mosphere. After the bubbling had ceased, the solution was stirred for an additional 3 hr and then permitted to warm to room temperature. The platinum black was removed by filtration and washed with a few milliliters of 50% methanol–water. The solution and washing were evaporated to a constant weight using a rotatory evaporator and a steam bath to give 3.9 g of crude **12** as a thick, light orange oil that solidified upon standing at room temperature. Final drying of the crude N-oxide was accomplished in a vacuum desiccator containing silica gel. The crude product melted at 35–37°. The picrate of **12**, after three crystallizations from 95% ethanol, melted at 161–162°.

Anal. Calcd for $C_{19}H_{24}N_4O_8$: C, 52.29; H, 5.54; N, 12.83. Found: C, 52.27; H, 5.34; N, 12.30.

Pyrolysis of N-Oxide 12.—The pyrolysis tube was a 250 × 22 mm Pyrex tube wound with a nichrome wire heater and filled to a height of 80 mm with $^3/_8$-in. glass helices. The tube was mounted vertically and a short Liebig condenser attached to the top. A dropping funnel with a nitrogen inlet was connected to the condenser. The bottom end of the tube opened directly into a flask that had an outlet leading to a second trap. Both traps were cooled in a Dry Ice bath.

A solution of 3.85 g (0.0185 mole) of crude **12** in 40 ml of freshly dried and distilled tetrahydrofuran was dried further by addition of 3 g of Linde 4A Molecular Sieve pellets. After 3 hr in contact with the sieves, the solution was filtered through glass wool and dripped (10 drops/sec) into the pyrolysis chamber, which was maintained at 320°. After addition of 25 ml of pentane to the pyrolysate, the solution was washed with 50 ml of water and the water layer was extracted with 25 ml of fresh pentane. The combined pentane extracts were washed twice with 15 ml of cold 10% sulfuric acid and then with small portions of water until the washings were neutral. Concentration of the dried (magnesium sulfate) pentane solution in a rotatory evaporator gave 1.7 g of product, which was *ca.* 85% pure according to glpc analysis on a 4% Carbowax 20 M column. Preparative glpc on a 20% Carbowax 20 column gave 0.5 g (22%) of product, bp 56° (7 mm). The amine was recovered in 17% yield as described under the pyrolysis of **11**.

Registry No.—**1**, 6572-54-9; **7**, 13619-10-8; **6**, 13619-06-2; **9**, 13619-07-3; **10**, 13619-08-4; **11**, 13619-09-5; **12**, 13618-84-3; **12**, picrate, 13618-85-4; *endo*-2-dimethylaminolucyclo[2.2.1]hept-5-ene-7-spiro-1′-cyclopentane methiodide, 13618-86-5; **8**, 13619-11-9.

Cyclopropanes from Reactions of Ethyl (Dimethylsulfuranylidene)acetate with α,β-Unsaturated Compounds

GEORGE B. PAYNE

Shell Development Company, Emeryville, California

Received May 4, 1967

Ethyl (dimethylsulfuranylidene)acetate has been isolated in 90–95% yield as an analytically pure liquid and stored successfully for several weeks at −10°; it decomposed slowly at room temperature. Reaction of the ylide with a variety of α,β-unsaturated esters, ketones, aldehydes, and nitriles readily afforded cyclopropyl compounds in yields of 40–90%.

Recent publications concerned with several different resonance-stabilized sulfonium ylides have covered their preparation and spectral properties, but relatively few of their chemical reactions have been described.[1] Most recently, the preparation and properties of a number of sulfonium and oxosulfonium carbalkoxymethylides were reported.[2] Here again, the emphasis was on synthesis of new ylides rather than on their utilization as chemical intermediates.

Ethyl (dimethylsulfuranylidene)acetate (**1**, EDSA) was recently prepared by the reaction of the requisite sulfonium halide with sodium hydride (NaH) in tetrahydrofuran (THF), and its reaction *in situ* with Schiff bases was described.[1a] In later reports, nuclear magnetic resonance (nmr) and infrared spectral data were recorded.[1b]

$$^-X(CH_3)_2S^+CH_2CO_2C_2H_5 \xrightarrow[THF]{NaH} \underset{1}{(CH_3)_2S{=}CHCO_2C_2H_5}$$

Owing to its ease of preparation (by a new procedure described below), as well as to the potential utility of its derivatives, EDSA has undergone independent studies in these laboratories. We are reporting here a general synthesis of cyclopropyl derivatives by reaction of EDSA with a variety of α,β-unsaturated compounds.

Preparation of EDSA.—Treatment of a vigorously stirred chloroform solution of carbethoxymethyl dimethylsulfonium bromide with saturated potassium carbonate solution containing 1 molar equiv of sodium hydroxide afforded EDSA as an analytically pure residue in 90–95% yield. The reaction required 15 min at 10–20° and the product was isolated by vacuum removal of chloroform from the dried organic layer. EDSA was best stored at −10°; there it suffered little change during 1-month's time. At room temperature EDSA deteriorated gradually, and the nature of its decomposition is discussed below.

Exposure to moisture caused rapid conversion of EDSA to the inner salt (**2**). For this reason, it was important to use anhydrous reagents in reactions involving EDSA. Indeed, the successful isolation of this ylide from the water-containing reaction mixture used in its preparation must be attributed to its great solubility in chloroform relative to saturated aqueous potassium carbonate.

$$(CH_3)_2S{=}CHCO_2C_2H_5 + H_2O \longrightarrow \underset{2}{(CH_3)_2S^+CH_2COO^-} + C_2H_5OH$$

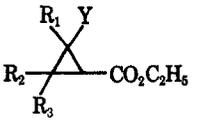
Summary of Results.—Reaction of EDSA with α,β-unsaturated systems has generally led to substituted cyclopropanes. The mechanism undoubtedly

(1) (a) A. J. Speziale, C. C. Tung, K. W. Ratts, and A. Yao, *J. Am. Chem. Soc.*, **87**, 3460 (1965); (b) K. W. Ratts and A. Yao, *J. Org. Chem.*, **31**, 1185, 1689 (1966); (c) A. W. Johnson and R. T. Amel, *Tetrahedron Letters*, No. 8, 819 (1966); (d) B. M. Trost, *J. Am. Chem. Soc.*, **89**, 138 (1967); (e) K. W. Ratts, *Tetrahedron Letters*, No. 39, 4707 (1966); (f) H. Nozaki, M. Takaku, and K. Kondo, *Tetrahedron*, **22**, 2145 (1966); (g) H. König, H. Metzger, and K. Seelert, *Chem. Ber.*, **98**, 3712, 3724, 3733 (1965); (h) A. Hochrainer and F. Wessely, *Monatsh. Chem.*, **97**, 1 (1966); (i) A. Hochrainer, *ibid.*, **97**, 823 (1966); (j) A. Hochrainer and W. Silhan, *ibid.*, **97**, 1477 (1966).

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

TABLE I

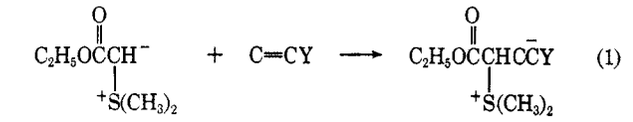
CYCLOPROPANES FROM α,β-UNSATURATED ALDEHYDES, KETONES, AND ESTERS



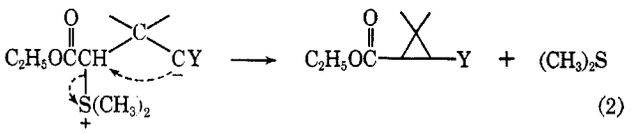
Starting material	Product[a]	Solvent[b]	Reaction temp, °C	Reaction time, hr	Yield, % on EDSA	Isomer ratio, *trans–cis*[c]
Acrolein	(3) Y = CHO	A	60	0.3	63	83:17
Crotonaldehyde	(4) Y = CHO; R_2 = CH_3	A	60	0.3	50	82:18
Methacrolein	(5) Y = CHO; R_1 = CH_3	B	80	1	86	68:32
Methyl vinyl ketone	(6) Y = $COCH_3$	C	45	2.5	87	98:2
Mesityl oxide	(7) Y = $COCH_3$; R_2, R_3 = CH_3	B	80	18	75	100:0[d]
2-Cyclohexen-1-one	(8) Y, R_2 = $CO(CH_2)_3$	B	80	18	71	*e*
Diethyl fumarate	(9) Y, R_2 = $CO_2C_2H_5$	B	80	2	91	100:0
Diethyl maleate	(10) Y, R_2 = $CO_2C_2H_5$	C	45	3	79	*e*
Ethyl acrylate	(11) Y = $CO_2C_2H_5$	C	25	18	84	97:3
Methyl methacrylate	(12) Y = CO_2CH_3; R_1 = CH_3	C	45	18	69	91:9
Ethyl crotonate	(13) Y = $CO_2C_2H_5$; R_2 = CH_3	C	45	18	71	57:43
Dimethyl itaconate	(14) Y = CO_2CH_3; R_1 = $CH_2CO_2CH_3$	B	80	18	89	*f*

[a] R = H unless otherwise specified. [b] A = acetone; B = benzene; C = methylene chloride; D = excess ester as solvent. [c] Glpc analysis; assignments confirmed chemically with products **3**, **7**, **9**, **11**, **12**, and **13**. [d] No separate peak for *cis* isomer. [e] Two isomers not resolved completely; approximately 2:1 ratio of peaks. [f] Not determined.

involves a nucleophilic attack by ylide carbon (step 1), followed by ring closure with elimination of dimethyl sulfide (step 2). This carbethoxymethylene transfer



(1)



(2)

to the α,β-carbon–carbon double bond is reminiscent of the methylene transfer achieved by Corey and Chaykovsky in their reactions with dimethyloxo-sulfoniummethylide.[3] The electron-withdrawing groups (Y) found effective were CHO, C(=O)R, C(=O)OR, CN, $(CN)_2$, $(CO_2R)_2$, and (CN, CO_2R). In addition, cyclopropanes were formed in 80–90% yields from substrates (diethyl maleate and diethyl fumarate) having electron-withdrawing groups at each end of the double bond.

In the several cases investigated, the reaction was shown to proceed with *trans* stereochemistry predominating (Y *trans* to $CO_2C_2H_5$). The ratio of *trans–cis* isomers varied from about 60:40 to 98:2.

Cyclopropane formation was usually achieved by allowing equimolar amounts of EDSA and the α,β-unsaturated compound to react in an aprotic solvent such as benzene at ambient temperature or at reflux. Substances with terminal vinyl groups (methyl vinyl ketone, acrolein, acrylonitrile) reacted exothermally and required no further heating. Efficient reactions of EDSA with more highly substituted double bonds (mesityl oxide, etc.) were facilitated by use of an excess of such reactants. Products were isolated by direct distillation of the reaction mixtures.

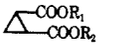
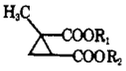
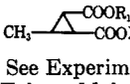
α,β-Unsaturated Aldehydes, Ketones, and Esters.—Table I summarizes results obtained from a study of the reaction of EDSA with these materials. Excellent yields (75–90%) of the expected cyclopropanes were secured from methacrolein, methyl vinyl ketone, mesityl oxide, diethyl fumarate, diethyl maleate, ethyl acrylate, and dimethyl itaconate, while 50–75% yields were obtained in other cases.

Stereochemistry.—Products **3**, **7**, **9**, **11**, **12**, and **13** (Table I) were subjected to oxidation and/or hydrolysis in order to establish the stereochemistry (see Experimental Section). In all cases the *trans* isomer predominated; in addition, this isomer always showed the shortest retention time on gas–liquid partition chromatography (glpc) analysis.[4] This then allowed a reasonably firm (but tentative) assignment of isomer distributions in those cases where rigorous examinations were not made.

It was of particular interest to contrast yields and stereochemistry of products formed in the present study with those reported for the Darzens reaction of α,β-unsaturated esters with α-halo esters to produce cyclopropanes.[5] Table II summarizes those three cases where a direct comparison with the literature could be made.

TABLE II

COMPARISON OF SULFONIUM YLIDE AND DARZENS METHODS OF PREPARING SUBSTITUTED CYCLOPROPANES

Compound	R_1	R_2	Yield, %	*cis*, %	*trans*, %	Method
	C_2H_5	C_2H_5	84	3	97	Ylide
	C_2H_5	C_2H_5	51	81	19	Darzens[a]
	C_2H_5	CH_3	43	60	40	Darzens[b]
	CH_3	C_2H_5	69	9	91	Ylide
	CH_3	CH_3	70	80	20	Darzens[b]
	C_2H_5	C_2H_5	71	43	57	Ylide
	C_2H_5	C_2H_5	28	50	50	Darzens[b]

[a] See Experimental Section. [b] R. Oda, T. Shono, A. Oku, and H. Takao, *Makromol. Chem.*, **67**, 124 (1963).

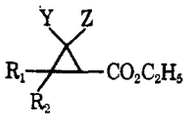
(3) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965).

(4) A cyanoethylated silicone (XF-1150) on Chromosorb W column was used exclusively; the *cis* and *trans* peaks were usually well separated.

(5) See L. L. McCoy, *J. Am. Chem. Soc.*, **84**, 2246 (1962), for leading references to this type of Darzens reaction.

TABLE III

CYCLOPROPANES FROM α,β-UNSATURATED DIFUNCTIONAL COMPOUNDS

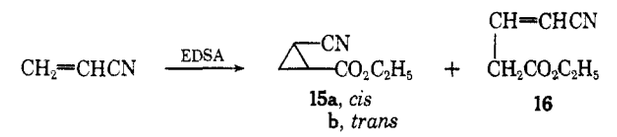


Starting material	Product[a]	Reaction temp, °C	Reaction time, hr	Yield, % on EDSA
Isopropylidenemalononitrile	(**18**) Y, Z = CN; R_1, R_2 = CH_3	45–25	18	85
Ethyl isopropylidenecyanoacetate	(**19**) Y = CN; Z = $CO_2C_2H_5$; R_1, R_2 = CH_3	45–25	18	91
Diethyl ethylidenemalonate	(**20**) Y, Z = $CO_2C_2H_5$; R_1 = CH_3	42–45	18	90
Diethyl isopropylidenemalonate	(**21**) Y, Z = $CO_2C_2H_5$; R_1, R_2 = CH_3	80	18	65

[a] R = H unless otherwise specified.

Acrylonitrile.—This compound reacted exothermally with EDSA in methylene chloride to give a mixture of three isomers in 70% total yield. Glpc analysis indicated a 75:8:17 distribution. The major component (**15b**) was isolated by fractional distillation and its structure assigned as ethyl *trans*-2-cyanocyclopropanecarboxylate following acid hydrolysis to *trans*-1,2-cyclopropanedicarboxylic acid. Similarly, the 17% component was isolated by glpc trapping and its *cis* configuration established by conversion to the *cis*-diethyl ester of 1,2-cyclopropanedicarboxylic acid.

The minor component was not isolated. However, the nuclear magnetic resonance (nmr) spectrum of the mixture showed absorption at δ 3.3 which was consistent with a methylene group flanked by both carbonyl and C=C. Partly for this reason, but mainly because of the isolation of an analogous product from the reaction of crotononitrile and EDSA,[6] the minor component was assigned the structure ethyl 4-cyano-3-butenoate (**16**).

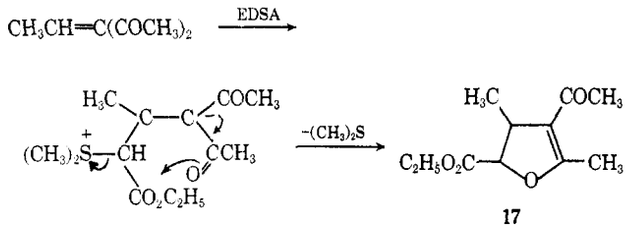


15a, *cis*
b, *trans*

16

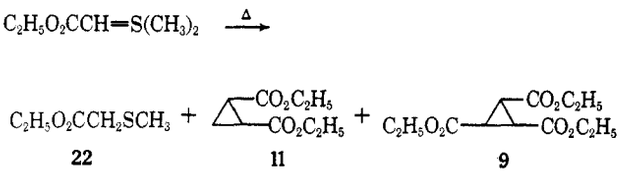
α,β-Unsaturated Difunctional Compounds.—Reaction of EDSA with compounds containing two activating groups attached to the same carbon proceeded readily and in good yield to give the expected cyclopropane. Table III summarizes results obtained with several such materials.

Reaction of 3-ethylidene-2,4-pentanedione with EDSA led to ethyl 4-acetyl-3,5-dimethyl-2,3-dihydrofuran-2-carboxylate (**17**) rather than to a cyclopropane derivative. Structure **17** was assigned on the basis of elemental, nmr, and ultraviolet analyses.



17

Decomposition of EDSA.—In view of the relative instability of EDSA at room temperature, its decomposition in refluxing solvents was investigated. On heating in dimethoxyethane at 125° for 2 hr (autoclave), three products (**9**, **11**, and **22**) were obtained in nearly equal amounts by weight. They were isolated by distillation and identified by comparison with authentic samples.



22 **11** **9**

When EDSA was allowed to reflux in benzene (80°), it decomposed to the extent of 35% in 3 hr. In refluxing dimethoxyethane (86°), 82% deterioration was noted in the same time span.

Experimental Section[7]

Carbethoxymethyl Dimethylsulfonium Bromide.—A solution of 265 g (1.59 moles) of ethyl bromoacetate and 114 g (1.84 moles) of dimethyl sulfide in 500 ml of acetone was stored in a water bath for 3 days. Filtration gave 326 g (90%) of the sulfonium bromide, mp 78–80° dec (lit.[1a] mp 85–87°).

The nmr spectrum showed singlets at δ 3.5 (6 H, $S(CH_3)_2$) and 5.3 (2 H, CH_2), a triplet at δ 1.3 (3 H, CO_2CCH_3), and a quartet at δ 4.3 (2 H, CO_2CH_2–).

Ethyl (Dimethylsulfuranylidene)acetate (EDSA).—A solution of 163 g (0.71 mole) of sulfonium bromide in 565 ml of chloroform was stirred vigorously at 5–10° with ice-bath cooling and treated in one portion with a mixture of 425 ml of saturated potassium carbonate solution[8] and 56.6 ml of 12.5 *N* sodium hydroxide. The reaction mixture warmed to 15–20° and was held there for an additional 15 min. After removal of salt by filtration, the filtrate was separated and the upper chloroform layer was dried for 2 hr over potassium carbonate. Removal of solvent under vacuum (Rinco) at 25° and 1 mm gave the light yellow ylide with constant weight of 100 g (95% yield), $n^{25}D$ 1.5253–1.5263.

Anal. Calcd for $C_6H_{12}O_2S$: C, 48.6; H, 8.2; S, 21.6. Found: C, 48.6, 48.7; H, 8.1, 8.1; S, 21.8. The infrared spectrum (chloroform) showed delocalized carbonyl absorption at 6.24 μ and other significant bands at 7.2, 7.3, 7.6, 8.8, 9.1, 9.4, 9.8, 10.3, and 11.2 μ; the 11.2-μ band was the strongest of these. The ultraviolet spectrum showed $\lambda_{max}^{isooctane}$ 267 mμ (ε 7800) and λ_{max}^{EtOH} 256 mμ (ε 4020). The nmr showed a triplet at δ 1.2 (3 H, $COOCCH_3$), a quartet at δ 3.9 (2 H, CO_2CH_2), and a singlet with a shoulder at δ 2.7–2.8 [7 H, $CH=S(CH_3)_2$].

The ylide was stored at −10° using a bottle fitted with a Teflon-lined screw cap, and wrapped with tape.

(6) G. B. Payne, unpublished results, Shell Development Co.

(7) Melting points are corrected; boiling points are uncorrected. Nmr spectra were obtained in $CDCl_3$ with a Varian A-60 spectrometer using tetramethylsilane as internal standard. Glpc analyses were done on an F & M Model 720 instrument using a 10-ft column packed with 5% of XF-1150 on Chromosorb W.

(8) Prepared by dissolving 650 g of $K_2CO_3 \cdot 1.5H_2O$ in 500 ml of water, adding 170 ml of anhydrous carbonate, stirring overnight, and filtering. Any salt that precipitated later was redissolved by warming on the steam bath.

TABLE IV

CHARACTERIZATION DATA ON SUBSTITUTED CYCLOPROPANES[a]

Compd	Bp, °C (mm)	$n^{25}D$	Formula	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found
3	45 (<1)	1.4488	$C_7H_{10}O_3$	59.1	59.3	7.1	6.9
4	40–43 (<1)	1.4498	$C_8H_{12}O_3$	61.5	61.5	7.7	7.8
5	45 (<1)	1.4487	$C_8H_{12}O_3$	61.5	61.4	7.7	7.8
6	65–68 (1)	1.4446	$C_8H_{12}O_3$	61.5	61.4	7.7	7.8
7	69–70 (1)	1.4555	$C_{10}H_{16}O_3$	65.2	64.4[b]	8.8	8.7
8	94–96 (1)	1.4845	$C_{10}H_{14}O_3$	65.9	65.5	7.7	7.7
9	110–113 (<1)[c]	1.4474					
10	105–107 (<1)[d]	1.4493					
11	70–71 (1)[e]	1.4392					
12	75–78 (2)	1.4420	$C_9H_{14}O_4$	58.1	57.8	7.6	7.6
13	62–67 (<1)	1.4422	$C_{10}H_{16}O_4$	60.0	59.8	8.1	8.1
14	102–105 (<1)	1.4510	$C_{11}H_{16}O_5$	54.0	53.8	6.7	6.7
18	93–94 (<1)	1.4624	$C_{10}H_{12}O_2N_2$	62.5	62.4	6.3	6.3
19	104–106 (<1)	1.4560	$C_{12}H_{14}O_4N$	60.2	60.0	7.2	7.2
20	96–99 (<1)	1.4446	$C_{13}H_{20}O_6$	57.4	57.1	7.4	7.5
21	109–111 (<1)	1.4460	$C_{14}H_{22}O_6$	58.8	58.4	7.7	7.8

[a] On mixtures of isomers; all new compounds showed infrared and nmr spectra in agreement with the assigned structures. [b] Low owing to presence of diethyl 1,2-cyclopropanedicarboxylate as an impurity. [c] G. Maier (*Chem. Ber.*, **95**, 611 (1962)) reports bp 92° (0.04 mm). [d] Glpc indicated *trans-cis* isomers in a ratio of about 2:1. [e] A. T. Blomquist and D. T. Longone (*J. Am. Chem. Soc.*, **81**, 2012 (1959)) report bp 111–113° (1–0 mm), $n^{25}D$ 1.4374–1.4378.

Decomposition of EDSA.—A nitrogen-purged solution of 32.2 g (0.22 mole) of EDSA in 75 g of dry dimethoxyethane (DME) was heated wih stirring at 125° for 2 hr in a 300-ml-capacity autoclave (Magnedrive). The cooled mixture was flashed at 25° and 5 mm to give recovered DME containing 9.1 g (68%) of dimethyl sulfide (glpc). The residue of 22 g was analyzed by glpc: DME (26%) and products A (27%), B (25%), and C (22%).

Product A was isolated by fractional distillation, bp 50–52° (5 mm), $n^{25}D$ 1.4561. It was identified as ethyl (methylthio)-acetate by infrared and glpc comparisons with the product obtained from thermal decomposition of the sulfonium bromide (see below).

Product B was also isolated by fractional distillation, bp 73–74° (1 mm), $n^{25}D$ 1.4386. It was identified as *trans*-diethyl 1,2-cyclopropanedicarboxylate by glpc and infrared comparisons with the product prepared from EDSA and ethyl acrylate.

Claisen distillation of the heavy ends from isolation of A and B gave product C, bp 106–108° (1 mm), $n^{25}D$ 1.4487; it was identified as triethyl 1,2,3-cyclopropanetricarboxylate by glpc and infrared comparisons with the product from EDSA and diethyl fumarate.

Saponification of C gave *trans*-1,2,3-cyclopropanetricarboxylic acid, mp 214–217° (lit.[9] mp 213–217°).

Ethyl (Methylthio)acetate.—A 25-g (0.11 mole) sample of carbethoxymethyl dimethylsulfonium bromide was heated at 5 mm with a hot air gun. In less than 0.5 hr, 11.0 g of product was collected, bp 40–60°. Glpc analysis showed it to be a 20:80 mixture of ethyl bromoacetate and ethyl (methylthio)acetate. The yields were 12 and 60%, respectively. A pure sample of the methylthio compound was isolated by glpc trapping.

Reaction of EDSA with Acrolein.—To a stirred solution of 14.8 g (0.10 mole) of EDSA in 100 ml of refluxing dry acetone was added dropwise over 5 min 7.0 ml (0.10 mole) of acrolein. After 10 min longer the mixture was Claisen distilled to give 9.0 g (63%) of ethyl 2-formylcyclopropanecarboxylate, bp 45° (<1 mm), as an 83:17 mixture of *trans-cis* isomers (glpc) (see Table IV, **3**, for analysis).

The infrared spectrum ($CHCl_3$) showed carbonyl absorption at 5.85 μ and other significant bands at 7.2, 7.6, 7.8, 8.5, 9.1, 9.8, 10.2, 11.4, and 11.7 μ. Nmr showed a triplet at δ 1.3 (3 H, CO_2CCH_3), a quartet at δ 4.2 (2 H, CO_2CH_2–), a multiplet at δ 1.5–2.5 (4 H, cyclopropyl protons), and a singlet at δ 9.3 (1 H, CHO). Glpc trapping of the mixture allowed the isolation of 99% purity *cis*-ethyl 2-formylcyclopropanecarboxylate with an nmr spectrum virtually the same as the 83:17 mixture.

Conversion of Ethyl 2-Formylcyclopropanecarboxylate to *trans*-1,2-Cyclopropanedicarboxylic Acid.—A stirred solution of 7.1 g (0.05 mole) of formyl ester (83:17 mixture) in 50 g of 98% formic acid was held at 50–55° as 4.8 g (0.07 mole) of 50% hydrogen peroxide was added over 10 min. After standing overnight, the mixture was treated with 0.2 g of 5% palladium on charcoal and distilled slowly through a 0.7 × 50 cm glass spiral packed column. After 4 hr, 5 ml had been removed and the head temperature had risen from 88 to 98°. The mixture was vacuum concentrated to an oily residue; this was crystallized from ether–hexane to give 2.3 g (35%) of *trans*-1,2-cyclopropanedicarboxylic acid, mp 157–167°. Recrystallization gave 1.0 g with mp 172–174°; a mixture melting point with the product derived from EDSA and ethyl acrylate (see below) was not depressed (lit.[10] mp 175°).

Esterification of 0.8 g of acid was carried out by fractional distillation with 10 g of ethyl orthoformate.[11] Glpc comparison of the solution with the diester product from EDSA and ethyl acrylate confirmed the *trans* stereochemistry of that material.

Reaction of EDSA with Ethyl Acrylate.—A solution of 5.0 g (0.05 mole) of ethyl acrylate and 7.4 g (0.05 mole) of EDSA in 75 ml of methylene chloride was held overnight at 25°. Claisen distillation gave 7.8 g (84%) of diethyl 1,2-cyclopropanedicarboxylate, bp 70–71° (1 mm) (see Table IV, **11**). Glpc analysis indicated a 97:3 ratio of *trans-cis* isomers. An authentic sample of the *cis* isomer (see below) showed the same emergence time as the minor component.

Saponification gave the known *trans*-1,2-cyclopropanedicarboxylic acid, mp 169–173° (lit.[10] mp 175°), after one crystallization from ether–hexane.

***cis*-Diethyl 1,2-Cyclopropanedicarboxylate.**—A literature procedure[12] was followed, substituting ethyl acrylate for methyl acrylate. From 50 g of ethyl acrylate and 61 g of ethyl chloroacetate was obtained 52.7 g of crude mixture, bp 50–90° (1 mm). Glpc analysis indicated the presence of 10% of ethyl chloroacetate, 17% of *trans* diester, and 73% of *cis* diester. The latter was isolated by fractional distillation to give 20 g, bp 83–84° (1 mm), $n^{25}D$ 1.4404, showing 97% *cis* content by glpc.

Triethyl *trans*-1,2,3-Cyclopropanetricarboxylate.—The following procedure was generally used with those compounds that reacted exothermally with EDSA. To a solution of 43 g (0.25 mole) of diethyl fumarate in 125 ml of benzene was added a solution of 37 g (0.25 mole) of EDSA in benzene. The mixture warmed to 45–50°; when no longer exothermic, it was refluxed for 1 hr. Vacuum concentration, followed by Claisen distillation, gave 59.0 g (91%) of triester, bp 110–113° (<1 mm) (see Table IV, 9). Glpc analysis indicated a purity of 98%, with 2% of diethyl fumarate as the impurity.

The **trishydrazide** was prepared in methanol containing excess hydrazine at reflux for 10 min. Chilling gave a 50% yield, mp 200–203° dec (lit.[13] mp 203–205°).

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trans-1-Methyl-1,2-Cyclopropanedicarboxylic Acid.—A 5.0-g sample of the diester obtained from EDSA and methyl methacrylate (Table IV, **12**) was allowed to reflux for 7 hr with 80% formic acid. Concentration under vacuum, followed by crystallization of the residue from acetonitrile gave 0.5 g (17% yield) of *trans*-1-methyl-1,2-cyclopropanedicarboxylic acid, mp 162–165°; another crystallization gave mp 168–169° (lit.[12] mp 170°).

3-Methyl-*trans*-1,2-cyclopropanedicarboxylic Acid and 3-Methyl-*cis*-1,2-cyclopropanedicarboxylic Anhydride.—A 13.0-g (0.065 mole) sample of the 60:40 mixture of *trans-cis* diesters derived from ethyl crotonate and EDSA (Table IV, **13**) was boiled overnight with 60 ml of 80% formic acid. Vacuum concentration gave 10 g of crude residue which was treated with 25 ml of thionyl chloride. After 2 hr at 25°, followed by 3 hr at reflux, the mixture was concentrated at the water pump; the residue was distilled through a glass spiral packed column to give 5.5 g of fraction 1, bp 50–51° (2 mm), and 1.0 g of fraction 2, bp 51–57° (1 mm). Warming the base of the column melted solid material that had collected there. Recrystallization from ether gave 0.4 g, mp 78–80° (lit.[12] mp 75–78° for the *cis* anhydride).

Fraction 1 was identified as 3-methyl-*trans*-1,2-cyclopropanedicarbonyl chloride by its boiling point (lit.[14] bp 68° (8 mm)) and by its reaction with hot water to give the *trans* diacid, mp 144–147° (lit.[12] mp 148–149°) after two crystallizations from acetonitrile.

A 1-ml portion of fraction 1 was boiled for 15 min with 5 ml of ethanol to give a solution containing the *trans*-diethyl ester. Its emergence time (glpc) coincided with that of the major component in the original ester mixture.

Reaction of the *cis* anhydride with acidic ethanol at reflux gave a solution containing the *cis*-diethyl ester. Its glpc emergence time was the same as that of the minor component in the original mixture.

Ethyl 4-Acetyl-3,5-dimethyl-2,3-dihydrofuran-2-carboxylate.—To a solution of 7.4 g (0.05 mole) of EDSA in 50 ml of benzene was added 6.3 g (0.05 mole) of 3-ethylidene-2,4-pentanedione. An exothermic reaction carried the temperature to 60°. After standing overnight the mixture was distilled to give 8.4 g (83%) of product, bp 87–90° (<1 mm), $n^{25}D$ 1.4761.

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.2; H, 7.6. Found: C, 61.8; H, 7.7. Ultraviolet analysis showed $\lambda_{max}^{isooctane}$ 265 mμ (ε 8900). Nmr analysis showed multiplets at δ 1.0–1.5 (6 H, CH_3 and CO_2CCH_3), at 2.1–2.5 (6 H, $COCH_3$ and $C{=}CCH_3$), and at δ 3.4 (1 H, C=CCH) as well as a quartet at δ 4.2 (2 H, CO_2CH_2), and a doublet at δ 4.5 (1 H, CHO).

Reaction of EDSA with Acrylonitrile.—To a refluxing solution of 22.2 g (0.15 mole) of EDSA in 100 ml of methylene chloride was added dropwise over 10 min a solution of 8.5 g (0.16 mole) of acrylonitrile in 15 ml of solvent. After 0.5 hr longer at reflux the mixture was held at 25° for 18 hr. Claisen distillation gave 14.7 g (70%) of product, bp 60–75° (<1 mm). Glpc analysis showed components A (75%), B (8%), and C (17%). Product A was isolated by fractional distillation, bp 80–82° (3 mm), $n^{25}D$ 1.4458, and assigned the structure of ethyl *trans*-2-cyanocyclopropanecarboxylate.

Anal. Calcd for $C_7H_9NO_2$: C, 60.4; H, 6.5. Found: C, 60.7; H, 6.7. Nmr analysis showed multiplets at δ 1.1–1.7 (5 H, $H_2\triangle CO_2CCH_3$) and δ 1.8–2.4 (2 H, H△H) and a quartet at δ 4.2 (2 H, CO_2CH_2).

Product C of 68% purity, bp 84–87° (1 mm), was obtained by distillation; glpc trapping then gave 99% purity material, $n^{5}D$ 1.4503, with analyses in support of ethyl *cis*-2-cyanocyclopropanecarboxylate.

Anal. Calcd for $C_7H_9NO_2$: C, 60.4; H, 6.5; mol wt, 139. Found: C, 60.3; H, 6.5; mol wt, 139 (mass spectrum). The nmr spectrum was virtually identical with that of the *trans* isomer; infrared analysis showed a nitrile band at 4.45 μ.

Product B was assigned the tentative structure of ethyl 4-cyano-3-butenoate (see discussion above). Products A and C were assigned the *trans* and *cis* stereochemistry, respectively, by the following procedure. A 3.0-g sample of 75:8:17 mixture of isomers A–C was warmed on the steam bath for 3 hr with 30 ml of concentrated hydrochloric acid. After concentration to dryness at 40° (water pump), the residue was boiled three times with ether and the ether extracts were dried and concentrated to an oily residue of 1.9 g. Esterification with ethyl orthoformate[11] gave a solution which, by glpc analysis, contained *trans*- and *cis*-ethyl 1,2-cyclopropanedicarboxylates in the relative amounts of 84 and 16%, respectively.

Saponification of Ethyl 2-Acetyl-3,3-dimethylcyclopropanecarboxylate.—A mixture of 31 g (0.17 mole) of keto ester (Table IV, **7**), 75 ml of ethanol, and 100 ml of 2 *N* sodium hydroxide was allowed to reflux for 3 hr. After vacuum removal of most of the ethanol, the residue was acidified and extracted with chloroform. Removal of chloroform from the washed and dried solution gave 25 g (95%) of 2-acetyl-3,3-dimethylcyclopropanecarboxylic acid, mp 108–110°. Recrystallization from chloroform–hexane gave material with mp 111–112° (lit.[15] mp 108–110°).

Anal. Calcd for $C_8H_{12}O_3$: C, 61.5; H, 7.7. Found: C, 61.7; H, 7.8. Nmr analysis showed a pair of singlets at δ 1.2 and 1.4 (6 H, two CH_3 groups), singlets at δ 2.3 (3 H, $COCH_3$) and 11.5 (1 H, COOH), and a multiplet at δ2.5 (2 H, cyclopropyl protons).

Registry No.—**3** (*trans*), 13949-93-4; **3** (*cis*), 13950-12-4; **4** (*trans*), 13949-94-5; **4** (*cis*), 13950-13-5; **5** (*trans*), 13949-97-8; **5** (*cis*), 13950-14-6; **6** (*trans*), 13949-95-6; **6** (*cis*), 13950-15-7; **7** (*trans*), 13949-96-7; **8**, 13949-98-9; **9** (*trans*), 13949-99-0; **10** (*cis*), 13950-16-8; **11** (*trans*), 3999-55-1; **11** (*cis*), 710-43-0; **12** (*trans*), 13950-03-3; **12** (*cis*), 13950-18-0; **13** (*trans*), 4104-67-0; **13** (*cis*), 13950-19-1; **14**, 13950-01-1; **18**, 13952-91-5; **19**, 13952-92-6; **20**, 13952-93-7; **21**, 13952-94-8; EDSA, 5697-31-4; *trans*-1,-2-cyclopropanedicarboxylic acid, 696-75-3; ethyl *trans*-2-cyanocyclopropanecarboxylate, 3999-56-2; ethyl 4-acetyl-3,5-dimethyl-2,3-dehydrofuran-2-carboxylate, 13952-98-2; carbethoxymethyl dimethyl sulfonium bromide, 5187-82-6; ethyl(methylthio) acetate, 4455-13-4.

(14) Reference *b*, Table II.

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