

190.0815), 189 (41), 188 (41), 137.0079 (PhSCO⁺, 100; calcd 137.0061), 125.0620 (c-H₂OCO⁺, 50; calcd 125.0602).

O- α -Styryl S-phenyl thiocarbonate: crude oil obtained after standard workup and evaporation crystallized from pentane and then ether; mp 50–51 °C; NMR (CDCl₃) δ 5.05 (1 H, d, J = 2.4 Hz), 5.36 (1 H, d, J = 2.4 Hz), 7.1–7.6 (10 H, m); mass spectrum, m/e (relative intensity) 256.0556 (M⁺, 72; calcd 256.0557), 229 (72), 228.0605 (M⁺ - CO, 100; calcd 228.0608), 212.0677 (M⁺ - CO₂, 50; calcd 212.0659), 196.0883 (M⁺ - COS, 15; calcd 196.0887).

O- n -Butenyl S-phenyl thiocarbonate: bp 80–88 °C (0.2 torr) (62:38 Z/E¹⁸ from the enol silane, 61:39 Z/E); NMR (CDCl₃) δ 0.98 (3 H, t, J = 7.5 Hz), 1.8–2.5 (2 H, m), 4.91 (0.62 H, dt, J = 7, 7 Hz, Z), 5.50 (0.38 H, dt, J = 13, 7 Hz, E), 6.95–7.2 (1 H, m), 7.3–7.8 (5 H, m); ¹³C NMR (CDCl₃) for Me δ 13.7 (Z) and 13.8 (E), for CH₂ δ 17.7 (Z) and 20.5 (E), for EtCH= δ 116.4 (Z) and 117.3 (E), for C=O δ 167.2 (Z) and 167.4 (E), for =CHO and aryl δ 129.2 (Z), 129.7 (E), and, in common, 134.2, 134.7, 134.8, 135.1, 135.6, 135.7; mass spectrum, m/e (relative intensity) 208.0557 (M⁺, 100; calcd 208.0557), 181 (53), 180.0612 (M⁺ - CO, 79; calcd 180.0608), 179.0532 (M⁺ - COH, 16; calcd 179.0530), 151 (49), 149 (25). Product Z/E ratios (VPC) at partial reaction times of 15, 27, 35, and 45 h were 65:35, 66:34, 63:37, and 63:37, respectively.

O-Propenyl S-phenyl thiocarbonate: bp 89–91 °C (0.6 torr) (75:25 Z/E¹⁸ from the enol silane, 74:26 Z/E); NMR (CDCl₃) δ 1.57 and 1.61 (3 H, 2 d's, each J = 7 Hz), 4.82 (0.75 H, dq, J = 7, 7 Hz, Z), 5.26 (0.25 H, dq, J = 12, 7 Hz, E), 6.8–7.05 (1 H, m), 7.15–7.6 (5 H, m); mass spectrum, m/e (relative intensity) 194.0418 (M⁺, 32; calcd 194.0401), 170 (20), 137 (70), 110 (PhSH⁺, 34), 109.0107 (PhS⁺, 100; calcd 109.0112).

O-Vinyl S-Phenyl Thiocarbonate. Alternate Procedure.

This was made in 68 and 65% yields by the standard method (Table I). The compound also was prepared by stirring a mixture of S-phenyl thiochloroformate (12.9 g, 0.0746 mol), (vinylloxy)-trimethylsilane (8.26 g, 94% pure, 0.0668 mol), KF (5.2 g, 0.09 mol), and 18-crown-6 (0.74 g, 4 mol %) in 50 mL of THF at room temperature followed by the usual workup: yield 7.95 g (66%, VPC pure); bp 69–73 °C (0.5 torr) [lit.⁶ 67–69 °C (0.4 torr)]; NMR (CDCl₃) δ 4.52 (1 H, dd, J = 7, 1 Hz), 4.85 (1 H, dd, J = 14, 1 Hz), 7.08 (1 H, dd, J = 14, 7 Hz), 7.2–7.6 (5 H, m).

O-(3-Methylbutenyl) S-Phenyl Thiocarbonate. Second Alternate Procedure. S-Phenyl thiochloroformate (3.59 g, 0.0208 mol) was stirred with KF (1.6 g, 0.028 mol) and 18-crown-6 (0.3 g, 5 mol %) in THF (30 mL) at room temperature until no chloroformate remained (51 h, VPC assay). Then [(3-methylbutenyl)oxy]trimethylsilane (3.11 g, 0.0196 mol, 54:46 Z/E) was added, stirring was continued for 23 h, and the title compound was isolated by the standard workup: yield 3.36 g (72%, 54:46 Z/E¹⁸); bp 99–106 °C (0.4 torr); NMR (CDCl₃) δ 1.00 and 1.03 (6 H, 2 d's, each J = 7 Hz), 2.0–3.0 (1 H, m), 4.87 (0.54 H, dd, J = 9, 7 Hz, Z), 5.46 (0.46 H, dd, J = 12, 7 Hz, E), 6.9–7.1 (1 H, m) 7.3–7.8 (5 H, m); mass spectrum, m/e (relative intensity) 222.0738 (M⁺, 75; calcd 222.0724), 194.0760 (M⁺ - CO, 84; 194.0775), 137 (PhSCO⁺, 100). This product was also made in 61% yield (54:46 Z/E) by the first alternate procedure using S-phenyl thiochloroformate (0.073 mol), KF (0.15 mol), 18-crown-6 (2 mol %), the enol silane (0.051 mol), and THF (40 mL) (92 h at room temperature).

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Registry No. 5 (R = R' = R'' = H), 6213-94-1; 5 (R = R' = Me, R'' = H), 6651-34-9; 5 (R = R' = H, R'' = Me), 1833-53-0; 5 (R = H, R' = R'' = (-CH₂CH₂CH₂CH₂-)), 6651-36-1; 5 (R = R' = H, R'' = Ph), 13735-81-4; (E)-5 (R = Me, R' = R'' = H), 39162-68-0; (Z)-5 (R = Me, R' = R'' = H), 50300-18-0; (E)-5 (R = Et, R' = R'' = H), 19980-23-5; (Z)-5 (R = Et, R' = R'' = H), 19980-22-4; (E)-5 (R = CHMe₂, R' = R'' = H), 73397-84-9; (Z)-5 (R = CHMe₂, R' = R'' = H), 73397-85-0; 6, 2286-39-7; 7 (R = R' = R'' = H), 70872-45-6; 7 (R = R' = Me, R'' = H), 73397-86-1; 7 (R = R' = H, R'' = Me), 73397-87-2; 7 (R = H, R' = R'' = (-CH₂CH₂CH₂CH₂-)), 73397-88-3; 7 (R = R' = H, R'' = Ph), 73397-89-4; (E)-7 (R = Me, R' = R'' = H), 73397-90-7; (Z)-7 (R = Me, R' = R'' = H), 73397-91-8; (E)-7 (R = Et, R' = R'' = H), 73397-92-9; (Z)-7 (R = Et, R' = R'' = H), 73397-93-0; (E)-7 (R = CHMe₂, R' = R'' = H), 73397-94-1; (Z)-7 (R = CHMe₂, R' = R'' = H), 73397-95-2; S-phenyl thiochloroformate, 13464-19-2.

Flash Vacuum Pyrolysis of 2-Methylbenzophenones and 2-Methyldiphenyl Ketimines

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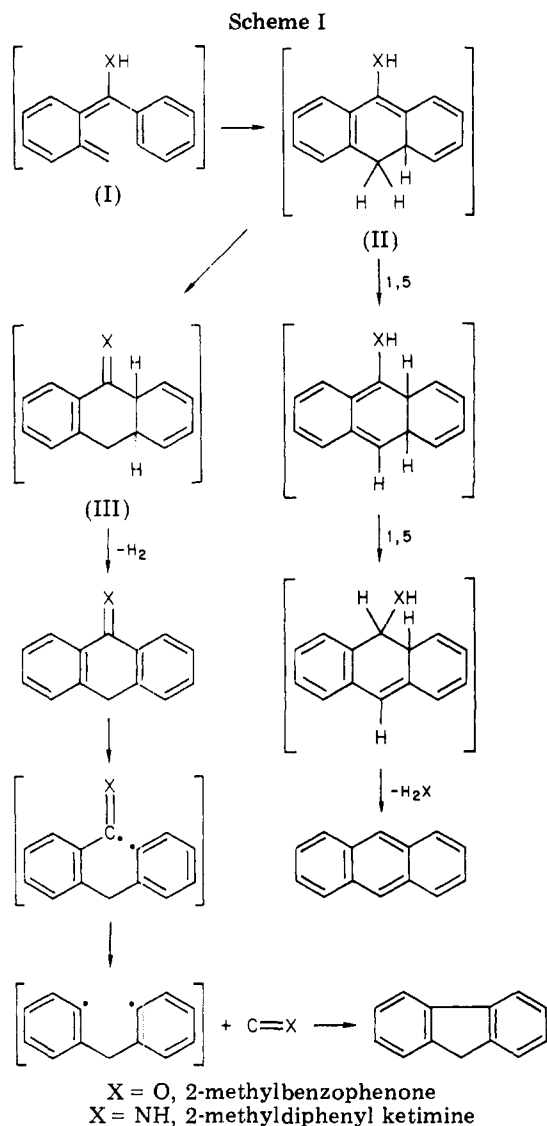
The solution-phase pyrolysis of 2-methylbenzophenone at 300–400 °C—the Elbs reactions—gives low yields of anthracene and water.^{1–15} We hoped that the gas-phase pyrolysis of 2-methylbenzophenones would give higher yields and fewer side products than the Elbs reaction carried out in solution phase.

Gas-phase vacuum pyrolysis of 2-methylbenzophenone in a flow system at temperatures below 750 °C resulted only in recovery of starting material. At temperatures between 800 and 900 °C, reaction occurred, with higher conversions of starting material to products being obtained at higher temperatures: 800 °C (7%), 900 °C (36%) (see Table I). The highest yield of volatile products was only 40–50%. Anthracene, the expected product, was obtained in 7 to 11% yield while fluorene was found in 32 to 39% yield. We believe that the formation of anthracene and fluorene may occur as outlined in Scheme I. Tautomerization of 2-methylbenzophenone yields the previously proposed dienol intermediate (I).^{16,17} Electrocyclic reaction of the dienol and the benzene nucleus may result in formation of 4a,10-dihydro-9-anthranol (II),^{18–25} which reacts further to yield both anthracene and fluorene. Consecutive 1,5-sigmatropic hydrogen rearrangements²⁶

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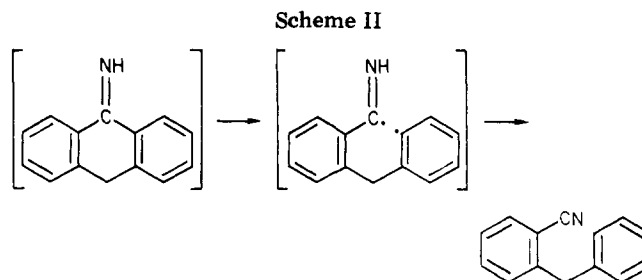
Table I. Vacuum Pyrolysis of 2-Methylbenzophenone

pyrolysis temp, °C	% conversion	anthracene, % yield	fluorene, % yield
800	7	7	32
825	13	8	34
850	16	7	32.5
875	20	10.5	38.5
900	36	9.5	35



lead to 9,9a-dihydro-9-anthranol which can lose water in a 1,2 sense to yield anthracene. Tautomerization of II yields 4a,9a-dihydroanthrone (III); loss of a molecule of hydrogen from III yields anthrone. Anthrones have, in fact, occasionally been isolated in low yields from the Elbs reactions.^{27,28} Further, anthrone will decarbonylate under the gas-phase pyrolysis conditions via scission of an acyl-aryl carbon-carbon single bond to yield a radical pair which loses carbon monoxide to form a pair of aryl radicals which recombine to yield fluorene.^{29,30}

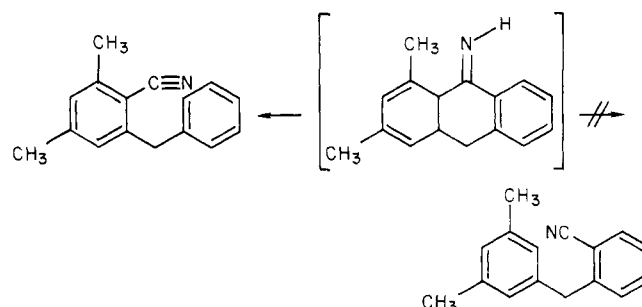
Likewise, gas-phase vacuum pyrolysis of 2-methyldiphenyl ketimine between 800 and 900 °C in the flow system yields anthracene (26–30%), fluorene (2–3%), 2-



benzoylbenzotrile (6–10%), benzotrile (22–34%), *o*-tolunitrile (25–28%), benzene, and toluene (see Table II). Quantitative recovery of these latter two volatile products was difficult under our flow pyrolysis conditions. Scission of an aryl-imine bond of the anthrone ketimine intermediate would lead to a radical pair in which intramolecular hydrogen transfer from the nitrogen of the imine to the aryl radical could lead to 2-benzoylbenzotrile (see Scheme II). Homolytic cleavage of an aryl-imine carbon-carbon single bond of the starting material may occur to give two different radical pairs, one of which disproportionates to yield benzotrile and toluene while the other yields *o*-tolunitrile and benzene.

Gas-phase pyrolysis of 2,4,6-trimethylbenzophenone yields 2,4-dimethylfluorene (11.2%) and 1,3-dimethylanthracene (1.6%), the expected products. In addition, a number of other aromatic hydrocarbons which have lost methyl groups are formed: 2-methylfluorene (3.7%), 4-methylfluorene (3.9%), fluorene (1.9%), 1-methylanthracene (1%), 2-methylanthracene (1%), and anthracene (2%). Loss of methyl^{31,32} groups has been previously observed in the Elbs reaction as well as in the gas-phase pyrolysis of alkylated aromatic compounds.^{33,34}

Likewise pyrolysis of 2,4,6-trimethyldiphenyl ketimine yields 1,3-dimethylanthracene (19%), 2-methylanthracene (15.5%), 2-benzyl-4,6-dimethylbenzotrile (11%), 2,4,6-trimethylbenzotrile (21%), and benzotrile (25%). No 2-(3',5'-dimethylbenzyl)benzotrile was formed.



On the basis of the present results, it appears that gas-phase pyrolysis offers little or no synthetic advantage over the solution-phase Elbs reaction.

Experimental Section

IR spectra were determined as CCl₄ solutions on a Perkin-Elmer 281 spectrometer. NMR spectra were recorded on a Varian XL-100 or T-60 spectrometer, using 5% solutions in CDCl₃ or 10% solutions in CCl₄ with an internal standard of chloroform. Mass spectra were determined on a Dupont 21-492 at an ionizing voltage of 70 eV. UV spectra were run on a Beckman Acta M spectrometer on solutions made in spectro-grade cyclohexane. Samples of all compounds for spectral analysis were purified by

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Table II. Vacuum Pyrolysis of 2-Methyldiphenyl Ketimine

pyrolysis temp, °C	% conversion	products, % yield				
		anthracene	2-benzylbenzonitrile	benzonitrile	<i>o</i> -tolunitrile	fluorene
800	30	26	8	24	27	2
850	59	30	10	22	25	3
875	98	29	7	34	26	3
900	98	26	6	32	28	3

preparative vapor-phase chromatography on a Hewlett Packard F&M 700. Yields of products were determined by GLPC with triphenylmethane added as an internal standard.

Most of the starting materials and products are known compounds. They have physical and spectral properties in complete agreement with literature values. In those cases where spectral data have not been previously reported, we have included these data.

2-Methylbenzophenone was obtained from Aldrich. 2,4,6-Trimethylbenzophenone was prepared by addition of methyl benzoate (27.2 g, 200 mmol) to solution of mesitylmagnesium bromide, made from 15 g (75 mmol) of bromomesitylene (Aldrich) and 2.0 g (83 mmol) of magnesium turnings in tetrahydrofuran. It was purified by distillation, bp 130 °C (0.2 mm) [lit.³⁵ bp 180–182 °C (8.5 mm)], 10.1 g (45 mmol, 60%).

2-Methyldiphenyl ketimine was prepared by the reaction of *o*-tolunitrile (Aldrich) (11 g, 95 mmol) and phenylmagnesium bromide, made from 15 g (95.5 mmol) of bromobenzene and 2.4 g (100 mmol) of magnesium turnings, by the method of Moureu.³⁶ A yield of 14 g (72 mmol, 76%) of 2-methyldiphenyl ketimine, bp 114 °C (0.3 mm) [lit.³⁷ bp 136 °C (4 mm)], was obtained: NMR δ 9.15 (s, 1 H), 7.68–6.98 (m, 9 H), 2.08 (s, 3 H); IR 3240 (NH), 1595 (C=N) cm⁻¹; UV λ 2410 Å (ϵ 1.36 \times 10⁴), 2700 (1.74 \times 10³, sh).

2,4,6-Trimethyldiphenyl ketimine was prepared as above by reaction of mesitylmagnesium bromide with benzonitrile (5.3 g, 52 mmol) in 70% yield: bp 119–121 °C (0.1 mm); NMR δ 9.10 (s, 1 H), 7.82–7.64 (m, 2 H), 7.53–7.27 (m, 3 H), 6.89 (br s, 2 H), 2.32 (s, 3 H), 2.08 (s, 6 H); IR 3250 (NH) 1605 (C=N) cm⁻¹, mass spectrum, *m/e* 223 (P, 28%) (calcd for C₁₆H₁₇N 223.1361, found 223.1354), 222 (P - 1, 100%), 207 (23.5%), 77 (17%).

Pyrolysis of 2-Methylbenzophenone. 2-Methylbenzophenone was pyrolyzed under reduced pressure (0.5 mm) at various temperatures from 800 to 900 °C (see Table I).

The pyrolyses were performed in a 30-cm vertical-tube oven. A 5-mL round-bottom flask charged with 1 g of 2-methylbenzophenone was connected to the bottom end of a quartz tube (14 mm o.d., 12 mm i.d., 34 cm long). A short-path bulb-to-bulb distillation apparatus was attached on the top of the pyrolysis tube, the other end of which was equipped with a 25-mL pear-shaped flask which was cooled in liquid nitrogen. The outlet of the short-path was connected to a vacuum pump. The pyrolysis tube was heated to the desired temperature which was measured by using a Leeds and Northrup potentiometer and an iron-constantan thermocouple. 2-Methylbenzophenone was distilled under vacuum into the pyrolysis tube by heating the 5-mL round-bottom flask to 140–160 °C with an oil bath. All of the 2-methylbenzophenone passed through the pyrolysis tube within 20 min. The product as collected in the 25-mL pear-shaped flask. The crude pyrolysate was bulb-to-bulb distilled at 0.02 mm. The volatile products were analyzed by GLPC on a 1.25 ft. \times 0.25 in. 20% poly(phenyl ether) (6-ring) on a Chromosorb P 60/80 mesh column.

Pyrolysis of 2-Methyldiphenyl Ketimine. 2-Methyldiphenyl ketimine was pyrolyzed as above (see Table II). In order to improve the conversion, the pyrolysis tube used here was a quartz tube (9 mm o.d., 8 mm i.d., 250 cm long). It was wrapped in the shape of a helical spiral (3 cm o.d.) of 30 turns. The height of the spiral was 30 cm. The pyrolysis products were identified as anthracene (26–30%), 2-benzylbenzonitrile⁴⁰ (6–10%), fluorene (2–3), benzonitrile (24–32%), and *o*-tolunitrile (25–28%). Ben-

zonitrile and *o*-tolunitrile can be separated from the rest of the products very easily by column chromatography on activated alumina with *n*-hexane. The nitriles eluted last.

2-Benzylbenzonitrile was identified by comparison of its NMR, IR, and UV spectra and GLPC retention time with an authentic sample which was prepared as follows: Clemmenson reduction³⁸ of 2-chlorobenzophenone (Aldrich) (14 g, 64.6 mmol) gave 5.5 g (27 mmol, 42%) of (2-chlorophenyl)phenylmethane which was purified by distillation: bp 86 °C (0.2 mm) [lit.³⁹ bp 144 °C (5 mm)]; NMR δ 7.48–7.05 (m, 9 H), 4.15 (s, 2 H). 2-Benzylbenzonitrile⁴⁰ was prepared by heating (2-chlorophenyl)phenylmethane (1 g, 5 mmol) and cuprous cyanide (0.7 g, 7.8 mmol) in 1.5 mL of DMF at 200 °C for 48 h.⁴¹ After a workup with 2 g of ferric chloride, the reaction mixture was bulb-to-bulb distilled to yield 0.3 g (1.5 mmol, 32%) of 2-benzylbenzonitrile which was purified by preparative GLPC: NMR δ 7.62–7.00 (m, 9 H), 4.12 (s, 2 H); IR 2210 (C \equiv N); UV 2750 Å (ϵ 1.45 \times 10⁻³), 2840 (1.50 \times 10⁴).

Pyrolysis of 2,4,6-trimethylbenzophenone was carried out as above at 870 °C. The crude product was purified by column chromatography on activated alumina. The hydrocarbon fraction was eluted with *n*-hexane. It was further analyzed and purified by analytical and preparative charge-transfer TLC⁴² with 2,4,7-trinitrofluorenone⁴³ or 2,4,5,7-tetranitrofluorenone⁴⁴ on silica gel and GLPC. The results indicated the formation of 2,4-dimethylfluorene⁴⁵ (11.2%), 2-methylfluorene⁴⁶ (3.7%), 4-methylfluorene⁴⁶ (3.9%), fluorene (1.9%), dimethylantracene⁴⁷ (1.6), 1-methylantracene⁴⁸ (1%), 2-methylantracene⁴⁸ (1%), and anthracene (2%). 1,3-Dimethylantracene⁴⁷ NMR δ 8.46 (s, 1 H), 8.29 (s, 1 H), 8.06–7.83 (m, 2 H), 7.63–7.15 (m, 4 H), 2.78 (s, 3 H), 2.49 (s, 3 H).

Pyrolysis of 2,4,6-Trimethyldiphenyl Ketimine was carried out as above at 875 °C and was analyzed as above to yield 1,3-dimethylantracene⁴⁷ (19%), 2-methylantracene⁴⁸ (15.5%), 2,4,6-trimethylbenzonitrile⁴⁹ [21%, NMR δ 6.90 (s, 2 H), 2.47 (s, 6 H), 2.31 (s, 3 H); mass spectrum, *m/e* 145 (P, 53.6%), 130 (P - 15, 100%)], benzonitrile (25%), and 2-benzyl-4,6-dimethylbenzonitrile [11%; NMR δ 7.26 (br s, 5 H), 7.09 (br s, 2 H), 4.13 (s, 2 H), 2.49 (s, 3 H), 2.29 (s, 3 H); IR 2220 (C \equiv N) cm⁻¹; mass spectrum, *m/e* 221 (P, 100%) (calcd. for C₁₆H₁₅N 221.120; found 221.122), 220 (P - 1, 16.7%), 206 (P - 15, 19.2%), 190 (10.5%), 91 (14.4%), 77 (9.4%).

Acknowledgment. This work has been supported by the Air Force Office of Scientific Research, Grant 80-0006, and the National Cancer Institute, DHEW Grant 1R01-CA-19444-01.

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Registry No. 2-Methylbenzophenone, 131-58-8; anthracene, 120-12-7; fluorene, 86-73-7; 2-methyldiphenyl ketimine, 22627-00-5; 2-benzylbenzointrile, 56153-61-8; benzointrile, 100-47-0; *o*-tolunitrile, 529-19-1; 2,4,6-trimethylbenzophenone, 954-16-5; bromomesitylene, 576-83-0; methyl benzoate, 93-58-3; bromobenzene, 108-86-1; (2,4,6-trimethylphenyl)phenyl ketimine, 65232-41-9; 2-chlorobenzophenone, 5162-03-8; (2-chlorophenyl)phenylmethane, 29921-41-3; 2,4-dimethylfluorene, 2928-44-1; 2-methylfluorene, 1430-97-3; 4-methylfluorene, 1556-99-6; 1,3-dimethylantracene, 610-46-8; 1-methylantracene, 610-48-0; 2-methylantracene, 613-12-7; 2,4,6-trimethylbenzointrile, 2571-52-0; 2-benzyl-4,6-dimethylbenzointrile, 73466-76-9.

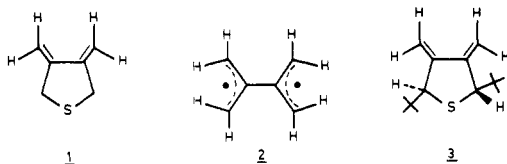
Synthesis and Reactions of a 3,4-Dimethylenethiolane Derivative

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A structurally interesting but little known compound type is represented by 3,4-dialkylidenethiolanes. The parent compound, 3,4-dimethylenethiolane (1), is, for in-



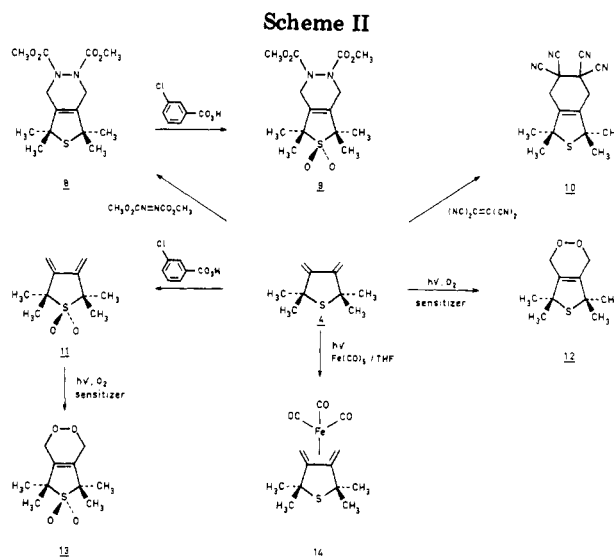
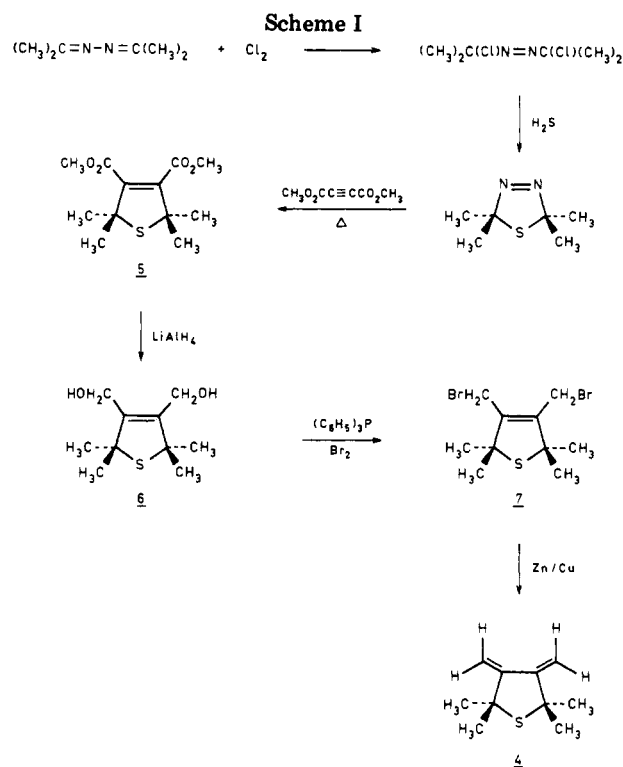
stance, an unusual (double) exocyclic isomer of 3,4-dimethylthiophene. One notes also that the carbon framework of 1 corresponds to that of tetramethyleneethane (2); for the case of 3, for which we developed a synthesis, the sulfur bridge separating the 3,4-dimethylenethiolane from a tetramethyleneethane was removed by means of an indirect route.¹

Syntheses of 3,4-dialkylidenethiolanes have been restricted to 1,² which polymerizes readily, and 3.¹ We report here a synthesis of 2,2,5,5-tetramethyl-3,4-dimethylenethiolane (4) following the path used for the synthesis of 3.

Appropriate manipulation of the cycloadducts (5) obtained from 1,3-dipolar cycloaddition of a thiocarbonyl ylide³ to dimethyl acetylenedicarboxylate forms the basis of the synthesis (Scheme I). All the reactions proceeded without notable complications once optimum conditions were found (see Experimental Section). The thiolane 4 is somewhat unstable toward polymerization, at least directly after its preparation from zinc/copper couple, perhaps owing to trace amounts of metal in the diene. It was usually prepared directly before use from dibromide 7. The debromination proceeds quantitatively, and removal of metal by filtration leaves virtually pure 4 in solution. Well-purified samples of 4 are entirely stable.

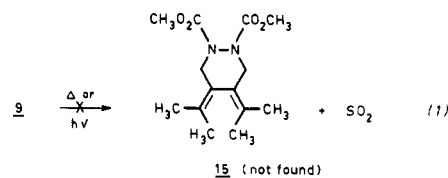
Some of the reactions carried out on 4 are shown in Scheme II.

Oxidation of 4 to sulfone 11 proceeded smoothly without detectable amounts of reaction at the double bonds. 11 is extremely stable, not undergoing decomposition or polymerization even on vigorous heating; 11 is also very insoluble and dissolves poorly only in chlorinated solvents.



Cycloadditions with dimethyl azodicarboxylate or tetracyanoethylene failed with 11.

These dienophiles reacted smoothly, however, with 4 to give cycloadducts 8 and 10, respectively. The former was oxidized readily to sulfone 9; all attempts, either thermal or photochemical, to remove SO₂ from 9 (eq 1) failed.



The failure to obtain 15 prevented us from going any further in a tetramethyleneethane synthesis along the lines described earlier.¹ Difficulty in removing SO₂ from 2,2,5,5-tetramethylbutadiene sulfones has been encountered before;⁴ apparently steric crowding of opposing

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