7.25; S, 11.05%.

Reaction of IIIa with Benzenethiol. When a mixture of IIIa (0.300 g, 1 mmol) and benzenethiol (0.110 g, 1 mmol) in 15 m*l* of dry benzene was stirred at room temperature, the crystals of IIIa gradually disappeared to give an almost clear solution after 6 hr. Stirring was continued overnight and the solvent was removed under reduced pressure. The resulting viscous oil was chromatographed over silica gel. Elution with ether-petroleum ether (1: 1) gave 1-phenylthio-2,3-dicarbomethoxy-4-oxocyclooctene (XIIa), mp 118.5—119.5°C (*n*-hexane), in 80% yield. Further elution with the same mixture afforded 1-methylthio-2,3-dicarbomethoxy-4-oxocyclooctene (XII, R=MeS) in 18% yield.

In a similar way, reactions of IIIa with ethanethiol, hydrogen cyanide and methanol gave 1-substituted-4-oxocyclooctene derivatives(XIIc—d) in high yields without concomitant formation of XII(R=MeS). In the case of hydrogen cyanide, the reaction was carried out with twofold excess of hydrogen cyanide generated *in situ* from potassium cyanide and acetic acid. The yields, melting points, NMR spectra and analytical values of XIIa—d are shown in Table 3.

Reaction of IIIa with Acetylacetone. A solution of IIIa (0.300 g, 1 mmol) and acetylacetone (0.100 g, 1 mmol) in 10 m*l* of dry DMSO was heated at 90—100°C for 18 hr. The reaction mixture was poured into ice-water and worked up with ether to give a semi-crystalline viscous oil which was chromatographed over silica gel. Elution with methylene chloride afforded 1-methylthio-2,3-dicarbomethoxy-4-oxocyclooctene (XII, R=MeS) in 23% yield, mp 124—125°C (*n*- or *c*-hexane). Found: C, 54.69; H, 6.47; S, 11.10%. Calcd for $C_{13}H_{18}O_5S$: C, 54.54; H, 6.34; S, 11.18%. IR (KBr): 1703, 1650, 1618, and 1553 cm^{-1}. NMR: δ 1.2—2.85 (8H, m, C_4H_8), 3.37 (3H, s, MeS), 3.68 (3H, s, MeOCO), 3.70 (3H, s, MeOCO), and 12.67 (1H, s, CO–CH–CO_2Me) ppm.

Similarly, reactions of IIIa with diethyl malonate, malononitrile, ethyl acetoacetate, dibenzoylmethane and trifluoroacetylacetone in various solvents such as DMSO, DMF, acetonitrile, methylene chloride, THF, dioxane or benzene also gave XII (R=MeS) in 23—74% yields.

Reaction of IIIa with Benzoyl Chloride. When a mixture of I (0.310 g, 1.03 mmol) and benzoyl chloride (0.149 g, 1.05 mmol) in 15 m*l* of dry benzene was stirred at room temperature, the yellow crystals of IIIa gradually disappeared. After being stirred overnight, the solvent was evaporated to give a viscous oil which was chromatographed over silica gel. 1-Methylthio-2,3-dicarbomethoxy-4-benzoyloxy-1,3-cyclooctadiene (XIIIa), mp 138.5—139.5°C, was obtained in 68%

18) H. Meerwein, "Methoden der Organischen Chemie," Vol. 6 (III), p. 336.

19) The sulfonium salt was prepared from dimethyl sulfide, 2-bromocyclopentanone and silver 2,4,6-trinitrobenzenesulfonate.[11]

yield by elution with ether-petroleum ether (2: 3). NMR (DMSO-d_6): δ 1.1—2.9 (8H, m, C_4H_8), 2.40 (3H, s, MeS), 3.42 (3H, s, MeOCO), 3.47 (3H, s, MeOCO) and 7.4—8.1 (5H, m, C_6H_5) ppm.

In a similar way, the reactions of IIIa with acetyl chloride, methyl iodide and benzyl bromide afforded the corresponding diene ester (XIIIb) and diene ethers (XIIIc, d). The results are recorded in Table 4.