

zones in the mixture (sulfuric acid spray, silica gel G,³³ solvent B).

The preceding experiment was also carried out using the carbonate form of Dowex-I anion exchange resin with identical results.

Use of *n*-propylamine as base at room temperature resulted in the cleavage of the glycoside to a similar 2,4-dinitrophenyl- α -aminoacrylic acid derivative described above (solvent A on silica gel G³³) and a carbohydrate component as above. However, a yellow, slower moving zone component gave evidence of a certain amount de-*O*-acetylation without cleavage of the glycoside. This product is under further investigation.

With all the above conditions a selection of temperatures ranging from -30 to 50° were tried. Below -20° no glycoside cleavage was observed, whereas on visual estimation of products with thin layer chromatographic resolution, the base-catalyzed elimination was considerably accelerated at temperatures above room temperature.

The "acid-base" compound (V) described above could be synthesized by treating the isolated unsaturated *N*-2,4-dinitro-

phenyl- α -aminoacrylic acid methyl ester (IV) with barium or sodium methoxide in methanol.

Acid-catalyzed hydrolysis of the glycoside (III) in sulfuric acid (2 *N*) for 6 hr at 95° , neutralization with barium carbonate, and isolation of the hydrolysate by centrifuging gave a solution which was resolvable into two zones on thin layer chromatographic examination (silica gel G, solvent B) corresponding to 2-amino-2-deoxy-D-glucose and *N*-2,4-dinitrophenylserine (ninhydrin and silver nitrate location reagents³³).

Acknowledgment.—The authors are indebted to Dr. R. A. Gibbons, National Institute for Research in Dairying, Shinfield, Reading, Berkshire, England, for suggesting the original problem and to Dr. Derek Horton, Department of Chemistry, The Ohio State University, Columbus, Ohio, for his helpful counsel on the course of experimentation.

Organic Sulfur Compounds. XVIII. Selective Addition of Thiols and Thiol Acids to Diallyl Maleate and Fumarate^{1a}

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Aliphatic and aromatic thiols and thiolacetic acid were selectively added to the allylic double bonds of diallyl maleate and fumarate with a free-radical, ultraviolet light initiated mechanism (at 16°). The "allylic" radical addition was mostly of anti-Markovnikov orientation, but minor amounts (up to 5%) of the Markovnikov-type (branched) allylic adducts were also formed. No isomerization of the maleic compound to the fumarate isomer occurred during these additions. The high specificity of the attack of thiol radicals was attributed to their highly electrophilic nature. Base catalysis of the above reactions with triethylenediamine resulted in anionic Michael additions to the maleic or fumaric double bonds. These reactions were probably preceded by isomerization of the diallyl maleate to the fumarate, which indicates their reversibility.

In contrast to still widely held beliefs, free-radical reactions may show a remarkable selectivity. Earlier studies of free-radical addition reactions of thiol compounds to dienes and acetylenes in this laboratory^{1b,2,3} showed that such reactions have a specific course which can be predicted on the basis of the structure of the starting olefin. Our more recent studies are concerned with selectively reacting certain groups in polyfunctional molecules while leaving others intact. In particular, this paper deals with selective free-radical additions of thiol compounds to the allylic double bonds of diallyl esters of maleic and fumaric acid. Anionic additions to the maleic and fumaric double bonds of the above compounds are also described.

Thiol compounds were a logical selection as model compounds for a study of both free-radical and ionic addition reactions of diallyl maleate and fumarate. In the presence of free-radical catalysts and often even in their absence, aliphatic and aromatic thiols are known to react in a clean, free-radical manner with olefinic double bonds. Base-catalyzed addition of thiols to maleic anhydride has also been described.^{4,5}

It was reasonable to assume that, under the proper conditions, thiols are especially likely to add to diallyl maleate by either a free-radical or an ionic mechanism and, therefore, are ideal reagents for testing the possibility of selective reactions. Although diallyl maleate and fumarate have been known for some time, none of their possible selective addition reactions has been previously studied to our knowledge.

In this study mostly equimolar amounts of simple aliphatic and aromatic thiols, thiolacetic acid, and diethylphosphorodithioic acid were allowed to react with diallyl maleate and fumarate without solvent at ambient temperatures. The reaction mixtures were analyzed by a combination of n.m.r. spectroscopy and gas-liquid partition chromatography (g.l.p.c.). The adducts formed were isolated by fractional distillation *in vacuo*. N.m.r. spectra of the benzenethiol monoadducts are shown in Figure 1 for illustration of the distinctive spectral characteristics of the "allylic and maleic or fumaric adducts."

Results

Dependent on the reaction conditions, either the allylic or the maleic (fumaric) bonds of diallyl maleate (fumarate) could be selectively reacted.

Free-Radical Additions.—Methane-, ethane-, and benzenethiol could be selectively added under the effect of ultraviolet irradiation at 16° to the allylic double bonds of diallyl maleate and fumarate to form the corresponding anti-Markovnikov-type "allylic" mono- and diadducts (Tables I and II). No isomeri-

(1) (a) The contents of this paper were part of a presentation before the Organic Chemistry Division at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p. 47P. (b) A. A. Oswald, K. Griesbaum, W. A. Thaler, and B. E. Hudson, Jr., *J. Am. Chem. Soc.*, **84**, 3897 (1962).

(2) K. Griesbaum, A. A. Oswald, E. R. Quiram, and W. Naegle, *J. Org. Chem.*, **28**, 1952 (1963).

(3) A. A. Oswald, K. Griesbaum, B. E. Hudson, Jr., and J. M. Bregman, *J. Am. Chem. Soc.*, **86**, 2877 (1964).

(4) F. B. Zienty, B. D. Vineyard, and A. A. Schlepplnik, *J. Org. Chem.*, **27**, 3140 (1962).

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TABLE I
FORMATION OF ISOMERIC MONO- AND DIADDUCTS ON THE ADDITION OF THIOL COMPOUNDS TO DIALLYL MALEATE AND FUMARATE

Catalyst	Time, hr.	Temp., °C	Reaction conditions		Starting compounds, moles		Starting compounds (except thiols)		Compounds in reaction mixture, wt. % (i.e., % area g.l.p.c.)		Allylic adducts with maleic or fumaric unsaturation	
			Thiol used	Thiol maleate	Diallyl maleate	Diallyl fumarate	Diallyl maleate	Diallyl fumarate	Mono- or fumaric adducts	Dl- ^c	Monoadducts	Diadducts
Ultraviolet	4	16	Methanethiol ^b	1	1	5	0.5	0.5	27	56
Ultraviolet	7	16	Ethanethiol	1	1	43	1	1	3	2	42	6
Ultraviolet	7	16	Ethanethiol	1	1	0	58	30	5	3	30	3
Ultraviolet	4	16	Benzenethiol ^c	1	1	10	10	10	23	...	57	...
Ultraviolet	4	16	Benzenethiol ^c	1	1	...	42	42	1	...	54.5	...
...	Thiolacetic acid ^d	1	1	30	3	3	2	...	43	19 ^e
...	Thiolacetic acid ^d	1	1	...	41	41	2.5	...	54.5	...
...	Diethyldithiophosphoric acid	2	1	...	2	2	98 ^e
...	Ethanethiol	1	1	100
R ₃ N ^f	1/6	<30	n-Dodecanethiol	1	1	...	5	5	95
R ₃ N ^f	1/6	90	2-Methyl-2-propanethiol	1	1	...	24	24	76
R ₃ N ^f	...	<30	Benzenethiol	1	1	100
R ₃ N ^f	...	<30	Benzenethiol	1	2	...	50	50	50
R ₃ N ^{f/g}	...	<30	Thiolacetic acid	1	1	12	10	10	70	5	3	...

^a The second thiol molecule was added to one of the allylic double bonds. ^b The tabulation does not include the 10% triadduct formed. ^c Diadducts could not be analyzed by g.l.p.c. and therefore are not included in these data. For their n.m.r. estimation, see the Experimental Section. ^d The diadduct peak is a wide one; it may include more than this one isomer. ^e The unreacted diethyldithiophosphoric acid was removed before g.l.p.c. analysis of the mixture. ^f 5 mole % triethylenediamine. ^g The amine formed a solid salt precipitate with the acid.

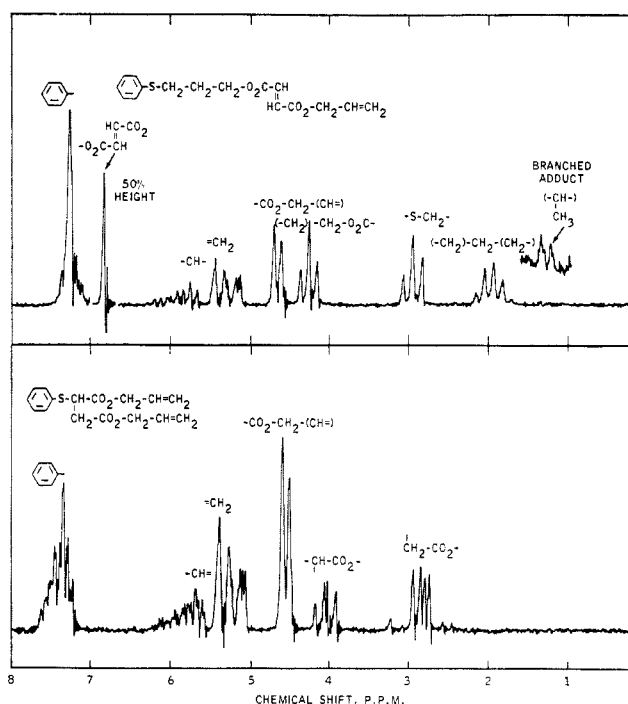
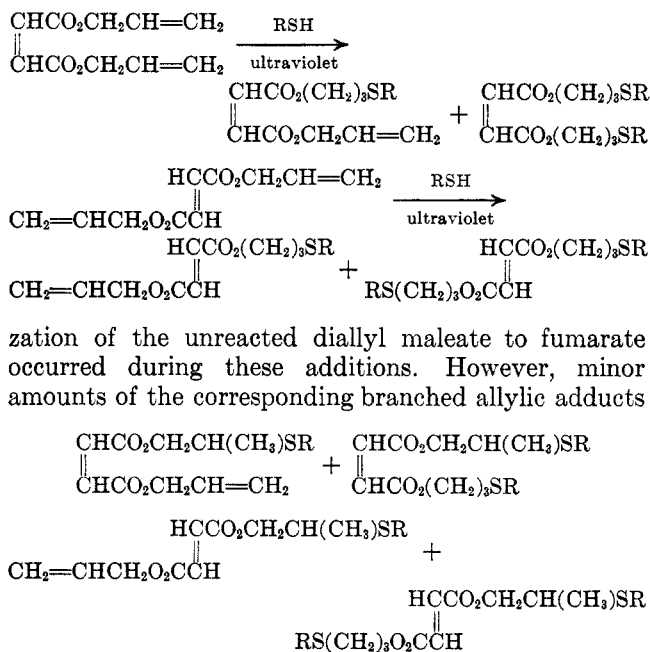


Figure 1.—N.m.r. spectra of benzenethiol-diallyl fumarate mono-adducts.



(Table I) were formed. No oligomerization was observed in any of these reactions.

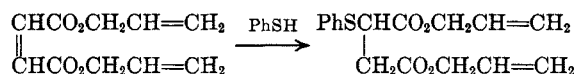
A reaction of 2 moles of methanethiol with 1 mole of diallyl maleate yielded the allylic mono- and diadducts and the triadduct as the major products (Table I). Only trace amounts of the isomeric mono- and diadducts were formed. The reaction of an equimolar amount of ethanethiol with diallyl maleate formed only the allylic mono- and diadducts as major products. However, this latter reaction resulted in more of the branched isomers (Table I). A similar reaction of ethanethiol with diallyl fumarate yielded significant amounts of the corresponding fumaric adduct.

When a equimolar amount of benzenethiol was added to diallyl maleate some spontaneous "maleic" addition occurred. On subsequent irradiation of the mixture

TABLE II
SOME PHYSICAL AND ANALYTICAL DATA OF THIOL MONOADDUCTS OF DIALLYL MALEATE AND FUMARATE

Catalyst	Diallyl starting compound	R	Formula	Structure	B.p., °C. (mm.)	Calcd., %				Found, %			
						C	H	O	S	C	H	O	S
Ultraviolet	Maleate	Methyl	C ₁₁ H ₁₄ O ₄ S	I	116-117 (0.1)	54.08	6.60	26.20	13.12	53.93	6.57	26.4	13.16
Ultraviolet	Maleate	Ethyl	C ₁₃ H ₁₈ O ₄ S	I	120-123 (0.1)	55.79	7.02	24.78	12.41	55.82	7.09	24.6	12.22
Ultraviolet	Fumarate			II	124-127 (0.1)					55.94	7.12	24.5	12.32
R ₃ N	Maleate			III	103-104 (0.1)					55.77	7.08	24.8	12.47
R ₃ N	Maleate	<i>t</i> -Butyl	C ₁₄ H ₂₀ O ₄ S	III	107-109 (0.1)	58.72	7.74	22.35	11.19	59.06	7.73	22.5	10.96
Ultraviolet	Maleate	Phenyl	C ₁₅ H ₁₈ O ₄ S	I	159-162 (0.2)	62.78	5.92	20.89	10.46	62.88	6.00	20.8	10.45
Ultraviolet	Fumarate			II	164-167 (0.2)					62.69	5.95	20.7	10.50
R ₃ N	Maleate			III	152-153 (0.2)					62.67	6.02	20.9	10.29
R ₃ N	Fumarate			III	153-155 (0.2)					62.78	5.96	20.7	10.64
Ultraviolet	Maleate	Acetyl	C ₁₂ H ₁₄ O ₄ S	I	133-136 (0.1)	52.93	5.92	29.38	11.77	52.84	5.90	29.1	11.95
Ultraviolet	Fumarate			II	134-137 (0.1)					52.96	5.95	29.2	11.85
R ₃ N	Maleate			III	135-137 (0.7)					52.93	5.93	29.3	11.56
Nil	Maleate	(C ₂ H ₅ O) ₂ P(S)	C ₁₄ H ₂₀ OPS ₂ ^a	III		43.97	6.06	25.11	16.77	43.72	6.04	25.0	16.95

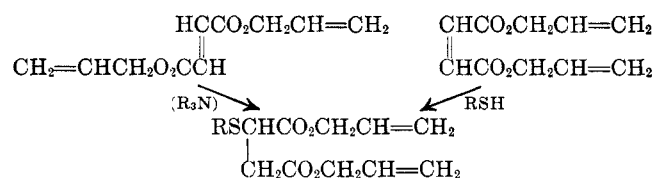
^a Anal. Calcd.: P, 8.09. Found: P, 8.2.



for 4 hr., however, an adduct mixture consisting mainly of the isomeric allylic monoadducts in a 1:1 ratio was obtained. In the case of diallyl fumarate, reaction with benzenethiol under similar conditions resulted in an almost exclusively allylic addition (Figure 1).

The addition of thiolacetic acid to diallyl maleate and fumarate also occurred in the absence of irradiation. Nevertheless, the addition of thiolacetic acid, unlike that of benzenethiol, took place selectively at the allylic bonds of both the maleate and the fumarate.

Ionic Additions.—In the presence of a basic catalyst, such as aliphatic amines, exclusive Michael addition of thiol compounds to the maleic and fumaric bond could be carried out. Owing to the fast rates of such additions, free-radical addition to the allylic double bonds is insignificant.



A strongly acidic thiol compound, diethyldithiophosphoric acid, could be added to the maleic and the fumaric double bonds even without the use of a base catalyst. A similar, exclusively maleic course of addition was observed with this compound in the presence of a free-radical inhibitor, methylhydroquinone.

In the case of less acidic thiol compounds, which are not effective enough to catalyze the reaction themselves, 5 mole % of triethylenediamine (1,4-diazabicyclo[2.2.2]octane) was added to the thiol before the addition of the diallyl maleate or fumarate. The conjugate addition of ethane-, *n*-dodecane-, and benzenethiol under such conditions occurred readily and quantitatively. These reactions were exothermic; ice-water cooling was necessary to keep them under control. In contrast, a tertiary aliphatic thiol, 2-methyl-2-propanethiol, did not react at ambient temperatures. Heating of the reaction mixture to 90° was necessary to effect reaction.

Thiolacetic acid formed an almost insoluble salt with triethylenediamine; consequently, only minor amounts (about 5%) of the allylic adducts were formed in this case.

In all the amine-catalyzed maleic additions the unconverted diallyl maleate reactant was isomerized to the fumarate. To determine the effect of the amine, benzenethiol was added to diallyl maleate solutions containing varying amounts of triethylenediamine at 25-30° and the resulting mixtures were analyzed by n.m.r. spectroscopy for composition. The results of these experiments are given in the Table III.

TABLE III
ADDITION OF BENZENETHIOL TO DIALLYL MALEATE IN THE PRESENCE OF VARYING AMOUNTS OF TRIETHYLENEDIAMINE^a

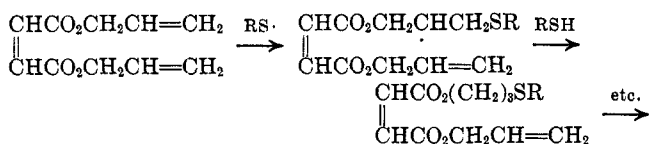
Amine added, mole %	Components of reaction mixtures by n.m.r., mole %				
	Monoadducts formed		Reactants and isomers		
	Allylic	Maleic	Maleate	Fumarate	Thiol
Nil	5	0	46	2	47
0.005	45	21	9	8	17
0.010	17	50	0	17	16
0.025	0	70	0	15	15
0.050	0	76	0	12	12
0.100	0	84	0	8	8
0.166	0	88	0	6	6
0.500	0	88	0	6	6

^a This data cannot be used to estimate over-all addition rates because the conditions of the reactions, especially the times, were not strictly uniform.

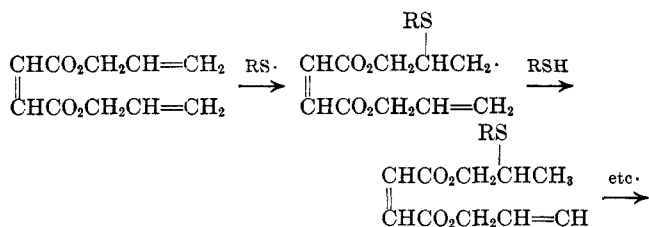
It is interesting to observe that in these mixtures the presence of amine results not only in addition to the maleate double bond but in isomerization of it. In fact, time studies in the presence of small amounts of amine indicated that isomerization of the maleate to the fumarate precedes the addition reaction. The amine alone does not isomerize the maleate under the reaction conditions.

Discussion

Selective free-radical addition of thiols to the allylic double bonds of diallyl maleate and fumarate apparently occurs by the usual chain mechanism as illustrated. The formation of the Markovnikov-type,



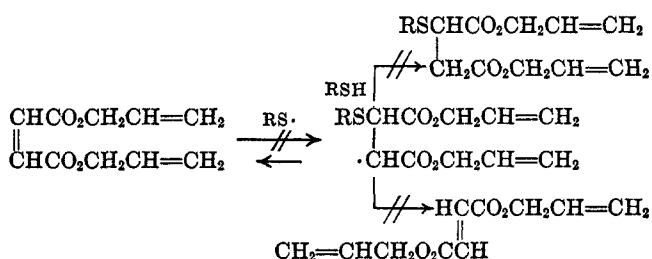
branched allylic adducts as minor by-products takes place by a similar mechanism involving a primary rather than a secondary radical intermediate.



The above branched adducts are completely absent as products of the amine-catalyzed anionic addition of thiols to diallyl maleate. An acid-catalyzed ionic addition mechanism can also be ruled out because about the same amounts of these branched by-products are formed on the addition of thiolacetic acid as that of the much less acidic aliphatic thiols. Aliphatic thiols do not add cationically to allyl esters under the reaction conditions used in the present study.

The formation of these "Markovnikov-type" adducts of a radical mechanism as minor by-products is postulated. As expected on the basis of the relative stability of the two intermediate radicals involved, the terminal radical is formed predominantly but not exclusively.

Selective free-radical addition of thiols to the allylic double bonds of diallyl maleate without concurrent isomerization of the latter to the fumarate is evidence of a high degree of selectivity of the first addition step. Since the reversible formation of a mercaptosuccinyl radical would probably lead to isomerization, the absence of isomerization suggests that initial attack on the maleic bond by thiyl radicals is negligible. The absence of such an attack in preference to attack on the allylic double bonds is attributed to the electron deficiency at the maleic sites. The maleic carbon atoms



have decreased electron density since they are both in α -position to an electron-withdrawing carboxylate group. As a consequence the electron-poor maleic carbon atoms are less preferred points of attack than allylic carbons for the strongly electrophilic thiyl radicals.

The formation of even very minor amounts of maleic adducts under free-radical conditions may be the result of concurrent ionic addition rather than of a lack of specificity of free thiyl radical addition.

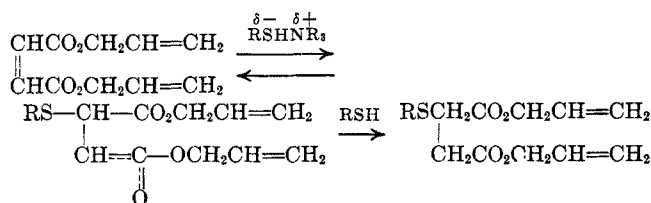
The same specificity for allylic additions is not found in the case of diallyl fumarate. This is apparent in the case of ethanethiol additions, where a fumaric addi-

tion to diallyl fumarate occurs to a significant extent. On the other hand, the ionic reactivity of diallyl fumarate at the fumaric site is also smaller than at the maleic as was shown by a comparison of the non-catalyzed benzenethiol additions.

Thiol compounds of increasing acidity, in general, showed less selectivity for allylic addition because of increasing rates of concurrent ionic additions to the maleic double bond. Thiolacetic acid was found to be somewhat of an exception; although it is a stronger acid than benzenethiol, it shows less of a tendency for maleic addition. This exception, however, might be explained by the smaller reactivity of thiolacetic acid in ionic additions. The ionic additions take place at a slower rate at the fumaric double bonds. For example, benzenethiol slowly adds to diallyl maleate even in the absence of added catalyst, while an amine catalyst is necessary for its addition to diallyl fumarate. This difference is apparently due to steric crowding in the case of the fumarate. However, a very strong thiol acid such as diethyldithiophosphoric acid adds to both diallyl maleate and fumarate without any catalyst, indicating that the acidity has a greater effect on the reaction rate than steric factors.

The amine-catalyzed anionic addition of aliphatic and aromatic thiols and thiolacetic acids also occurs at greater rates with thiols of increasing acidity. The latter is in agreement with the results of similar additions to maleic anhydride, studied by Dmuchovsky, Vineyard, and Zienty.⁵

In our experiments it is interesting to observe the isomerization of the starting diallyl maleate to diallyl fumarate. This isomerization probably always precedes the formation of the succinate adducts. For this isomerization to occur in the presence of thiols, very small quantities of the amine are sufficient. It is proposed that this is a result of the reversibility of the addition of the thiolate anion to the maleic double bond. The idea of such a reversibility is indirectly supported by the reported base and thermal reversal of the Michael reaction.⁶



Experimental Section

Starting Materials.—Diallyl maleate and diallyl fumarate from the Borden Chemical Co. were washed with 5% aqueous sodium hydroxide solution to remove the methylhydroquinone inhibitor and then fractionally distilled before use under vacuum. The maleate so obtained contained about 5% of the fumarate isomer. The fumarate was pure as indicated by g.l.p.c. Methane-, ethane-, 2-methyl-2-propane-, dodecane-, and benzenethiols were C.P. Eastman Organic Chemicals. Thiolacetic acid from Wateree Chemical Co., Lugoff, S. C., was redistilled before use. It contained 5% acetic acid as an impurity. O,O'-Diethylphosphorodithioic (diethyldithiophosphoric) acid was synthesized from ethanol and phosphorus pentasulfide and purified as described by Bacon and LeSuer.⁷

(6) C. F. H. Allen, J. O. Fournier, and W. J. Humphlett, *Can. J. Chem.*, **42**, 2616 (1964).

(7) W. E. Bacon and W. M. LeSuer, *J. Am. Chem. Soc.*, **76**, 670 (1954).

TABLE IV
PARAMETERS OF P.M.R. SPECTRA OF ALLYLIC ADDUCTS^a OF THIOL COMPOUNDS TO DIALLYL MALEATE
(AND FUMARATE)

R	R-S-	Chemical shifts of structural units, p.p.m. ^b							
		-CH ₂ -	-CH ₂ -	-CH ₂ O-	-CCH=CHC-		-OCH ₂ -	-CH=	=CH ₂
					<i>cis</i>	<i>trans</i>			
CH ₃ -	2.05 (s)	2.54 (t) ^c	1.91 (m)	4.23 (t) ^d	6.27 (s)	[6.80 (s)]	4.65 (d) ^e	5.65-6.30 (m)	5.10-5.50 (m)
CH ₃ CH ₂ -	1.25 (t), ^f 2.54 (g)	2.6 (t) ^e	1.96 (m)	4.30 (t) ^d	6.26 (s)	[6.83 (s)]	4.70 (d) ^e	5.70-6.35 (m)	5.15-5.55 (m)
C ₆ H ₅ -	7.05-7.50 (m)	2.95 (t) ^c	1.94 (m)	4.26 (t) ^d	6.17 (s)	[6.82 (s)]	4.64 (d) ^e	5.65-6.30 (m)	5.05-5.50 (m)
CH ₃ CO-	2.30 (s)	2.92 (t) ^e	1.92 (m)	4.18 (t) ^d	6.26 (s)	...	4.62 (d) ^e	5.65-6.30 (m)	5.10-5.50 (m)
	2.31 (s)	2.97 (t) ^e	1.97 (m)	4.25 (t) ^d	...	[6.85 (s)]	4.70 (d) ^e	5.70-6.35 (m)	5.10-5.55 (m)

^a N.m.r. parameters for the straight allylic diadducts were found to be identical with those for the corresponding groups in the monoadducts. The branched allylic mono- and diadducts are characterized by a doublet for the side-chain methyl group between 1.30 and 1.35 p.p.m. ^b Downfield from TMS, internal standard, in CCl₄ solution. ^c *J* = 6.5 c.p.s. ^d *J* = 6.3 c.p.s. ^e *J* = 5.5 c.p.s. ^f *J* = 7.2 c.p.s. ^g *J* = 7.0 c.p.s.

TABLE V
PARAMETERS OF P.M.R. SPECTRA OF MALEIC AND FUMARIC ADDUCTS OF THIOL COMPOUNDS TO DIALLYL
MALEATE AND FUMARATE, RESPECTIVELY

R	Chemical shifts of structural units, p.p.m. ^a					
	R-S	-CH-CO-	CH ₂ -CO-	-O-CH ₂ - ^m	-CH= ^m	=CH ₂ ^m
CH ₃ CH ₂ -	1.25 (t)	2.69 (q)	3.66 (q) ^{b,c}	2.79 (m) ^{d,e}	4.47-4.68 (m)	5.60-6.30 (m)
CH ₃ (CH ₂) ₁₀ CH ₂ -	0.90 (t) 1.28 (s)	2.65 (t)	3.64 (q) ^{b,f}	2.78 (m) ^{d,e}	4.50-4.70 (m)	5.62-6.30 (m)
(CH ₃) ₃ C-		1.35 (s)	3.55 (q) ^{b,g}	2.76 (m) ^{c,h}	4.47-4.66 (m)	5.60-6.30 (m)
C ₆ H ₅ -	7.15-7.65 (m)		4.04 (q) ^{b,i}	2.82 (m) ^{c,h}	4.54 (d) ^j	5.55-6.23 (m)
CH ₃ CO-	2.35 (s)		4.55 ^{b,k}	2.89 (m) ^{c,k}	4.50-4.70 (m)	5.63-6.30 (m)
(CH ₃ CH ₂ O) ₂ P-	1.35 (t) ^f	4.16 (dq) ^l	~4.55 ^{b,k}	2.97 (m) ^{c,k}	4.48-4.70 (m)	5.60-6.30 (m)

^a Downfield from TMS, internal standard, in CCl₄ solution. ^b X part of an ABX spin system. ^c *J*_{AX} = 6.5 c.p.s., *J*_{BX} = 9 c.p.s. ^d AB part of an ABX spin system, eight-line pattern. ^e *J*_{AB} = 16.5 c.p.s. ^f *J*_{AX} = 6.3 c.p.s., *J*_{BX} = 9 c.p.s. ^g *J*_{AX} = 6.5 c.p.s., *J*_{BX} = 9.5 c.p.s. ^h *J*_{AB} = 17 c.p.s. ⁱ *J*_{AX} = 6.8 c.p.s., *J*_{BX} = 8.3 c.p.s. ^j *J* = 5.5 c.p.s. ^k X part is obscured by -OCH₂- absorption; AB part is not sufficiently resolved to determine coupling constants. ^l *J*_{H-C-O-P} = 10.0 c.p.s. ^m Parameters of the two allylic groups of these adducts are essentially the same.

N.m.r. spectrometry was carried out on a Varian A-60 instrument using 30% solutions in CCl₄. Tetramethylsilane (TMS) was used as an internal standard. Chemical shifts are recorded in parts per million from TMS as zero. The degree of splitting is indicated in the following manner: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet. Coupling constants, *J*, are given in cycles per second.

Free-radical additions were, in general, carried out in quartz vessels equipped with magnetic stirrers. In the case of volatile thiols, such as methanethiol, a quartz tube equipped with a Teflon pressure valve was used. Nonvolatile thiols were allowed to react after nitrogenation of the reaction mixture under a nitrogen atmosphere. For reaction initiation, a Hanau ultraviolet immersion lamp with a 70-w. high-pressure mercury arc was used. Both the reaction vessel and the lamp were immersed into a water bath thermostated at 16 ± 1°. Analyses of samples from the reaction mixtures by g.l.p.c. are shown in Table I. The rest of the samples were fractionally distilled *in vacuo* to separate the adducts. Some physical and analytical data of the monoadducts so obtained are shown in Table II. N.m.r. spectra of the adducts were also determined. Chemical shifts of the monoadducts from the reaction of the allylic bonds are shown in Table IV. N.m.r. data of the products from additions to the maleic and fumaric double bonds are shown in Table V.

Addition of Methanethiol to Diallyl Maleate.—A magnetically stirred mixture of 24 g. (0.5 mole) of methanethiol and 49 g. (0.25 mole) of diallyl maleate in a closed quartz tube reacted for 4 hr. at 16° under the effect of ultraviolet light. The mixture was then fractionally distilled to yield 15 g. (22.5%) of allylic monoadduct as a colorless liquid having the physical and analytical data shown in Tables II and III. The allylic diadduct was isolated as a colorless liquid distillate as the next fraction, boiling between 155 and 158° at 0.05 mm., 37 g. (50% yield).

Anal. Calcd. for C₁₂H₂₀O₄S₂ (diadduct): C, 49.29; H, 6.89; O, 21.89; S, 21.93. Found: C, 49.27; H, 6.94; O, 21.9; S, 22.6.

The n.m.r. spectrum indicated a 90:10 ratio of allylic diadducts having maleic and fumaric configuration.

As a distillation residue, 8 g. of a yellow liquid remained. An n.m.r. spectrum of this residue indicated that about 75% of this residue was the triadduct. The absence of allylic unsaturation and the appearance of a quartet at 3.56 p.p.m., the X part of the ABX spin system (*J*_{AX} = 6.3 c.p.s., *J*_{BX} = 9.0 c.p.s.) originating from thiol addition across the maleic double bond was taken as qualitative and quantitative evidence of the triadduct. All the other triadduct peaks were obscured by overlapping peaks.

Addition of Ethanethiol to Diallyl Maleate.—A stirred mixture of 18.6 g. (0.3 mole) of ethanethiol and 58.8 g. (0.3 mole) of diallyl maleate was irradiated for 7 hr. at 16°. The mixture was then fractionated *in vacuo* to recover the unreacted diallyl maleate and separate the adducts. The allylic monoadduct was obtained as a colorless liquid in 32% (25 g.) yield (physical and analytical properties in Tables II and III). The allylic diadduct (8 g., 8%) was also a colorless liquid boiling at 177-182° at 0.2 mm. Its analysis indicates some monoadduct as an impurity.

Anal. Calcd. for C₁₄H₂₄O₄S₂ (diadduct): C, 52.47; H, 7.54; S, 20.02. Found: C, 53.26; H, 7.29; S, 17.62.

Addition of ethanethiol to diallyl fumarate was carried out as described in the previous example to yield mainly the corresponding allylic monoadduct (Tables I-III). Significant reaction was observed with the fumaric double bonds. This resulted in the formation of the fumaric monoadduct and the fumaric-allylic diadduct.

Addition of Benzenethiol to Diallyl Maleate.—To 22 g. (0.2 mole) stirred and nitrogenated benzenethiol, 39.2 g. (0.2 mole) of diallyl maleate was added in 5 min. An n.m.r. spectrum of a sample of the resulting reaction mixture indicated that 27% of the maleic bonds disappeared to form the corresponding maleic adduct. Some isomerization of the maleic bonds also occurred as shown by a 10:1 maleate:fumarate ratio.

Subsequent ultraviolet irradiation of the mixture for 4 hr. in the usual manner resulted in considerable allylic addition (Table I). Fractional distillation of the product mixture yielded two yellow liquid adduct fractions. The first product fraction, b.p. 163-170°, consisted of a 7:3 ratio of the isomeric, maleic

and allylic monoadducts. The other fraction, b.p. 180–183°, had the same isomers in a 3:7 ratio. (For physical and analytical data see Tables II–IV.)

Addition of benzenethiol to diallyl fumarate with ultraviolet irradiation under the conditions of the above experiment occurred selectively at the allylic bonds. N.m.r. and g.l.p.c. analyses of the reaction mixture before irradiation showed about 50% reaction (45% allylic monoadduct). Irradiation resulted in a somewhat increased conversion but no great change of product distribution (Table I). Fractional distillation of the reaction mixture yielded 15 g. (20%) of the allylic monoadduct as a slightly yellow liquid (Figure 1, Tables II and III) and 10 g. (11%) of a distillation residue consisting of about a 1:1 mixture of mono- and diadducts.

Addition of thiolacetic acid to diallyl maleate occurred on mixing without irradiation. On fractional distillation of the reaction mixture from 0.2 mole of each reactant, 22 g. (40%) of allylic monoadduct was obtained as a colorless liquid distillate. The distillation residue (20 g.) contained a major amount (66%) of the diadduct together with some of the above monoadduct (34%).

Addition of thiolacetic acid to diallyl fumarate took place in the manner described in the above experiment to give the results shown in Tables I and II.

Addition of Diethyldithiophosphoric Acid to Diallyl Maleate.—To 19.6 g. (0.1 mole) of stirred and nitrogenated diallyl maleate, 37.2 g. (0.2 mole) of the acid was added with ice cooling in 20 min. Subsequent n.m.r. analysis indicated that all the maleate disappeared to form 96% of the expected maleic monoadduct. The crude product was dissolved in 150 ml. of ether, washed twice with 200 ml. of 5% aqueous sodium hydrogen carbonate to remove the excess acid, dried over anhydrous sodium sulfate, concentrated to remove the ether, and heated at 80° at 0.1 mm. to distil off the fumarate to yield the purified monoadduct (Tables I and II). A similar addition to diallyl maleate containing 5 mole % dissolved methylhydroquinone yielded the same product.

Anionic Additions.—The catalyst, usually 5 mole % triethylenediamine, was dissolved in the diallyl maleate or fumarate, and the thiol compound was slowly added to the solution under nitrogen with stirring and ice-water cooling. Maleic or fumaric addition was usually complete within 1 hr. The reaction mixtures were worked up by distillation, which produced recovered triethylenediamine in the forerun.

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Electrophilic Substitution of the Benzenethiols. III. New Thiol Protective Groups and Cleavage Reagents¹

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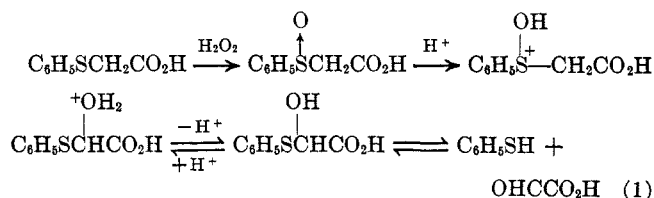
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The sulfur atom of benzenethiols must be protected prior to carrying out electrophilic substitution reactions in the benzene ring. The general requirements of a protective group in this series are that the group be unaffected by electrophilic reagents and that it may be easily cleaved. The present paper indicates that further general requirements of a sulfur-protective group for benzenethiols are that the group should contain hydrogen on the carbon atom adjacent to sulfur, and that this carbon should be "activated" by an electron-withdrawing group. Such groups are then readily removed by acidic oxidizing agents. It is shown that the acetyl group and the cyanomethyl group have only limited usefulness as sulfur-protective groups in electrophilic substitution reactions in the benzenethiol series. Finally, the present paper points out the utility of nitric acid and acid permanganate as cleavage reagents.

In an earlier paper Walker and Leib³ demonstrated that phenylmercaptoacetic acid could be cleaved in high yield to benzenethiol and glyoxylic acid by adding hydrogen peroxide to a boiling mineral acid suspension of phenylmercaptoacetic acid, and removing the benzenethiol as it was formed, by passing steam into the reaction mixture. This reaction was shown to proceed through phenylsulfinylacetic acid, which compound underwent rearrangement to phenylmercaptohydroxyacetic acid in the presence of mineral acid. This hemimercaptal then disproportionated to give benzenethiol and glyoxylic acid. Equation 1⁴ describes the reaction.

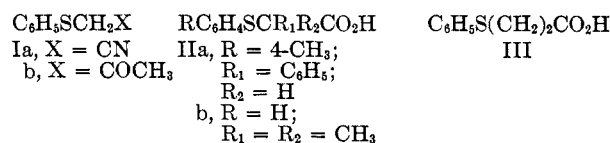
The rapid oxidative cleavage of the carboxymethyl group suggested the utility of this group as a readily removable sulfur-protective species which would enable electrophilic substitution of the aromatic ring of



benzenethiols to be carried out. A number of halo- and acylarylthiols were subsequently prepared using this scheme.

The present paper describes experiments with other sulfur-protective groups and with oxidizing agents other than hydrogen peroxide.

Since the carboxymethyl group of phenylmercaptoacetic acid is readily cleaved with hydrogen peroxide and mineral acid, and since simple aryl alkyl sulfides do not undergo this reaction, it seemed reasonable to expect that compounds of type I, wherein X is an electron-withdrawing group, would undergo cleavage,



(5) D. Walker and J. Leib, *J. Org. Chem.*, **27**, 4455 (1962).

(6) D. Walker and J. Leib, *ibid.*, **28**, 3077 (1963).

(1) The work described in this paper is the subject of Canadian, United States, and other patent applications.

(2) Arapahoe Chemicals, Inc., Boulder, Colo. 80301.

(3) D. Walker and J. Leib, *Can. J. Chem.*, **40**, 1242 (1962).

(4) The rearrangement of sulfoxides described by eq 1 has been the subject of considerable work in recent times. It is now not certain that the hydroxyl group attached to positive sulfur migrates to the adjacent carbon atom as implied in eq 1. For further mechanistic considerations, the interested reader is referred to the following papers: H.-D. Becker, *J. Org. Chem.*, **29**, 1358 (1964); W. E. Parham and M. D. Bhavsar, *ibid.*, **28**, 2686 (1963); H.-D. Becker, G. J. Mikol, and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3410 (1963).