dl-diol peak which had no trace of a shoulder. Hence, if this *dl*-diol was not completely free of *meso* isomer, it surely contained considerably less than 10% of this isomer. The high-boiling material gave the bis(4-nitrobenzoate), m.p. and m.m.p. 129.0–129.5°, lit.[17] m.p. 128°. After distillation of the high-boiling material a residue of 0.25 g. remained.

cis-**2-Butene.**—Alkene used was 41.5 mmoles; ozone introduced was 39.4 mmoles; Grignard reagent reacted was 147 mmoles. Refluxing the ozonation mixture–Grignard reagent reaction mixture gave 15.6 mmoles of propene and 30.4 mmoles of propane. After removal of the solvent the reaction products gave a negative test for α-diol with periodic acid. The more volatile material (6.27 g.) was found to contain by v.p.c. isopropyl alcohol (28.5 mmoles), methylisopropylcarbinol (49.3 mmoles), and unidentified material (0.04 g.). There was a distillation residue of 0.26 g.

1-Butene.—Alkene used was 45.3 mmoles; ozone introduced was 40.8 mmoles; Grignard reagent reacted was 155 mmoles. Refluxing the ozonation mixture–Grignard reagent reaction mixture gave 20.5 mmoles of propene and 39.7 mmoles of propane. The more volatile material (4.63 g.) was found by v.p.c. to contain isopropyl alcohol (31.6 mmoles), isobutyl alcohol (14.2 mmoles), ethylisopropylcarbinol (17.9 mmoles), and unidentified material (0.19 g.). The high-boiling material was analyzed by v.p.c. and found to contain butane-1,2-diol (9.0 mmoles) and unidentified material (0.35 g.). The bis(4-nitrobenzoate) of the high-boiling material was prepared and had m.p. and m.m.p. 95–96°.

Anal.[22] Calcd. for $C_{18}H_{16}N_2O_8$: C, 55.7; H, 4.2; N, 7.2. Found: C, 56.3; H, 4.4; N, 7.3.

There was a distillation residue of 0.04 g.

Ethylene.—Ozone introduced was 40.0 mmoles; Grignard reagent reacted was 144 mmoles. Refluxing the ozonation mixture–Grignard reagent reaction mixture gave 19.9 mmoles of propene and 37.3 mmoles of propane. After removal of solvent the reaction products gave a negative test for α-diol with periodic acid. The more volatile material (4.15 g.) was found by v.p.c. to contain isopropyl alcohol (21.9 mmoles), isobutyl alcohol (38.5 mmoles), and unidentified material (0.41 g.). There was a distillation residue of 0.42 g.

(22) By S. M. Nagy, Massachusetts Institute of Technology Microchemical Laboratory.

Detection of ethylene glycol in the aqueous layer was attempted by v.p.c. (10% Ethofat on Fluoropak column), but none could be detected either in the initial aqueous layer or after it had been concentrated to 75 g. on a rotary evaporator. Control experiments showed that the glycol could be detected without difficulty in a 0.5 wt. % aqueous solution, and that this solution could be concentrated on a rotary evaporator without loss of the glycol.

Preparation of Molozonides in *n*-Pentane.—The alkene (7.0–10 mmoles) was dissolved in 75 ml. of *n*-pentane. The solution was cooled to −110° and 2.50 mmoles of ozone was added to the solution. Ethylene was introduced simultaneously with the ozone into the *n*-pentane. The ozone–oxygen stream contained about 1.5 vol. % of ozone. All of the ozone was retained by the reaction mixture. With the C_2, C_4, and C_5 alkenes solid material separated in the reaction mixture from the very early stages of the ozonation. The C_6 molozonides were sufficiently soluble in the pentane to necessitate a reduction of the volume of *n*-pentane to 50 ml. The molozonides of the *trans* C_4 and C_5 alkenes were more soluble than were those from the corresponding *cis*-alkenes.

The ozonation flask was removed from the apparatus, and a thermometer (precooled in liquid nitrogen) was placed carefully into the reaction mixture. In the case of *cis*-2-pentene the thermometer went into the reaction mixture with a sizzling noise, and when the thermometer bulb touched the bottom of the reaction flask one could hear and feel a small explosion at the end of the thermometer. In this first experiment the reaction mixture exploded as the reaction flask was being raised from the cooling bath. This was attributed to the thermometer bulb crushing some of the solid on the bottom of the reaction flask. Thereafter, the cooling bath was lowered carefully from the reaction flask. The reaction mixture was allowed to warm slowly, and the temperature was noted when the warming rate increased rapidly. At this point the white solid in the reaction mixture disappeared rapidly. The temperatures at which these rapid decompositions began for the various alkene molozonides follow: ethylene, −68°; *cis*-2-butene, −95°; *trans*-2-butene, −68°; *cis*-2-pentene, −90°; *trans*-2-pentene, −60°; 1-pentene, −66°; *cis*-3-hexene, −70 and −68°; and *trans*-3-hexene, −67°.

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The Synthesis of 4,1-Benzothiazepines and 5,1-Benzothiazocines

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Synthesis of 3,5-dihydro-4,1-benzothiazepin-2(1H)-one (V) and 1,3,4,6-tetrahydro-2H-5,1-benzothiazocin-2-one (XI) are described. Lithium aluminum hydride reduction of V and XI gave 1,2,3,5-tetrahydro-4,1-benzothiazepine and 2,3,4,6-tetrahydro-1H-5,1-benzothiazocin, respectively.

The first report on a compound with a benzothiazepine structure appeared about 40 years ago. Mayer and Horst[1] reacted β-chloropropionic acid with *o*-nitrothiophenol and the resulting β-(*o*-nitrophenylmercapto)propionic acid was then reduced to its amino analog, which, when heated, cyclized to 2,3-dihydro-1,5-benzothiazepin-4(5H)-one.[2,3] This compound was reduced by lithium aluminum hydride to 2,3,4,5-tetrahydro-1,5-benzothiazepine.[4] Several alternative approaches to this class of compounds have been developed. They are based upon the condensation of *o*-aminothiophenol with α,β-unsaturated acids,[5] α,β-unsaturated esters,[6] α,β-unsaturated ketones,[7–9] acetoacetic ester, or diketene.[10] The significance of the substituted derivatives of 2,3-dihydro-1,5-benzothiazepin-4(5H)-one and 1,5-benzothiazepin-4(5H)-one as pharmacologically useful agents was brought to light by the work of Krapcho and his co-workers.[11–13] The isomeric 1,4-benzothiazepine structure was ob-

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CHART I

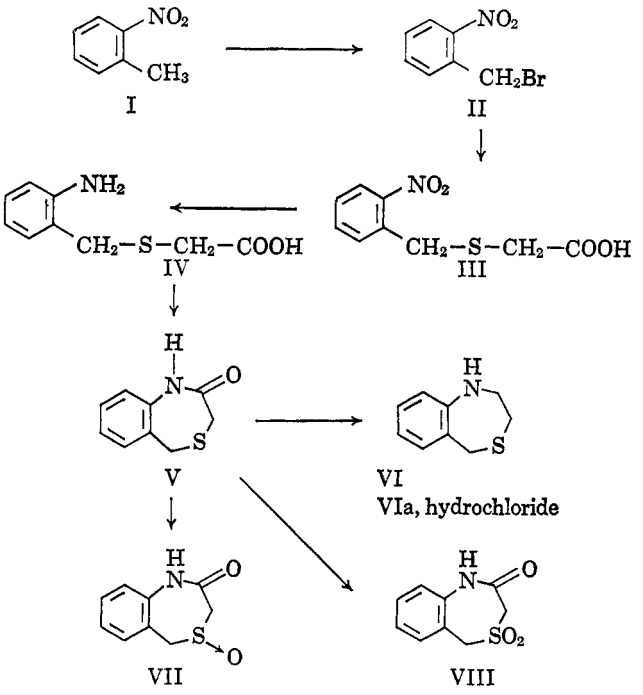
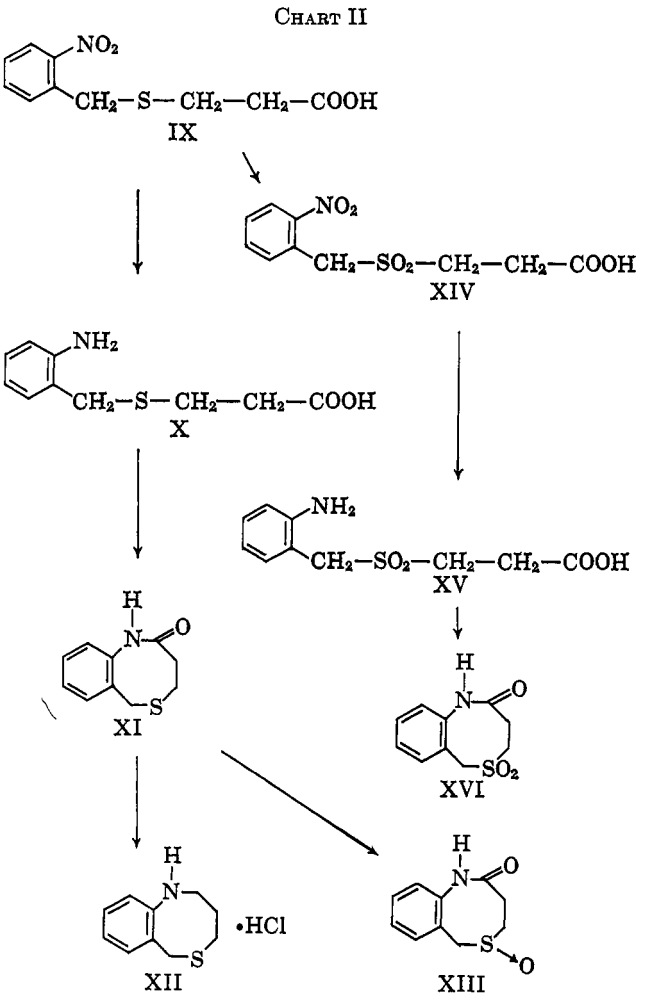


CHART II



tained by McClelland, Rose, and Stammers[14] upon dehydration of 2-carbamylphenylthioacetic acid to 1,4-benzothiazepine-3,5(2H,4H)-dione. Recently Jacob and Schlack[15] described the reaction of *o*-mercaptobenzoic acid with ethylenimine to obtain 2,3-dihydro-1,4-benzothiazepin-5(4H)-one. This paper reports a novel synthesis of the hitherto unknown 4,1-benzothiazepine, as well as the application of this method to the preparation of 5,1-benzothiazocine.

The scheme of the synthesis is shown in Chart I. The principal step consists of a smooth cyclization of (2-aminobenzylmercapto)acetic acid (IV) to 3,5-dihydro-4,1-benzothiazepin-2(1H)-one (V). For the synthesis of this acid, *o*-nitrotoluene was first brominated with N-bromosuccinimide.[16] The resulting crude 2-nitrobenzyl bromide (II) was condensed with mercaptoacetic acid in sodium hydroxide solution at 0° to yield (2-nitrobenzylmercapto)acetic acid (III). The nitro group was reduced catalytically with a palladium-on-carbon catalyst in methanol solution. The product was a mixture of the expected amino acid IV and the cyclized product V. The cyclization was completed by refluxing the xylene solution of this mixture for 2 hr. 3,5-Dihydro-4,1-benzothiazepin-2(1H)-one (V) is a white, crystalline, high-melting substance, insoluble in most organic solvents. Its structure is supported by a satisfactory microanalysis and by an infrared spectrum which shows absorptions for N–H (3400 cm.$^{-1}$), a methylene group next to a carbonyl (2980 and 1425 cm.$^{-1}$), and the lactam carbonyl group (1680 cm.$^{-1}$). Compound V also shows an ultraviolet absorption maximum at 237 mμ (ϵ 8200). The presence of the lactam group is indicated further by reduction with lithium aluminum hydride to the fully identified 1,2,3,5-tetrahydro-4,1-benzothiazepine (VI). The cyclic sulfide group was confirmed by oxidation of V with 30% hydrogen peroxide which gave 3,5-dihydro-4,1-benzothiazepin-2(1H)-one 4,4-dioxide (VIII). The infrared spectrum of VIII shows absorptions at 1320 and 1128 cm.$^{-1}$, characteristic of a sulfo group. When V was oxidized with sodium periodate,[17] 3,5-dihydro-4,1-benzothiazepin-2(1H)-one 4-oxide (VII) was formed, exhibiting strong sulfoxide absorption at 1045 cm.$^{-1}$.

When, in the same reaction sequence, β-mercaptopropionic acid was used instead of mercaptoacetic acid, a 5,1-benzothiazocine system was formed (Chart II). Formation of an eight-membered ring from 3-(2-aminobenzylmercapto)propionic acid (X) is a much slower process. After 2 hr. in a boiling xylene solution only 22% of 1,3,4,6-tetrahydro-2H-5,1-benzothiazocin-2-one (XI) was obtained. This result has to be compared with an 83% over-all yield from III to V under the same conditions. The amide carbonyl of XI is shown in the infrared spectrum at 1656 cm.$^{-1}$. In the ultraviolet region compound XI is characterized by the inflections at 233–234 mμ (ϵ 9000) and 275 mμ (ϵ 900) superimposed on a strong end absorption. Reduction of XI with lithium aluminum hydride in tetrahydrofuran solution at room temperature gave 2,3,4,6-tetrahydro-1H-5,1-benzothiazocine, characterized as the hydrochloride XII.

Oxidation of XI with hydrogen peroxide in acetic acid solution gave a dark mixture. Chromatography on an alumina column resulted only in the isolation of

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1,3,4,6-tetrahydro-2H-5,1-benzothiazocin-2-one 5-oxide (XIII). The structure of the last compound was supported by analysis and infrared spectrum. The desired sulfo compound was obtained by an alternative sequence of reactions. The acid IX was first oxidized with hydrogen peroxide to give 3-(2-nitrobenzylsulfonyl)propionic acid (XIV). The nitro group was then reduced by catalytic hydrogenation. Cyclization of 3-(2-aminobenzylsulfonyl)propionic acid (XV) thus obtained proceeded very slowly; after 2 hr. in refluxing xylene solution, only 2% of 1,3,4,6-tetrahydro-2H-5,1-benzothiazocin-2-one 5,5-dioxide (XVI) was formed. On the other hand, by maintaining XV as a molten mass at 200° for 10 min., a 20% conversion to XVI was accomplished.

Experimental[18]

(2-Nitrobenzylmercapto)acetic Acid (III) from *o*-Nitrotoluene (I).—To the solution of 69 g. of *o*-nitrotoluene in 300 ml. of carbon tetrachloride was added 90 g. of N-bromosuccinimide and 2 g. of benzoyl peroxide, and the suspension was refluxed for 3 hr. After cooling, succinimide was separated by filtration, and the solution was evaporated to dryness. The crude *o*-nitrobenzyl bromide was dissolved in 200 ml. of acetone, and this solution was added dropwise to an ice-cold stirred solution of 46 g. of mercaptoacetic acid and 40 g. of sodium hydroxide in 300 ml. of water. The reaction mixture was stirred for 24 hr. at room temperature, diluted with water, extracted with methylene chloride, then acidified with acetic acid and extracted again with methylene chloride. The last extract was washed with water, dried over anhydrous sodium sulfate, and evaporated. The crystalline residue was recrystallized from an acetone–hexane mixture to give 47.5 g. of III (42%): m.p. 99–103°; infrared (in $CHCl_3$) 2630, 2540, 1708 (–COOH), 1528, and 1344 cm.$^{-1}$ (–NO_2); ultraviolet λ_{max} 237–257 mμ (ϵ 5200).

Anal. Calcd. for $C_9H_9NO_4S$ (227.24): C, 47.57; H, 3.99; N, 6.16; S, 14.11. Found: C, 47.53; H, 3.91; N, 6.23; S, 14.29.

3,5-Dihydro-4,1-benzothiazepin-2(1H)-one (V) from III.—To a solution of 22.7 g. of III in 1200 ml. of methanol was added 3.8 g. of 10% palladium-on-carbon catalyst, and the suspension was hydrogenated at room temperature at a pressure of 65–100 p.s.i. until the theoretical amount of hydrogen was absorbed. The catalyst was filtered and the solution was evaporated to dryness. The infrared spectrum of the semicrystalline residue showed it to be a mixture of the amino acid IV and the cyclized product V. This residue was taken up in 2 l. of xylene, and the solution was refluxed for 2 hr. with a slow distillation of xylene. After cooling, the crystalline precipitate was filtered and recrystallized from acetone to give 15 g. of V (84%): m.p. 218–223°; infrared (in $CHCl_3$) 3400 (N–H), 2980, 1425 (–CH_2– next to a carbonyl), and 1680 cm.$^{-1}$ (amide carbonyl); ultraviolet λ_{max} 237 mμ (ϵ 8200).

Anal. Calcd. for C_9H_9NOS (179.24): C, 60.31; H, 5.06; N, 7.82; S, 17.89. Found: C, 60.31; H, 4.92; N, 8.25; S, 18.10.

1,2,3,5-Tetrahydro-4,1-benzothiazepine (VI) from V.—To a suspension of 4 g. of lithium aluminum hydride in 400 ml. of anhydrous tetrahydrofuran, cooled to 0°, was added slowly a solution of 4.5 g. of V in 350 ml. of anhydrous tetrahydrofuran. The mixture was stirred for 24 hr. at room temperature. After cooling in an ice bath for a short time, a saturated solution of sodium sulfate was added slowly until hydrogen evolution ceased; then anhydrous sodium sulfate was added, and the mixture was filtered. The solution was evaporated to dryness and the crystalline residue was recrystallized from methanol to give 3 g. of VI (72%): m.p. 85.5–87.5°; infrared (in $CHCl_3$) 3370 (N–H), 2930, 2900, and 2850 cm.$^{-1}$ (–CH_2 groups); ultraviolet λ_{max} 241–242 mμ (ϵ 6500) and 284–285 mμ (ϵ 1750).

Anal. Calcd. for $C_9H_{11}NS$ (165.26): C, 65.41; H, 6.71; N, 8.48; S, 19.40. Found: C, 65.76; H, 6.57; N, 8.40; S, 19.36.

The hydrochloride of VI was prepared by addition of an ether solution of hydrogen chloride to an acetone solution of the base. After evaporation, the noncrystalline residue was crystallized from ethanol–ether to give VIa, m.p. 193–197° dec.

Anal. Calcd. for $C_9H_{11}NS \cdot HCl$ (201.72): C, 53.59; H, 6.00; Cl, 17.58; N, 6.94; S, 15.90. Found: C, 53.31; H, 5.70; Cl, 17.23; N, 6.92; S, 16.08.

3,5-Dihydro-4,1-benzothiazepin-2(1H)-one 4-Oxide (VII) from V.—To an ice-cold suspension of 3.6 g. of V in 250 ml. of methanol was added 42 ml. of 0.5 *M* sodium periodate. This mixture was stirred for 7 hr. in an ice bath, then 3 days at room temperature. The precipitate (sodium iodate) was filtered, and the solution was evaporated to dryness. The residue was recrystallized from acetone to give 3.4 g. of VII (87%): m.p. 255.5–256° after transformation at 250–255°; infrared (KBr) 3130 (N–H), 2910, 2840 (–CH_2–), 1650 (carbonyl), 1045, and 1023 cm.$^{-1}$ (sulfoxide); ultraviolet λ_{max} 220–222 mμ (ϵ 21,200) and 260–262 mμ (ϵ 2850).

Anal. Calcd. for $C_9H_9NO_2S$ (195.24): C, 55.37; H, 4.65; N, 7.17; S, 16.42. Found: C, 55.51; H, 4.88; N, 7.36; S, 16.45.

3,5-Dihydro-4,1-benzothiazepin-2(1H)-one 4,4-Dioxide (VIII) from V.—A mixture of 3.58 g. of V dissolved in 150 ml. of glacial acetic acid and 4.5 ml. of 30% hydrogen peroxide was heated for 2 hr. at 100°, and then it was evaporated to dryness. The crystalline residue was recrystallized from acetone to give 2 g. of VIII (42%): m.p. 241–242°; infrared (KBr) 3170 (N–H), 2980, 1430 (–CH_2–), 1670 (carbonyl), 1320, and 1128 cm.$^{-1}$ (–SO_2–); ultraviolet λ_{max} 232–234 mμ (ϵ 9300).

Anal. Calcd. for $C_9H_9NO_3S$ (211.24): C, 51.17; H, 4.29; N, 6.63; S, 15.18. Found: C, 51.86; H, 4.31; N, 6.62; S, 14.91.

3-(2-Nitrobenzylmercapto)propionic Acid (IX) from I.—An acetone solution of *o*-nitrobenzyl bromide, prepared as described above, was added to an ice-cold stirred solution of 53 g. of β-mercaptopropionic acid and 40 g. of sodium hydroxide in 300 ml. of water. The reaction mixture was then stirred for 24 hr. at room temperature. After this time, the solution became neutral. It was diluted with 1 l. of water, made alkaline to pH 9, extracted with methylene chloride, then acidified with acetic acid, and extracted again with methylene chloride. The last extract was washed with water, dried over sodium sulfate, and evaporated to dryness. The residue crystallized from an acetone–hexane mixture to give 65 g. of IX (54%): m.p. 83–85°; infrared (in $CHCl_3$) 2660, 2560, 1710 (–COOH), 1528, and 1346 cm.$^{-1}$ (–NO_2); ultraviolet λ_{max} 247–248 mμ (ϵ 5200).

Anal. Calcd. for $C_{10}H_{11}NO_4S$ (241.27): C, 49.78; H, 4.60; N, 5.81; S, 13.29. Found: C, 50.03; H, 4.95; N, 5.72; S, 13.44.

3-(2-Aminobenzylmercapto)propionic Acid (X) from IX.—A mixture of 24.1 g. of IX dissolved in 1000 ml. of methanol and 5.5 g. of 10% palladium-on-carbon catalyst was hydrogenated at room temperature and 90 p.s.i. pressure until the theoretical amount of hydrogen was absorbed, then filtered, and evaporated to dryness. The residue was crystallized from ether–petroleum ether (b.p. 30–60°) to give 17 g. of X (80%): m.p. 84–85°; infrared (in $CHCl_3$) 3450, 3340 (–NH_2), 2750, 2610, and 1710 cm.$^{-1}$ (–COOH).

Anal. Calcd. for $C_{10}H_{13}NO_3S$ (211.29): C, 56.85; H, 6.20; N, 6.63; S, 15.80. Found: C, 56.69; H, 6.30; N, 6.45; S, 15.44.

1,3,4,6-Tetrahydro-2H-5,1-benzothiazocin-2-one (XI) from X.—A solution of 5 g. of X in 200 ml. of xylene was boiled for 2 hr. with slow distillation of xylene. After evaporation to dryness, the residue was chromatographed on a column of 150 g. of neutral Woelm alumina (grade I). The crystalline fractions eluted with benzene gave, after recrystallization from acetone, 1 g. of XI (22%): m.p. 194–198.5°; infrared (in $CHCl_3$) 3370 (N–H) and 1656 cm.$^{-1}$ (carbonyl group); ultraviolet shoulder at 233–234 mμ (ϵ 9000) and 275 mμ (ϵ 900). (The material eluted later from the column gave 3.5 g. of the starting acid X.)

Anal. Calcd. for $C_{10}H_{11}NOS$: C, 62.15; H, 5.74; N, 7.25; mol. wt., 193.27. Found: C, 62.08; H, 5.86; N, 6.73; S, 16.69; mol. wt., 193 (mass spectrum).

1,3,4,6-Tetrahydro-2H-5,1-benzothiazocin-2-one 5-Oxide (XIII) from XI.—A solution of 15.2 g. of XI and 17.3 ml. of 30%

(18) All melting points are corrected. Elemental microanalyses were performed by Dr. A. Steyermark. Ultraviolet spectra were taken in isopropyl alcohol on a Cary Model 14M spectrophotometer. Infrared spectra were taken on a Perkin-Elmer Model 21 spectrophotometer.

hydrogen peroxide in 150 ml. of acetic acid was heated at 100° for 10 min. The solution turned very dark. After evaporation, the resinous residue was chromatographed on a column of 300 g. of neutral Woelm alumina (grade I). The fractions eluted with benzene were crystallized from acetone to give 1.5 g. of XIII (9%): m.p. 230–232°; infrared (KBr) 3200 (N–H), 1660 (carbonyl), and 1032 cm.$^{-1}$ (sulfoxide); ultraviolet inflection at 238 mμ (ε 8000).

Anal. Calcd. for $C_{10}H_{11}NO_2S$ (209.27): C, 57.39; H, 5.30; N, 6.69; S, 15.32. Found: C, 56.88; H, 5.50; N, 6.66; S, 15.22.

2,3,4,6-Tetrahydro-1H-5,1-benzothiazocine Hydrochloride (XII) from XI.—To a solution of 4 g. of lithium aluminum hydride in 400 ml. of anhydrous tetrahydrofuran was added slowly at 0° a solution of 3.9 g. of XI in 220 ml. of anhydrous tetrahydrofuran. The mixture was stirred 24 hr. at room temperature. After cooling in an ice bath, a saturated solution of sodium sulfate was added slowly until hydrogen evolution ceased; then crystalline sodium sulfate was added, and the mixture was filtered. The solution was evaporated, and the starting material was separated as material insoluble in ether (1 g., m.p. 188–192°). The ether solution was evaporated, the oily residue was dissolved in acetone, and an ethereal solution of hydrogen chloride was added. After evaporation to dryness, the residue was crystallized from 95% ethanol to give 1.1 g. of XII (25%): m.p. 216–220° with transformation above 205°; infrared (KBr) 2900, 2860, 2800 (–CH_2–), 2720–2410 (amino salt), and 1580 cm.$^{-1}$ (anilino C–N); ultraviolet λ_{max} 245–255 mμ (ε 5300) and 309–310 mμ (ε 1300).

Anal. Calcd. for $C_{10}H_{13}NS\cdot HCl$ (215.75): C, 55.67; H, 6.54; Cl, 16.43; N, 6.49; S, 14.86. Found: C, 55.44; H, 6.54; Cl, 16.36; N, 6.46; S, 14.99.

3-(2-Nitrobenzylsulfonyl)propionic Acid (XIV) from IX.—A solution of 4.8 g. of IX and 5 ml. of 30% hydrogen peroxide in 100 ml. of acetic acid was heated for 4 hr. at 100° and then evaporated. The crystalline residue was recrystallized from ether to give 5.2 g. of XIV (96%): m.p. 126–127°; infrared (KBr) 2700, 2570, 1700 (–COOH), 1524, 1342 (–NO_2), 1316, and 1130 cm.$^{-1}$ (–SO_2–); ultraviolet λ_{max} 251–258 mμ (ε 4900).

Anal. Calcd. for $C_{10}H_{11}NO_6S$ (273.27): C, 43.95; H, 4.06; N, 5.13; S, 11.73. Found: C, 44.00; H, 4.17; N, 4.93; S, 11.72.

3-(2-Aminobenzylsulfonyl)propionic Acid (XV) from XIV.—A solution of 5.2 g. of XIV in 300 ml. of methanol was hydrogenated over 0.5 g. of 10% palladium-on-carbon catalyst at room temperature and 90–115 p.s.i. pressure; then it was filtered and evaporated. The residue was crystallized from a methanol–ether mixture to give 4.6 g. of XV (99%): m.p. 168–172°; infrared (KBr) 3400, 3330 (–NH_2), 2740, 2640, 2530, 1710 (–COOH), 1318, and 1105 cm.$^{-1}$ (–SO_2–); ultraviolet λ_{max} 240–241 mμ (ε 7800) and 294–295 mμ (ε 3200).

Anal. Calcd. for $C_{10}H_{13}NO_4S$ (243.29): C, 49.37; H, 5.39; N, 5.76; S, 13.18. Found: C, 49.65; H, 5.46; N, 5.76; S, 13.47.

1,3,4,6-Tetrahydro-2H-5,1-benzothiazocin-2-one 5,5-Dioxide (XVI) from XV.—A boiling solution of 4.5 g. of XV in 1000 ml. of xylene was distilled slowly over 2 hr. After cooling, the crystalline starting material (4.2 g., m.p. 166–172°) was filtered, and the solution was evaporated. Recrystallization of the residue from acetone gave 100 mg. of XVI, m.p. 287–292°. The same cyclization occurred by melting XV at 200° for 10 min. From 3 g. of XV, 0.6 g. of XVI (22%) was obtained in this way. The spectral data for XVI are: infrared (KBr) 3200 (N–H), 1668 (carbonyl group), 1317, and 1115 cm.$^{-1}$ (–SO_2–); ultraviolet inflections at 234–235 mμ (ε 6500), 270 mμ (ε 490), 277 mμ (ε 320), and 300 mμ (ε 130).

Anal. Calcd. for $C_{10}H_{11}NO_3S$ (225.27): C, 53.32; H, 4.92; N, 6.22. Found: C, 53.82; H, 5.19; N, 6.19.

Acknowledgment.—We are indebted to Dr. A. Steyermark for the microanalyses, to Dr. V. Toome for the ultraviolet spectra, and to Mr. S. Traiman for the infrared spectra.

The Reaction of Carbon Tetrachloride in a Radiofrequency Glow Discharge[1a]

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The action of a glow discharge produced by radiofrequency energy on carbon tetrachloride in the gas phase at room temperature produces a chlorinated polymer, hexachloroethane, tetrachloroethylene, dichloroacetylene, hexachlorobenzene, and chlorine. These products are formed primarily through the initial generation of a trichloromethyl radical. Any dichlorocarbene is not present in sufficient amounts to be detected.

Several methods are generally available for the generation of free radicals in the gas phase.[2–7] This may be conveniently accomplished by electron impact in an electric discharge, thermally, or by photolysis. Electron impact in an electric discharge may be obtained by several known techniques: electrical discharge tubes, low-frequency discharge, radiofrequency discharge, and microwave discharge.[8] Little or no work on the decomposition of organic compounds in a radiofrequency discharge has been carried out and there are only a few reports of decomposition of organic compounds in a microwave discharge.[9]

Decomposition of carbon tetrachloride at reduced pressure over activated carbon at 1200–1350° has been carried out.[10,11] The preliminary report,[10] which disclosed the isolation of dichlorocarbene, was later corrected[11] to show that the dichlorocarbene reported was actually a mixture of dichloroacetylene and chlorine in equal molar amounts. The trichloromethyl radical was demonstrated to be the primary decomposition fragment, as is the case in the thermal decomposition of carbon tetrachloride under reduced pressure without a catalyst.[12,13] The mass spectral analysis of the particles from the decomposition of carbon tetrachloride

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