in the solvent (10 mL) was stirred at 25 °C for 60 min (reaction in water), 20 min (reaction in methanol), or 30 min (reaction in acetic acid), quenched with solid $NaHCO_3$ and saturated aqueous $NaHCO_3$ (in the case of the reaction in acetic acid the mixture was previously diluted with water), and thoroughly extracted with ether. Evaporation of the washed (NaCl-saturated H_2O) ether extracts yielded mixtures consisting of diols **5** and **6** (reaction in water), hydroxy ethers **2–4** (reaction in methanol), or monoacetates (reaction in acetic acid) which were analyzed by GLC (see Table II), except for the reaction carried out in acetic acid. The crude product obtained from the reaction in acetic acid was analyzed by GLC after saponification of the monoacetates to the corresponding diols **5** and **6** as described later for the reactions of **1** with trichloroacetic acid. The reaction of **1** in methanol and that in acetic acid were also performed in the presence of anhydrous $LiClO_4$ (1.0 M) to give the results reported in Table II.

The solvolysis addition products of these reactions were completely stable under the reaction conditions used.

Reactions of Epoxide 1 with Trichloroacetic Acid in Several Solvents. The reactions were carried out in anhydrous benzene, cyclohexane, CCl_4, $CHCl_3$, and CH_2Cl_2 in the following way. A solution of **1** (0.100 g, 0.81 mmol) in the solvent (9 mL) at 25 °C was treated with a 1 M solution of trichloroacetic acid in the same solvent (1.0 mL), stirred 1 h at the same temperature, washed with saturated aqueous $NaHCO_3$ and water, and evaporated to dryness. The residue obtained, consisting mainly of mixtures of monotrichloroacetates was hydrolyzed in the following way. The crude product was dissolved in freshly distilled THF (8 mL), treated with 1 M KOH in ethanol (2.5 mL), and then left 5 h at room temperature. The reaction mixture was diluted with water, saturated with NaCl and extracted four times with ether. Evaporation of the washed (NaCl-saturated H_2O) and dried ether extracts yielded a mixture of **5** and **6** which was analyzed by GLC (see Table II). Reaction of **1** in each solvent carried out under the same conditions, but being stopped after a longer reaction time of contact with the acid, yielded the same product composition within experimental error. Experiments were carried out in order to verify if the diols **5** and **6** are stable under the saponification conditions, and if the method of saponification used does not alter the stereoselectivity of the reactions.

Reaction of 1 with Methanol in Methylene Dichloride in the Presence of *p*-Toluenesulfonic Acid. To the epoxide **1** (0.100 g, 0.81 mmol) was added a solution of *p*-toluenesulfonic acid monohydrate and methanol in a molar ratio (expoxide/acid/methanol) of 1:0.1:6 in anhydrous CH_2Cl_2 (10 mL) at 25 °C. The resulting mixture was stirred for 1 h at the same temperature and then treated with solid $NaHCO_3$ and saturated aqueous $NaHCO_3$. Evaporation of the washed (H_2O) organic solvent gave a residue, which was analyzed by GLC.

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Registry No. **1**, 932-03-6; **2**, 75476-39-0; **3**, 75476-40-3; **4**, 28144-12-9; **5**, 75476-41-4; **6**, 75476-42-5; **7**, 75476-43-6; **8**, 931-49-7.

Aromatic Substitution. 46. Methyl (Ethyl) Thio(Dithio)carboxylation of Aromatics with *S*-Methyl (*S*-Ethyl) Thiocarboxonium and Dithiocarboxonium Fluoroantimonates[1a]

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S-Methyl(*S*-ethyl)thio(dithio)carboxinium ions were prepared by reacting methyl (ethyl) fluoride–antimony pentafluoride with carbonyl sulfide (carbon disulfide) and studied with ^1H and ^{13}C NMR spectroscopy. The ions were subsequently used in the novel carboxylation reaction of arenes to *S*-methyl (*S*-ethyl) thio(dithio)benzoates. The method was also found to be adaptable to the carboxylation of polystyrene to poly(styrenecarboxylic acid) without degradation of the polymer backbone.

Aromatic carboxylic acids can be synthesized by Friedel–Crafts reactions using phosgene, oxalyl chloride, or carbamoyl chlorides and hydrolyzing (deaminating) the intermediate carboxylic acid derivatives.[2] Arenethiocarboxylic esters can be prepared[3,4] by reacting aromatic hydrocarbons with alkyl chlorothioformates in the presence of $AlCl_3$ or other Friedel–Crafts catalysts (eq 1). The dithiocarboxylic acids of pyrroles have been prepared by Friedel–Crafts reaction with carbon disulfide and $AlCl_3$.[5-7]

$$ArH + ClC(O)SR \xrightarrow{AlCl_3} ArC(O)SR + HCl \quad (1)$$

In these methods generally a 2-mol excess of the strong Lewis acid catalyst is needed, and significant side reactions take place, including alkylations. Yields are modest and applicability is limited.

We now report an efficient and mild method for the preparation of methyl and ethyl thio(dithio)benzoates by electrophilic substitution of aromatic hydrocarbons with *S*-methyl(*S*-ethyl)thiocarboxonium and -dithiocarboxonium fluoroantimonates, readily prepared by methylating (ethylating) carbonyl sulfide and carbon disulfide,

(1) (a) For part 45, see G. A. Olah, G. C. Narang, J. A. Olah, R. L. Pearson, and C. A. Cupas, *J. Am. Chem. Soc.*, **102**, 3507 (1980). (b) Postdoctoral fellow 1979–1980, CNRS, Strasbourg, France.

(2) For a review of acid syntheses see G. A. Olah and J. A. Olah in "Friedel–Crafts and Related Reaction", Vol. 3, Wiley-Interscience, New York, 1964, Part 2, Chapter 39.

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Table I. NMR Spectroscopic Data for *S*-Alkylthiocarboxonium and *S*-Alkyldithiocarboxonium Hexafluoroantimonates[a]

species	^{13}C NMR, δ			^{1}H NMR, δ	
	CH_2	CH_3	X=C=Y	CH_2	CH_3
S=C=S			192.8		
O=C=S			154.2		
$[S{=}C{\cdots}SCH_3]^+ SbF_6^-$ (1a)		22.36	200.7		3.4
$[S{=}C{\cdots}SC_2H_5]^+ SbF_6^-$ (1b)	42.01 (157.6)	15.54 (131.3)	200.3	4.1 (7.7)	
$[O{=}C{\cdots}SCH_3]^+ SbF_6^-$ (2a)		21.04 (156.4)	160.0		3.5
$[O{=}C{\cdots}SC_2H_5]^+ SbF_6^-$ (2b)	44.25 (158.0)	17.14 (131.8)	160.0	4.5 (8.0)	1.8

[a] Spectra measured in SO_2 at −65 °C; Me_4Si used as external reference.

Table II. Preparation of Methyl Arenedithiocarboxylates from 1a

substrate	reaction conditions: temp, °C	time, min	yield, %	bp, °C (pressure, torr): obsd	bp, °C (pressure, torr): lit.[a]	^{1}H NMR ($CDCl_3$),[b] δ	IR,[c] cm^{-1}
benzene	−30	20	72	90 (0.8)	142 (12)	8.6-7.8 (m, 5 H), 3.2 (s, 3 H)	3060, 2910, 1590, 1445, 310, 1230, 1050 (br, C=S), 765, 960
toluene	−70	5	81	80 (0.15)	125 (2.5)	8.7-7.7 (q, 4 H), 3.3 (s, 3 H), 2.9 (s, 3 H)	3030, 2980, 2920, 1610, 1410, 1310, 1240, 1185, 1055 (br, C=S), 820
o-xylene	−70	5	83	122 (0.25)		8.3-7.4 (m, 3 H), 3.1 (s, 3 H), 2.6 (s, 6 H)	3020, 2950, 1600, 1450, 1250, 1065 (br, C=S), 835
m-xylene	−70	5	72	92-95 (0.15)		7.7-7.2 (q, 3 H), 3.1 (s, 3 H), 2.6 (s, 6 H)	3020, 2920, 1615, 1450, 1250, 1060 (br, C=S), 820
p-xylene	−70	5	62	88 (0.15)		7.6 (s, 3 H), 3.1 (s, 3 H), 2.7 (s, 6 H)	3030, 1500, 1450, 1260, 1180, 1075 (br, C=S), 815
anisole	−70	5	84	120 (0.2)	148 (0.8)	8.5-7.0 (q, 4 H), 4.0 (s, 3 H), 3.0 (s, 3 H)	3010, 2840, 1600, 1500, 1420, 1250 (br), 1175, 1050 (br, C=S), 840
cumene	−70	5	80	116 (0.8)		8.6-7.6 (q, 4 H), 3.6-2.9 (m, 1 H), 3.1 (s, 3 H), 2.6 (d, 6 H)	3030, 2980, 1605, 1415, 1250, 1185, 1060 (br, C=S), 840
mesitylene	−70	5	82	90 (0.1)		7.4 (s, 2 H), 3.1 (s, 3 H), 2.7 (s, 6 H), 2.6 (s, 3 H)	2920, 1615, 1450, 1250, 1065 (br, C=S), 855
fluorobenzene	−30	20	60	106 (1.2)	106 (1.2)	8.6-2.3 (m, 4 H), 3.0 (s, 3 H)	3060, 2910, 1600, 1500, 1410, 1235 (br), 1160, 1055 (br, C=S), 890

[a] See ref 4. [b] From external Me_4Si in $CDCl_3$; s = singlet, q = quartet, m = multiplet, d = doublet. [c] Neat; br = broad.

respectively, with methyl (ethyl) fluoride–antimony pentafluoride.[8]

Results and Discussion

When an SO_2 solution of CS_2 is added to an SO_2 solution of methyl fluoride–antimony pentafluoride and the mixture is slowly warmed to −25 °C (−65 °C with SO_2ClF as solvent), the ^{1}H NMR spectrum reveals the disappearance of the peak at δ 5.56 due to methylated sulfur dioxide and the appearance of a new peak at δ 3.4 indicating S-methylation of CS_2 to give **1a** (eq 2). COS is similarly

$$[RO{=}S{=}O]^+ SbF_6^- + S{=}C{=}X \xrightarrow[SO_2]{-25\ °C} [R\text{-}S{\cdot\cdot}C{=}X]^+ SbF_6^-$$

1a, X = S; R = CH_3
b, X = S; R = C_2H_5
2a, X = O; R = CH_3
b, X = O; R = C_2H_5 (2)

S-methylated to give **2a**. The ^{13}C and ^{1}H NMR parameters for alkylated CS_2 (and COS) are given in Table I. Examination of the ^{13}C shifts of these species shows a significant deshielding of the thiocarbonyl carbon of 1 and 2 from the chemical shift of the carbon atom of COS or CS_2 indicative of the carbon atom's increased electrophilicity. Dimethylchloronium hexafluoroantimonate[9] also S-methylates COS and CS_2, but this reaction is too slow and incomplete to be practical.

Ethylation of COS and CS_2 with ethyl fluoride–antimony pentafluoride in SO_2 at −60 °C is quantitative and instantaneous, confirming the more powerful alkylating ability of this complex. An equimolar mixture of ethylene and fluorantimonic acid (HF/SbF_5) in SO_2 can also be used in place of CH_3CH_2F/SbF_5 with similar results and represents a simple and efficient way to prepare **1b** and **2b**.[10]

$$CH_2{=}CH_2 + HF/SbF_5 \xrightarrow[\leq -30\ °C]{SO_2} [CH_3CH_2O{=}S{=}O]^+ SbF_6^- \xrightarrow{X{=}C{=}S} \textbf{1b or 2b} \quad (3)$$

Thiocarboxylation of aromatics is simply effected by dropwise addition of an SO_2 solution of the aromatic to a well-stirred solution of 1 or 2. S-Alkylation of COS or CS_2 sufficiently increases the carbon atom's electrophilicity

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(9) G. A. Olah, J. R. Demember, Y. K. Mo, J. J. Svoboda, P. Schilling, and J. A. Olah, *J. Am. Chem. Soc.*, 96, 884 (1974).

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Table III. Preparation of Methyl Arenethiocarboxylates from 2a

substrate	reaction conditions: temp, °C	reaction conditions: time, min	yield, %	bp, °C (pressure, torr): obsd	bp, °C (pressure, torr): lit.[a]	^{1}H NMR ($CDCl_3$),[b] δ	IR,[c] cm^{-1}	yield of acid,[d] %
benzene	−50	20	60	62 (0.8)	116 (16)	8.5–7.6 (m, 5 H, ring H), 2.7 (s, 3 H, ester CH_3)	3060, 2980, 2930, 1665 (br, C=O), 1605, 1585, 1450, 1280, 1210, 1110, 920, 720, 690	69
toluene	−70	10	77	70 (0.45)	135 (16)	8.3–7.4 (q, 4 H, ring H), 2.6 (s, 3 H, ester CH_3), 2.5 (s, 3 H, ring CH_3)	2920, 1660 (br, C=O), 1605, 1575, 1510, 1420, 1310, 1170, 915, 840	81
o-xylene	−70	10	71	82 (0.4)	154 (16)	8.2–7.5 (m, 3 H, ring H), 2.7 (s, 3 H, ester CH_3), 2.5 (s, 6 H, ring CH_3)	2980, 2930, 1670 (br, C=O), 1610, 1500, 1450, 1290, 1260, 1240, 1210, 1165, 1125, 1025, 980, 860, 830	72
m-xylene	−70	10	78	84 (0.8)	145 (16)	8.2–7.3 (m, 3 H, ring H), 2.8 (s, 3 H, ester CH_3), 2.7 (s, 3 H, ortho CH_3), 2.6 (s, 3 H, para CH_3)	3020, 2940, 1670 (br, C=O), 1617, 1500, 1450, 1215, 1135, 955, 875 875, 825	78
anisole	−70	10	78	100 (0.55)	164 (16)	8.5–7.2 (q, 4 H), 4.2 (s, 3 H, OCH_3), 2.8 (s, 3 H)	3070, 2980, 2930, 2840, 1650 (br, C=O), 1605, 1580, 1510, 1420, 1310, 1220, 1115, 1030, 920, 650	58
cumene	−70	10	77	99 (0.5)	162 (16)	8.4–7.4 (q, 4 H), 3.4–2.9 (m, 1 H), 2.6 (s, 3 H, ester CH_3), 1.4 (d, 6 H)	3030, 2960, 2930, 1670 (br, C=O), 1610, 1465, 1415, 1215, 1060, 920, 850	84
mesitylene	−70	10	64	85 (0.4)	150 (16)	7.2 (s, 2 H, ring H), 2.8 (s, 3 H, ester CH_3), 2.6 (s, 9 H, ring CH_3, br)	2920, 1670 (br, C=O), 1610, 1440, 1380, 1210, 890, 855	
fluorobenzene	−40	20	62	50 (0.5)	116 (16)	8.5–7.3 (m, 4 H, ring H), 2.8 (s, 3 H, CH_3)	3080, 2940, 1670 (br, C=O), 1610, 1510, 1410, 1230, 1160, 1105, 925, 845	62
chlorobenzene	−40	20	55	92 (1.0)	151 (20)	8.4–7.7 (q, 4 H), 2.8 (s, 3 H)	2920, 1665 (br, C=O), 1595, 1575, 1490, 1400, 1210, 1095, 930, 840	68
benzene	−40	20	50	96 (0.4)	170 (16)	8.4–7.9 (q, 4 H), 2.8 (s, 3 H)	2940, 1650 (br, C=O), 1590, 1395, 1210, 920, 840, 760, 720, 650	59

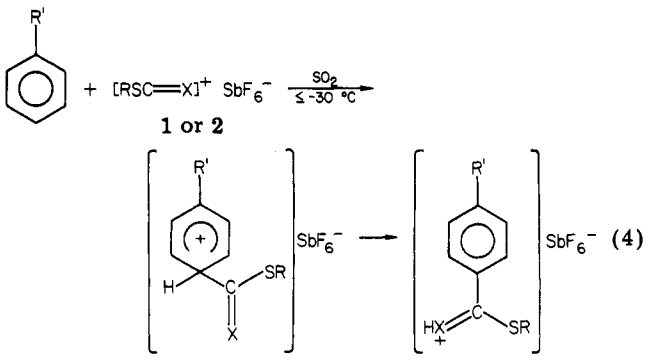
[a] See ref 4. [b] From external Me_4Si in $CDCl_3$. [c] Neat; br = broad. [d] After hydrolysis with 20% NaOH for 1 h. [e] In Me_2SO-d_6 at 90 °C.

Table IV. Preparation of Ethyl Arenethiocarboxylates from 2b

substrate[e]	yield, %	bp,[a] °C (pressure, torr)	^{1}H NMR ($CDCl_3$),[b] δ	IR,[c] cm^{-1}
benzene[d]	10	58 (0.25)	8.4-7.3 (m, 5 H, ring H), 3.3 (q, 2 H), 1.5 (t, 3 H)	3060, 2970, 2930, 2880, 1660 (br, C=O), 1595, 1580, 1445, 1375, 1210, 915, 695, 655
toluene	76	73 (0.2)	8.1-7.3 (q, 4 H), 2.5 (s, 3 H, ring CH_3), 1.5 (t, 3 H, ester CH_3), 3.2 (q, 2 H, ester CH_2)	3020, 2980, 2925, 2870, 1655 (br, C=O), 1600, 1570, 1445, 1375, 1200, 1175, 915, 825, 790
anisole	76	98 (0.2)	8.15-6.95 (q, 4 H), 3.9 (s, 3 H, OCH_3), 3.15 (q, 2 H, ester CH_2), 1.5 (t, 3 H, ester CH_3)	3080, 2970, 2940, 2880, 2840, 1655 (br, C=O), 1600, 1575, 1505, 1455, 1375, 1260, 1220, 1170, 1030, 920, 845
m-xylene	81	77 (0.2)	8.05-7.3 (m, 3 H), 2.7 (s, 3 H, ring *o*-CH_3), 2.5 (s, 3 H, ring *p*-CH_3), 1.55 (t, 3 H, ester CH_2), 3.2 (q, 2 H, ester CH_3)	3020, 2970, 2930, 2880, 1660 (br, C=O), 1610, 1450, 1375, 1210, 955, 865, 820, 730, 640
ethylbenzene	77	81 (0.2)	8.3-7.4 (q, 4 H, ring H), 3.3 (q, 2 H, ester CH_2), 2.9 (q, 2 H, ring CH_2), 1.45 (t, 3 H, ring CH_3), 1.5 (t, 3 H, ester CH_3)	3024, 2960, 2930, 2875, 1655 (br, C=O), 1605, 1450, 1375, 1215, 1175, 930, 845

[a] Observed boiling point. [b] From external Me_4Si; s = singlet, t = triplet, q = quartet, m = multiplet. [c] Neat; br = broad. [d] Minor products; major product is that of **2b** with $(C_2H_5)C_6H_5$. [e] The reaction temperature was −78 °C and the reaction time 15 min in each case.

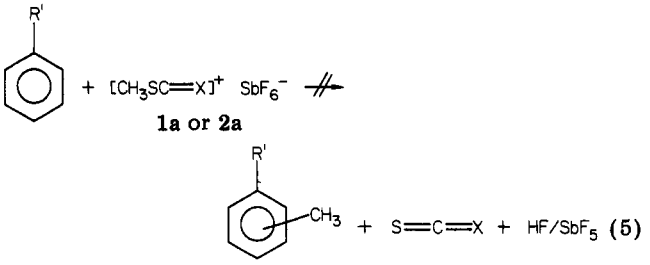
for reaction with aromatics. The suggested mechanism of the reactions is depicted as shown in eq 4.



(4)

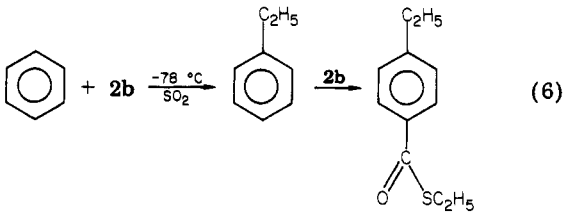
The thiocarboxylation reaction of activated aromatics is instantaneous and nearly quantitative, despite low reaction temperatures. In monosubstituted aromatics, substitution occurs nearly exclusively at the para position as determined from aromatic proton NMR coupling patterns. The isomeric selectivity was further confirmed by TLC. Ortho thiocarboxylation can occur, however, as evidenced in the reactions of **1a** and **2a** with *m*- and *p*-xylene. The thiocarboxonium ions **2** were found to be more reactive than the corresponding dithiocarboxonium ions **1**. Thiocarboxonium ion **2a** reacted quantitatively with benzene at −50 °C while dithiocarboxonium ion **1a** does not begin to react with benzene below −30 °C. We have found that while **2a** readily reacts with halobenzenes at low temperature, **1a** will not react with these deactivated aromatics in the temperature range studied. We have also found that the carbonyl and thiocarbonyl groups, respectively, of the products can act as internal bases which neutralize the fluoroantimonic acid formed in the reactions (eq 5 and 6).

Competitive alkylation occurs only in the reactions of **1b** and **2b** with benzene or halobenzenes, as determined by GLC analysis of the products, in agreement with Olah and Schilling's[4] finding in Friedel–Crafts reactions with *S*-alkyl chlorothioformates. Thus, **1a** and **2a** do not transfer methylate the substrates (eq 5), while **2b** seems



(5)

to react with benzene to give ethylbenzene which subsequently reacts with another molecule of **2b** to give *S*-ethyl *p*-ethylthiobenzoate[11] (eq 6). The ambident electro-



(6)

philicity of **2b** is easily explained by considering the fact that the incipient ethyl cation is more stable than the methyl cation and thus is more readily tranferred to a less reactive aromatic.

The reaction mixtures were worked up by pouring them slowly into a pentane–ice mixture at the end of the reaction times listed. They were then extracted with pentane to minimize acid-catalyzed hydrolysis of the products, especially halothiobenzoic acid esters. The pure thio- and dithioesters were isolated by distillation and characterized by IR and ^{1}H NMR spectroscopy. For preparation of the corresponding benzoic acids, the crude esters can be hydrolyzed by refluxing them in 20% NaOH for 1 h, followed by acid workup. Reaction conditions, yields, and product data for the esters are given in Tables II–IV.

(11) In similar reactions with liquid CO_2 under pressure, only alkylation occurred with activated and deactivated aromatics.

The high positional selectivity inherent in the reaction of **1** and **2** with monosubstituted aromatics is partially attributable to steric interactions between the bulky attacking electrophile and a substituent in the ortho position. However, in agreement with the results of Olah and Schilling,[4] high para selectivity can also be attributed to formation of a thermodynamically more stable para σ complex under superacid conditions, particularly at the low temperatures involved.

The fact that CS_2 is often used as a solvent in Friedel–Crafts reactions raises the question whether it is alkylated by RX/AlX_3 to form a species like **1a**. To our knowledge, however, the formation of dithioesters as a side reaction in Friedel–Crafts alkylation has not been reported.[12]

Experimental Section

All staring materials were commercially available. Antimony pentafluoride (Cationics, Inc.) was doubly distilled in glass under an inert atmosphere before use. Ethyl fluoride (PCR), methyl fluoride (Matheson), and ethylene (Airco) were used as received. Carbonyl sulfide (Matheson) was purified through a drying train of calcium chloride, calcium sulfate, and mercuric oxide. Carbon disulfide (Mallinckrodt) was stored over molecular sieves.

Infrared and ^1H NMR spectra were recorded on Perkin-Elmer Model 297 and Varian Associates Model A56-60 spectrometers, respectively. Tetramethylsilane was used as an external standard. Thin-layer chromatography was performed on silica gel plates with hexane as eluent.

The general procedure for the carboxylation of aromatics with **1** or **2** in SO_2 was as follows. A solution of the alkylating agent was prepared by introducing a slight excess of alkyl fluoride into a solution of antimony pentafluoride (10.0 mmol) in SO_2 (15 mL) at −78 °C. Excess carbon disulfide or carbonyl sulfide was then added to this vigorously stirred solution, and in the case of methyl fluoride-antimony pentafluoride, the solution temperature was allowed to rise to −30 °C for 15 min to ensure complete formation of **2a**. Ethylation with ethyl fluoride–antimony pentafluoride of **1b** or **2b** was instantaneous at −60 °C. The progress of the reaction is indicated by the disappearance of the upper layer of CS_2 as **1a** is formed.

The aromatic substrate (10 mmol) was then dissolved in 5 mL of SO_2, cooled to the reaction temperature, and added dropwise to the well-stirred, light yellow solution of the carboxylating agent. After being stirred for the specified time, the reaction mixture was poured over ice, extracted three times with 100-mL portions of 10% $NaHCO_3$ solution and distilled water, respectively, and dried over anhydrous $MgSO_4$. After removal of pentane from the product by rotary evaporation, the pure ester was obtained by vacuum distillation or recrystallization. The compounds obtained gave satisfactory elemental analysis (Galbraith Laboratories).

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Registry No. 1a, 75599-66-5; **1b**, 75599-68-7; **2a**, 75626-81-2; **2b**, 75599-70-1; methyl benzenedithiocarboxylate, 2168-78-7; methyl toluenedithiocarboxylate, 75599-50-7; methyl *o*-xylenedithiocarboxylate, 75599-51-8; methyl *m*-xylenedithiocarboxylate, 75599-52-9; methyl *p*-xylenedithiocarboxylate, 75599-71-2; methyl anisoledithiocarboxylate, 75626-80-1; methyl cumenedithiocarboxylate, 75599-53-0; methyl mesitylenedithiocarboxylate, 58863-45-9; methyl fluorobenzenedithiocarboxylate, 75599-54-1; methyl benzenethiocarboxylate, 5925-68-8; methyl toluenethiocarboxylate, 75599-55-2; methyl *o*-xylenethiocarboxylate, 75599-56-3; methyl *m*-xylenethiocarboxylate, 75599-57-4; methyl anisolethiocarboxylate, 75599-58-5; methyl cumenethiocarboxylate, 75599-59-6; methyl mesitylenethiocarboxylate, 39248-77-6; methyl fluorobenzenethiocarboxylate, 75599-60-9; methyl chlorobenzenethiocarboxylate, 75599-61-0; methyl bromobenzenethiocarboxylate, 75599-62-1; polystyrene, 9003-53-6; ethyl benzenethiocarboxylate, 1484-17-9; ethyl toluenethiocarboxylate, 75599-63-2; ethyl anisolethiocarboxylate, 75599-64-3; ethyl *m*-xylenethiocarboxylate, 75599-65-4; ethyl ethylbenzenethiocarboxylate, 75599-72-3; CS_2, 75-15-0; COS, 463-58-1.

(12) G. A. Olah, "Friedel–Crafts and Related Reaction", Vol. 3, Wiley-Interscience, New York, 1964, Part 2, Chapter 39.

Notes

Syntheses of Seven-Membered Cyclic Azo Compounds[1]

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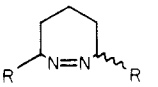
The chemistry of both cyclic and acyclic azo compounds has been investigated extensively in our laboratory since 1949.[1] Attention has been focused recently on the study of seven- to ten-membered-ring systems. Previous thermal and photochemical decomposition studies of medium-sized cyclic azo compounds in solution and in the solid state have provided interesting data on the stereoselectivity of product formation observed in these reactions and the characteristics of the radical intermediates that were produced during decomposition.

In conjunction with this research effort, we report the synthesis of the seven-membered cyclic azo compounds of this series. The compounds 1,2-diaza-(*Z*)-1-cycloheptene (**1**) and *cis*- and *trans*-3,7-dimethyl-1,2-diaza-(*Z*)-1-cycloheptenes (**2** and **3**, respectively) have been synthesized and characterized. The synthesis of *cis*-3,7-diphenyl-1,2-diaza-(*Z*)-1-cycloheptene (**4**) has been reported previously.[4,5]



1, R = H
2, R = CH_3 (cis)
3, R = CH_3 (trans)
4, R = C_6H_5 (cis)

(1) This is the 53rd in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper see C. G. Overberger and Minn-Shong Chi, *J. Org. Chem.*, companion paper in this issue.
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(3) Taken in part from the Ph.D. Thesis of T. F. Merkel, The University of Michigan, 1973.

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