Electrolyses.—A 1 *M* solution of lithium chloride (50 ml) in the appropriate solvent was placed in the cathode compartment; the anolyte was identical, but also contained 5 ml of 95% hydrazine. The solvent was purified by pre-electrolysis in a nitrogen stream for 30 min at a cathode potential of −1.1 V *vs.* Ag-AgCl for **1a**, **c**, and **d**, and −2.0 V for **1b**. The dihalide (5–7 mmol) was added and electrolysis was allowed to proceed until current had decayed to background. The catholyte was poured into water, extracted with pentane, washed with water, and dried over magnesium sulfate. The pentane was carefully distilled; the **2**–**3** mixtures were analyzed by nmr spectroscopy by the method of Seyferth, *et al.*[9] Results generally agreed with results of independent vpc analyses. Yields of halocyclopropanes were in the range 80–90%.

Registry No.—**1a**, 15649-61-3; **1b**, 15649-62-4; **1c**, 15649-58-8; **1d**, 15834-79-4.

Acknowledgment.—Financial support by the Petroleum Research Fund is gratefully acknowledged.

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[9] D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

Ethyl (Dimethylsulfuranylidene)acetate. II. Reactions with α,β-Unsaturated Esters in Ethanol Solutions

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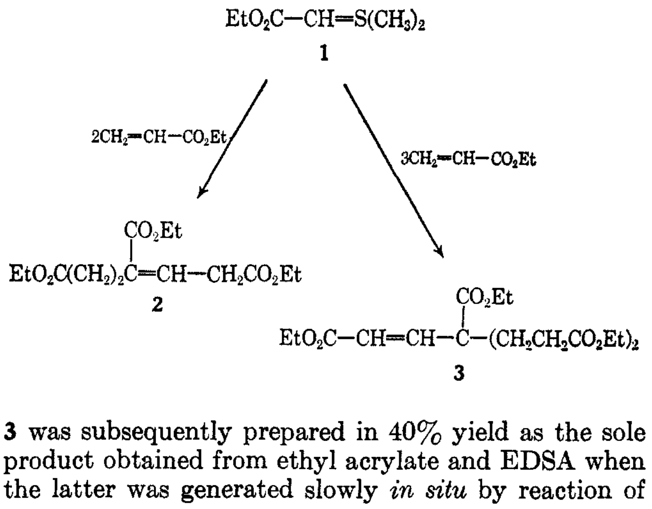
Received October 10, 1967

The general reaction between ethyl (dimethylsulfuranylidene)acetate (EDSA, **1**) and α,β-unsaturated compounds in aprotic solvents to produce substituted cyclopropanes was recently reported.[1] We now report that reaction of EDSA with certain α,β-unsaturated esters in ethanol solution leads not to cyclopropanes but rather to open-chain products of varying complexity.

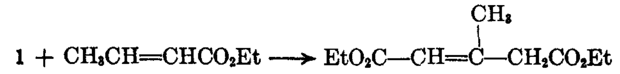
Results and Discussion

Reaction of EDSA with 4 molar equiv of ethyl acrylate in ethanol at 30–35° afforded a 69% yield (based on EDSA) of triethyl 2-pentene-1,3,5-tricarboxylate (**2**) along with a 20% yield of triethyl 3-(2-ethoxycarbonylethyl)-1-pentene-1,3,5-tricarboxylate (**3**). Tetraester **3** was subsequently prepared in 40% yield as the sole product obtained from ethyl acrylate and EDSA when the latter was generated slowly *in situ* by reaction of carbethoxymethyl dimethylsulfonium bromide with anhydrous potassium carbonate.



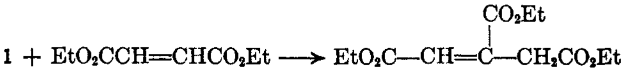
$$EtO_2C{-}CH_2\overset{+}{S}(CH_3)_2Br^- + 3CH_2{=}CH{-}CO_2Et \xrightarrow{K_2CO_3} \mathbf{3}$$

Ethyl crotonate and EDSA afforded a 75% yield of diethyl 3-methylglutaconate (**4**) as a 50:50 mixture of *cis–trans* isomers while EDSA and diethyl fumarate gave triethyl aconitate (**5**) in 87% yield as a 70:30 mixture of *trans–cis* isomers.



$$\mathbf{1} + CH_3CH{=}CHCO_2Et \longrightarrow EtO_2C{-}CH{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH_2CO_2Et$$

4



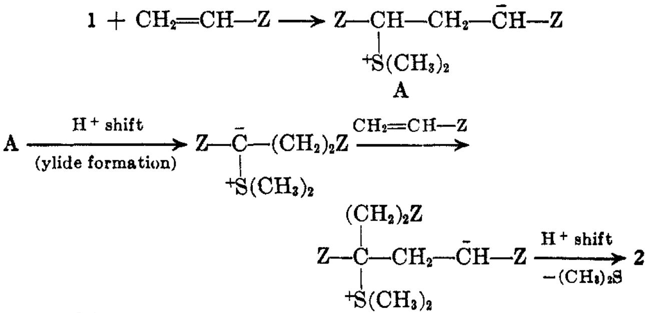
$$\mathbf{1} + EtO_2CCH{=}CHCO_2Et \longrightarrow EtO_2C{-}CH{=}\overset{\overset{\displaystyle CO_2Et}{|}}{C}{-}CH_2CO_2Et$$

5

Compound **2** was identified by elemental and nmr analyses and by hydrogenation followed by saponification to the known 1,3,5-pentanetricarboxylic acid. Structure **3** was assigned on the basis of elemental and nmr analyses. Saponification of **4** gave the known 3-methylglutaconic acid as a mixture of *cis–trans* isomers, and **5** was identified by comparison with an authentic sample of triethyl aconitate.

The formation of **2** has been rationalized according to Scheme I.

SCHEME I[a]

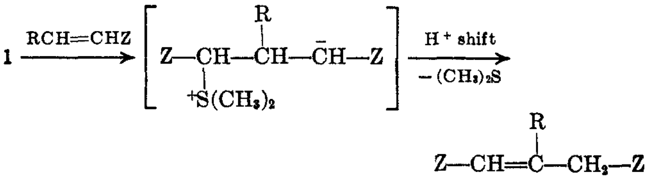


[a] Z = CO_2Et

Compound **3** can be visualized as being formed *via* intermediates A and B by Michael reaction of the latter with 2 mol of ethyl acrylate.

$$A \xrightarrow[-(CH_3)_2S]{H^+\ shift} \underset{\displaystyle B}{Z{-}CH{=}CH{-}CH_2{-}Z} \xrightarrow{2CH_2{=}CH{-}Z} \mathbf{3}$$

The conversions of ethyl crotonate into **4** and diethyl fumarate into **5** are believed to occur by the same mechanism.



$$\mathbf{1} \xrightarrow{RCH{=}CHZ} \left[Z{-}\underset{\underset{\displaystyle ^+S(CH_3)_2}{|}}{CH}{-}\overset{\overset{\displaystyle R}{|}}{C}H{-}\bar{C}H{-}Z \right] \xrightarrow[-(CH_3)_2S]{H^+\ shift} Z{-}CH{=}\overset{\overset{\displaystyle R}{|}}{C}{-}CH_2{-}Z$$

4, R = CH_3
5, R = CO_2Et

Experimental Section[2]

Reaction of EDSA with Ethyl Acrylate.—To a solution of 20.0 g (0.20 mol) of ethyl acrylate in 50 ml of absolute ethanol was

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

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

added a solution of 7.4 g (0.05 mol) of EDSA[1] in 25 ml of ethanol. Ice cooling was needed to hold the temperature at 30–35°.

After an overnight stand at 25°, the mixture was flashed into a Dry Ice cooled trap at 5 mm and 25°. Glpc analysis of the volatiles indicated the presence of 0.048 mol of dimethyl sulfide and 0.080 mol of ethyl acrylate.

Distillation of the residue gave 9.8 g (69%) of triethyl 2-pentene-1,3,5-tricarboxylate, bp 106–109° (<1 mm) and $n^{25}\mathrm{D}$ 1.4553, and 4.1 g of residue (21% yield calculated as **3**).

Anal. Calcd for $C_{14}H_{22}O_6$: C, 58.7; H, 7.7. Found: C, 58.7; H, 7.8.

The nmr spectrum showed multiplets at δ 1.3 (9 H, $-CO_2CCH_3$), 2.0–2.7 (4 H, $C{=}C(CH_2)_2COOR$), and 3.9–4.4 (6 H, CO_2CH_2-), a triplet at 7.0 (1 H, $-CH{=}CCOOR$), and a doublet at 3.4 (2 H, $-C{=}CCH_2COOR$).

Distillation of the residue gave material with bp 170–175° (<1 mm) in good recovery. It was shown by infrared analysis to be identical with compound **3** prepared below.

2-Pentene-1,3,5-tricarboxylic Acid.—A solution of 8.0 g (0.028 mol) of triester in 50 ml of concentrated hydrochloric acid was warmed on the steam bath for 4 hr and then allowed to stand overnight. Filtration of the resulting precipitate gave 3.4 g, mp 181–182°; concentration of the filtrate followed by crystallization from acetone gave another 0.5 g, mp 178–180° (70% combined yield). Recrystallization of the two crops gave product with mp 181–182°.

Anal. Calcd for $C_8H_{10}O_6$: C, 47.5; H, 5.0. Found: C, 47.8; H, 5.1.

The nmr spectrum showed a multiplet at δ 2.0–2.7 (4 H, $C{=}C(CH_2)_2COO-$), a doublet at 3.3 (2 H, $-O_2CCH_2C{=}C-$), a triplet at 6.9 (1 H; $-CH{=}C-$), and a singlet at 11.1 (3 H, $-COOH$).

Hydrogenation of the unsaturated acid was carried out in a Parr hydrogenator using 5% palladium-on-carbon catalyst, ethyl alcohol as solvent, and a pressure of 40 psi. One molar equivalent of hydrogen was absorbed in 0.5 hr to give 1,3,5-pentanetricarboxylic acid, mp 112–114°. A mixture melting point with an authentic sample (mp 113–115°)[3] was not depressed. The infrared spectra were identical.

Reaction of Carbethoxymethyl Dimethylsulfonium Bromide with Potassium Carbonate and Ethyl Acrylate.—A mixture of 22.9 g (0.10 mol) of sulfonium bromide,[1] 30.0 g of ethyl acrylate, 21 g of anhydrous potassium carbonate, and 100 ml of absolute ethanol was allowed to stir for 18 hr at 25°.

Filtration followed by Claisen distillation gave 15.3 g (40% yield) of relatively pure product, bp 174–187° (<1 mm) and $n^{25}\mathrm{D}$ 1.4605. Redistillation through a small Vigreux column gave analytically pure triethyl 3-(2-ethoxycarbonylethyl)-1-pentene-1,3,5-tricarboxylate: bp 203–206° (1 mm), $n^{25}\mathrm{D}$ 1.4616.

Anal. Calcd for $C_{19}H_{30}O_8$: C, 59.1; H, 7.8; mol wt, 386. Found: C, 59.4; H, 7.9; mol wt, 395 ± 12 (ebullioscopic, benzene).

The nmr showed multiplets at δ 1.3 (12 H, RCO_2CCH_3), 1.8–2.8 (8 H, $-CH_2-$), and 4.2 (8 H, RCO_2CH_2-) and doublets at 6.0 (1 H, $RO_2CCH{=}C$) and 7.1 (1 H, $RO_2C-C{=}CH-$).

Reaction of EDSA with Ethyl Crotonate.—A mixture of 11.4 g (0.10 mol) of ethyl crotonate, 7.4 g of EDSA (0.05 mol), and 50 ml of ethanol was held at room temperature for 4 days and then heated under reflux for 1 hr.

Claisen distillation gave 7.5 g (75%) of diethyl 3-methylglutaconate, bp 65–66° (<1 mm), $n^{25}\mathrm{D}$ 1.4488 (lit.[4] *cis*, bp 131° (9 mm), $n^{20}\mathrm{He}$ 1.452; *trans*, bp 127° (12 mm), $n^{20}\mathrm{He}$ 1.452).

Anal. Calcd for $C_{10}H_{16}O_4$: C, 60.0; H, 8.1. Found: C, 59.9; H, 8.1.

Nmr analysis indicated an approximately 1:1 mixture of *cis* and *trans* isomers showing a triplet at δ 1.2 (6 H, RCO_2CCH_3), two doublets at 2.0 and 2.2 (3 H, $C{=}C{-}CH_3$), two singlets at 3.2 and 3.7 (2 H, $C{=}C{-}CH_2{-}COOR$), a quartet at 4.2 (4 H, RCO_2CH_2-), and a multiplet at 5.8 (1 H, $-HC{=}C-$).

Saponification by aqueous ethanolic sodium hydroxide gave an 86% yield of isomers, mp 95–110°. Recrystallization from benzene afforded a mixture with constant mp 111–115°.[5]

Anal. Calcd for $C_6H_8O_4$: C, 50.0; H, 5.6; neut equiv, 72. Found: C, 50.3; H, 5.7; neut equiv, 72.

Nmr analysis indicated an approximately 2:1 ratio of *cis-trans* isomers ($COOH-CH_2COOH$): a pair of doublets at δ 2.0 and 2.2 (3 H, $C{=}C{-}CH_3$), a doublet at 3.3 (J = 1–2 cps), and a singlet at 3.7 in the ratio of 2:1 (2 H, $-C{=}C{-}CH_2{-}COO-$), a singlet at 4.7 (2 H, $-COOH$), and a multiplet at 5.9 (1 H, $-CH{=}C-$).

Triethyl Aconitate.—The reaction was carried out as above using 34.4 g (0.20 mol) of diethyl fumarate and 14.8 g (0.10 mol) of EDSA in 75 ml of ethanol.

After 18 hr the mixture was Claisen distilled to give 17.1 g (0.10 mol) of recovered diethyl fumarate, bp 60–70° (<1 mm), and 22.5 g (87%) of triethyl aconitate, bp 97–99° (<1 mm), $n^{25}\mathrm{D}$ 1.4515 (lit.[6] bp 165° (12 mm), $n^{20}\mathrm{D}$ 1.4556).

Glpc analysis indicated a 70:30 mixture of *trans-cis* isomers.[7] The early emerging peak was confirmed as the *trans* isomer by saponifying and then reesterifying Pfizer technical grade triethyl aconitate (all *trans*). The Pfizer triester and the 70:30 mixture showed nearly identical infrared spectra.

An nmr analysis was carried out on the 70:30 product showing multiplets at δ 1.3 (9 H, RCO_2CCH_3) and 4.2 (6 H, RCO_2CH_2-) and singlets at 3.9 (2 H, $-C{=}CCH_2{-}CO_2R$) and 6.9 (1 H, $RO_2CH{=}C-$). A minor multiplet at 2.5 indicated the presence of a small amount of impurity. The latter was not resolved by glpc analysis.

Registry No.—**1**, 5697-31-4; **2**, 15649-51-1; $C_8H_{10}O_6$, 15717-32-5; **3**, 15649-53-3; **4** (*cis*), 15649-54-4; **4** (*trans*), 1466-21-3; $C_6H_8O_4$ (*cis*), 15649-56-6; $C_6H_8O_4$ (*trans*), 372-42-9.

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[3] R. P. Mariella, R. Clutter, and H. G. Ebner, *J. Org. Chem.*, **20**, 1702 (1955).

[4] "Dictionary of Organic Compounds," Vol. 4, Oxford University Press, New York, N. Y., 1965, p 2311.

[5] For a discussion of these *cis* and *trans* isomers, see L. M. Jackman and R. H. Wiley, *Proc. Chem. Soc.*, 196 (1958).

[6] Reference 4, Vol. 1, p 33.

[7] J. Casanova, Jr., and D. A. Rutolo, Jr. (*Chem. Commun.*, 1224 (1967)) have reported the formation of *trans*-trimethyl aconitate from the reaction of methyl (dimethylsulfuranylidene)acetate with dimethyl fumarate in methanol solution.

Ethyl (Dimethylsulfuranylidene)acetate. III. Reaction with α-Bromo Acrylic Compounds

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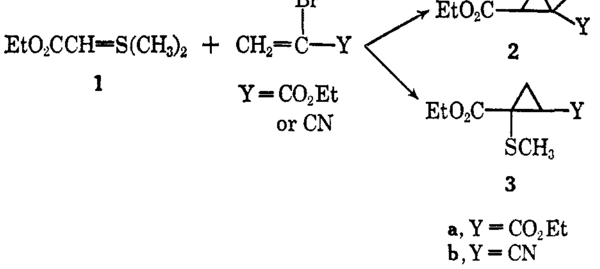
Received October 17, 1967

Earlier reports have described the synthesis[1] of ethyl (dimethylsulfuranylidene)acetate (**1**, EDSA), its reaction with α,β-unsaturated compounds in aprotic solvents to produce cyclopropanes,[1] and its reaction with α,β-unsaturated esters in ethanol solution to give esters of acyclic polybasic acids.[2]

The reactions of EDSA with 2-bromoacrylonitrile and ethyl 2-bromoacrylate were carried out with the expectation that bromocyclopropanes **2** might be produced.



Whereas **2a** was indeed produced (36% yield) from the reaction of EDSA with ethyl 2-bromoacrylate at room temperature *in benzene solution*, very little was

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

[2] G. B. Payne, *ibid.*, **33**, 1284 (1968).