0.50; mp 92–98 °C (from isooctane); IR (KBr) 1770 $cm^{-1}$; NMR $\delta_{Me_4Si}$ 4.96 (d, $J$ = 6.0 Hz, C-6 methine), ~4.0 (m, ketal), 1.12 (s, C-7 $CH_3$), 1.03 (d, $J$ = 7.2 Hz, C-2 $CH_3$); MS $m/e$ 280 ($M^+$), 265, 235, 219, 100, 99, 86. The contaminating C-2 $\alpha$-$CH_3$ isomer showed $\delta_{Me_4Si}$ 4.96 (d, $J$ = 8.4 Hz), 1.07 (s, C-7 $CH_3$) and 0.9 (d, $J$ = 5.4 Hz, C-2 $CH_3$).

**Ethylene Ketal of (*t*-2,7-Dimethyl-*t*-6-hydroxy-8-oxo-*r*-1*H*-bicyclo[5.3.0]dec-5-yl)β-hydroxypropionic Acid γ-Lactone (21).** The procedure of Minato and Horibe[18] was employed. To a suspension of 76 mg of 55% sodium hydride suspension in 4 mL of ether was added at 0 °C a solution of 0.323 g (1.15 mmol) of lactone **20** and 0.17 mL (2 mmol) of ethyl formate in 4 mL of ether dropwise over 2 min. The suspension was stirred for 1 h at 0 °C and for an additional 7 h at room temperature. The reaction mixture was poured into a saturated ammonium chloride solution and extracted with ether. Workup yielded 0.342 g (97%) of crude product; no purification of this product was attempted.

To a solution of 50 mg (1.31 mmol) of sodium borohydride in 3 mL of absolute methanol was added at −18 °C a solution of 0.342 g (1.11 mmol) of the above α-formyl-γ-butyrolactone in 2 mL of absolute methanol. The solution was stirred at −18 °C for 1 h, slowly brought to room temperature, and poured into a saturated ammonium chloride solution. The product was isolated with ether and purified by column chromatography on silica gel using 50% ethyl acetate–isooctane, yielding 0.206 g (60%) of a white crystalline solid: $R_f$ (2) 0.34; NMR $\delta_{Me_4Si}$ 4.93 (d, $J$ = 9.3 Hz, C-6 methine), ~3.9 (m, ethylene ketal), ~3.8 (m, $CH_2OH$), 1.10 (s, C-7 $CH_3$), 1.06 (d, $J$ > 6.6 Hz, C-2 $CH_3$). The contaminating C-2 α-$CH_3$ isomer showed $\delta_{Me_4Si}$ 1.06 (s, C-7 $CH_3$) and 0.90 (d, $J$ = 5.4 Hz, C-2 $CH_3$).

**(*t*-2,7-Dimethyl-8-oxo-*t*-6-hydroxy-*r*-1*H*-bicyclo[5.3.0]-dec-5-yl)-β-hydroxypropionic Acid γ-Lactone (22).** A solution of 0.206 g (0.66 mmol) of ethylene ketal **21** in 5 mL of 40% 3 M hydrochloric acid–methanol was stirred at 0 °C for 15 min. Methanol was evaporated in vacuo, water was added, and the product extracted with ether. Isolation and purification by column chromatography on solica gel using 25% isooctane–ethyl acetate yielded 0.144 g (81%) of **22** as a colorless oil: $R_f$ (2) 0.13; NMR $\delta_{Me_4Si}$ 4.56 (d, $J$ = 8.7 Hz, C-6 methine), 4.1 (m, $CHCH_2OH$), 3.9 (m, $CH_2OH$), 2.9 (m, C-5 methine), 1.13 (s, C-7 $CH_3$), 1.07 (d, C-2 $CH_3$); MS $m/e$ 266 ($M^+$, 2), 251 (100), 233 (25), 97 (50). The isomeric ketone **22a** showed: $R_f$ (2) 0.17; $\delta_{Me_4Si}$ 4.66 (d, $J$ > 7.2 Hz, C-6 methine), 1.09 (s, C-7 $CH_3$), 1.00 (d, $J$ = 5.4 Hz, C-2 $CH_3$).

**(±)-Damsin (1).** A solution of 0.144 g (0.54 mmol) of the above β′-hydroxy-γ-butyrolactone **22** and 126 mg of *p*-toluenesulfonyl chloride in 1.6 mL of freshly distilled pyridine was stirred for 24 h at 0 °C. The solution was poured into water and the product isolated with chloroform, yielding 0.227 g (100%) of a yellow oil. A solution of the above crude tosylate in 2 mL of pyridine was heated at reflux for 4 h. The solution was cooled and poured into water; extraction with ether and evaporation of the solvent gave 0.134 g (100%) of yellow oil. Purification by column chromatography on silica gel using 50% ethyl acetate–isooctane yielded 73 mg (51%) of white crystalline product, whose spectra and TLC behavior were identical with those of naturally occurring damsin (1): $R_f$ (2) 0.35; mp 122–124 °C; IR (KBr) 2950, 2875, 1760, 1735, 1655, 1280, 1165, 1155, 1130, 1060, 1000, 985, 970, 955, 820 $cm^{-1}$; NMR $\delta_{Me_4Si}$ 6.27 and 5.53 (d, $J$ = 3.1 and 2.75 Hz, respectively, vinyl H's), 4.53 (d, $J$ = 8.5 Hz, C-6 methine), 3.30 (m, C-7 methine), 1.08 (d, $J$ = 7.5 Hz, C-2 $CH_3$), 1.08 (s, C-7 $CH_3$); MS $m/e$ 248 ($M^+$, 5), 2.33 (100), 123 (36), 97 (42), 95 (30), 55 (50). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.61; H, 8.14.

(±)-2-*epi*-Damsin (**1a**), contaminated with (±)-damsin (a fraction of the above mentioned column chromatography), was purified by preparative TLC using 50% ethyl acetate–isooctane, affording 2 mg of white crystalline compound: $R_f$ (2) 0.41; NMR $\delta_{Me_4Si}$ 6.26 and 5.57 (d, $J$ = 2.5 and 2.0 Hz, respectively, vinyl H's), 4.53 (d, $J$ = 7.75 Hz, C-6 methine), 3.11 (m, C-7 methine), 1.00 (d, $J$ = 6.5 Hz, C-2 $CH_3$), 1.11 (s, C-7 $CH_3$).

**Ethyl [2,*t*-7-Dimethyl-*c*-8-(2′-tetrahydropyranyloxy)-6-oxo-*r*-1*H*-bicyclo[5.3.0]dec-2-en-5-yl]acetate (23).** A suspension of 0.364 g (1.0 mmol) of olefin **13** and 10 mg of 5% palladium on carbon in 1 mL of absolute ethanol was hydrogenated at room temperature and atmospheric pressure. After 6 h the suspension was filtered and concentrated in vacuo, yielding 0.362 g (100%) of trisubstituted olefin **23**: $R_f$ (1) 0.49; IR (film) 1740, 1700, 1195, 1175, 1160, 1130, 1115, 1025, 985 $cm^{-1}$; NMR $\delta_{Me_4Si}$ 5.83 (m, vinyl H), 4.20 (q, $J$ = 7.2 Hz, $COOCH_2CH_3$), 1.26 (t, $J$ = 7.2 Hz, $COOCH_2CH_3$), 0.95 (s, C-7 $CH_3$).

**Acknowledgment.** We thank the "Nationaal Fonds voor Wetenschappelijk Onderzoek" for financial support to the laboratory.

**Registry No.**—**1**, 60133-11-1; **1a**, 63039-02-1; **3**, 62990-77-6; **4**, 62990-78-7; **5**, 62990-79-8; **6**, 62990-80-1; **7**, 62990-81-2; **8**, 62990-82-3; **9**, 62990-83-4; **10**, 62990-84-5; **11**, 62990-85-6; **12**, 62990-86-7; **13**, 62990-87-8; **14**, 62990-88-9; **15**, 62990-89-0; **16**, 62990-90-3; **17**, 62990-91-4; **18**, 62990-92-5; **18a**, 62990-93-6; **19**, 60090-71-3; **19a**, 62990-94-7; **20**, 60090-72-4; **21**, 62990-95-8; **22**, 62990-96-9; **23**, 62990-97-0; **20** $C_2$ isomer, 63039-03-2.

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(8) Dione **3** is now available in 60% overall yield from 2-methyl-2-cyclopentenone using slight modifications of procedures in ref 5: unpublished results of the laboratory.
(9) W. Hückel and L. Schnitzspahn, *Justus Leibigs Ann. Chem.*, **505**, 274 (1933); J. A. Marshall and W. F. Huffman, *J. Am. Chem. Soc.*, **92**, 6358 (1970).
(10) This feature could be used to reverse the stereochemistry expected from control by the angular methyl group; this laboratory, work in progress.
(11) C. V. Wilson, *Org. React.*, **9**, 332 (1957).
(12) The alcohol i (with epimeric C-2), synthesized by Marshall,[4] yielded under the same circumstances a mixture of three double bond isomers (25% exo, 60% trisubstituted, and 15% tetrasubstituted). Consideration of this and our own results tend to assign the still unknown configuration of franserin at C-2 as depicted in i′, since dehydration with thionyl chloride–pyridine leads to a trisubstituted olefin and not a tetrasubstituted one as would be expected from dehydratation of i″; J. Romo, A. Romo de Vivar, A. Vélez, and E. Urbina, *Can. J. Chem.*, **46**, 1535 (1968).
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(14) To the best of our knowledge this cleavage of a 2-tetrahydropyranyl ether under neutral but rather drastic (70 h, 4 bar) conditions is unprecedented and could prove to be useful in certain circumstances.
(15) For the sake of consistency we have retained the same numbering for this compound as has been used throughout the paper; the generally accepted numbering for pseudoguaianolides (ref 2a) would indicate this product as (±)-10-*epi*-damsin. The α configuration was assigned to the C-2 $CH_3$ group of the a isomers (**1a**, **18a–22a**), the only marked difference between the NMR data of the natural products and their a isomers being the chemical shifts and vicinal exocyclic $J$ values of the C-2 $CH_3$ groups. Especially significant is the larger value of the exo coupling constant in the natural products compared to the corresponding a isomers, in accordance with the higher strain present in the former compounds; M. Anteunis, *Bull. Soc. Chim. Belg.*, **80**, 3 (1971); Z. Samek, *Tetrahedron Lett.*, 1709 (1971).
(16) We thank Dr. J. Romo for kindly sending a sample of natural damsin.
(17) Reaction products were isolated by the addition of water and extracted with the specified solvent. The combined extracts were washed with saturated brine and dried over anhydrous magnesium sulfate. The solvent was removed from the filtered solutions on a rotary evaporator. $R_f$ values are quoted for Merck silica gel 60 $GF_{254}$ TLC plates of thickness 0.25 mm; $R_f$ (1) refers to the solvent system acetic acid–ethyl acetate–isooctane = 2:15:20; $R_f$ (2) to acetic acid–ethyl acetate–isooctane = 2:15:10. IR spectra were recorded on a Perkin-Elmer 337 spectrometer, $^1H$ NMR spectra on a Varian EM-390 spectrometer ($CDCl_3$), and mass spectra on an AEI MS-50 mass spectrometer. Melting points are uncorrected. Stereochemical designations of substituents in bicyclic compounds are indicated by *c* (cis) and *t* (trans) relative to a reference substituent *r*.
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## Thermal Decomposition of Phenylmethyldiazirine. Effect of Solvent on Product Distribution

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The thermal decomposition of phenyl-*n*-butyldiazirine[1] in $Me_2SO$ at 100 °C resulted in a quantitative evolution of nitrogen and the formation of *cis*- and *trans*-1-phenyl-1-pentenes plus less than 5% of valerophenone. In addition, 1-phenyldiazopentane has been isolated as an intermediate

**Table I. Product Distribution in the Thermal Decomposition of Phenylmethyldiazirine**

| Reaction conditions | Azine | Products, % Acetophenone | Styrene | Cyclopropyl derivatives |
|---|---|---|---|---|
| Neat 16 h at 130 °C | 65 | 3–4 | Trace | 30 |
| 5% Solution in $Me_2SO$, 16 h at 65 °C and 6 h at 110 °C | 40 | 50 | Trace | 8–10 |
| 10% Solution in nitrobenzene, 16 h at 130 °C | 95 | 0 | Trace | 5 |
| 5% Solution in hexane, 72 h at 68 °C | 45 | 17–19 | Trace | 35 |
| 5% Solution in isooctane, 16 h at 99 °C | 40 | 3–4 | Trace | 56 |
| 0.6% Solution in nitrobenzene 16 h at 130 °C | 32 | 32 | Trace | 35 |
| 0.6% Solution in chlorobenzene, 16 h at 130 °C | 40 | 10 | Trace | 48–50 |
| 0.01 Torr at 120 °C | — | — | 98 | Trace |

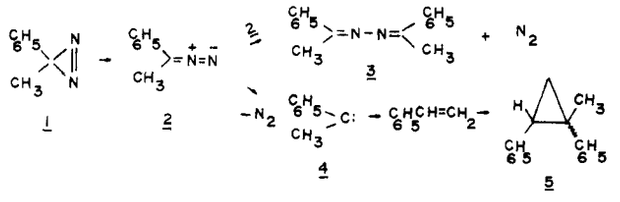
during this decomposition. In the light of the above observation, it is then reasonable to assume the intermediacy of 1-phenyldiazoethane **2** in the thermal decomposition of phenylmethyldiazirine **1**.

Overberger and Anselme[3] could not duplicate the synthesis of **1** as reported by Schmitz and Ohme.[3] However, in the decomposition of **2**, Overberger and Anselme[3] reported acetophenone azine **3** as the only product. No styrene was detected although Schmitz and Ohme[2] reported it as the sole decomposition product of **1** in nitrobenzene. Due to this apparent difference, we have reinvestigated the thermal decomposition of **1** with a view to resolve these inconsistencies.

**1** is a colorless liquid and is stable at 0 °C for several weeks. When **1** was heated neat or in solvents listed in Table I, the solution turned red. The red material has a strong IR absorption at 2040 $cm^{-1}$ and was isolated and identified as **2**.[4] The red color of the solution persisted even after heating a solution of **1** or **2** in hexane at 68 °C for over 48 h. **2** begins to decompose significantly at temperatures greater than 100 °C.

Thermal decomposition of **1** carried out in different solvents under varying conditions results in the formation of a mixture of products as given in Table I. A decrease in the amount of **3** and a corresponding increase in cyclopropyl derivatives was observed with decreasing solvent polarity. The same effect was observed for a decrease in concentration of **1** in the decomposition mixture. Only trace amounts of styrene could be detected, a fact which contradicts the results obtained by Schmitz and Ohme,[2] who reported styrene as the only product in the decomposition. However, the gas phase (0.01 Torr) decomposition of **1** gave styrene as the major product with trace amount of **5**.

The following scheme shows the two probable pathways for the decomposition of **1**. Polar solvents stabilize better the



transition state for dimerization of **2** and thus the formation of **3** is favored over further fragmentation to the carbene **4**, but in nonpolar solvents, due to the lack of such stabilization, further decomposition to **4** is favored. **4** is a precursor to styrene and cyclopropyl derivatives. An alternative possibility involved the attack of carbene **4** on either **1** or **2** to produce the azine **3**.[5,6] However, we consider this only as a minor possibility as it has to compete with the intramolecular rearrangement of **4** to styrene. The formation of cyclopropyl derivatives is presumably the result of the 1,3-dipolar reaction of **2** with styrene followed by elimination of $N_2$. It is to be noted that in nonpolar solvents, the formation of **3** is still considerable. However, only traces of styrene are detected as most of it gets converted to the cyclopropyl derivatives. Also in dilute solutions, the probability for dimerization to **3** is less and hence the formation of **4** is favored. The presence of fairly large amounts of acetophenone in $Me_2SO$ is due to solvent participation in the oxidation of **2** whereas its presence in small quantities in other solvents is presumably due to aerial oxidation of **2**. The absence of azine in the decomposition of phenyl-*n*-butyldiazirine[1] could well be explained in terms of a steric effect.

In the photolysis of 1-phenyldiazoethane **2** at 5 °C, the formation of acetophenone azine **3** was reported.[7] However, in recent studies by Moss and Joyce[8] on the photolysis of **2** in isobutene matrices, **3** was not detected.

## Experimental Section

**General.** NMR spectra were recorded from a Varian T-60 instrument using $CDCl_3$ as solvent and $Me_4Si$ as internal standard. IR spectra were obtained from a Perkin-Elmer 137 spectrophotometer asd mass spectra with VG Micromass MM601 spectrometer. A Perkin-Elmer Model F11 gas chromatograph was used for VPC analysis (20% Carbowax column). All the solvents used were of Analar grade.

**3-Phenyl-3-methyldiazirine (1).** This compound was prepared by the procedure of Schmitz and Ohme[2] with minor modification. *N*-Benzyl-methylphenylketimine (20.9 g, 100 mmol) in methanol (200 mL) was added dropwise to liquid ammonia (100 mL) and stirred at −60 °C for 3 h. A solution of hydroxylamine-*O*-sulfonic acid (14.0 g, 150 mmol) in methanol (100 mL) was added and stirred for 2 h. The reaction mixture was allowed to warm up to room temperature and the excess ammonia was allowed to evaporate; the residue was extracted with ether and concentrated to a yellow oil. This oil was oxidized with freshly prepared silver oxide (from silver nitrate (25.5 g, 150 mmol) and sodium hydroxide (6.5 g, 160 mmol)) in a solution of 1:1 MeOH + $H_2O$ (600 mL) at room temperature for 3 h. The silver salts were filtered out and the product was extracted with ether, dried, and concentrated to a pale yellow oil. Chromatography over silica gel afforded 5.28 g of **1** (40%): IR 1600 $cm^{-1}$ (N=N); NMR $\tau$ 2.8 (m, 3, meta and para aromatics), 3.2 (m, 2, ortho), 8.52 (s, 3, methyl); $UV_{max}$ (methanol) 368 nm ($\epsilon$ 187).

**Thermal Decomposition of 1.** The same general procedure was employed for the decomposition of **1** in all the solvents mentioned in Table I. A solution of **1** of desired concentration was taken in a round-bottomed flask equipped with a reflux condenser and drying tube. The flask was immersed in an oil bath and heated at temperature and period indicated in Table I. In all cases the solution turned red in a few minutes and this red material, IR 2040 $cm^{-1}$, was identified as phenyldiazoethane.[4] When the red color had completely disappeared, the solvent was removed under vacuum and the residue was analyzed by recording its NMR spectra. The residue was then chromatographed over silica gel and the products were separated. The products were identified as acetophenone azine, *m/e* 236, mp 120 °C (lit.[3] mp 119–120 °C), acetophenone (>C=O, 1695 $cm^{-1}$), and a mixture of cyclopropanes *m/e* 208, NMR $\tau$ 2.70–3.45 (m, 10H); 7.50–8.00 (m, 1H); 8.50 and 8.90 (2s, 3H); and 8.50–8.90 (m, 2H).[9] No styrene was isolated but VPC analysis indicates its presence in trace amounts. In the case of decomposition in $Me_2SO$, the solvent was first removed by repeated washing with water.

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**Registry No.**—**1**, 63269-86-3; **2**, 22293-10-3; **3**, 729-43-1; *cis*-**5**,

14161-72-9; *trans*-**5**, 1416173-0; acetophenone, 98-86-2; *N*-benzylmethylphenylketimine, 14428-98-9; hychoxylamine-*O*-sulfonic acid, 2950-43-8.

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## Aromatic Electrophilic Substitution by Pummerer Rearrangement Intermediates


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Sulfoxides have been developed extensively as synthetic reagents. The most common reactions are $\beta$ elimination for the introduction of double bonds[1] and [2,3] sigmatropic rearrangement for allylic transposition of alcohols.[2] Sulfoxides have also been ingeniously used for benzo[*b*]thiophene synthesis, i.e., the Thyagarajan rearrangement.[3] Replacement of the sulfoxide moiety with an *N*-oxide resulted in a new general synthesis of indoles.[4]

The present study was initiated in the hope that replacement of the acetylenic moiety with a cyano group might result in a general 4,5-benzoisothiazole synthesis via a pathway analogous to the Thyagarajan process. In the event, however, a very different sequence intervened leading to a novel electrophilic aromatic substitution reaction, the first example of intermolecular attack of Pummerer rearrangement intermediates on an aromatic ring.

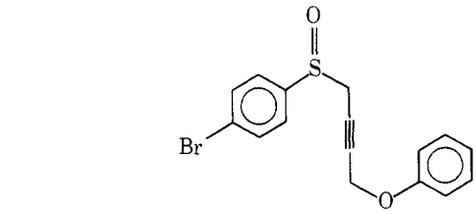
Compound **1** was found to be inert under conditions which converted **2** into the benzo[*b*]thiophene skeleton[3] (refluxing chloroform). Indeed, **1** proved to be quite thermally stable, being recovered unchanged after prolonged reflux in benzene, carbon tetrachloride, ethanol, 1-butanol, and toluene. However, **1** in refluxing xylene formed two products, *p*-bromophenyl disulfide and a crystalline solid, $\alpha$-(4-bromophenylthio)-2,5-xylylacetonitrile (**3**), corresponding to a condensation of **1** with *p*-xylene and loss of a water molecule. This structure was deduced from spectral data. The IR showed a nitrile absorption and lacked a sulfoxide band. The NMR showed two nonidentical methyl groups ($\delta$ 2.32 and 2.42), a methine singlet ($\delta$ 4.97), and seven aromatic hydrogens, and the mass spectrum showed a molecular ion at *m/e* 333/331.

A similar reaction took place when **1** was refluxed in anisole, yielding *p*-bromophenyl disulfide, the ortho and para condensation products **5** and **6**, and bis(4-methoxyphenyl)acetonitrile (**4**).[12]

In view of the unexpected nature of the reaction of **1**, several analogous compounds (**7–10**) were synthesized and refluxed in anisole to delineate the scope and mechanism of this transformation.

Compound **7** gave the corresponding condensation product **11**, and **8** led to **12**. Compounds **9** and **10** do not provide condensation products in refluxing anisole or xylene.[5]

The reactions are reminiscent of the Pummerer rearrangement,[6] an acid-catalyzed reaction of sulfoxides in which sulfur becomes reduced with concomitant functionalization of the $\alpha$-carbon. The catalysts normally used are HCl or *p*-toluenesulfonic acid. The present examples are rare cases of "uncatalyzed"[7] Pummerer rearrangements and are the first examples of reaction with such weakly nucleophilic species as xylene and anisole.[8]



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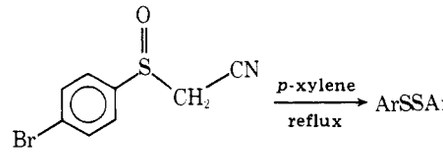

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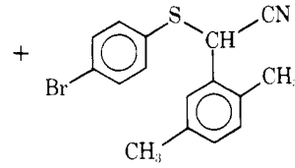

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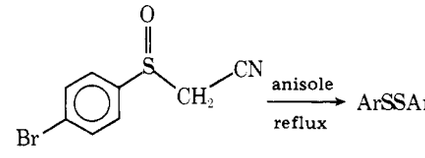

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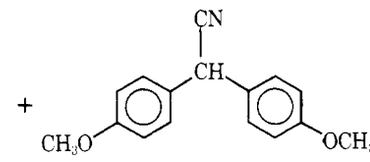

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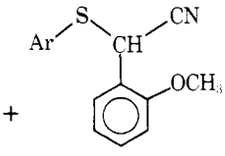

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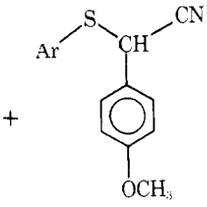

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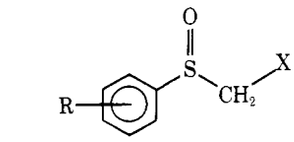
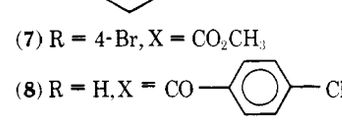


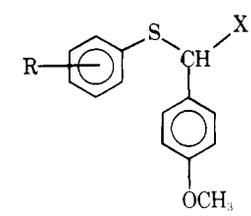
(7) R = 4-Br, X = $CO_2CH_3$



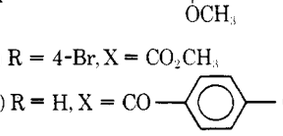
(8) R = H, X = CO—Cl

(9) R = 2-CN, X = Ph

(10) R = H, X = Ph



(11) R = 4-Br, X = $CO_2CH_3$



(12) R = H, X = CO—Cl