SULFUR YLIDES.

4. CYCLOPROPANATION OF FULVENES BY ETHYL (DIMETHYLSULFURANYLIDENE)ACETATE UNDER INTERPHASE CATALYSIS CONDITIONS

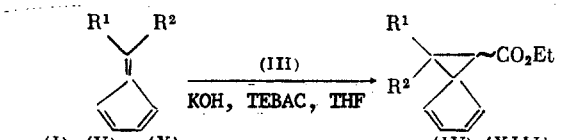
G. A. Tolstikov, F. Z. Galin,
V. N. Iskandarova, and S. N. Lakeev,
L. V. Spirikhin, and L. M. Khalilov

UDC 542.97:547.514.71:547.512

The reaction was studied of fulvenes with ethyl (dimethylsulfuranylidene)acetate generated under interphase catalysis conditions from the sulfonium salt $[Me\overset{+}{S}CH_2CO_2Et)]Br^-$ by the action of 85% KOH in the presence of triethylbenzylammonium chloride.

3-Phenoxybenzyl esters of spirocyclopropanecarboxylic acids have high insecticidal activity and belong to the class of synthetic pyrethroids [1]. The acid component of the pyrethroid molecules of this type is usually synthesized by cyclopropanation of fulvenes by sulfur ylides [2]. We have earlier proposed a convenient modification of cyclopropanation of α, β-unsaturated ketones by sulfur ylides generated under interphase catalysis conditions (a solid phase–liquid system) [3]. However, the reaction of azomethines with sulfur ylides under similar conditions leads to unexpected products, the derivatives of cyclopropanedicarboxylic acid [4].

It was therefore of interest to study the reaction of fulvenes with sulfur ylides generated under interphase catalysis conditions. We found that the reaction of 6,6-dimethylfulvene (I) with ethyl (dimethylsulfuranylidene)acetate (II), (carbethoxymethyldimethylsulfonium bromide (III), KOH, triethylbenzylammonium chloride (TEBAC), THF, 20°C) proceeds in a practically quantitative yield in the course of 2 h, leading to ester (IV)



(I), (V)–(X) (IV), (XIII)–(XVIII)

$R^1 = R^2 = CH_3$ (I), (IV); $R^1 = C_2H_5$, $R^2 = CH_3$ (V), (XIII);
R^1 = cyclopropyl, $R^2 = CH_3$ (VI), (XIV); $R^1 = (CH_2)_3OAc$, $R^2 = CH_3$ (VII), (XV);
$R^1 = R^2 = (CH_2)_4$ (VIII), (XVI); R^1 = α-furyl, $R^2 = H$ (IX), (XVII);
$R^1 = C_6H_5$, $R^2 = CH_3$ (X), (XVIII).

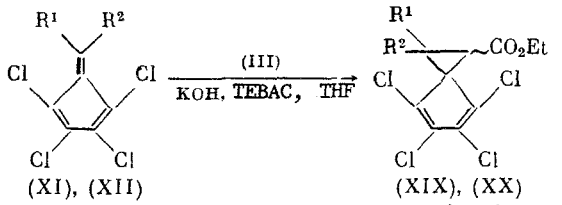
Replacement of one of the methyl groups of fulvene by ethyl does not subtantially influence the yield of the cyclopropanation product. Introduction of bulkier substituents (cyclopropyl (VI), acetoxypropyl (VII)) at the C^6 atom of fulvene lowers the yield of the desired end product (to 60%). In the case of 6,6-tetramethylenefulvene (VIII), the yield of (XVI) is only 40%. In the cyclopropanation of 6-α-furylfulvene, the yield of ester (XVII) does not exceed 35%; although the conversion of the starting fulvene is fairly high (70%), considerable resinification is observed. 6-Phenyl-6-methylfulvene (X) was found to be least reactive.

Introduction of four chlorine atoms into the fulvene molecule activates the exocyclic double bond of fulvene. Thus, the cyclopropanation of fulvene (XII) under the above conditions produces the ethyl ester (XX) in a 90% yield. Conversion of fulvene (XI) under these conditions is also high, but the yield of compound (XIX) does not exceed 37% because of resinification.

The reaction with (II) of fulvenes having various substitutents at the C^6 atom under interphase catalysis conditions proceeds with the formation of a mixture of cis and trans

Institute of Chemistry, Bashkir Scientific Center. Urals Branch of the Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk USSR, Seriya Khimicheskaya, No. 6, pp. 1373-1377, June, 1990. Original article submitted April 17, 1989.

0568-5230/90/3906-1238$12.50



(XI), (XII) (XIX), (XX)

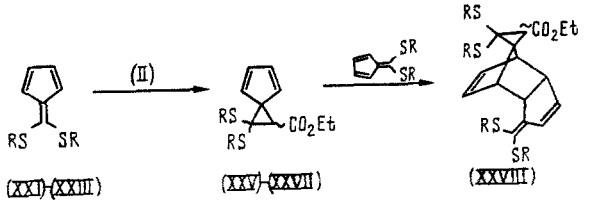
$R^1 = \alpha$-furyl, $R^2 = H$ (XI), (XIX); $R^1 = C_6H_5$, $R^2 = H$ (XII), (XX).

isomers of cyclopropanecarboxylic acid derivatives with trans isomers predominating. Only in the case of 6-phenyl-6-methylfulvene (X) is a cis isomer preferentially formed.

The assignment of the cyclopropanecarboxylic acid ethyl ester derivatives having only one substituent at the C^2 atom (XVII), (XIX), (XX) to the cis or trans series, was made according to the SSCC value for vicinal protons in the cyclopropane ring. For (XIII)-(XV), (XVIII), the assignment of the isomers was carried out on the basis of the chemical shift values of protons at C^1 and in the methyl group (an electronegative substituent in the cis position to the Me group shifts the signals of the methyl protons to the weak field). In the case of the trans isomers of (XIV) and (XVIII), the proton signals at C^1 of the cyclopropane ring are present in a stronger field than in the case of the cis isomers. In contrast to these, the cis and trans isomers of (XIII) and (XV) differ in the PMR spectra only with respect to the methyl group signals.

It should be noted that the cyclopropanation of fulvenes having an α-furyl substituent at the C^6 atom of fulvene (IX) or (XI) proceeds very stereospecifically with the formation of trans isomers. Data are not available in the literature on the reaction of fulvenes having hetero atoms attached to the C^6 atom [5, 6] with sulfur ylides.

The reaction of thiofulvenes with (II) generated under interphase catalysis conditions is accompanied by strong resinification. Heating of thiofulvene (XXI) with (II) in THF for 2 days results in the formation of a cyclopropanation product (XXV) in a yield of not more than 20%. We increased the yield of (XXV) to 60%, by carrying out the reaction in vacuo ($p \approx 5$ torr) at a lower temperature (25°C), which substantially reduced the degree of resinification. It should be noted that product (XXV) formed in the course of the reaction, readily enters the Diels—Alder reaction with the initial (XXI) giving the adduct (XXVIII).



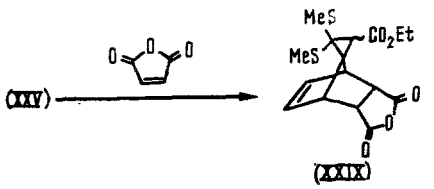
(XXI)-(XXIII) (XXV)-(XXVII) (XXVIII)

R = CH_3 (XXV), (XXVIII); C_2H_5 (XXVI), CH_2 (XXVII).

The structure of compounds (XXV)-(XXVII) was established on the basis of PMR data. The proton signals of the thioalkyl groups undergo a shift to the weak field compared with the signals of the analogous alkyl groups in the corresponding dialkylspiroheptadienecarboxylates. Thus two singlets at 2.15 and 2.18 ppm correspond to the protons of the thiomethyl groups of compound (XXV) (in compound (IV) at 1.40 and 1.55 ppm). The cyclopropane ring proton in (XXV) also resonates in a weaker field (3.3 ppm) than (IV) (2.6 ppm).

Adduct (XXVIII) is produced in the form of a single isomer, the structure of which was established by ^{13}C NMR method. The content of adducts of type (XXVIII) in the mixture of (XXV) and (XXVIII) is determined by the duration of the reaction.

The reaction of (XXV) with maleic anhydride leads to a single product (XXIX) in 94% yield.



(XXIX)

EXPERIMENTAL

The NMR spectra were obtained on "Tesla-497" (1H, 100 MHz, relative to TMS) and "Jeol-FX-90Q" (^{13}C, 22.5 MHz, relative to TMS) spectrometers. The chemical shifts are given in a δ scale. The IR spectra were run on a UR-20 spectrophotometer (thin film) and the UV spectra on a "Specord UV-VIS" spectrophotometer in ethanol or chloroform. The mass spectra were recorded on an MX-1320 spectrometer. The synthesis of ethyl (dimethylsulfuranylidene)acetate (II) and sulfonium salt (III) was carried out according to [7].

Fulvenes (I), (V), (VI), (VIII), (X) were synthesized according to a method in [8], (IX) – [9], [XI], [XII] – [10]. Their spectral characteristics and physical constants are similar to those described in [9-13].

6-Methyl-6-cyclopropylfulvene (VI) (63%). The UV spectrum [λ_{max}^{EtOH}, nm (log ε)]: 287 (4.09); 355 (2.45). PMR spectrum ($CDCl_3$): 0.78 s (CH_2), 0.85 s (CH_2), 1.75 s (CH_3), 2.00-2.48 m (CH), 6.23-6.67 m (4H, CH). Found: C 90.74; H 9.20%. $C_{10}H_{12}$. Calculated: C 90.85; H 9.12%.

6-Methyl-6-acetoxypropylfulvene (VII) (66%), bp 95-97°C (1 mm). UV spectrum [λ_{max}^{EtOH}, nm log ε)]: 268 (4.32), 360 (2.46). PMR spectrum ($CDCl_3$): 1.60-1.90 m (CH_2), 2.00 s (CH_3), 2.16 s (CH_3), 2.40-2.75 m (CH_2), 4.06 t (J = 6 Hz, CH_2), 6.45 narrow m (4H, CH). Found: C 74.90; H 8.29%. $C_{12}H_{16}O_2$. Calculated: C 74.97; H 8.39%.

6,6-Diethylthiofulvene (XXII). A 6.6 g portion (0.1 mole) of KOH powder and 0.01 g of TEBAC were added to a solution of 1.2 g (0.01 mole) of cyclopentadiene in 20 ml of THF, and then 1.4 g (0.02 mole) of CS_2 was added dropwise. After 15 min, 4.4 g (0.04 mole) of CH_3CH_2Br was added, the mixture was stirred for another 30 min, and then the reaction mixture was filtered, evaporated and passed through a column with SiO_2 (eluent – chloroform). Yield, 1.2 g (50%) of a dark-red liquid. UV spectrum [λ_{max}^{EtOH}, nm (log ε)]: 248 (4.02); 308 (3.75); 353 (2.65). PMR spectrum ($CDCl_3$): 1.58 t (J = 8 Hz, 6H, CH_3), 2.82 q (J = 8 Hz, 4H, CH_2), 6.48 m (4H, CH). Found: C 60.51; H 7.10; S 31.96%. $C_{10}H_{14}S_2$. Calculated: C 60.55; H 7.12; S 32.33%.

6,6-Dibenzylthiofulvene (XXIV) was obtained in a similar way as (XIX), yield 30%. UV spectrum [λ_{max}^{EtOH}, nm (log ε)]: 277 (3.90); 311 (2.88); 354 (2.32). PMR spectrum ($CDCl_3$): 4.49 narrow m (CH_2), 6.37 m (4H, CH), 7.40 m (C_6H_5). Found: C 74.50; H 5.9; S 19.75%. $C_{20}H_{18}S_2$. Calculated: C 74.49; H 5.62; S 19.89%.

Thiofulvenes (XXI) and (XXIII) were obtained in a similar way as (XXII) in a yield of 80 and 65%, respectively, and the spectral characteristics coincide with those described in [5].

Ethyl Ester of 2,2-Dimethylspiro[2,4]hepta-4,6-diene-1-carboxylic acid (IV). A mixture of 6.15 g (58 mmoles) of 6,6-dimethylfulvene, 13.3 g (58 mmoles) of sulfonium salt (III), 3.86 g of 85% KOH powder, and 0.17 g (0.8 mmole) of TEBAC in 80 ml of THF was vigorously stirred for 1.5 h at room temperature. The reaction mixture was filtered, and the solvent was evaporated. After distillation, 10 g (90%) of a light yellow oil was obtained, bp 64°C (1 mm), n_D^{23} 1.5104. IR spectrum (ν, cm^{-1}): 1735 (C=O). UV spectrum [λ_{max}^{EtOH}, nm (log ε)]: 221 (3.60); 262 (2.60). PMR spectrum ($CDCl_3$): 1.2 t (J = 7 Hz, CH_3), 1.40 s (CH_3), 1.55 s (CH_3), 2.60 s (CH), 4.02 q (J = 7 Hz, CH_2), 5.88-6.68 m (4H, CH). Found: 74.90; H 8.43%. $C_{12}H_{16}O_2$. Calculated: C 74.93; H 8.40%. Mass spectrum (m/z): M^+ 192.

Compounds (XIII)-(XX) were obtained in a similar way as (IV).

Ethyl Ester of 2-Ethyl-2-methylspiro[2,4]hepta-4,6-diene-1-carboxylic Acid (XIII). (90%). Ratio of trans/cis isomers = 55:45, bp 78°C (1 mm). IR spectrum (ν, cm^{-1}): 1740 (C=O). UV spectrum [λ_{max}^{EtOH}, nm (log ε)]: 222 (3.43); 262 (2.59). PMR spectrum ($CDCl_3$): trans 1.25 t (J = 7 Hz, CH_3), 1.43 s (CH_3) 1.68-2.18 m (CH_2), 2.75 s (CH), 4.49 q (J = 7 Hz, CH_2), 6.00-6.93 m (4H, CH); cis 1.25 t (J = 7 Hz, CH_2), 1.56 s (CH_3), 1.68-2.18 m (CH_2), 2.75 s (CH), 4.49 q (J = 7 Hz, CH_2), 6.00-6.93 m (4H, CH). Found: C 75.54; H 8.84%. $C_{13}H_{18}O_2$. Calculated C 75.68; H 8.81%. Mass spectrum (m/z): M^+ 206.

Ethyl Ester of 2-Cyclopropyl-2-methylspiro[2,4]hepta-4,6-diene-1-carboxylic Acid (XIV), (60%). Rf (XIV) trans = 0.68, Rf (XIV) cis = 0.52 (hexane–ethyl acetate = 10/1). Ratio of trans/cis isomers = 60/45. IR spectrum (ν, cm^{-1}): 1725 (C=O). UV spectrum [λ_{max}^{EtOH}, nm (log ε)]: 287 (4.09); 355 (2.45). PMR spectrum ($CDCl_3$): trans 1.18 t (J = 7 Hz, CH_3), 1.57 s (CH_3), 2.63 s (CH), 4.07 q (J = 7 Hz, CH_2), 5.87-7.07 m (4H, CH); cis 1.21 t (J = 7 Hz, CH_3), 1.80 s (CH_3), 2.78 s (CH), 4.11 q (J = 7 Hz, CH_2), 5.87-7.07 m (4H, CH). Found: C 77.15; H 8.07%. $C_{14}H_{18}O_2$. Calculated: C 77.02; H 8.33%. Mass spectrum (m/z); M^+ 218.

Ethyl Ester of 2-Acetoxypropyl-2-methyl[2,4]hepta-4,6-diene-1-carboxylic Acid (XV), (70%). Ratio of trans/cis isomers = 50/50. R_f = 0.45 (hexane–ethyl acetate = 10/1). IR spectrum (ν, cm^{-1}): 1730 (C=O), 1740 (C=O). PMR spectrum ($CDCl_3$): trans 1.27 t (J = 7 Hz, CH_3), 1.45 s (CH_3), 1.59-2.00 m (4H, CH_2), 2.03 s (CH_3), 2.73 s (CH), 3.83-4.28 m (4H, CH_2), 5.70-6.20 m (4H, CH); cis 1.27 t (J = 7 Hz, CH_3), 1.58 s (CH_3), 1.58-2.00 m (4H, CH_2), 2.03 s (CH_3), 2.73 s (CH), 3.83-4.28 m (4H, CH_2), 5.70-6.20 m (4H, CH). Found: C 69.00; H 7.95%. $C_{16}H_{22}O_4$. Calculated: C 69.03; H 7.98%. Mass spectrum (m/z): M^+ 278.

Ethyl Ester of 2,2-Tetramethylene[2,4]hepta-4,6-diene-1-carboxylic Acid (XVI), (40%). R_f 0.6 (hexane/ethyl acetate = 10/1), IR spectrum (ν, cm^{-1}): 1730 (C=O). UV spectrum [λ_{max}^{EtOH}, nm (log ε): 230 (3.7); 267 (2.9). PMR spectrum ($CDCl_3$): 1.25 t (J = 7 Hz, CH_3), 1.58-1.72 m (4H, CH_2), 2.83 s (CH), 4.12 q (J = 7 Hz, CH_2), 6.09-6.73 m (4H, CH), Found: C 77.21; H 8.27%. $C_{14}H_{18}O_2$. Calculated: C 77.02; H 8.33%. Mass spectrum (m/z): M^+ 218.

Ethyl Ester of 2-α-Furylspiro[2,4]-hepta-4,6-diene-1-carboxylic Acid (XVII),(35%). Ratio of trans/cis isomers 95/5. R_f trans = 0.60; R_f cis = 0.46 (hexane/ethyl acetate = 10/1). IR spectrum (ν, cm^{-1}): 1730 (C=O). UV spectrum [λ_{max}^{EtOH}, nm (log ε)]: 218 (2.90); 306 (3.23); 327 (3.10). PMR spectrum ($CDCl_3$): trans 1.26 t (J = 7 Hz, CH_3), 3.34 d (J = 7 Hz, CH), 4.19 q (J = 7 Hz, CH_2), 6.15-6.33 m (4H, CH), 6.50 d (J = 1.5 Hz, 2H, CH), 7.31 br. s (CH); cis 1.26 t (J = 7 Hz, CH_3), 3.74 d (J = 6.5 Hz, CH), 4.19 q (J = 7 Hz, CH_2), 6.16-6.33 m (4H, CH), 6.50 d (J = 1.5 Hz, 2H, CH), 7.31 br. s (CH). Found: C 73.48; H 6.23%. $C_{14}H_{14}O_3$. Calculated: C 73.02; H 6.14%. Mass spectrum (m/z): M^+ 230.

Ethyl Ester of 2-Phenyl-2-methylspiro[2,4]hepta-4,6-diene-1-carboxylic Acid (XVIII), (10%). Ratio of trans/cis isomers 35/65. R_f trans = 0.60; R_f cis = 0.47 (hexane/ethyl acetate = 10/1). IR spectrum (ν, cm^{-1}): 1730 (C=O). UV spectrum [λ_{max}^{EtOH}, nm (log ε)]: 265 (3.73); 230 (4.02). PMR spectrum ($CDCl_3$): trans 1.25 t (J = 7 Hz, CH_3), 1.67 s (CH_3), 3.01 s (CH), 4.05 q (J = 7 Hz, CH_2), 5.45-6.98 m, (4H, CH), 7.02 narrow m (5H, CH); cis 1.30 t (J = 7 Hz, CH_3), 1.83 s (CH_3), 3.31 s (CH), 4.21 q (J = 7 Hz, CH_2), 5.45-6.95 m (4H, CH), 7.02 narrow m (5H, CH). Found: C 80.44; H 7.18%. $C_{17}H_{18}O_2$. Calculated: C 80.27; H 7.15%. Mass spectrum (m/z): M^+ 254.

Ethyl Ester of 2-α-Furyl-4,5,6,7-tetrachlorospiro[2,4]hepta-4,6-diene-1-carboxylic acid (XIX). (30%), mp 63-65°C. IR spectrum (ν, cm^{-1}): 1740 (C=O). UV spectrum [λ_{max}^{EtOH}, nm (log ε)]: 255 (3.96); 267 (3.90); 298 (3.54). PMR spectrum ($CDCl_3$): trans 1.29 t (J = 7 Hz, CH_3), 3.45 d (J = 10 Hz, CH), 3.79 d (J = 10 Hz, CH), 6.38 s (CH). Found: C 46.01; H 2.50; Cl 38.44%. $C_{14}H_{10}Cl_4O_3$. Calculated: C 45.59; H 2.74; Cl 38.53%. Mass spectrum (m/z): M^+ 368.

Ethyl Ester of 2-Phenyl-4,5,6,7-tetrachlorospiro[2,4]hepta-4,6-diene-1-carboxylic Acid (XX), (90%). Ratio of trans/cis isomers 55/45, mp 63-65°C. IR spectrum (ν, cm^{-1}): 1740 (C=O). UV spectrum [λ_{max}^{EtOH}, nm (log ε)]: 255 (3.96); 267 (3.90); 298 (3.50). PMR spectrum ($CDCl_3$): trans 1.12 t (J = 7 Hz, CH), 3.03 d (J = 10 Hz, CH), 3.59 d (J = 10 Hz, CH), 4.05 q (J = 7 Hz, CH_2), 7.18 narrow m (5H, CH); cis 1.22 t (J = 7 Hz, CH_3), 3.18 d (J = 4.5 Hz, CH), 3.42 d (J = 4.5 Hz, CH), 4.17 q (J = 7 Hz, CH_2), 7.23 narrow m (5H, CH). Found: C 50.54; H 3.21; Cl 36.98%. $C_{16}H_{12}Cl_4O_2$. Calculated: C 50.82; H 3.18; Cl 37.51%. Mass spectrum (m/z): M^+ 378.

Ethyl Ester of 2,2-Dimethylthiospiro[2,4]hepta-4,6-diene-1-carboxylic Acid (XXV). A mixture of 1.7 g (0.1 mole) of a freshly prepared fulvene (XXI) and 1.5 g (0.1 mole) of ylide (II) was evacuated at P = 1 mm for 2 h. After separation on a column with SiO_2 (hexane/ethyl acetate, 10/1), 1.5 g (60%) of (XXV) and 0.4 g of (XXVIII) (40% based on the starting fulvene) were obtained. IR spectrum (ν, cm^{-1}): 1740 (C=O). UV spectrum [λ_{max}^{EtOH} nm (log ε)]: 210 (3.4); 270 (2.9). PMR spectrum ($CDCl_3$): 1.28 t (J = 7 Hz, CH_3), 2.15 s (C_3), 2.18 s (CH_3), 2.8 s (CH_3), 3.30 s (CH), 4.11 q (J = 7 Hz, CH_2), 6.15 m (4H, CH). Found: C 56.18; H 6.22; S 25.02%. $C_{12}H_{16}O_2S_2$. Calculated: C 56.12; H 6.29; S 25.01%.

Compounds (XXVI, (XXVII) were obtained in a similar way as (XXV).

Ethyl Ester of 2,2-Diethylthiospiro[2,4]hepta-4,6-diene-1-carboxylic Acid (XXVI), (54%). IR spectrum (ν, cm^{-1}): 1740 (C=O). UV spectrum [λ_{max}^{EtOH}, nm (log ε)]: 220 (4.2); 275 (2.4). PMR spectrum ($CDCl_3$): 1.30 t (J = 7 Hz, CH_3), 2.18 s (CH_3), 1.38 t (J = 8 Hz, 6H, CH_3), 1.70-2.00 m (4H, CH_2), 3.30 s (CH), 4.22 q (J = 7 Hz, 2H, CH), 6.10 m (4H, CH). Found: C 59.09: H 7.05; S 22.50%. $C_{14}H_{20}O_2S_2$. Calculated: C 59.12; H 7.09: S 22.55%

Ethyl Ester of 2,2-Diethylenethiospiro[2,4]hepta-4,6-diene-1-carboxylic Acid (XXVII), (30%). IR spectrum (ν, cm^{-1}): 1735 (C=O). UV spectrum [λ_{max}^{EtOH}, nm (log ε)]: 232 (3.9); 290 (2.9). PMR spectrum ($CDCl_3$): 1.25 t (J = 7 Hz, CH_3), 2.60-1.82 m (4H, CH_2), 3.21 s (CH), 4.16 q (J = 7 Hz, CH_2), 6.00-6.72 m (4H, CH). Found: C 56.61; H 5.51; S 25.18%, $C_{12}H_{14}O_2S_2$. Calculated: C 56.66; H 5.55; S 25.21%.

Spiro-{3',3'-dimethylthio-2'-carbethoxycyclopropane-10,1'-(5-dimethylthiomethylene)-endo-tricyclo[5.2.1.$O^{2,6}$]deca-3,8-diene} (XXVIII), (40%). IR spectrum (ν, cm^{-1}): 1735. PMR spectrum ($CDCl_3$): 1.27 t (J = 7.4 Hz, CH_3), 2.07 s, 2.13 s, 2.20 s, 2.32 s (12H, CH_3), 2.16 s (CH), 3.36-3.54 m (2H, CH, CH), 3.54-3.80 m (2H, CH, CH), 4.14 q (J = 7.4 Hz, CH_2O), 5.94 t (2H, CH), 6.03 d.d (J_1 = 2.4, J_2 = 5.9 Hz, CH), 6.54 d.d (J_1 = 5.9, J_2 = 1.4 Hz, CH). ^{13}C NMR spectrum ($CDCl_3$): 14.20, 14.25, 16.47; 17.50 (CH_3), 14.90 (CH_3CH_2), 34.41 (S—C—S), 36.41 (CH—CO_2), 46.78, (47.90, 50.60, 51.62 (CH), 60.63 (CH_3—O), 65.60 (—C—), 121.85 (S>C=S), 131.82 (CH=CH), 140.38 (CH=CH), 133.77, 136.10 (CH=CH), 154.79 (—C=), 168.06 (CO_2). Found: C 56.25; H 6.10; S 29.18%. $C_{20}H_{26}O_2S_4$. Calculated: C 56.30; H 6.14; S 30.06%.

Spiro-{3,3-dimethylthio-2-carbethoxycyclopropane-1,7-endo-bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic Acid Anhydride (XXIX). A 0.05 g portion (0.5 mmole) of maleic anhydride was added to a solution of 0.12 g (0.5 mmole) of (XXV) in 5 ml of benzene and the reaction mixture was boiled with stirring for 4 h. The solvent was evaporated, the mixture obtained was crystallized from a hexane—ether (5:1) mixture, and the precipitate was filtered. Yield, 0.16 g (94%), of a white crystalline compound, mp 149-151°C. IR spectrum (ν, cm^{-1}): 1730 (C=O), 1780, 1860, ($(CO)_2O$). PMR spectrum ($CDCl_3$): 1.30 t (J = 7.1 Hz, CH_3), 2.08 s, 2.14 s (6H, CH_3), 3.5 br. s (CH), 3.68-4.01 m (4H, CH), 4.20 m (CH_2), 6.45 m (2H, CH). ^{13}C NMR spectra ($CDCl_3$): 14.15, 14.20 (CH_3S), 14.89 (CH_3CH_2), 32.22 ($CHCO_2$), 44.66 (S—C—S), 46.38, 47.20, 49.94, 47.23 (CH), 61.42 (CH_2—O), 66.01 (C), 134.77, 136.20 (CH=CH), 166.64, 166.74 (—CO—O—CO—), 168.17 (CO_2). Found: C 54.24; H 5.08; S 17.98%. $C_{16}H_{18}O_5S_2$. Calculated: C 54.22; H 5.12; S 18.09%.

LITERATURE CITED

1. K. Neumann, Chemistry of Plant Protection and Combatting of Pests. Chemistry of Synthetic Pyrethroid Insecticides [in German], Vol. 7, R. Wegler, Berlin (1981).
2. W. I. Fanta and J. I. Shulman, US Patent 3,823,177; Ref. Zh. Khim., 220298 P (1975).
3. G. A. Tolstikov, F. Z. Galin, and V. N. Iskandarova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1210 (1983).
4. G. A. Tolstikov, F. Z. Galin, and V. N. Iskandarova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 7, 1668 (1984).
5. R. Gompper and E. Kutter, Chem. Ber., 98, 1966 (1965).
6. S. N. Lakeev, F. Z. Galin, and G. A. Tolstikov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 213 (1989).
7. G. B. Payne, J. Org. Chem., 32, 3351 (1967).
8. W. Freiesleben, Angew. Chem., 75, 576 (1963).
9. C. H. Schmidt, Chem. Ber., 90, 1352 (1957).
10. E. T. McBee and R. K. Meyers, J. Am. Chem. Soc., 77, 86 (1955).
11. K. J. Stone and D. R. Little, J. Org. Chem., 49, 1849 (1984).
12. K. Hafner, Liebigs Ann. Chem., 79, 606 (1957).
13. J. L. Kice, J. Am. Chem. Soc., 80, 3792 (1958).