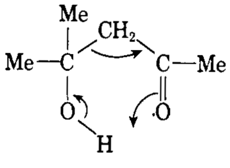
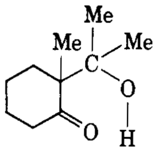
proposed for the pyrolysis of esters,[3a] β-hydroxy olefins,[3b] and β,γ-unsaturated acids.[4]

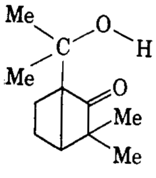
Further evidence for a cyclic transition state mechanism was presented by Mole[5] who reported the condensed phase thermal decomposition of β-hydroxy ketones. He showed that 2-methyl-2-(1-hydroxy-1-methylethyl)cyclohexanone (II) pyrolyzes into 2-methylcyclohexanone and acetone and that the rate in petroleum ether was uneffected by the nature of the surface of the reaction vessel or by small traces of acids or bases. They reported that 3,3-dimethyl-1-(1-hydroxy-1-methylethyl)bicyclo[2.2.1]heptanone (III) is essentially stable to heat. This compound cannot form a cyclic transition state and products without forming a double bond at the bridgehead.



I



II



III

As 4-hydroxy-4-methyl-2-pentanone is the only β-hydroxy ketone whose pyrolysis rate has been measured in the vapor state, comparative studies are a little premature. However, it is noteworthy that the temperature required for the pyrolysis of 4-hydroxy-4-methyl-2-pentanone (200–250°) is much lower than that for simple aliphatic esters (300–400°),[3a] β-hydroxy olefins (350–400°),[3b] and β,γ-unsaturated acids (369–378°).[4] This indicates that although the acidity of the hydrogen, which is thought to be involved in the transition state, is not particularly important,[3b] the greater basicity of the C═O bond in the β-hydroxy ketones over that of C═C bond is significant.

Experimental

4-Hydroxy-4-methyl-2-pentanone.—4-Hydroxy-4-methyl-2-pentanone was obtained commercially and fractionated before use, b.p. 65–66° (17 mm.), $n^{20}\text{D}$ 1.4215 [lit.[6] b.p. 67–69° (19 mm.), $n^{20}\text{D}$ 1.4213].

Method of Pyrolysis.—4-Hydroxy-4-methyl-2-pentanone was pyrolyzed at temperatures ranging from 221.9 to 255.2° in a stainless steel reactor of constant volume (200 ml.), whose design and operation have been described.[7] The reaction was followed automatically using a stainless steel diaphragm closing one end of the reactor as a null gauge and a pressure transducer connected to a strip chart recorder. The temperature was maintained to within 0.02° with a large glass wool lagged, electrically heated aluminum block, and was measured with two Chromel–Alumel thermocouples in series; these were calibrated to 0.1° against a platinum resistance thermometer.

Product Analysis.—The product from several pyrolyses of 4-hydroxy-4-methyl-2-pentanone was trapped in a liquid nitrogen trap attached directly to the reaction vessel, and was analyzed by v.p.c. on a Dow silicone 710 column and by fractional distillation. In the v.p.c. analysis only one peak was obtained, corresponding in retention time to acetone, and the fractionation only yielded acetone and unreacted 4-hydroxy-4-methyl-2-pentanone which were identified by their refractive indices and infrared spectra.

TABLE I

KINETIC DATA FOR THE PYROLYSIS OF 4-HYDROXY-4-METHYL-2-PENTANONE

$k \times 10^3$, sec.$^{-1}$	Temp., °C.	Activation energy, kcal.	Log A	Entropy of activation at 500°K., e.u.
16.7	255.2			
8.77	243.9			
4.05	231.1	32.3	11.63	−8.3
2.27	221.9			

Acknowledgment.—This work was supported in part by the United States Air Force, Air Force Office of Scientific Research under Grant No. AF-62-628 and by the Utah State University Research Council. Grateful acknowledgment is given for this support.

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The Reaction of Aromatic–Aliphatic Sulfones with N-Bromosuccinimide[1]

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Received June 18, 1964

In 1955 the author attempted to prepare 1,5-dibromo-1,2,4,5-tetrahydro-3-benzothiepine 3,3-dioxide by allowing 1-bromo-1,2,4,5-tetrahydro-3-benzothiepine 3,3-dioxide to react with N-bromosuccinimide.[2] The yields were disappointingly low (2–7%), even though the reaction conditions were varied. These results were surprising since numerous benzylic-type compounds had been successfully brominated with N-bromosuccinimide.[3]

Although Maerov[4] was unable to brominate 2,3,4,5-tetrahydrothiepine 1,1-dioxide with N-bromosuccinimide, Traynelis and Love[5] reported the successful bromination of 2,3-dihydro-1-benzothiepine 1,1-dioxide with N-bromosuccinimide. In view of these results, it seemed worthwhile to determine whether N-bromosuccinimide could be generally used for the bromination of benzylic methylene groups at least once removed from sulfone groups.

Since the 2-phenethylsulfonyl grouping in 2-phenethyl phenyl sulfone is similar to that found in 1,2,4,5-tetrahydro-3-benzothiepine 3,3-dioxide, this compound was selected for initial study. 2-Phenethyl phenyl sulfone was treated with N-bromosuccinimide and a 46% yield of 2-bromo-2-phenethyl phenyl sulfone was realized. The bromo compound was dehydrohalogenated with triethylamine to yield phenyl ω-styryl sulfone which was compared with an authentic sample.[6]

Initial attempts to form bis(2-bromo-2-phenethyl) sulfone by vigorously refluxing bis(2-phenethyl) sulfone with N-bromosuccinimide in carbon tetrachloride were

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[1] Acknowledgment is made to the American Medical Association Education and Research Foundation for partial support of this research.

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unsuccessful. The sulfone underwent decomposition with the elimination of sulfur dioxide. When the temperature for the bromination was held slightly under the reflux temperature of carbon tetrachloride, a 32% yield of the dibromo sulfone was realized. Apparently the lower reaction temperature resulted in less decomposition of the bromo sulfone. Although it was impossible to obtain a sample of bis(2-bromo-2-phenethyl) sulfone with a sharp melting point (160–170°), the dibromo sulfone was readily dehydrohalogenated in good yield (95%) to distyryl sulfone with triethylamine in boiling benzene.

Since considerable difficulty was experienced in the purification of bis(2-bromo-2-phenethyl) sulfone, the compound was synthesized by another route. Diphenacyl sulfide was reduced with sodium borohydride to bis(2-hydroxy-2-phenethyl) sulfide which was oxidized with 30% hydrogen peroxide to bis(2-hydroxy-2-phenethyl) sulfone. Treatment of this compound with phosphorus tribromide yielded bis(2-bromo-2-phenethyl) sulfone which had the same melting point characteristics (m.p. 162–171°) as that prepared by the N-bromosuccinimide method. Repeated crystallizations of this material from a variety of solvents did not appreciably alter the melting point. However, no melting point depression was observed when the two dibromo sulfones were mixed.

Treatment of 2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide with N-bromosuccinimide resulted in a 27% yield of 3-bromo-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide. The six-membered ring sulfone, thiochroman 1,1-dioxide, was converted in 51% yield to 4-bromothiochroman 1,1-dioxide when treated with N-bromosuccinimide. The structure was established by comparing it with a sample prepared by treating thiochroman-4-ol 1,1-dioxide with phosphorus tribromide. When 1,2-dihydro-3-benzothiepine 3,3-dioxide, formed by the dehydrohalogenation of 1-bromo-1,2,4,5-tetrahydro-3-benzothiepine 3,3-dioxide with triethylamine, was allowed to react with N-bromosuccinimide, the desired compound (1-bromo-1,2-dihydro-3-benzothiepine 3,3-dioxide) was not formed. Likewise 3-benzothiepine 3,3-dioxide, which conceivably could have been formed by bromination and dehydrohalogenation, was not formed. When a long reaction time (24 hr.) and low temperature (60–65°) were employed, starting material and a high-melting solid (m.p. 195–199°) were isolated. Admixture of this high-melting solid with an authentic sample of 1,2-dibromo-4,5-dihydro-3-benzothiepine 3-dioxide gave no depression in melting point and the infrared spectra of both were identical.

The results of this work indicate that N-bromosuccinimide can be used with fair results to brominate benzylic methylene groups once removed from sulfone groups. 1,2,4,5-Tetrahydro-3-benzothiepine 3,3-dioxide and 1,2-dihydro-3-benzothiepine 3,3-dioxide failed to undergo bromination with N-bromosuccinimide.

Experimental[7]

2-Bromo-2-phenethyl Phenyl Sulfone.—A solution of 5.0 g. (0.020 mole) of 2-phenethyl phenyl sulfone (prepared according to the procedure of Ashworth and Burkhardt[8]), 150 ml. of carbon tetrachloride, 0.25 g. of benzoyl peroxide, and 4.0 g. (0.022 mole) of N-bromosuccinimide was refluxed for 41 hr. The solution was illuminated with the light from an unfrosted 150-w. bulb during the reaction period. The solvent was evaporated and the remaining solid was treated with aqueous sodium thiosulfate. Recrystallization of the material from methanol yielded 3 g. (46%) of solid, m.p. 98–101°.

Anal. Calcd. for $C_{14}H_{13}BrO_2S$: C, 51.70; H, 4.03. Found: C, 51.74; H, 4.01.

A solution of 2-bromo-2-phenethyl sulfone (2.0 g., 0.0062 mole) and triethylamine (8.2 g., 0.081 mole) in 50 ml. of benzene was refluxed for 30 min. The benzene was evaporated and the solid was recrystallized from aqueous methanol to give 1.4 g. (93%) of product, m.p. 73–74°. A mixture melting point with a sample prepared by allowing benzene to react with ω-styrenesulfonyl chloride in the presence of aluminum chloride[6] showed no depression.

Bis(2-hydroxy-2-phenethyl) Sulfide.—Diphenacyl sulfide was prepared from ω-bromoacetophenone and sodium sulfide according to the procedure of Tafel and Mauritz.[9] A solution of 3.00 g. (0.0794 mole) of sodium borohydride, dissolved in 40 ml. of 50% water–dioxane, was slowly added to a cooled solution of 5.0 g. (0.19 mole) of diphenacyl sulfide in 50 ml. of dioxane and 30 ml. of methanol. The resulting solution was allowed to stand for 12 hr. at room temperature and heated at 60° for 1 hr. The solvent was evaporated at 40° and the remaining material was treated with ice and concentrated hydrochloric acid. The solid was separated and crystallized first from benzene and then hexane to yield 2.6 g. (50%) of white crystalline product, m.p. 95–96°.

Anal. Calcd. for $C_{16}H_{18}O_2S$: C, 70.06; H, 6.57. Found: C, 70.10; H, 6.57.

Bis(2-hydroxy-2-phenethyl) Sulfone.—A solution of 5.0 g. (0.018 mole) of bis(2-hydroxy-2-phenethyl) sulfide and 100 ml. of glacial acetic acid was cooled to 15° and treated with 12 ml. of 30% hydrogen peroxide. The solution was then allowed to stand 24 hr. at room temperature. The volume of glacial acetic acid was reduced to 15 ml. and diluted with ice–water. The resulting solid (4 g., 73%) was recrystallized from benzene, m.p. 104–105°.

Anal. Calcd. for $C_{16}H_{18}O_4S$: C, 62.72; H, 5.88. Found: C, 62.59; H, 5.95.

Bis(2-bromo-2-phenethyl) Sulfone.—A solution of bis(2-phenethyl) sulfone (3.0 g., 0.011 mole), prepared according to the procedure of Rheinboldt and Giesbrecht,[10] 250 ml. of carbon tetrachloride, 0.58 g. of benzoyl peroxide, and 6.9 g. (0.039 mole) of N-bromosuccinimide was vigorously refluxed for 12 hr. and the solvent was evaporated. During the reflux period the odor of sulfur dioxide was noted. The material remaining after the removal of solvent was washed three times with diethyl ether and then with warm methanol. One gram of unchanged bis(2-phenethyl) sulfone was recovered along with a red oil which could not be crystallized.

In a second experiment 6.0 g. (0.022 mole) of bis(2-phenethyl) sulfone, 300 ml. of carbon tetrachloride, 0.50 g. of benzoyl peroxide, and 7.80 g. (0.0438 mole) of N-bromosuccinimide were heated at 70° for 15 hr. and the solvent was removed. The resulting material was washed three times with diethyl ether and then with warm methanol. The remaining crystals were washed with warm 5% sodium thiosulfate and water and recrystallized from benzene and acetone. These crystals (3.0 g., 32%) melted mainly at 168–170°. However, some of the material melted at 160°. Recrystallization of this material from methanol, chloroform, hexane, cyclohexane, ethyl acetate, and glacial acetic acid did not significantly alter the melting point.

Anal. Calcd. for $C_{16}H_{16}Br_2O_2S$: C. 44.46; H, 3.73. Found: C, 44.37; H, 3.75.

A solution of 2.00 g. (0.00463 mole) of bis(2-bromo-2-phenethyl) sulfone, 1.50 g. (0.0149 mole) of triethylamine, and 50 ml. of benzene was refluxed for 30 min. The benzene was evaporated and the resulting solid was crystallized from methanol to give 1.19 g. (95%) of bis(styryl) sulfone, m.p. 100–101° (lit.[11] m.p. 99–100°).

A 4.0-g. (0.013-mole) sample of bis(2-hydroxy-2-phenethyl) sulfone was cooled to 0° and allowed to react with 3.6 g. (0.013 mole) of phosphorus tribromide. The resulting solid (4.5 g.,

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(7) Melting points were taken using a Nalge–Axelrod melting point apparatus and are uncorrected.

(8) F. Ashworth and G. N. Burkhardt, *J. Chem. Soc.*, 1791 (1928).

(9) J. Tafel and A. Mauritz, *Ber.*, **23**, 3474 (1890).

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(11) H. J. Backer, *Rec. trav. chim.*, **72**, 119 (1953).

80%) was recrystallized from benzene and then acetone, m.p. 162–171°. Recrystallization from various solvents did not improve the melting point. On admixture with the dibromo sulfone prepared with N-bromosuccinimide no depression in melting point was observed.

3-Bromo-2,3-dihydrobenzo[*b*]thiophene 1,1-Dioxide.—Benzo[*b*]thiophene in glacial acetic acid was oxidized to the sulfone with 30% hydrogen peroxide[12] and then reduced to 2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide with zinc and sodium hydroxide.[13]

A mixture of 5.0 g. (0.030 mole) of 2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide, 0.58 g. of benzoyl peroxide, 5.5 g. (0.031 mole) of N-bromosuccinimide, and 300 ml. of carbon tetrachloride was refluxed for 5 hr. The carbon tetrachloride was evaporated and the residue was taken up in diethyl ether and washed with aqueous sodium thiosulfate and water. Evaporation of the ether yielded a liquid which was taken up in benzene and chromatographed over aluminum oxide using benzene as an eluting solvent. The initial fractions were collected, evaporated to dryness, taken up in methanol, and refrigerated. The resulting crystals (2 g., 27%) melted at 91–92° (lit.[14] m.p. 91–92°). Treatment of this material with triethylamine in hot benzene yielded benzo[*b*]thiophene 1,1-dioxide.

Thiochroman-4-ol 1,1-Dioxide.—3-Phenylmercaptopropanoic acid, prepared from thiophenol and 3-chloropropanoic acid,[15] was converted by means of concentrated sulfuric acid to thiochroman-4-one.[15] The cyclic keto sulfide was oxidized to thiochroman-4-one 1,1-dioxide with 30% hydrogen peroxide.[16]

To 10 g. (0.051 mole) of thiochroman-3-one 1,1-dioxide dissolved in 100 ml. of warm dioxane was slowly added 1.17 g. (0.0310 mole) of sodium borohydride dissolved in 40 ml. of 50% aqueous dioxane. The solution was kept at room temperature for 1 hr. and heated at 90° for an additional 0.5 hour. The dioxane was evaporated and the residue was treated with ice and 5% hydrochloric acid. The resulting solid (7.4 g., 73%) was recrystallized from boiling water, m.p. 95–97°.

Anal. Calcd. for $C_9H_{10}O_3S$: C, 54.53; H, 5.09. Found: C, 54.62; H, 5.23.

4-Bromothiochroman 1,1-Dioxide.—The thiochroman-4-one was converted by means of the Wolff–Kishner reduction to thiochroman which was then oxidized with 30% hydrogen peroxide to thiochroman 1,1-dioxide.[17]

Thiochroman 1,1-dioxide (2.7 g., 0.015 mole), 2.6 g. (0.015 mole) of N-bromosuccinimide, 0.5 g. of benzoyl peroxide, and 300 ml. of carbon tetrachloride were refluxed for 8 hr. The carbon tetrachloride was evaporated and the residue (3.5 g.) was treated with aqueous sodium thiosulfate and recrystallized from methanol and then benzene. The 4-bromothiochroman 1,1-dioxide (2 g., 51%) melted at 138–139°.

Anal. Calcd. for $C_9H_9BrO_2S$: C, 41.39; H, 3.47. Found: C, 41.64; H, 3.57.

A mixture of 5.0 g. (0.025 mole) of thiochroman-4-ol 1,1-dioxide and 9.5 g. (0.35 mole) of phosphorus tribromide was allowed to stand for 14 hr. at room temperature and was then heated on a steam bath for 10 min. The mixture was treated with ice-water and washed with cold, dilute sodium bicarbonate. The resulting 4-bromothiochroman 1,1-dioxide (4.2 g., 64%) was recrystallized from methanol and then benzene, m.p. 138–139°. Admixture of this material with the 4-bromo-1-thiochroman 1,1-dioxide prepared with N-bromosuccinimide gave no depression in melting point.

1,2-Dihydro-3-benzothiepine 3,3-Dioxide.—A solution of 10.0 g. (0.0364 mole) of 1-bromo-1,2,4,5-tetrahydro-3-benzothiepine 3,3-dioxide,[18] 4.00 g. (0.0396 mole) of triethylamine, and 200 ml. of benzene was heated at 80° for 0.5 hr., cooled, and filtered. Evaporation of the benzene afforded 6 g. (85%) of crystals, m.p. 135–137° [from methanol and petroleum ether (b.p. 35–37°)].

Anal. Calcd. for $C_{10}H_{10}O_2S$: C, 61.87; H, 5.18. Found: C, 62.07; H, 5.30.

The Reaction of 1,2-Dihydro-3-benzothiepine 3,3-Dioxide with N-Bromosuccinimide.—A solution of 300 ml. of carbon tetrachloride, 2.00 g. (0.0103 mole) of 1,2-dihydro-3-benzothiepine 3,3-dioxide, 1.79 g. (0.0101 mole) of N-bromosuccinimide, and 0.50 g. of benzoyl peroxide was heated at 70° for 9 hr. and refluxed for an additional 2 hr. Evaporation of the carbon tetrachloride and treatment of the resulting material with diethyl ether left a solid which after being washed with aqueous sodium thiosulfate and recrystallized from methanol proved to be starting material (1 g.). The ether-soluble red oil could not be crystallized.

In a second experiment the quantities remained the same but the reaction mixture was heated at 60–65° for 24 hr. The carbon tetrachloride was evaporated and the remaining material was extracted with diethyl ether. The undissolved solid was washed with aqueous sodium thiosulfate, water, and recrystallized from methyl alcohol. One gram of 1,2-dihydro-3-benzothiepine 3,3-dioxide was recovered. The volume of the ether was reduced and the crystalline material which separated was collected. The crystalline solid (0.3 g., 8.2%) after repeated crystallization from methanol melted at 195–199° and gave a positive test for halogen. This product was shown by mixture melting points and infrared spectra to be identical with 1,2-dibromo-4,5-dihydro-3-benzothiepine 3,3-dioxide.

Anal. Calcd. for $C_{10}H_{10}Br_2O_2S$: C, 33.92; H, 2.85. Found: C, 33.52; H, 2.75.

In a third experiment the reaction mixture was refluxed for 6 hr. The reaction mixture was worked up as described above. Starting material and some red oil were recovered.

1,2-Dibromo-4,5-dihydro-3-benzothiepine 3,3-Dioxide.—A solution of bromine (5.0 g., 0.031 mole) and 1,2-dihydro-3-benzothiepine 3,3-dioxide (6.1 g., 0.031 mole) in 50 ml. of chloroform was decolorized in the dark. The crystalline precipitate (7.7 g., 70%) which formed was collected and crystallized from methanol, m.p. 195–199°.

Anal. Calcd. for $C_{10}H_{10}Br_2O_2S$: C, 33.92; H, 2.85. Found: C, 33.61; H, 2.79.

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The Structure of Secondary Amine–Sulfur Dioxide Salts

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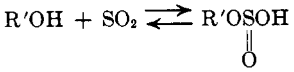
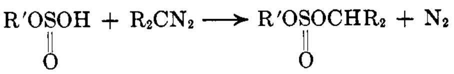
Received December 11, 1964

Staudinger and co-workers found that amines and alcohols reacted with diazoalkanes at low temperatures in the presence of sulfur dioxide.[1] The intermediate was postulated as $Ph_2C{=}SO_2$. Reinvestigation of the amine reaction in 1952 substantiated these results.[2] However, Hesse and Majmudar[3] found that sulfite esters were formed in the alcohol reaction. In the mechanism proposed sulfur dioxide is in equilibrium with the alcohol forming a hydrogen alkyl sulfite which then reacts with the diazoalkane as a carboxylic acid.



$$R'OH + SO_2 \rightleftharpoons R'O\underset{\overset{\|}{O}}{S}OH \qquad (1)$$



$$R'O\underset{\overset{\|}{O}}{S}OH + R_2CN_2 \longrightarrow R'O\underset{\overset{\|}{O}}{S}OCHR_2 + N_2 \qquad (2)$$

Investigations of the structure of amine–sulfur dioxide salts are limited; substituted anilines,[4] pyri-

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