what higher compared to that of aromatic olefins with an open side chain.[10]

Evidence for the presence of a cyclobutene ring in II was provided by the infrared spectrum, which showed the following adsorption maxima (in cm.$^{-1}$; intensity: s, strong; m, medium; w, weak): 668 (w), 700 (s), 834 (w), 844 (w), 868 (m), 891 (m), 927 (w), 966 (w), 1002 (m), 1012 (m), 1037 (m), 1077 (m), 1138 (w), 1163 (w), 1188 (w), 1241 (w), 1271 (w), 1376 (e), 1461 (s), 1491 (w), 1508 (s), 1540 (w), 1575 (w), 1600 (w), 1612 (s), 1754 (w), 1813 (w), 1880 (w), 1960 (w), 2900 (m), 2970 (s), 3070 (m), 3130 (m).

As seen, the =C—H stretching absorption appears at 3130 cm.$^{-1}$, which is characteristic[11] for a cyclobutene without a substituent at the double bond (cyclobutene,[11] 3126 cm.$^{-1}$; 3-methylcyclobutene,[9] 3130 cm.$^{-1}$). Also, typically for a strained four-membered ring[11] the C=C stretching frequency is very low (1575 cm.$^{-1}$), as found in cyclobutene (1565 cm.$^{-1}$) and 3-methylcyclobutene (1566 cm.$^{-1}$). It is significant that apart from the band at 1575 cm.$^{-1}$ the spectrum of II contains a second weak band at 1600 cm.$^{-1}$, which is also observed in the spectrum of 3-methylcyclobutene.[9] The well-defined doublet exhibited by the latter compound (1566–1600 cm.$^{-1}$) seems to be characteristic for cyclobutenes with an alkyl or aryl substituent in the 3 position; a similar doublet has been observed at higher frequencies in the spectra of 3-alkylcyclopentenes[12] (1616–1650 cm.$^{-1}$) and 3-alkylcyclohexenes[13] (1650–1685 cm.$^{-1}$). The specific absorption pattern[14] in the 1700–2000-cm.$^{-1}$ range and the strong band at 700 cm.$^{-1}$ show that the benzene ring in II is monosubstituted.

Ozonation of II under the above conditions (see compound V) gave as the sole product (yield, 94%) a semisolid acid, which failed to crystallize from a number of solvents, including carbon tetrachloride. The acid contained two carboxylic groups, as determined by neutralization in alcoholic solution, and analyzed for the expected α-methyl-α′-phenylsuccinic acid.

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.20; H, 5.94.

Sources and Synthesis of Pure Hydrocarbons.—1,3-Diphenyl-2-methylpropane (III) and **1,3-diphenyl-2-methylpentane (VI)** were available from previous work.[15] **1-Phenyl-1,3-pentadiene** was synthesized by N. C. Sih of our laboratory.

1,5-Diphenyl-2-methylpentane.—This compound was synthesized through the Grignard reaction of 1-bromo-3-phenylpropane with phenyl-2-propanone. The intermediate carbinol, **1,5-diphenyl-2-methyl-2-pentanol**, b.p. 213–214° (18 mm.), n^{20}D 1.5568, was obtained in 64% yield. It was dehydrated over Harshaw alumina[15] at 330–340° and the resulting mixture of two double-bond isomers was hydrogenated at 150° and 120-atm. hydrogen pressure over chromia–alumina. After distillation the obtained 1,5-diphenyl-2-methylpentane was 99% pure, b.p. 126–127° (0.4 mm.), n^{20}D 1.5413.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.65; H, 9.31. Found: C, 90.53; H, 9.35.

1,4-Diphenyl-2,3-dimethylbutane (IV).—This compound was obtained by reacting an ethereal solution of 1-phenyl-2-chloropropane at reflux temperature with magnesium turnings. The chloride was prepared by reacting 1 mole of 1-phenyl-2-propanol dissolved in 1 mole of pyridine with 1.3 moles of thionyl chloride.

The 1,4-diphenyl-2,3-dimethylbutane obtained consisted of a 40:60% mixture of *erythro* and *threo* isomers, having retention times identical with the compound IV obtained from the dimerization of β-methylstyrene.

Analytical.—Preparative fractional distillation of reaction products was carried out at reduced pressure on a 20 cm. × 12 mm. column, filled with stainless steel wire gauze packing, or when necessary (*e.g.*, in the isolation of compound II) on a Piros–Glover spinning band column.

Quantitative analyses of product components, as well as of hydrogenation or ozonation products, were carried out by gas chromatography on a programmed temperature apparatus (F and M, Model 300). Several types of columns were used including (a) a 9-ft. column, filled with 10% silicone gum rubber on Chromosorb P; and (b) a 14-ft. column with 8% silicone (DC 550 fluid) on the same support. In the analysis of acids the liquid phase was silicone, containing 10% stearic acid.

N.m.r. spectra were measured on a Varian spectrometer.

Acknowledgment.—Thanks are due to Mr. Ed M. Lewicki for valuable laboratory assistance.

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Synthesis of 1-Butene-2,4-sultam

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The chlorosulfonylation of 1,4-dichlorobutane has been effected in refluxing sulfur dioxide solution to give 1,4-dichlorobutane-2-sulfonyl chloride. The latter has been converted to 4-chloro-1-butene-2-sulfonamide by treatment with triethylamine and ammonia, and the chlorobutenesulfonamide has been cyclized to 1-butene-2,4-sultam by treatment with alcoholic alkali. The sultam is a colorless, uncrystallizable oil which darkens on exposure to air and polymerizes on distillation at reduced pressure. Its crystalline N-benzenesulfonyl derivative melted at 134–135°. The sultam polymerized by Michael addition in the presence of strong base, giving a water-insoluble solid, m.p. 170–190°, [η] 0.08 dl./g. Preliminary investigation has indicated that the sultam can also polymerize by radical-initiated olefin addition and by sustained ring opening.

In a general study of the preparation and polymerization of aliphatic sultams,[2] we have examined the effect of an exocyclic double bond on the reactivity of the five-membered sultam ring. Although the literature contains no examples of simple methylene-substituted sultams, it seemed reasonable to suppose the chlorosulfonylation[3] of aliphatic dihalides would afford a synthetic route to unsaturated sultams by the transformations indicated below for the preparation of 1-butene-2,4-sultam (I).[4]

The attempted chlorosulfonylation of II by the method successfully applied to 1-chlorobutane by

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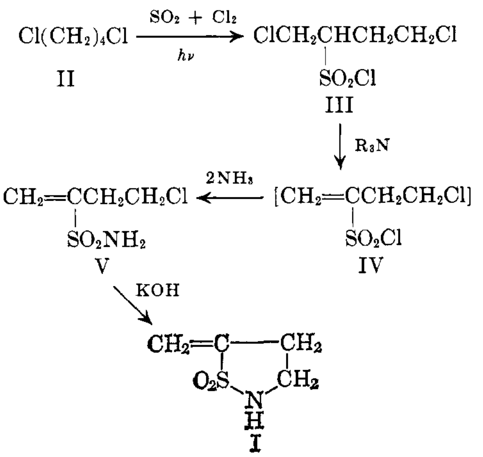
[2] (a) A. D. Bliss, W. K. Cline, C. E. Hamilton, and O. J. Sweeting, *J. Org. Chem.*, **28**, 3537 (1963); (b) A. D. Bliss, W. K. Cline, C. E. Hamilton, and O. J. Sweeting, *J. Polymer Sci.*, to be published.

[3] C. F. Reed, U. S. Patent 2,046,090 (June 30, 1936); *Chem. Abstr.*, **30**, 5593 (1936).

[4] We have followed the common practice of naming sultams as derivatives of the longest hydrocarbon chain to which both sulfur and nitrogen are attached [B. Helferich, K. Geist, and H. Plümpe, *Ann.*, **651**, 17 (1962), *q.v.*] rather than by the cumbersome and seldom-used heterocyclic nomenclature suggested in "The Naming and Indexing of Chemical Compounds from Chemical Abstracts," American Chemical Society, 1962, in which I would be named 5-methyleneisothiazolidine 1,1-dioxide.



Helberger, Manecke, and Fischer[5] led exclusively to the formation of chlorinated products, principally 1,2,4-trichlorobutane and some tetrachlorobutane. Similarly, the use of sulfuryl chloride with a pyridine catalyst in the presence of light[6] merely resulted in the chlorination of II. The preparation of III was effected by treating an illuminated solution of II in 3 moles of refluxing sulfur dioxide with a 1:1 mixture of chlorine and sulfur dioxide. The reaction could be catalyzed by benzoyl peroxide[7] or α,α'-azodiisobutyronitrile[8] in the presence of light, but the accelerating effect of these materials was short lived. The best catalyst for the reaction was an acetyl alkanesulfonyl peroxide generated *in situ* by initially adding acetic anhydride and benzoyl peroxide to the sulfur dioxide solution and passing in a small amount of oxygen with the mixture of sulfur dioxide and chlorine.[9]

Despite the high concentration of sulfur dioxide employed and the low temperature of the reaction, both factors which tend to favor chlorosulfonylation over chlorination,[6] III was formed in only 30% yield, the major product being a mixture of polychlorinated butanes. The symmetry of 1,4-dichlorobutane (II) and the effect of the two chlorine atoms in suppressing attack on the carbons to which they are attached[5] prevents the formation of monosulfonyl chlorides other than III. The yield of III could be increased by using still larger amounts of liquid sulfur dioxide, but the reaction then became very slow and excessive amounts of sulfuryl chloride were formed.

When the reaction was initiated in excess liquid sulfur dioxide, and chlorine alone was passed in, the rate of hydrogen chloride evolution increased as the reaction proceeded, as a result of the depletion of sulfur dioxide. The sulfonyl chlorides obtained under these conditions, unlike III, evolved both hydrogen chloride and sulfur dioxide and formed black tars upon attempted distillation at reduced pressure.

The reaction of III with ethereal ammonia resulted in a partial elimination of the chlorine in the 1-position and gave a 35% yield of 4-chloro-1-butene-2-sulfonamide (V) along with large amounts of what appeared to be polymeric aminoalkane sulfonamides. The infrared spectra of these products showed strong primary sulfonamide absorptions, but were distinctly different from that of poly-4-chloro-1-butene-2-sulfonamide prepared by treating a chloroform solution of V with benzoyl peroxide. The polymers were tentatively identified as condensation products of 1-amino-4-chlorobutane-2-sulfonamide (VI), which probably was formed by direct displacement of chlorine from the 1-position of 1,4-dichlorobutane-2-sulfonamide. Since V could be recovered unchanged after standing for 1 week at room temperature in an ethereal ammonia solution, VI and its condensation products cannot have arisen by the addition of ammonia to the double bond of V. This contrasts with the behavior of ethenesulfonamide, which has been shown to add ammonia readily.[10-12] It was found, however, that the stronger base, butylamine, did react slowly with V at room temperature, producing butylamine hydrochloride and probably also giving some addition to the double bond, although identification of the addition products was not certain. It appears possible to account for the by-products in the reaction of III with ammonia as condensation products of VI along with some products of addition of V and VI.

One mole of triethylamine reacted rapidly and quantitatively with III at 0° and presumably formed 4-chloro-1-butene-2-sulfonyl chloride (IV), in a manner analogous to the formation of ethenesulfonyl chloride from 2-chloroethanesulfonyl chloride and 2,6-lutidine.[12] The intermediate was not isolated, but was caused to react directly with 2 moles of ammonia to give V in a yield of 85%.

The cyclization of V occurred readily in dilute alcoholic solutions of alkali hydroxides, forming salt in 96% yield, a small amount of ether-insoluble gum, and a 90% yield of a colorless oil with the spectral characteristics of 1-butene-2,4-sultam (I). The oil resisted all attempts at crystallization and darkened rapidly upon attempted vacuum distillation. The material instantly decolorized acidic potassium permanganate solution and rapidly added bromine (neither reaction is shown by propanesultam or 1,4-butanesultam). The reaction of benzenesulfonyl chloride with a solution of the oil in aqueous sodium hydroxide gave a 91% yield of the crystalline N-benzenesulfonyl derivative, which also decolorized permanganate and added bromine. The nuclear magnetic resonance spectrum of the N-benzenesulfonyl derivative showed resonances at 5.7 and 6.0 p.p.m. (from internal tetramethylsilane standard) proving the presence of the exocyclic methylene group. The sultam ring protons on C-3 gave a resonance at 2.95 p.p.m. and those on C-4 at 3.68 p.p.m. The protons of the aromatic ring were in the normal position for a sulfone. There was also an indication that a small amount of the isomeric N-benzenesulfonyl-2-butene-2,4-sultam was present. Resolution was not sufficiently high to permit quantitative estimation of the amount, but it could not have exceeded 4%.

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(8) Soc. Anon. des Manufactures des Glaces et Produits Chimiques de Saint-Gobain, French Patent 1,023,736 (March 23, 1953); *Chem. Abstr.*, **52**, 5459 (1958).

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(10) A. S. Matlack, *J. Org. Chem.*, **23**, 729 (1958).

(11) A. A. Goldberg, *J. Chem. Soc.*, 464 (1945).

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When the cyclization of V was run in solutions more concentrated than about 0.5 *M*, substantial amounts of a solid, water-insoluble polymeric material formed. The same polymer could be prepared by treatment of an alcohol solution of I with catalytic amounts of alkalies or sodium alkoxides or by the bulk polymerization of I with a sodium hydride catalyst. The infrared spectra of these polymers showed strong SO_2 absorptions, but no NH or unsaturation. The spectrum, the mode of formation, and the analysis of the material strongly suggested that it was a polymer formed by the sustained Michael addition of I. Breslow, Hulse, and Matlack[13] have shown that this type of polymerization can occur with ethenesulfonamide, acrylamide, and other materials which, like I, contain an activated double bond and an acidic function.

Very cursory investigation has indicated that I can polymerize by ring opening under the same conditions as propanesultam[2,14] and by radical-initiated olefin addition as well as by sustained Michael addition.

Experimental

1,4-Dichlorobutane-2-sulfonyl Chloride (III).—A 500-ml., three-necked flask, fitted with a stirrer, Dry Ice reflux condenser, gas inlet tube, and drying tube was cooled by means of a Dry Ice–acetone bath and charged with approximately 135 ml. (3 moles) of anhydrous sulfur dioxide. To this was added 127 g. (1.0 mole) of 1,4-dichlorobutane (Eastman White Label), 5.0 ml. of acetic anhydride, and a small amount of benzoyl peroxide.[9] The mixture was stirred, allowed to reflux, illuminated with a 500-w. incandescent lamp placed approximately 3 in. from the flask, and treated with a gaseous mixture of oxygen (20 ml./min.), sulfur dioxide (190 ml./min.), and chlorine (190 ml./min.). Reaction started immediately and hydrogen chloride was evolved.

By passing the exit gas through a Dry Ice trap and then into a known amount of standard alkali, it was estimated that 1 mole of hydrogen chloride would be evolved in 2.75 hr. (1.3 moles of chlorine); the chlorine and sulfur dioxide were shut off at the end of that time, but oxygen input and illumination were continued. Hydrogen chloride continued to evolve for about 10 min. and then stopped abruptly. The oxygen flow and the illumination were interrupted and the liquid sulfur dioxide was allowed to evaporate. Dissolved gases and most of the sulfuryl chloride produced were removed at room temperature and 50-mm. pressure. The residue, which weighed 200.7 g., was distilled at a pressure of 13 mm. The distillation produced 27.6 g. of sulfuryl chloride (which passed into the Dry Ice trap), 97.0 g. of a chlorinated butane mixture boiling over the range 29–43°, 63.5 g. of a sulfonyl chloride boiling at 99–100°, and 7.9 g. of black, tarry residue. The chlorinated butane fraction was found by vapor phase chromatography and infrared spectroscopy to contain 0.15 mole of 1,4-dichlorobutane, approximately 0.5 mole of 1,2,4-trichlorobutane, and a small amount of an unidentified higher boiling component. The sulfonyl chloride fraction was redistilled at 12.5 mm., yielding 6.5 g. boiling at 95–98°, 37.6 g. boiling at 98.0–98.3°, 11.3 g. boiling at 98.3–100.0°, and 6.1 g. of brown liquid residue. The center cut was shown by vapor phase chromatography to consist of a single major component. The detection of minor constituents was not possible because of some decomposition of the material on the chromatographic column. Infrared and nuclear magnetic resonance spectroscopy identified the material as III. Principal infrared absorptions (μ) were 3.30 (w), 3.38 (w), 6.87 (m), 6.95 (m), 7.25 (vs), 7.55 (w), 7.70 (m), 7.80 (w), 8.20 (m), 8.61 (vs), 12.4 (m), 13.1 (m), 13.6 (m), 14.2 (m), and 14.8–15.0 (m).

The nuclear magnetic resonance spectrum showed resonances (from internal tetramethylsilane standard) at 4.05 (multiplet) for the protons of C-1, 4.2 (multiplet) for the methine, 2.65 for the C-3 methylene, and 3.78 p.p.m. (multiplet) for the C-4 methylene.

Anal. Calcd. for $C_4H_7Cl_3O_2S$: C, 21.30; H, 3.13; Cl, 47.16. Found: C, 21.57; H, 3.33; Cl, 48.96, 48.14.

4-Chloro-1-butene-2-sulfonamide (V).—A solution of 5.0 g. (22 mmoles) of III in 100 ml. of anhydrous ether was cooled in ice and treated with 2.2 g. (22 mmoles) of triethylamine in 20 ml. of ether. A white precipitate formed immediately. The mixture was allowed to warm to room temperature and filtered. The solid, washed with ether and dried, 3.0 g. (100%), melted at 251–253°, unchanged on admixture with authentic triethylamine hydrochloride. The filtrate, which had the characteristic odor of a sulfonyl chloride, was again cooled in an ice bath and treated with anhydrous ammonia until it became basic. A white solid was removed by filtration, washed with ether, dried, and found to weigh 1.4 g. (The calculated quantity of ammonium chloride is 1.2 g.) The extraneous material was not identified. Ether was removed from the filtrate at reduced pressure, yielding a slightly yellow oil, which did not completely redissolve in 50 ml. of anhydrous ether. The solution was decanted from 0.5 g. of viscous yellow oil, treated with decolorizing carbon, and filtered. The colorless filtrate was treated with petroleum ether (b.p. 30–60°) to faint turbidity and chilled, producing 3.2 g. (85%) of a white crystalline compound which melted at 67–68°.[15] Two recrystallizations from mixed ether and petroleum ether raised the melting point to 68–69°. The substance was identified as V by infrared spectroscopy and elemental analysis. Principal infrared absorptions (μ) were 2.90 (s), 3.00 (s), 3.18 (m), 3.33 (m), 6.45 (s), 6.85 (m), 6.98 (m), 7.60 (vs), 8.45 (m), 8.70 (vs), 8.80 (vs), 10.5 (s), 11.0 (s), 11.7 (m), 13.2 (s), and 14.3–15 (s).

Anal. Calcd. for $C_4H_8ClNO_2S$: C, 28.32; H, 4.75; N, 8.26; Cl, 20.90. Found: C, 28.46; H, 4.87; N, 8.15; Cl, 21.20.

1-Butene-2,4-sultam (I).—To a solution of 9.203 g. (54.3 mmoles) of V in 50 ml. of anhydrous methanol containing 0.2 g. of N,N-dimethylaniline, was added a solution of 2.173 g. (54.3 mmoles) of sodium hydroxide in 50 ml. of methanol. An intense yellow color developed immediately, but faded to pale yellow within 1 min. After the solution had refluxed for 2 hr., bumping caused by precipitated salt became severe and the mixture was cooled and filtered. The salt was washed with 20 ml. of methanol and the filtrate and washings were combined and again refluxed. After a total of 8 hr. at reflux, the solution had become neutral and was cooled and filtered. The filtrate was evaporated at reduced pressure, leaving a yellow oil and a substantial amount of salt. The oil was dissolved in 15 ml. of anhydrous ethanol and filtered. The combined salt residues from all of the operations were dried and found to weigh 3.026 g. (95.7%). The ethanol filtrate was treated with ether to faint turbidity and chilled, but only a small amount of dark yellow gum separated. The solution was decanted and evaporated *in vacuo* to a yellow oil, which weighed 6.61 g. (91.4%). Treatment of an ethanol solution of the oil with decolorizing carbon gave, on evaporation of the alcohol, 6.35 g. of a colorless oil which resisted all attempts at crystallization and darkened and became viscous on attempted distillation at 0.8 mm. The oil instantly decolorized permanganate and rapidly added bromine. Upon exposure to the atmosphere, it slowly developed a reddish color. It was identified as I on the basis of its infrared spectrum and elemental analysis. Principal infrared absorptions (μ) were 3.05 (vs), 3.25 (m), 3.37 (m), 3.43 (m), 6.12 (w), 6.50 (w), 6.68 (m), 6.80 (m), 7.05 (s), 7.30 (s), 7.7 (vs), 8.60 (vs), 8.9 (vs), 9.65 (s), 10.0 (s), 10.4 (s), 10.75 (s), 11.4 (m), and 13.2 (b).

Anal. Calcd. for $C_4H_7NO_2S$: C, 36.07; H, 5.30; N, 10.52. Found: C, 36.30, 36.25; H, 5.74, 5.65; N, 10.84.

N-Benzenesulfonyl-1-butene-2,4-sultam.—To a solution of 1.4 g. (0.01 mole) of 1-butene-2,4-sultam in 20 ml. of water was added 0.8 g. (0.02 mole) of sodium hydroxide and 3.5 ml. (0.02 mole) of benzenesulfonyl chloride. The mixture was stirred for 6 hr. at room temperature. A substantial amount of white solid was removed by filtration and washed three times with 20-ml. portions of water and six times with 20-ml. portions of ethanol. The odorless, neutral product was dissolved in acetone, treated with charcoal to remove a slight yellow color, and filtered. Evaporation of the filtrate gave 2.5 g. (91%) of white crystals melting at 133–134°. Three recrystallizations from ethanol raised the melting point to 134–135°. The material rapidly decolorized aqueous acidic permanganate and slowly added bromine. Its

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[13] D. S. Breslow, G. E. Hulse, and A. S. Matlack, *J. Am. Chem. Soc.*, **79**, 3760 (1957).

[14] W. H. Libby, U. S. Patent 2,983,713 (May 9, 1961).

[15] In the first preparation of this compound, a different crystalline modification (needles) melting at 53.0–53.5° was obtained. This changed spontaneously to the higher melting form (without alteration of its spectrum or analysis) and was never obtained again.

infrared spectrum showed no NH absorptions. The nuclear magnetic resonance spectrum showed resonances (from internal tetramethylsilane standard) at 2.95, 3.68, 5.7, and 6.0 p.p.m. The protons of the aromatic ring were in the normal position for a sulfone.

Anal. Calcd. for $C_{10}H_{11}NO_4S_2$: C, 43.94; H, 4.06; N, 5.13. Found: C, 44.06; H, 4.02; N, 5.11, 5.13.

Ammoniation of the Products of Chlorosulfonylation of 1,4-Dichlorobutane.—The total reaction mixture from the chlorosulfonylation of 1 mole of II, after removal of dissolved gas and sulfuryl chloride, was dissolved in 1 lb. of anhydrous ether and filtered. The yellow filtrate was diluted with another pound of ether and placed in a 3-l. flask fitted with stirrer, thermometer, gas inlet tube, and calcium chloride drying tube. The solution was cooled to −10° with an ice–salt bath and treated with anhydrous ammonia at the rate of 250 ml./min. After a 1.3-mole addition of ammonia, the mixture became basic. Filtration and vacuum-drying yielded 90.4 g. of white solid, which was extracted with 500 ml. of hot ethanol, then with 500 ml. of hot acetone. The residue (66 g.) was shown by chloride analysis and vacuum sublimation of an aliquot to contain 54 g. (1.0 mole) of ammonium chloride, 12 g. of a polymeric solid (m.p. 150–170° to a viscous melt) which showed strong sulfonamide absorptions in the infrared, and a trace of an ammonium alkanesulfonate (barium nitrate precipitation). Evaporation of the alcohol–acetone extract gave 24 g. of dark oil which, except for about 1 g. of gum, dissolved readily in petroleum ether, had a strong odor of chlorinated butane, and gave a very poorly resolved infrared spectrum that showed no SO_2 absorptions. The ether filtrate of the reaction products, which after standing overnight at room temperature had deposited a small amount of yellow gum, was decanted and evaporated at reduced pressure to a yellow oil. The oil was washed three times by decantation with 250-ml. portions of petroleum ether. Evaporation of the petroleum ether extracts gave 85 g. of a mixture of chlorinated butanes, which showed no sulfonyl absorptions in the infrared. The residue from the extraction, 51.2 g., left a small gummy residue when treated with ether. The ether solution was decanted, treated with petroleum ether to faint turbidity, and chilled, which caused the separation of a dark yellow viscous oil. The solution was decanted, again treated with petroleum ether to turbidity, and cooled, whereupon a light yellow, fluid oil separated. Another repetition of this treatment gave 26 g. of yellow crystalline solid melting at 61–64°. Treatment of an ether solution of the material with decolorizing carbon and two recrystallizations from ether–petroleum ether gave 19 g. of white plates melting at 68–69°,[15] identified as V by infrared spectroscopy, elemental analysis, and mixture melting point. The spectra of the oily products were very similar to that of the crystalline sulfonamide.

Anal. Calcd. for $C_4H_8ClNO_2S$: C, 28.32; H, 4.75; N, 8.26; Cl, 20.90. Found: C, 28.40; H, 4.63; N, 8.31; Cl, 21.14.

Ammoniation of 1,4-Dichlorobutane-2-sulfonyl Chloride.—A solution of 10.05 g. (0.04 mole) of III in 100 ml. of ether was added slowly to an ice-cold mixture of 10 ml. of concentrated aqueous ammonia and 100 ml. of ether. Upon completion of the vigorous reaction, a small amount of water was added to the mixture to dissolve a white solid, and the layers were separated. A gummy white precipitate appeared during the drying of the ether layer over magnesium sulfate. The solution was filtered and evaporated at reduced pressure to 7.1 g. of colorless oil. Ether then dissolved only about half of this material. The solution was decanted, treated with petroleum ether to faint turbidity, and chilled, giving 2.8 g. of sticky white crystals. Recrystallization from mixed ether and petroleum ether gave 2.4 g. (35%) of a crystalline solid melting at 68–69°, unchanged on admixture with authentic V. Infrared examination showed the ether-insoluble oil to be a sulfonamide with a spectrum very similar to that of the crystalline material.

Treatment of V with Ammonia.—To a mixture of 1.5 ml. of concentrated aqueous ammonia and 10 ml. of ether was added 0.5 g. of V in 5 ml. of ether. The mixture was allowed to stand at room temperature for a week. The ether solution was then dried over magnesium sulfate, filtered, and evaporated, yielding 0.5 g. of white crystalline solid melting at 68–69°, unchanged on admixture with the starting material.

Treatment of V with Butylamine.—A solution of 0.5 g. of V in 10 ml. of ether was treated with 0.5 ml. of anhydrous butylamine and allowed to stand at room temperature for 4 days. The ether was decanted from a sticky white solid and evaporated to a colorless oil. The material oiled out of solutions of ether and petroleum ether upon cooling and did not crystallize when seeded with V. Its infrared spectrum showed a broad, poorly resolved absorption in the 2.95–3.10-μ region which was interpreted as a combination of amine N–H and sulfonamide N–H bonds.

Polymerization of V.—A solution of 1.0 g. of V in 5 ml. of chloroform was treated with a small amount of benzoyl peroxide and warmed on the steam bath. After about 5 min., a white precipitate began to appear. After 2 hr., the solution was cooled and filtered, giving 0.2 g. of slightly yellow solid which gave a viscous melt at 170–180°. The material was soluble in water, slightly soluble in alcohol, and insoluble in ether. Its infrared spectrum showed strong primary sulfonamide peaks, carbon–chlorine absorptions, and no definite indications of unsaturation. The spectrum was distinctly different, particularly in the 2.95–3.10-μ region, from the spectra of the polymeric sulfonamides obtained by the ammoniation of III.

Polymerization of I. A.—A solution of 5.0 g. of I in 50 ml. of chloroform was treated with a small amount of benzoyl peroxide and warmed on the steam bath. A white precipitate appeared after about 1 min., but apparently stopped coming out after approximately 5 min. The addition of more catalyst caused more solid to form, but the reaction again stopped after a few minutes. The solution was cooled and filtered, giving 0.5 g. of a light tan solid which gave a viscous melt at 190–210°. The infrared spectrum resembled that of I except for the absence of the double bond absorption at 6.10 μ and some differences in the 10.5–11.5-μ region. Its intrinsic viscosity in dimethyl sulfoxide solution was 0.04 dl./g.

B.—To a solution of 2.0 g. of I in 20 ml. of anhydrous ethanol was added 1 drop of N,N-dimethylaniline and 2 drops of a 2% solution of sodium ethoxide in ethanol. After 2 hr. at reflux, the mixture was cooled and filtered to remove a gummy white solid. The solid was washed with water and dried, yielding 0.5 g. of white powder which melted at 170–190°. Short, brittle fibers could be pulled from the viscous melt. The polymer had an intrinsic viscosity of 0.06 dl./g. in dimethyl sulfoxide. Its infrared spectrum showed strong sulfonyl absorptions, but no NH peaks and no unsaturation. The water-soluble portion of the reaction product was a viscous oil with weak sulfonamide NH absorptions in its infrared spectrum. Principal infrared absorptions (μ) were 3.31 (m), 3.45 (m), 6.91 (m), 7.28 (m), 7.75 (s), 8.02 (m), 8.50 (m), 8.84 (s), 9.70 (m), and 13.2–13.4 (s).

Anal. Calcd. for $C_4H_7NO_2S$: C, 36.07; H, 5.30; N, 10.52. Found: C, 35.71, 35.75; H, 5.39, 5.36; N, 10.11, 10.13.

C.—A small test tube was charged with 2.0 g. of I. The liquid was purged with dry nitrogen and heated to 127° for 30 min. To the hot sultam was then added 5 mg. of sodium hydride, and the mixture was allowed to react under nitrogen at 127° for 18 hr. The viscous brown liquid product was cooled and treated with 20 ml. of cold water. A yellow, granular solid was removed by centrifugation, washed five times with water and twice with acetone, and dried *in vacuo*. The material weighed 0.62 g. (30%), melted at 175–90°, and had an infrared spectrum identical with that of the polymer prepared in the preceding experiment. Its intrinsic viscosity in dimethyl sulfoxide was 0.08 dl./g. The water-soluble portion of the product was a yellow gum.

Formation of a Polymer of 1-Butene-2,4-sultam from 4-Chloro-1-butene-2-sulfonamide.—To a solution of 5.1 g. (0.03 mole) of V in 15 ml. of anhydrous ethanol containing 1 drop of N,N-dimethylaniline was added a solution of 1.2 g. (0.03 mole) of sodium hydroxide in 15 ml. of ethanol. The solution was refluxed for 3 hr.; it was then very weakly basic. A sudden precipitation of slightly gummy white solid ensued and continued for about 30 min. The mixture was cooled and filtered to give, after drying *in vacuo*, 3.75 g. of sticky white solid. This material, extracted three times with 20-ml. portions of water and twice with 20-ml. portions of ethanol, and dried *in vacuo*, weighed 1.2 g., melted at 170–90°, had an intrinsic viscosity of 0.07 dl./g. in dimethyl sulfoxide, and an infrared spectrum identical with those of the polymers prepared by the treatment of I with catalytic amounts of base. The alcoholic filtrate of the reaction products was evaporated at reduced pressure to a yellow oil. Extraction of the oil with ether left 0.7 g. of viscous dark yellow liquid. The ether extract was treated with decolorizing carbon and evaporated at reduced pressure to 1.3 g. (32%) of a colorless oil with an infrared spectrum identical with that of the 1-butene-2,4-sultam previously prepared.

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A Convenient, New Synthesis of *p*-Sexiphenyl from Biphenyl or *p*-Terphenyl in the Presence of Lewis Acid Catalyst–Oxidant[1]

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p-Sexiphenyl can be prepared in improved yield by a simple, one-step procedure involving treatment of biphenyl with aluminum chloride–cupric chloride, ferric chloride, or molybdenum pentachloride. Small amounts of *p*-quaterphenyl and higher molecular weight products were also formed. Under similar conditions, *p*-terphenyl yielded predominantly the dimer-type product, *p*-sexiphenyl. In attempted copolymerization of biphenyl and *p*-terphenyl, the main product obtained was *p*-sexiphenyl. Cuprous chloride proved to be a very effective inhibitor in the biphenyl–aluminum chloride–cupric chloride system. Studies were made of the relative rates of reaction for the monomers, benzene, biphenyl, and *p*-terphenyl, based on hydrogen chloride evolution. The theoretical aspects are discussed.

Aromatic hydrocarbons in the *p*-polyphenyl series have attracted considerable attention because of their good thermal stability, high melting points, insolubility, electronic configuration, and the interest in them as moderators in nuclear reactors. Previously, the individual, higher, isolable *p*-polyphenyls have usually been prepared by classical methods, such as the Ullmann coupling, Fittig reaction, or the Grignard synthesis. However, these routes suffer from one or more of the following limitations: very low yields, necessity of drastic conditions, tedious purifications, difficulties in reproducing results, multistep syntheses from the aromatic hydrocarbon precursor, and the formation of gross mixtures due to competing reactions.

Since our work is primarily concerned with *p*-sexiphenyl, discussion of the prior literature will be limited to this homolog. For example, in the Ullmann synthesis from 4-iodo-*p*-terphenyl and silver powder at 330°, Pummerer and Bittner[3] remarked on the difficulty of effecting condensation. Subsequently, this method was applied to a mixture of 4-iodobiphenyl, 4,4′-diiodobiphenyl, and copper powder, which provided a 25% yield based upon the iodo aromatics.[4a] In a modified version, Kuhn[4b] obtained *p*-sexiphenyl by zinc–acetic acid reduction of the product derived from 4,4′-diiodobiphenyl and copper. More recently,[5] Nozaki and co-workers[6] also investigated the Ullmann procedure with 4-iodo-*p*-terphenyl and reported a 10% yield based upon the *p*-terphenyl precursor in this multistep synthesis. In connection with their studies of *p*-polyphenyls and the corresponding methylated derivatives, Kern and Wirth[7] utilized the Ullmann and Grignard reactions for preparative purposes. In addition, the catalytic reduction of *p*-dibromobenzene in the presence of methanol afforded a gross mixture from which *p*-sexiphenyl was isolated in 0.7% yield.[8]

The objective of the present work was to effect the nuclear coupling of biphenyl and of *p*-terphenyl by treatment with a Lewis acid catalyst and oxidant, and to investigate the theoretical aspects.

Results and Discussion

We have succeeded in synthesizing *p*-sexiphenyl in good yield and high purity by a novel, one-step procedure involving biphenyl–Lewis acid catalyst–oxidant. Inexpensive, readily available starting materials are used. Under mild conditions, biphenyl was converted to the trimer-type product on treatment with aluminum chloride–cupric chloride, ferric chloride, or molybdenum pentachloride. Minor amounts of higher *p*-polyphenyls were formed, as well as small quantities of *p*-quaterphenyl. The isolated products were characterized by comparison with authentic materials (melting points and ultraviolet and infrared spectra). Apparently, the formation of *p*-sexiphenyl from biphenyl–aluminum chloride–cupric chloride proceeds as indicated below.

$$3\ \text{biphenyl} + 4\text{CuCl}_2 \xrightarrow{\text{AlCl}_3} p\text{-sexiphenyl} + 4\text{CuCl} + 4\text{HCl}$$

This transformation resembles the synthesis of bimesityl from mesitylene and ferric chloride.[9] Furthermore, analogy may be drawn to the conversion of benzene to *p*-polyphenyl,[10-12] except that the product from biphenyl is of much lower molecular weight.

The biphenyl reaction was investigated at some length with the aim, in part, of determining the optimum conditions for *p*-sexiphenyl formation (Table I). We found that the reaction, which proceeded with good rapidity, was quite sensitive to changes in the $AlCl_3$–$CuCl_2$ molar ratio. The yield of *p*-sexiphenyl attained a maximum

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[1] Paper VII: "Polymerization of Aromatic Nuclei," from the Ph.D. Thesis, 1964, of R. M. Lange, Case Institute of Technology; presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

[2] Department of Chemistry Fellow, Case Institute of Technology, 1962–1963.

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[5] NOTE ADDED IN PROOF.—J. A. Cade and A. Pilbean [*J. Chem. Soc.*, 114 (1964)] report a 29% yield (crude) of *p*-sexiphenyl from *p*-terphenyl *via* treatment of 4-bromo-*p*-terphenyl with butyllithium.

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