Discussion

The first isomerization experiment on *p*-bromochlorobenzene showed that there was halide exchange with the catalyst, disproportionation, and isomerization. The nature of disproportionation products depended on the reaction temperature. At reflux (*ca.* 175°) polybromochlorobenzene tars were formed in contrast to relatively pure dibromochlorobenzene formed at temperatures below 155°. Experimental conditions were selected to give a rapid rate of isomerization without tar formation. Equilibrium was approached by isomerizing each pure isomer to ensure accurate values. Any experiment having less than 95 mole % product accounting was repeated to minimize experimental error. The equilibrium mixture so obtained had an average composition of 3.1% *o*-, 63.4% *m*-, and 33.5% *p*-bromochlorobenzene. The equilibrium composition calculated from Run 10 data was 3.7% *o*-, 63.4% *m*-, and 32.9% *p*-bromochlorobenzene, and is in good agreement with the average.

The last experiment in Table II was sampled periodically during isomerization. The composition of each sample was determined and these data are shown in Table IV. The isomer distribution obtained in this experiment was 4.1% *o*-, 63.3% *m*-, and 32.6% *p*-bromochlorobenzene.

TABLE IV
ISOMERIZATION RATE DATA OF BROMOCHLOROBENZENE
Catalyst, Al_2Cl_6: temp. 110°

	Wt. % composition			
		Bromochlorobenzene		
	Chlorobenzene	*o*-	*m*-	*p*-
Charge start heating	19.1	12.1	4.0	64.8
0 min. at temp.	21.5	7.4	27.8	43.3
15	21.8	4.5	43.6	30.1
30	21.6	3.7	46.5	27.2
60	20.8	3.4	48.7	27.1
120	21.4	3.5	49.4	25.7
240	21.2	3.5	49.3	26.0
Cool to 25° during 18 hr.	20.3	3.3	50.4	26.0

The disproportionation products obtained as a residue by distillation of the combined product from the first 9 runs partly crystallized at room temperature. The solid was separated and purified by crystallization from methanol. It was characterized as 1,3-dibromo-5-chlorobenzene by infrared. Its melting point was 95.0–96.0 (reported m.p. 96°; 99.5°)[12] and its identity was further confirmed by elemental analysis. The liquid fraction was determined by infrared spectrum to be a mixture of the three dibromochlorobenzenes having 1,2,4-substitution. The 1,3,5-isomer accounted for 76.7% of the dibromochlorobenzene disproportionation product. No bromochlorobenzenes were detected.

Disproportionation was reduced in an amount predicted by the law of mass action, by the use of chlorobenzene as solvent in replicate isomerizations. Fairbrother and Scott[3] reported 17% disproportionation at the equilibrium. In this work we obtained 15–18% indicating probable approach to equilibrium ($K_{eq} = 0.09$).

Bromine-chlorine exchange occurred during the isomerization of *p*-bromochlorobenzene with water promoted aluminum chloride catalyst, to the extent of 2 mole % on the organic or 20 mole % on the catalyst. No exchange was observed during the isomerization of *o*- or *m*-bromochlorobenzene under identical conditions. Anhydrous aluminum chloride gave no halogen exchange even with the *para* isomer.

It is of interest to compare this isomerization with that of dichlorobenzene. Bromochlorobenzene can be isomerized, without special purification, to equilibrium composition using aluminum chloride with or without water promotion at temperatures as low as 100°. Dichlorobenzene does not isomerize to any extent using anhydrous aluminum chloride at 175°. However, at a temperature of 250° isomerization to equilibrium is obtained, even when technical grade dichlorobenzene is used. When water promoted aluminum chloride catalyst is used, equilibrium isomerization is obtained at 175° provided the dichlorobenzene is pure. The degree of isomerization of dichlorobenzene is very closely related to the trace amount impurities in the dichlorobenzene.

Reaction of Isobutyraldehyde and 2-Ethylhexaldehyde with Ammonium Sulfide. Reductive Thiolation

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The recent report of Harris and Sheppard[2] concerning the reductive thiolation of fluorocarbon carbonyl compounds prompts us to report our results regarding a similar reaction of isobutyraldehyde and 2-ethylhexaldehyde with ammonium sulfide.

The catalytic reductive thiolation of aldehydes and ketones has been investigated[3] and is reported to be effected only in the presence of sulfactive catalysts.[2] Under Willgerodt conditions,[4,5] cyclohexanone is transformed into cyclohexanethiol and

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dicyclohexyl disulfide.[6] Acetophenone is converted into di(α-phenylethyl) disulfide by ammonium polysulfide[7] and acetone into diisopropyl di-, tri-, and polysulfides by the action of hydrogen sulfide alone.[8] Thiols have also been postulated as intermediates in the Willgerodt reaction.[9]

Somewhat surprisingly, in the present investigation, the action of aqueous ammonium sulfide at 150° on both isobutyraldehyde and 2-ethylhexaldehyde produced considerable quantities (45 and 23%) of the respective thiols. Dialkyl di- and trisulfides accounted for the greater part of the remaining reaction products. That a reduction predominates, rather than the anticipated oxidation, can be assumed because of the relatively low ammonium polysulfide content of the reaction mixture as compared to the concentrations used in the Willgerodt reaction. Considerable variation in the ratio of thiol : disulfide : trisulfide isolated was frequently observed and may be caused by "minor" changes in the sulfide concentration and/or subtle differences in the work-up procedure, since all three products apparently can be in mutual equilibrium[9,10] in the presence of hydrogen sulfide and ammonia.

Experimental

Reaction of Isobutyraldehyde with Ammonium Sulfide.—A solution of 252 g. (7.9 moles) of hydrogen sulfide in 900 ml. (13.3 moles) of 28% aqueous ammonium hydroxide was charged, along with 144 g. (2 moles) of isobutyraldehyde, into a 3-l. stainless steel autoclave. The mixture was heated, with rocking, at 150° under autogenous pressure for 3.5 hr. and then cooled to 25°. Ether extraction of the reaction mixture followed by fractionation of the extracts yielded the following: (A) 80 g. (45%) of isobutyl mercaptan, b.p. 87°, n^{30}_{D} 1.4340; (B) 31 g. (18%) of diisobutyl disulfide, b.p. 60–75° (4.0 mm.), n^{30}_{D} 1.4882; (C) 9 g. (4%) of diisobutyl trisulfide, b.p. 86–92° (2.5 mm.), n^{30}_{D} 1.5215. The structure of A was confirmed by comparison of its physical properties to those of an authentic sample, b.p. 88°, n^{30}_{D} 1.4345, and the identity of the infrared spectra of the two.

From another experiment in which the mercaptan was not isolated there was obtained 65 g. (37%) of diisobutyl disulfide, b.p. 49–51° (0.45 mm.), n^{30}_{D} 1.4822, and 58 g. (27%) of diisobutyl trisulfide, b.p. 65–75° (0.3 mm.), n^{30}_{D} 1.5129–1.5219. Redistillation of the disulfide afforded pure material, of b.p. 55° (0.5 mm.), n^{30}_{D} 1.4822, which was found to be identical to an authentic sample, b.p. 43° (0.25 mm.), n^{30}_{D} 1.4819, prepared by the iodine oxidation of isobutyl mercaptan.

Anal. Calcd. for $C_8H_{12}S_2$: C, 53.91; H, 10.18; S, 35.91. Found: C, 53.91; H, 9.89; S, 35.80.

The structure of the trisulfide is based on its elemental analysis and infrared spectrum. A purified sample was obtained as a slightly yellow liquid, b.p. 70° (0.3 mm.), n^{30}_{D} 1.5219.

Anal. Calcd. for $C_8H_{16}S_3$: C, 45.70; H, 8.63; S, 45.67. Found: C, 46.00; H, 8.46; S, 45.42.

Reaction of 2-Ethylhexaldehyde with Ammonium Sulfide.—In the manner described for the preceding reaction of isobutyraldehyde, 258 g. (2 moles) of 2-ethylhexaldehyde was treated with a solution of 248 g. (7.3 moles) of hydrogen sulfide in 900 ml. (13.3 moles) of 28% aqueous ammonium hydroxide. The reaction products were isolated similarly to give the following: (A) 67 g. (23%) of 2-ethylhexyl mercaptan, b.p. 78–82° (20 mm.) n^{30}_{D} 1.4512; (B) 161 g. (55%) of di(2-ethylhexyl) disulfide, b.p. 144–146° (1.5 mm.), n^{30}_{D} 1.4820; and (C) 48 g. of higher sulfides 15% calculated as di(2-ethylhexyl) trisulfide, b.p. 155–181° (1.5–3.0 mm.), n^{30}_{D} 1.5075. Redistillation of A afforded the mercaptan as a colorless liquid, b.p. 67° (10 mm.), n^{30}_{D} 1.4512 [reported,[3] b.p. 74–80 (19 mm.), n^{25}_{D} 1.4541].

Anal. Calcd. for $C_8H_{18}S$: C, 65.68; H, 12.40; S, 21.92. Found: C, 65.75; H, 12.31; S, 21.71.

The disulfide fraction B was redistilled to give a pure sample as a slightly yellow liquid, b.p. 168° (5 mm.), n^{30}_{D} 1.4833.

Anal. Calcd. for $C_{16}H_{34}S_2$: C, 66.13; H, 11.79; S, 22.07. Found: C, 66.01; H, 11.78; S, 22.35.

Fraction C could not be further purified by distillation. The material decomposed at 200° (2–3 mm.) into 2-ethylhexyl mercaptan and a nonvolatile residue.

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A Diene–Retrodiene–Diene Reaction. The Synthesis of 2,3,5,6-Tetrakis(trifluoromethyl)-7-oxabicyclo[2.2.1]-2,5-heptadiene

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In connection with studies on the activity of 3,4-dicyanofuran as a diene component and the retrogressive cleavage of its adducts,[1] we deemed it of interest to investigate the reaction between 3,4-dicyanofuran and hexafluoro-2-butyne as a dienophile to obtain 2,3-bis(trifluoromethyl)-5,6-dicyano-7-oxabicyclo[2.2.1]-2,5-heptadiene (I). Its retrodiene fission may occur with the predominant formation of either dicyanoacetylene or hexafluoro-2-butyne as products of the cleavage together with the corresponding furan derivatives.

The two components were unaffected by heating them together at 140° over a twenty-four-hour period in a sealed tube. A reaction occurred, however, on raising the temperature to 160° and yielded 2,3,5,6-tetracyano-7-oxabicyclo[2.2.1]-2,5-heptadiene (IV) and 2,3,5,6-tetrakis(trifluoromethyl)-7-oxabicyclo[2.2.1]-2,5-heptadiene (V) as the only products. They could be separated easily

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