Ethyl (Dimethylsulfuranylidene)acetate. IV. Miscellaneous Reactions

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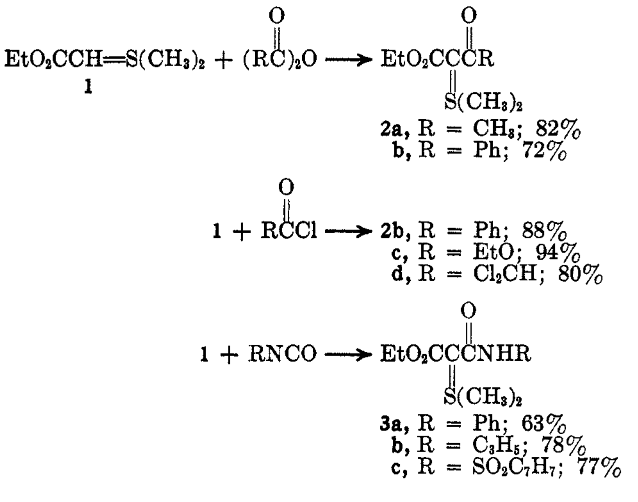
Ethyl (dimethylsulfuranylidene)acetate (EDSA) was allowed to react with a variety of materials known to be susceptible to nucleophilic attack. Stable sulfur ylides were obtained in 60–90% yields by treating EDSA with acid chlorides and anhydrides, isocyanates, acetylenic esters and ketones, ethoxymethylenemalononitrile, and diphenyl ketene. EDSA and α-dicarbonylic compounds (benzil, diacetyl, and ethyl pyruvate) gave epoxy esters in 40–90% yields. An epoxy compound was also obtained from chloral. Reaction of EDSA with trichloroacetonitrile in ether gave dichloroacetonitrile and a novel α-chloro ylide, ethyl chloro(dimethylsulfuranylidene)acetate, in high yields.

Our earlier reports have described the synthesis[1] of ethyl (dimethylsulfuranylidene)acetate (1, EDSA), its nucleophilic attack on α,β-unsaturated compounds in aprotic solvents to produce cyclopropanes,[1,2] and its reaction with α,β-unsaturated esters[3] in ethanol solution to give acyclic products. Further studies of reactions of EDSA with other electrophilic compounds have now led to a variety of new products. In many cases the course of the reaction was found to be markedly influenced by choice of solvent and/or reaction temperature.

Stable Sulfur Ylides.[4]—Acylation of EDSA to give stable sulfur ylides was carried out with acid anhydrides in pyridine solution, with acid chlorides in the presence of saturated potassium carbonate, and with isocyanates in benzene solution (for results, see Chart I). It should be noted that **2b** could be prepared in higher yield from benzoyl chloride than from the anhydride. In the case of **2c**, the 94% yield was calculated over-all from carbethoxymethyl dimethylsulfonium bromide, since EDSA was formed and utilized *in situ*. Compounds **2a** and **2b** were recently prepared from β-keto esters, dimethyl sulfoxide (DMSO), and acetic anhydride,[5] while **2c** was obtained in low yield by the reaction of ethyl chloroformate with dimethylsulfonium methylide.[6] Ylides **2a** and **2c** have also been prepared by reactions of DMSO and dicyclohexylcarbodiimide with ethyl acetoacetate and diethyl malonate, respectively.[4a]

CHART I



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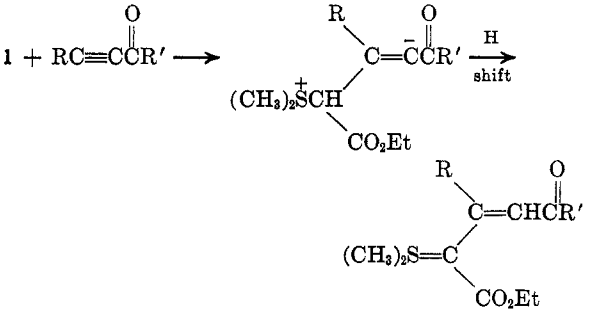
2a, R = CH_3; 82%
b, R = Ph; 72%

2b, R = Ph; 88%
c, R = EtO; 94%
d, R = Cl_2CH; 80%

3a, R = Ph; 63%
b, R = C_3H_5; 78%
c, R = $SO_2C_7H_7$; 77%

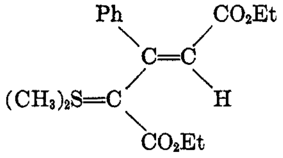
On attempted decomposition at 190–200° (10 mm), ylide **2a** distilled unchanged. It was also recovered unchanged from attempted cyclopropane formation by reaction with diethyl fumarate in refluxing dimethoxyethane for 18 hr.

Another synthesis of stable ylides involved reaction of EDSA with a conjugated acetylenic ester or ketone in ethanol solution. The yields of mixtures of *cis–trans* isomers (predominantly *trans*) were excellent, and the pure *trans* isomer was readily obtained by recrystallization.

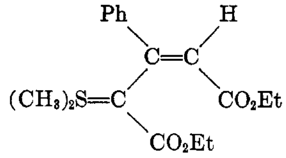


4a, R = H; R′ = OEt; 92%
b, R = Ph; R′ = OEt; 92%
c, R = H; R′ = CH_3; 86%

When ethyl phenylpropiolate and EDSA were allowed to react in ether in place of ethanol, the *cis* isomer of **4b** precipitated from the reaction mixture in 44% yield as a reasonably pure product.



4b (*trans*)
yellow; mp 86–88°;
$\lambda_{\max}^{\mathrm{EtOH}}$ 265 mμ (ε 17,100),
373 (10,400)



4b (*cis*)
colorless; mp 117–119°;
$\lambda_{\max}^{\mathrm{EtOH}}$ 265 mμ (ε 14,100),
337 (10,400)

EDSA underwent reaction with ethoxymethylenemalononitrile in ethanol to give the expected stable ylide **5** in 66% yield. An attempt to achieve further reaction of **5** with EDSA to give the cyclopropyl derivative **6** was not successful (Scheme I).

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(1) G. B. Payne, *J. Org. Chem.*, **32**, 3351 (1967).

(2) G. B. Payne and M. R. Johnson, *ibid.*, **33**, 1285 (1968).

(3) G. B. Payne, *ibid.*, **33**, 1284 (1968).

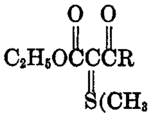
(4) Syntheses of a variety of stabilized sulfonium ylides have recently been reviewed: (a) A. F. Cook and J. G. Moffatt, *J. Amer. Chem. Soc.*, **90**, 740 (1968); (b) H. Nozaki, M. Takaku, D. Tunemoto, Y. Yamamoto, and K. Kondo, *Nippon Kagaku Zasshi*, **81**, 1 (1967).

(5) R. Oda and Y. Hayashi, *ibid.*, **87** (10), 1110 (1966); *Chem. Abstr.*, **66**, 85416 (1967).

(6) H. Nozaki, D. Tunemoto, S. Matubara, and K. Kondo, *Tetrahedron*, **23**, 545 (1967).

TABLE I

CHARACTERIZATION DATA ON STABLE SULFUR YLIDES

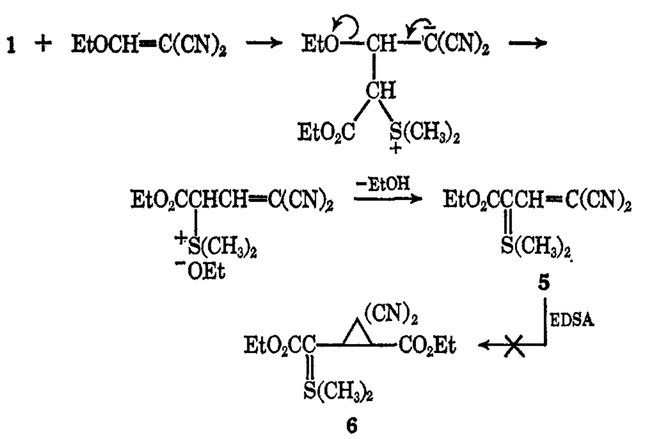


$C_2H_5OC(=O)C(=S(CH_3)_2)C(=O)R$

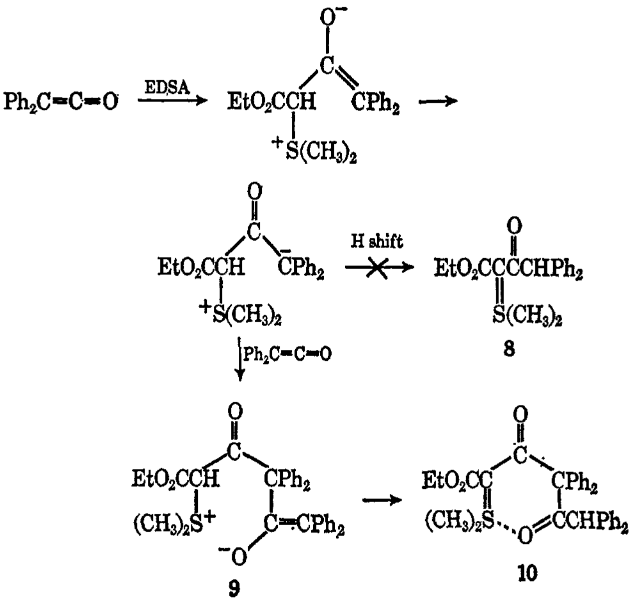
Compd	Registry no.	R	Mp, °C	Lit. mp, °C	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
2a	7039-34-1	CH_3	61–63	62–63[a]	$C_8H_{14}O_3S$	50.4	7.4	50.1	7.5
2b	14250-99-8	Ph	92–94	84–85[a]	$C_{13}H_{16}O_3S$	61.9	6.4	61.9	6.4
2c	14070-66-7	OC_2H_5	134–135	135–137[b]	$C_9H_{16}O_4S$	49.1	7.3	49.2	7.4
2d	16980-31-7	$CHCl_2$	141–142		$C_8H_{12}O_3SCl_2$	37.1	4.7	37.2	4.7
3a	16980-32-8	NHPh	137–139		$C_{13}H_{17}NO_3S$	58.4	6.4	58.5	6.4
3b	16980-51-1	NHC_3H_5	82–84		$C_{10}H_{17}NO_3S$	51.9	7.4	51.8	7.4
3c	16980-33-9	$NHSO_2C_7H_7$	135–136		$C_{14}H_{19}NO_5S_2$	48.7	5.5	48.8	5.6

[a] See ref 5. [b] See ref 6.

SCHEME I



SCHEME II

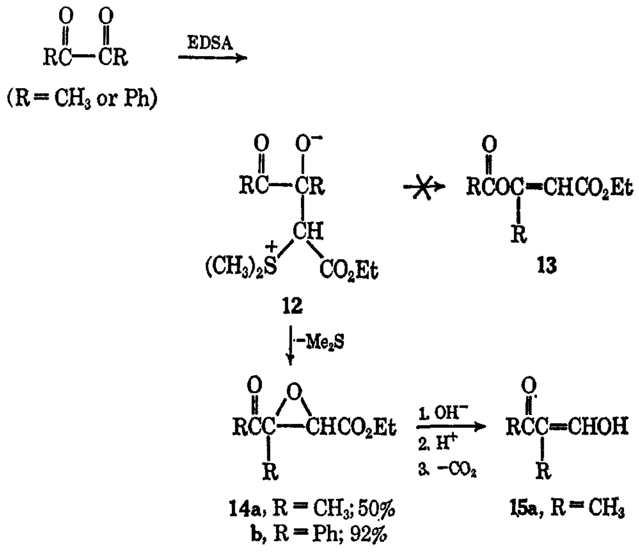


It was expected that EDSA might react with diphenylketene in benzene in a manner similar to that observed with an isocyanate to give a new ylide **8**. Interestingly, the product (85% yield) was not **8**, but one formed from 2 mol of the ketene and 1 of EDSA (Scheme II). We have tentatively assigned structure **10**, containing a quasi six-membered ring (loose bonding between carbonyl and ylide sulfur), to this material. However, structure **9**, with its "inner salt" arrangement, could not be ruled out on the basis of either infrared or nmr analysis.[7]

Characterization and nmr data appear in Tables I and II, respectively.

Epoxy Esters.—Benzil and diacetyl were selected for reaction with EDSA in benzene with the expectation that nucleophilic attack at carbonyl might bring about the type of carbon–carbon cleavage observed in the reaction of α-diketones with alkaline hydrogen peroxide[8] to give enol ester **13**. The latter was not observed; instead, dimethyl sulfide was eliminated directly from intermediate **12** to give epoxy ester **14**[9] (Scheme III).

SCHEME III



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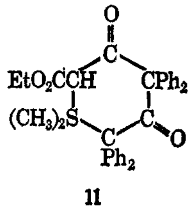
[7] A ring-closed structure such as **11** was not assigned, since various heterocyclic six-membered ring compounds having 1,3-diketo-2,2,4,4-tetraphenyl arrangements all showed carbonyl absorption at 1750–1790 cm^{-1} in contrast to the 1720-cm^{-1} value observed. See R. D. Kimbrough, Jr., *J. Org. Chem.*, **29**, 1242 (1964).



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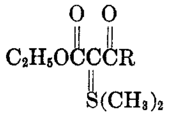
[8] C. A. Bunton, *Nature*, **163**, 444 (1949).

[9] The reaction of benzil with dimethylsulfonium methylide to give an epoxy ketone has been reported; no product from diacetyl could be isolated. See J. L. Pierre, R. Guidotti, and P. Arnand, *Bull. Soc. Chim. Fr.*, 1439 (1967).

TABLE II

NUCLEAR MAGNETIC RESONANCE DATA ON STABLE SULFUR YLIDES[a]



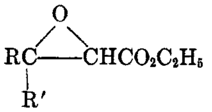
$C_2H_5O\overset{O}{\overset{\|}{C}}\underset{\underset{S(CH_3)_2}{\|}}{\overset{O}{\overset{\|}{C}}}CR$

Compd	R	$(CH_3)_2S$[b]	$OCCH_3$—[c]	OCH_2[d]	$\overset{O}{\overset{\|}{C}}CH_3$[b]	Ar[e]	$CHCl_2$[b]	NH[b]	NCH_2[e]	CH=C[e]	C=CH_2[e]	$ArCH_3$[b]
2a	CH_3	2.9 (6)	1.3 (3)	4.2 (2)	2.4 (3)							
2b	Ph	2.9 (6)	0.9 (3)	3.9 (2)		7.3 (5)						
2c	OC_2H_5	2.9 (6)	1.3 (6)	4.2 (4)								
2d	$CHCl_2$	3.0 (6)	1.3 (3)	4.2 (2)			7.5 (1)					
3a	NHPh	2.9 (6)	1.3 (3)	4.2 (2)				10.8 (1)				
3b	NHC_3H_5	2.9 (6)	1.3 (3)	4.2 (2)				8.7 (1)	3.9 (2)	5.9 (1)	5.2 (2)	
3c	$NHSO_2C_7H_7$	2.9 (6)	1.3 (3)	4.2 (2)		7.6 (4)		11.7 (1)				2.4 (3)

[a] $CDCl_3$ solution using tetramethylsilane (TMS) as an internal standard; chemical-shift values are in parts per million downfield from TMS; relative areas are in brackets. [b] Singlet. [c] Triplet. [d] Quartet. [e] Multiplet centered at value given.

TABLE III

CHARACTERIZATION DATA ON EPOXY ESTERS



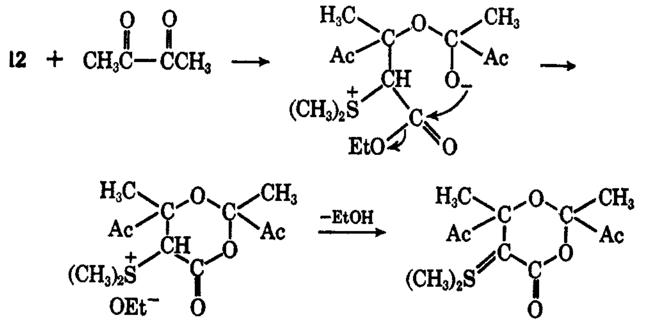
Compd	Registry no.	R	R′	Solvent[a]	Reaction Time, hr	Reaction temp, °C	Yield, %	Bp, °C (mm)	$n^{25}D$	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
14a	16980-39-5	$CH_3\overset{O}{\overset{\|}{C}}$—	CH_3	B	3[b]	45	50	56–57 (<1)	1.4327	$C_8H_{12}O_4$	55.7	7.0	55.8	7.0
14b	16980-40-8	$Ph\overset{O}{\overset{\|}{C}}$—	Ph	B	48	25	92[c]	Mp 50–60		$C_8H_{16}O_4$	73.0	5.4	73.1	5.4
17	16980-43-1	$EtO\overset{O}{\overset{\|}{C}}$—	CH_3	A	0.5[d]	55	42	72–73 (<1)	1.4390	$C_9H_{14}O_5$	53.5	7.0	53.8	6.9
18	10174-63-7	Cl_3C—	H	B	24[e]	25	22	65–68 (<1)	1.4714	$C_6H_7O_3Cl_3$	30.9	3.0	30.9	3.1

[a] Benzene (B); acetone (A). [b] EDSA solution added over 2 hr. [c] Mixture of isomers; one pure isomer (mp 59–60°) obtained by recrystallization from chloroform–hexane. [d] Ethyl pyruvate solution added over 10 min. [e] EDSA solution added over 20 min.

Structure **14a** was assigned on the basis of analysis and by Darzens degradation to the expected 4-hydroxy-3-methyl-3-buten-2-one (**15a**). Careful saponification of **14b** gave the corresponding epoxy acid as a crystalline derivative in high yield.

The addition of EDSA to 2 molar equiv of diacetyl in *ethanol* at 30–35° gave a crystalline water-soluble product in 58% yield. This has been assigned the ylide structure **16** on the basis of elemental, nmr spectral, and molecular weight analyses. Its formation is rationalized as given in Scheme IV.

SCHEME IV



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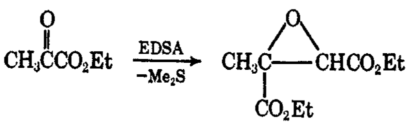
A brief study was made of the reaction of EDSA with ethyl pyruvate to give diethyl 2-methyl-2,3-epoxysuccinate (**17**). The highest yield (42%) was obtained by



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adding the ester dropwise to a boiling solution of ylide in acetone. Inferior yields were observed with other solvents such as benzene, ether, ethanol, acetonitrile, or dimethylformamide.

Reaction of EDSA with chloral was first carried out in benzene at room temperature by adding ylide to aldehyde. An exothermic reaction produced 0.45 molar equiv of dimethyl sulfide and a 22% yield of the desired epoxide, **18**. The latter was separated from a large quantity of residual material by distillation; its structure was assigned by analysis (Tables III and IV). An attempt at synthesis of an authentic sample *via* the Darzens reaction was not successful.

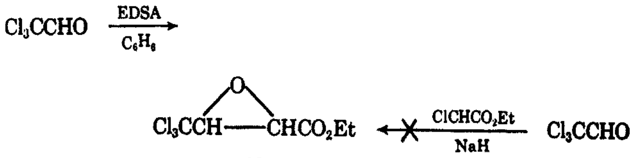

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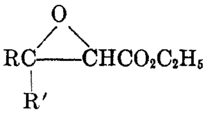
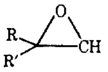
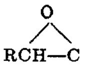
TABLE IV

NUCLEAR MAGNETIC RESONANCE DATA ON EPOXY ESTERS[a]

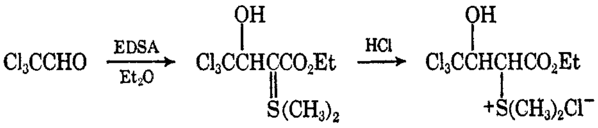


Compd	R	R′	$OCCH_3$[b]	OCH_2[c]		$CH_3\overset{O}{\overset{\|}{C}}$[d]	CH_3[d]	Ar[e]	
14a	$CH_3\overset{O}{\overset{\|}{C}}$	CH_3	1.2 (3)	4.2 (2)	3.5 (1)[d]	2.3 (3)	1.5 (3)		
14b	$Ph\overset{O}{\overset{\|}{C}}$	Ph	1.1 (3)	4.2 (2)	3.7 (1)[d]			7.7 (10)	
17	$C_2H_5O\overset{O}{\overset{\|}{C}}$	CH_3	1.3 (6)	4.2 (4)	3.7 (1)[f]		1.6 (3)		
18	Cl_3C	H	1.3 (3)	4.2 (2)	3.8 (1)[g]				4.0 (1)[g]

[a] See Table II, footnote *a*. [b] Triplet. [c] Quartet. [d] Singlet. [e] Multiplet centered at value given. [f] Doublet owing to presence of *cis–trans* isomers in ratio of about 4:1. [g] Doublet; J = 1.5 Hz.

Several attempts were made to improve the yield of **18**. These included reactions in acetone, ethanol, and benzene at different temperatures using a variety of procedures. In no case was the 22% yield exceeded.

In a final effort to achieve yield improvement, an ethereal solution of EDSA was added dropwise at 5° to a solution of chloral in ether. Surprisingly, a crystalline product precipitated in 65% yield. This has been assigned the ylide structure **19** on the basis of analysis and by its conversion into the expected sulfonium chloride (**20**). Ylide **19** was relatively stable when stored at −10°; in solution, however, it deteriorated readily.

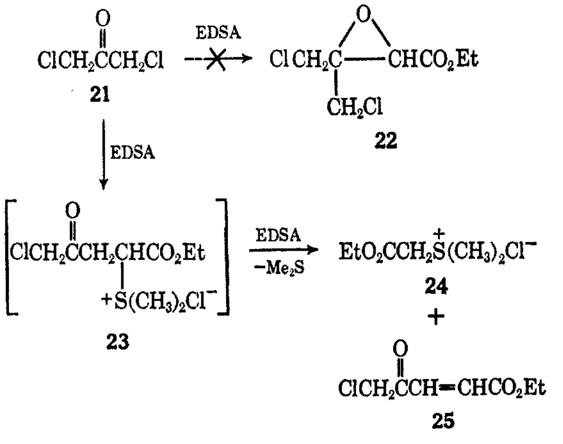


$$Cl_3CCHO \xrightarrow[Et_2O]{EDSA} Cl_3C\overset{OH}{\overset{|}{C}}H\underset{\underset{S(CH_3)_2}{\|}}{C}CO_2Et \xrightarrow{HCl} Cl_3C\overset{OH}{\overset{|}{C}}H\underset{\underset{+S(CH_3)_2Cl^-}{|}}{C}HCO_2Et$$

19 **20**

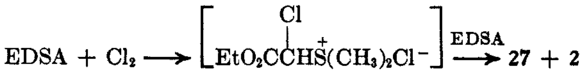
Treatment of EDSA with 1,3-dichloro-2-propanone (**21**) was carried out with the expectation that the carbonyl group might be activated enough to lead to the epoxy ketone, **22**. The latter was not isolated. Instead, equimolecular amounts of EDSA and **21** afforded *trans*-ethyl 5-chloro-4-oxo-2-pentenoate (**25**) in 41% yield along with the sulfonium chloride **24** (72%) and unchanged **21** (34%). See Scheme V. Attempts to improve the yield of **25** by using saturated potassium carbonate to dehydrohalogenate intermediate **23** were not successful.

SCHEME V



Trichloroacetonitrile (TCA).—This reactive nitrile and EDSA combined under a variety of conditions to give several unusual products. Scheme VI summarizes these results. Reaction in ether at 0–5° gave dichloroacetonitrile and a chloro ylide, ethyl chloro(dimethylsulfuranylidene)acetate (**27**), in 82 and 78% yields, respectively. The chloro ylide was a crystalline material that showed good stability at −10°; it deteriorated slowly in solution, however. Its structure was confirmed by reactions with both ethyl acrylate and acrylonitrile to give the expected[2] cyclopropyl derivatives (**28** and **29**) in 58 and 60% yields, respectively.

An attempt to prepare crystalline **27** by reaction of 2 mol of EDSA with 1 of chlorine was not successful. That **27** had been formed, however, was demonstrated



$$EDSA + Cl_2 \longrightarrow \left[EtO_2C\overset{Cl}{\overset{|}{C}}H\overset{+}{S}(CH_3)_2Cl^-\right] \xrightarrow{EDSA} \mathbf{27} + \mathbf{24}$$

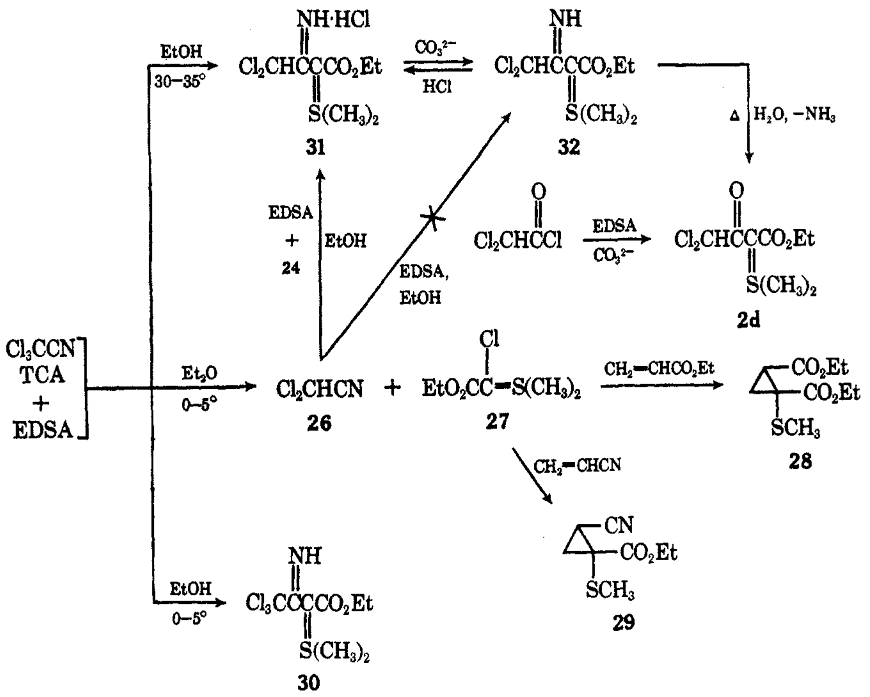
by treatment of a reaction mixture with acrylonitrile to give **29** in 65% yield.

TCA and EDSA reacted in ethanol at 0–5° to precipitate the 1:1 adduct (**30**) in 22% yield. No other pure product was obtained by distillation of the filtrate.

By adding TCA to EDSA in ethanol at 30–35° an entirely different product was secured (36% yield); this was the imine hydrochloride (**31**) derived from dichloroacetonitrile. Its mechanism of formation was investigated. It was shown, for example, that **26** and **27** reacted in ethanol at 25° to give **31**, but in only 16% yield. This then was clearly not a major pathway to **31**.

When dichloroacetonitrile and EDSA were allowed to react in ethanol, neither **31** nor **32** was isolated. In fact, no pure product was obtained. However, when a source of hydrogen chloride (sulfonium salt **24**) was included in the reaction mixture, **31** was formed in about 45% yield based on **26**. We conclude from this that **31** may be formed mainly by interaction of intermediate **26** with a second molecule of EDSA in the presence of a source of hydrogen chloride (a salt such

SCHEME VI

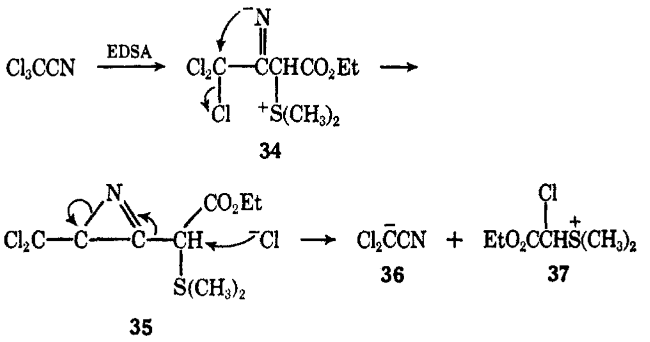


as **24**, for example, generated from EDSA by some unknown side reaction).

Treatment of **31** with base gave **32**; by boiling the latter with water, ammonia was evolved and the stable ylide **2d** produced. This was identical in all respects with the product formed from EDSA and dichloroacetyl chloride.

The formation of **26** and **27** in ether solution is rationalized as shown in Scheme VII. Nucleophilic attack by EDSA at the cyano group gives dipolar intermediate **34**. Intramolecular displacement of chloride ion produces a sulfonium salt containing a reactive azirene ring (**35**). Decomposition of the latter then follows by displacement of the conjugate base of dichloroacetonitrile (**36**) by chloride ion. Finally, the chloro ylide (**27**) is formed from **37** by reaction of the latter with either **36** or EDSA. An alternate mechanism involving nucleophilic displacement by ylide carbon directly on chlorine has been ruled out by failure of EDSA to react with ethyl trichloroacetate.[10]

SCHEME VII



then **36** + **37** $\longrightarrow$ **26** + **27**

and/or EDSA + **37** $\longrightarrow$ **24** + **27**

24 + **36** $\longrightarrow$ EDSA + **26**

Experimental Section[11]

Ethyl 2-(Dimethylsulfuranylidene)acetoacetate (2a).—A solution of 14.8 g (0.10 mol) of EDSA in 50 ml of dry pyridine was treated portionwise with 10 ml of acetic anhydride and held below 50° by cooling. After 15 hr at 25°, the mixture was vacuum stabilized at 60° (bath) and 1 mm. A chloroform solution of the residue was washed with half-saturated potassium carbonate and dried over magnesium sulfate. After removal of solvent *in vacuo*, the residue was crystallized from ether–hexane to give 15.5 g (82%) of **2a**, mp 61–63° (see Tables I and II).

Diethyl (Dimethylsulfuranylidene)malonate (2c).—To a stirred mixture of 45.8 g (0.20 mol) of carbethoxymethyl dimethylsulfonium bromide[1] and 160 ml of chloroform held at $<10°$ was rapidly added a mixture of 120 ml of *saturated* potassium carbonate[12] and 18.2 ml of 11.1 *N* sodium hydroxide. After stirring vigorously for 15 min at 10–20°, the mixture was cooled to $<10°$ and treated dropwise with 21.8 g (0.20 mol) of ethyl chloroformate. The mixture was stirred 1 hr longer at 10° and for 1.5 hr at 25°.

Following filtration to remove any salt, the upper chloroform layer was dried over magnesium sulfate. Vacuum concentration gave 41.5 g (94%) of **2c**, mp 132–134°.

Ethyl N-Allyl-2-(dimethylsulfuranylidene)malonamate (3b).—To a stirred solution of 7.4 g (0.05 mol) of EDSA in 25 ml of benzene was added a solution of 4.2 g (0.05 mol) of allyl isocyanate (Aldrich) in 25 ml of benzene. Cooling was used to hold the reaction temperature below 42°. After a 15-hr stand at 25°, the mixture was warmed on the steam bath and diluted with 150 ml of hexane. Chilling gave 9.0 g (78%) of **3b**, mp 82–84°.

Reaction of EDSA with Ethyl Propiolate.—To a stirred solution of 9.8 g (0.10 mol) of ethyl propiolate (Aldrich) in 50 ml of absolute ethanol was added dropwise at 20–25° over 1 hr a solution of 14.8 g (0.10 mol) of EDSA in 50 ml of ethanol. After an overnight stand, the mixture was vacuum concentrated to give 22.5 g (92%) of light orange solid, mp 75–82°. Its infrared spectrum was nearly identical with that of the recrystallized product (see below). The material was dissolved in 50 ml of chloroform and diluted with four 50-ml portions of petroleum

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[10] See D. G. Burton and J. R. Greenwald, *Tetrahedron Lett.*, No. 16, 1535 (1967), for a discussion of the reaction of triphenylphosphine with both TCA and methyl trichloroacetate.

[11] Boiling points are uncorrected; melting points are corrected. Nmr spectra were obtained with a Varian A-60 spectrometer using tetramethylsilane as an internal standard. Glpc analyses were done on an F & M Model 720 instrument using a 10-ft column packed with 5% of X-1150 on Chromosorb W.

[12] See ref 1, footnote 8.

ether (bp 40–60°). Filtration, then chilling gave 15.8 g (64%) of *trans*-diethyl 4-(dimethylsulfuranylidene)glutaconate (**4a**): mp 94–95°; ir ($CHCl_3$) 1620 and 1560 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.3 (2 t, 6, CO_2CCH_3), 3.0 (s, 6, $C{=}S(CH_3)_2$), 4.2 (m, 4, CO_2CH_2), 5.4 (d, 1, J = 15 Hz, C=CH—CO_2R), 7.8 (d, 1, J = 15 Hz, CH=C—CO_2R).

Anal. Calcd for $C_{11}H_{18}O_4S$: C, 53.6; H, 7.4; S, 13.0. Found: C, 53.7; H, 7.6; S, 13.0.

Reaction of EDSA with Ethyl Phenylpropiolate. A. In Ethanol.—To a cold solution of 19.8 g (0.10 mol) of 88% purity (glpc analysis) ethyl phenylpropiolate [Aldrich, redistilled; bp 90° (<1 mm)] in 50 ml of absolute ethanol was added a cold solution of 14.8 g (0.10 mol) of EDSA in 25 ml of ethanol. The mixture was allowed to warm to 25° and remain there for 5 days.

Vacuum concentration at 25° gave 30 g of residue. This was shaken with 50 ml of ether to allow removal of 3.1 g of insoluble gum. The filtrate was extracted with 50 ml of 3 *N* hydrochloric acid, then water, and finally dried. Claisen distillation of the ether solution gave 5.3 g of unchanged starting material, bp 90° (<1 mm).

The acid and water extracts were combined and basified with carbonate, and the liberated oil was extracted into chloroform. Concentration of the washed and dried organic layer gave 22.6 g (92% yield based on unrecovered starting material) of an oily mixture of isomers. This crystallized on standing for several days, mp 75–85°. The crushed and dried product was analyzed.

Anal. Calcd for $C_{17}H_{22}SO_4$: C, 63.3; H, 6.9; S, 9.9. Found: C, 63.2; H, 6.9; S, 9.7.

A 7.5-g sample was shaken with ether to give 0.3 g of an insoluble isomer, mp 105–115°. The filtrate was held at −10° to give 3.5 g, mp 85–88°. An additional 1.5 g, mp 83–89°, was recovered by treating the filtrate with hexane. The two crops (5.0 g) were recrystallized from ether–hexane to give 3.0 g of *trans*-diethyl 4-(dimethylsulfuranylidene)-3-phenylglutaconate (**4b**) as yellow crystals: mp 86–88°; ir ($CHCl_3$), 1660, 1610, and 1525 cm^{-1} (delocalized ester C=O); nmr ($CDCl_3$), δ 0.6 and 1.3 (2 t, 6, CO_2CCH_3), 3.7 and 4.2 (2 m, 4, CO_2CH_2), 3.0 (s, 6, $C{=}S(CH_3)_2$), 5.3 (s, 1, C=CH), 7.3 (s, 5, Ar).

B. In Ether.—When ether was used in place of ethanol, filtration of the reaction mixture gave 10.0 g of product, mp 102–106° (44% yield based on a 71% conversion of starting ester). Recrystallization from acetone–hexane gave 6.8 g, mp 111–116°. Two more crystallizations gave 3.0 g of *cis*-diethyl 4-(dimethylsulfuranylidene)-3-phenylglutaconate as colorless crystals: mp 117–119°; ir ($CHCl_3$), 1610 (sh 1650) and 1535 cm^{-1} (delocalized ester C=O); the nmr spectrum was nearly superimposable with that of the low-melting isomer.

Anal. Calcd for $C_{17}H_{22}O_4S$: C, 63.3; H, 6.9. Found: C, 63.3; H, 7.0

Reaction of EDSA with 3-Butyn-2-one.—The above reaction was repeated using 12.9 g (0.19 mol) of 3-butyn-2-one[13] and 28.0 g (0.19 mol) of EDSA. After 18 hr at 25° the mixture was vacuum concentrated to a residue of 35.6 g (86%). Recrystallization from chloroform gave 20.6 g (50%) of *trans*-ethyl 2-(dimethylsulfuranylidene)-5-oxo-3-hexenoate (**4c**) as light yellow crystals: mp 134–136°; nmr ($CDCl_3$), δ 1.3 (t, 3, CO_2CCH_3), 2.2 (s, 3, $COCH_3$), 3.0 (s, 6, $C{=}S(CH_3)_2$), 4.2 (m, 2, CO_2CH_2), 5.9 (d, J = 15 Hz, CH=C), 7.8 (d, J = 15 Hz, C=CH).

Anal. Calcd for $C_{10}H_{16}O_3S$: C, 55.6; H, 7.4; S, 14.8. Found: C, 55.5; H, 7.4; S, 14.6.

Reaction of EDSA with Ethoxymethylenemalononitrile.—To a stirred solution of 14.8 g (0.10 mol) of EDSA in 75 ml of absolute ethanol was added dropwise at 40° over 30 min a solution of 6.1 g (0.05 mol) of nitrile in 50 ml of ethanol.

After standing 15 hr longer at 25°, the resulting suspension was chilled and then filtered to give 7.4 g (66% yield based on dinitrile) of ethyl 4,4-dicyano-2-(dimethylsulfuranylidene)-3-butenoate (**5**), mp 184–185°. The melting point was not raised by recrystallization from ethanol. Nmr peaks ($CDCl_3$) were at δ 1.3 (t, 3, CO_2CCH_3), 3.1 (s, 6, $C{=}S(CH_3)_2$), 4.2 (m, 2, CO_2CH_2), and 7.8 (s, 1, C=CH).

Anal. Calcd for $C_{10}H_{12}N_2O_2S$: C, 53.5; H, 5.4; S, 13.6. Found: C, 53.6; H, 5.4; S, 14.3.

Reaction of EDSA with Diphenylketene.—To a stirred solution of 15.6 g (0.08 mol) of diphenylketene in methylene chloride was added portionwise at 10–15° a solution of 5.9 g (0.04 mol) of EDSA in 25 ml of solvent. After 1 hr at 10° and 30 min at 25°, the mixture was treated with pentane and chilled to give 18.2 g (85%) of ethyl 2-(dimethylsulfuranylidene)-4,4,6,6-tetraphenyl-3,5-diketohexanoate (**10**): mp 120–121°; ir ($CHCl_3$), 1720 and 1600 cm^{-1} (C=O); nmr ($CDCl_3$), δ 1.0 (t, 3, CO_2CCH_3), 2.3 (s, 6, $C{=}S(CH_3)_2$), 3.9 (m, 2, CO_2CH_2), 5.0 (s, 1 PhCH), 7.2 (d, 20, Ar).

Anal. Calcd for $C_{34}H_{32}O_4S$: C, 76.1; H, 6.0; S, 5.9. Found: C, 75.9; H, 6.1; S, 5.8.

Reaction of EDSA with Diacetyl. A. In Benzene.—A solution of 8.6 g (0.10 mol) of a diacetyl in 25 ml of benzene was added dropwise with stirring over 2 hr at 45–50° to a solution of 14.8 g (0.10 mol) of EDSA in 100 ml of benzene. After 1 hr longer at 45–50° and 18 hr at 25° the mixture was Claisen distilled to give 8.6 g (50%) of ethyl 2,3-epoxy-3-methyllevulinate (**14a**).

B. In Ethanol.—A solution of 7.4 g (0.05 mol) of EDSA in 25 ml of ethanol was added portionwise at 30–35° to a solution of 8.6 g (0.10 mol) of diacetyl in 50 ml of ethanol. After 18 hr at 25° the mixture was vacuum concentrated to a residue of 13.7 g. This was shaken mechanically with 50 ml of acetone for 30 min, chilled to −10°, and filtered to yield 8.0 g (58%) of 2,6-diacetyl-2,6-dimethyl-5-(dimethylsulfuranylidene)-*m*-dioxan-4-one (**16**): mp 166–169°; ir ($CHCl_3$), 1660 (sh 1700) cm^{-1}; nmr ($CDCl_3$), δ 1.3, 1.6 (2 s, 6, CH_3), 2.2 (s, 6, $COCH_3$), 2.9 (s, 6, $C{=}S(CH_3)_2$).

Anal. Calcd for $C_{12}H_{18}O_5S$: C, 52.6; H, 6.6; S, 11.7. Found: C, 52.5; H, 6.7; S, 11.4.

Reaction of EDSA with Chloral in Ether.—To a stirred solution of 7.4 g (0.05 mol) of chloral in 75 ml of ether was added dropwise at 5° over 30 min a solution of 7.4 g (0.05 mol) of EDSA in 75 ml of ether. After stirring at 5° for 2 hr longer, the mixture was filtered to give 9.6 g (65%) of ethyl 2-(dimethylsulfuranylidene)-3-hydroxy-4,4,4-trichlorobutyrate (**19**): mp 74–75°; ir ($CHCl_3$), 3330 (OH), 1600 cm^{-1} (delocalized C=O); an nmr spectrum was not definitive owing to decomposition.

Anal. Calcd for $C_8H_{13}O_3SCl_3$: C, 32.5; H, 4.4; S, 10.8; Cl, 36.0. Found: C, 32.4; H, 4.2; S, 10.8; Cl, 36.0.

The **sulfonium chloride** (**20**) was prepared by stirring a suspension of 3.0 g (0.01 mol) of the ylide in 50 ml of ether and adding dropwise 3.5 ml of 3.2 *N* ethanolic hydrochloric acid. Stirring caused crystallization of the initially gummy product; it was collected by filtration, washed with acetone, and dried to give 2.9 g (88%): mp 112–113° dec (when placed in a bath initially at 110°); nmr (D_2O), δ 1.4 (t, 3, CO_2CCH_3), 3.1 (d, 6, J = 4 Hz, $C{=}S(CH_3)_2$), 4.4 (m, 2, CO_2CH_2), 4.7 (s, 1, OH), 5.1 (s, 1, CH-O).

Anal. Calcd for $C_8H_{14}O_3SCl_4$: C, 28.9; H, 4.2. Found: C, 28.8; H, 4.3.

Degradation of Ethyl 2,3-Epoxy-3-methylevulinate.—A solution of 8.6 g (0.05 mol) of the subject compound in 75 ml of methyl alcohol was allowed to stand for 18 hr with 30 ml of 2 *N* sodium hydroxide added. The mixture was treated with a few small pieces of Dry Ice and vacuum concentrated to a residue. This was shaken with acetone and filtered to give 8.2 g of insoluble salt. Treatment with saturated ammonium sulfate containing 5 ml of concentrated hydrochloric acid gave an oil which was extracted three times with ether. The combined ether extracts were washed and dried. Vacuum concentration gave 5.3 g (74%) of 2,3-epoxy-3-methylevulinic acid as an oil. Glpc trapping at 200° gave 4-hydroxy-3-methyl-3-buten-2-one (**15a**), mp 70–71° (lit.[14] mp 72°) after recrystallization from hexane.

Anal. Calcd for $C_5H_8O_2$: C, 60.0; H, 8.0. Found: C, 60.0; H, 8.1.

3-Benzoyl-3-phenylglycidic Acid.—To a solution of 5.9 g (0.02 mol) of ethyl 3-benzoyl-3-phenylglycidate (mp 59–60°) in 50 ml of methanol was added 2.0 ml of 10.7 *N* sodium hydroxide. After 18 hr the mixture was treated with a few pieces of Dry Ice and vacuum concentrated at 25°. The residue thus obtained was dissolved in water, treated with 2 ml of concentrated hydrochloric acid, and extracted with ether. The ether extract was processed as above to give 5.3 g (98%) of product, mp 125–127° dec. Recrystallization from ether–hexane gave 4.2 g: mp 127–128° dec; nmr ($CDCl_3$), δ 3.7 (s, 1, CH—O), 7.7 (m, 10, Ar), 11.6 (s, 1, COOH).

Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.6; H, 4.5. Found: C, 71.7; H, 4.6.

***trans*-Ethyl 5-Chloro-4-oxo-2-pentenoate** (**25**).—To a stirred solution of 12.7 g (0.10 mol) of 1,3-dichloro-2-propanone in 75 ml of benzene was added dropwise over 30 min at 15–20° a solution of 14.8 g (0.10 mol) of EDSA in 50 ml of benzene. The mixture was stirred for 5 hr and then stored overnight at 25°.

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[13] H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, **83**, 2952 (1961).

[14] N. K. Kochetkov, *Chem. Abstr.*, **49**, 6090*h* (1955).

Filtration gave 6.7 g (72%) of carbethoxymethyl dimethylsulfonium chloride (**24**) as a hygroscopic white solid (infrared comparison with an authentic sample prepared from EDSA and hydrogen chloride). Distillation of the filtrate gave 4.3 g (34% recovery) of unchanged ketone: bp 73–74° (18 mm); mp and mmp 41–43°. The residue was recrystallized from ether to give 3.6 g (41% yield based on EDSA) of **25**: mp 75.5–76.5°; ir ($CHCl_3$), 1700 (conjd $C{=}O$) and 975 cm^{-1} (*trans* $C{=}C$); nmr ($CDCl_3$), δ 1.3 (t, C, CO_2CCH_3), 4.3 (m, 2, CO_2CH_2), 4.4 (s, 2, $ClCH_2$), 7.0 (m, 2, J = 16 Hz, $CH{=}CH$).

Anal. Calcd for $C_7H_9O_3Cl$: C, 47.5; H, 5.1; Cl, 20.1. Found: C, 47.1; H, 5.1; Cl, 20.0.

Reaction of EDSA with Trichloroacetonitrile. A. In Ether.—A solution of 7.2 g (0.05 mol) of trichloroacetonitrile (TCA) in 50 ml of ether was added dropwise at 0–5° over 30 min to a stirred solution of 7.4 g (0.05 mol) of EDSA in 50 ml of ether. After stirring for 1 hr longer in the cold, 7.2 g (78%) of ethyl chloro(dimethylsulfuranylidene)acetate (**27**) was collected by filtration, washed with cold ether, vacuum dried at −10°, and stored at that temperature: mp 78–83° dec; ir ($CHCl_3$), 1615 cm^{-1} (delocalized $C{=}O$); nmr ($CDCl_3$), δ 1.3 (t, 3, CO_2CCH_3), 2.7 (s, 6, $C{=}S(CH_3)_2$), 4.1 (m, 2, CO_2CH_2).

Anal. Calcd for $C_6H_{11}O_2SCl$: C, 39.4; H, 6.1; S, 17.6; Cl, 19.4. Found: C, 39.2; H, 6.0; S, 16.6;[15] Cl, 20.3.[15]

The **filtrate** from isolation of the chloro ylide was shown to contain 4.5 g (82%) of dichloroacetonitrile (**26**) by distillation, followed by glpc and infrared comparisons with an authentic sample.

B. In Ethanol at 0–5°.—Procedure A was repeated using ethanol in place of ether. After 4 hr longer at 0–5°, the mixture was filtered to recover 3.0 g (21%) of ethyl 2-(dimethylsulfuranylidene)-3-imino-4,4,4-trichlorobutyrate (**30**): mp 136–137° (this was not raised by recrystallization from acetone–hexane); ir ($CHCl_3$), 3230 ($C{=}NH$), 1630 ($C{=}O$), 1550 cm^{-1}; nmr ($CDCl_3$), δ 1.4 (t, 3, CO_2CCH_3), 2.9 (s, 6, $C{=}S(CH_3)_2$), 4.3 (m, 2, CO_2CH_2), 10.5 (s, 1, $C{=}NH$).

Anal. Calcd for $C_8H_{12}NO_2SCl_3$: C, 32.8; H, 4.1; S, 11.0; N, 4.8; Cl, 36.4. Found: C, 32.9; H, 4.3; S, 11.0; N, 4.8; Cl, 36.2.

C. In Ethanol at 30–35°.—Procedure B was carried out at 30–35°. After an overnight stand at 25°, the red-orange solution was vacuum concentrated at 25° to a residue of 11.8 g. This was shaken with 125 ml of acetone and filtered to give 5.3 g (36%) of ethyl 4,4-dichloro-2-(dimethylsulfuranylidene)-3-iminobutyrate hydrochloride (**31**), mp 158–159° dec. This was not changed by recrystallization from ethanol–acetone: ir (KBr), 1690 and 1640 cm^{-1} ($C{=}O$); nmr (D_2O), δ 1.5 (t, 3, CO_2CCH_3), 3.2 (s, 6, $C{=}S(CH_3)_2$), 4.5 (m, 2, CO_2CH_2), 4.8 (s, 2, $C{=}NH \cdot HCl$), 7.5 (s, 1, $CHCl_2$).

Anal. Calcd for $C_8H_{14}NO_2SCl_3$: C, 32.6; H, 4.8; S, 10.9. Found: C, 32.6; H, 4.9; S, 10.9.

Ethyl 4,4-Dichloro-2-(dimethylsulfuranylidene)-3-iminobutyrate (32).—A solution of 6.8 g (0.023 mol) of imine hydrochloride in 25 ml of water was shaken with a mixture of 25 ml of saturated potassium carbonate and 75 ml of chloroform. The chloroform layer was washed, dried, and vacuum concentrated to a residue. Recrystallization from chloroform–hexane gave 4.4 g (74%) of **32**: mp 92–94°; ir ($CHCl_3$), 1630 and 1560 cm^{-1} ($C{=}O$); nmr ($CDCl_3$), δ 1.3 (t, 3, CO_2CCH_3), 3.0 (s, 6, $C{=}S(CH_3)_2$), 4.2 (m, 2, CO_2CH_2), 7.2 (s, 1, $CHCl_2$), 8.9 (s, 1, $C{=}NH$).

Anal. Calcd for $C_8H_{13}NO_2SCl_2$: C, 37.2; H, 5.1; Cl, 27.5. Found: C, 37.3; H, 5.1; Cl, 27.7.

A small sample was dissolved in acetone and treated with ethanolic hydrogen chloride to regenerate the imine hydrochloride, mp 158–159° dec.

Ethyl 4,4-Dichloro-2-(dimethylsulfuranylidene)acetoacetate (2d).—A 1.7-g sample of **32** was boiled for 5 min with 75 ml of water (ammonia odor). After hot filtration, cooling gave 1.0 g (60%) of **2d**, mp 141–142°. A mixture melting point with the product from EDSA and dichloroacetyl chloride was not depressed and their infrared spectra were identical.

Reaction of EDSA with Dichloroacetonitrile in the Presence of Sulfonium Salt.—To a solution of 5.5 g (0.05 mol) of dichloroacetonitrile and 9.3 g (0.05 mol) of carbethoxymethyl dimethylsulfonium chloride[16] in 50 ml of ethanol was added 3.0 g (0.02 mol) of EDSA. After 24 hr the orange-red solution was vacuum concentrated to a residue. The latter was shaken with 100 ml of acetone and filtered to give 11.8 g of product, mp 150–153° (preliminary softening at about 90–100°). This was dissolved in 50 ml of water, treated with 25 ml of saturated potassium carbonate, and extracted with chloroform. Washing, drying, and concentration gave a residue which was recrystallized from chloroform–hexane to give 4.4 g (34% yield based on dichloroacetonitrile) of **32**, mp 91–93°. A mixture melting point with the product prepared above was not depressed.

Reaction of Ethyl Chloro(dimethylsulfuranylidene)acetate with Acrylonitrile.—To a freshly prepared solution of 6.7 g (0.037 mol) of the chloro ylide (**17**) in 75 ml of chloroform was added 5.3 g (0.10 mol) of acrylonitrile. The mildly exothermic reaction was held below 30°. After 18 hr the mixture was water washed, dried, vacuum concentrated, and Claisen distilled to give 3.9 g (58%) of ethyl 2-cyano-1-methylthiocyclopropanecarboxylate (**29**): bp 75–80° (<1 mm); n^{25}_D 1.4879. The product (30:70 ratio of *cis/trans* isomers) was identified by glpc and infrared comparisons with an authentic sample.[2]

Reaction of Ethyl Chloro(dimethylsulfuranylidene)acetate with Ethyl Acrylate.—The above reaction was repeated using ethyl acrylate in place of acrylonitrile. Distillation gave 5.1 g (60%) of diethyl 1-methylthio-1,2-cyclopropanedicarboxylate: bp 75–85° (<1 mm); n^{25}_D 1.4753. The product was identified by glpc and infrared comparisons with an authentic sample.[2]

Registry No.—**4a,** 16980-34-0; *cis* **4b,** 16980-35-1; *trans* **4b,** 16980-36-2; **4c,** 16980-52-2; **5,** 16980-37-3; **10,** 16980-38-4; 3-benzoyl-3-phenylglycidic acid, 16980-41-9; **16,** 16980-42-0; **19,** 16980-45-3; **20,** 16980-53-3; **25,** 16980-46-4; **27,** 16980-47-5; **30,** 16980-49-7; **31,** 16980-48-6; **32,** 16980-50-0.

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(15) Value obtained on sample with mp 70–73° dec.

(16) This compound was prepared by bubbling hydrogen chloride into a benzene solution of EDSA, followed by recrystallization from ethanol–ether: mp 99–100° dec.