

Fig. 3.—Heats of mixing in calories per mole of solution for the systems: chloroform with polyfluoro alkyl ethers.

The results obtained on mixing chloroform with the methyl, ethyl and *n*-propyl derivatives of 1,1,2-trifluoro-2-chloroethyl alkyl ethers are shown in Fig. 3 and Table I gives the heats of mixing per mole of solution at a mole fraction of 0.5.

TABLE I
HEATS OF MIXING OF 1,1,2-TRIFLUORO-2-CHLOROETHYL ALKYL ETHERS WITH CHLOROFORM AT 0°

Ether	ΔH , cal./mole
Methyl	93 = 3
Ethyl	62 = 4
<i>n</i> -Propyl	52 = 3

The isopropyl derivative gave heat effects of the same magnitude as the normal compound. Sufficient material was not on hand for quantitative study. In contrast to the behavior shown by diethyl ether and acetone, the heats of mixing were small and positive. The slight cooling effect produced indicates the lack of formation of hydrogen bonds, at least in large numbers.

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RECEIVED FEBRUARY 9, 1948

The Structure of Dioxadiene Dibromide

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Some time ago dioxadiene was found to react with only one molar equivalent of bromine to give a crystalline compound, dioxadiene dibromide, of unknown structure.² This was presumed to be 5,6-dibromo-*p*-dioxene. However, the possibilities that it had an oxonium bromide structure or that the dioxadiene ring had been ruptured were not excluded.

We have now found that I does not react with aqueous potassium iodide solution, a characteristic reaction of oxonium bromides.³ Furthermore, I reacts with the magnesium-magnesium iodide dehalogenating reagent² and with phenylmagnesium bromide to regenerate dioxadiene in high yield. Thus the structure of I must be 5,6-dibromo-*p*-dioxene.

(1) Present address, Chemistry Department, Antioch College, Yellow Springs, Ohio.

(2) Summerbell and Umhoefer, *THIS JOURNAL*, **61**, 3020 (1939).

(3) McIntosh, *ibid.*, **32**, 1330 (1910).

Attempted Reaction of I with Aqueous Potassium Iodide Solution.—To a solution of 1.0 g. of potassium iodide in 20 ml. of water was added 0.5 g. of I. No iodine was liberated on heating at 60° for twenty-four hours.

Reaction of I with Magnesium-Magnesium Iodide Reagent.—In a two-necked flask fitted with a mercury-sealed stirrer and a side-arm connected to a condenser arranged for downward distillation were placed 10 g. of magnesium turnings and 75 ml. of anhydrous butyl ether. To this was added slowly 4 g. of iodine. The solution was heated until distillation started and to it was added dropwise a solution of 10 g. (0.04 mole) of I in 50 ml. of butyl ether. A total of 100 ml. of distillate was collected during this addition. Redistillation through a 10-cm. Vigreux column gave 3.4 g. (97%) of dioxadiene, b. p. 74–75°, n_D^{20} 1.4351.

The Reaction of I with Phenylmagnesium Bromide.—To a solution of phenylmagnesium bromide prepared from 2.64 g. (0.11 atom) of magnesium and 17.3 g. (0.11 mole) of bromobenzene in 100 ml. of dry ether was slowly added a solution of 12.3 g. (0.05 mole) of I in 75 ml. of dry ether. After the moderately vigorous reaction subsided the mixture was allowed to stand for twelve hours and was then hydrolyzed by pouring into ice and ammonium chloride solution. The ether solution was separated and dried over magnesium sulfate. Distillation gave 5.9 g., b. p. 75–80°, and a sirupy residue. The distillate was dissolved in 50 ml. of carbon tetrachloride and to it was added dropwise a solution of bromine in carbon tetrachloride at 0° until a faint permanent color remained. Removal of the solvent *in vacuo* gave 9.6 g. of crystalline residue identified as I by mixture melting point. Assuming an average yield of 90% on the addition of bromine to dioxadiene this represents an 87% conversion to dioxadiene.

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RECEIVED APRIL 12, 1948

The Solubility of Aluminum Bromide in Cyclohexane¹

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During the course of a study of the isomerization of cyclohexane with aluminum bromide catalyst, the solubility of aluminum bromide in cyclohexane has been determined.

Materials.—Aluminum bromide was prepared and distilled into glass ampoules in the manner described by Leighton and Heldman.²

The cyclohexane was the gift of the Shell Oil Company. The stated analysis as received was 99.7 vol. % cyclohexane (by correlation of freezing point and mass spectrograph analysis), 0.0003 wt. % sulfur, less than 0.0005 vol. % benzene and less than 0.001 vol. % phenols. The freezing point was 6.0°. This material was further purified by "freezing out" cyclohexane crystals, followed by percolation of the remelted crystals through silica gel. The "freezing out" was performed as follows: About 300 ml. of cyclohexane contained in a 500-ml. Erlenmeyer flask was placed in a cooling bath of ice and water, and, with frequent hand stirring and scraping, a thick slurry of cyclohexane crystals was produced. The crystals were filtered off, melted, and the process repeated. The resultant cyclohexane was percolated through a column of silica gel to remove water and any trace of olefins. The product was stored over sodium in brown glass bottles. Physical properties of the purified cyclohexane were: m. p. 6.5°, n_D^{25} 1.4235.

(1) This work was supported by a grant from the Research Corporation.

(2) Leighton and Heldman, *THIS JOURNAL*, **65**, 2276 (1943).

Determination of Solubility.—The purified cyclohexane was placed in a flask attached to the vacuum system by a ground glass joint, thoroughly degassed, and distilled into the ampoules containing aluminum bromide. Each ampoule was sealed off from the vacuum line when it was estimated that it would be nearly full of solution upon reaching the solution temperature. Solution temperatures were determined as described by Heldman and Thurmond.³ All the solutions were clear and colorless. Samples were analyzed as follows: The aluminum bromide was precipitated in finely divided form² and the ampoule placed tip down in a long narrow flask equipped with standard taper joint and glass stopper. The flask and contents were weighed, and the flask shaken to break open the ampoule. The flask was then connected to a trap by all-glass connections using unlubricated standard taper joints. The trap was in turn connected to a vacuum pump. The vacuum pump was turned on and the flask cooled by immersion in a slurry of dry ice, chloroform, and carbon tetrachloride. After the system was evacuated, the dry ice slurry was removed and pumping continued until some time after the flask had reached room temperature. The cyclohexane was condensed in the trap. The aluminum bromide remained behind as a finely divided, white powder. The flask and contents were weighed and the cyclohexane calculated by difference. The aluminum bromide was removed by washing successively with nitrobenzene, water, and acetone. The flask and glass parts were weighed and the aluminum bromide calculated by difference.

TABLE I

SOLUTION TEMPERATURES OF ALUMINUM BROMIDE-CYCLOHEXANE MIXTURES

t_c , °C.	Al ₂ Br ₆		t_c , °C.	Al ₂ Br ₆	
	Mole fract.	Wt. % liq. phase		Mole fract.	Wt. % liq. phase
6.2	0.0503	25.1	38.7	0.178	57.9
8.8	.0568	27.6	39.8	.183	59.4
17.2	.0788	35.2	44.5	.220	64.2
26.4	.115	45.1	57.0	.333	76.0
28.5	.124	47.4	60.3	.380	79.5
36.0	.162	55.0	61.7	.393	80.4
37.6	.169	56.4	97.5	1.000	100.0

Results

The solution temperatures and compositions of the solutions examined are given in Table I. The moles of aluminum bromide are calculated on the basis of the formula Al₂Br₆. No correction was made for the cyclohexane in the vapor phase because of the comparatively low vapor pressure of cyclohexane and the small vapor volume present in the ampoules. The results show that aluminum bromide is appreciably more soluble in cyclohexane than in *n*-butane² or *n*-hexane⁴ when calculated on a mole fraction basis. On a weight basis aluminum bromide is more soluble in cyclohexane than in *n*-hexane throughout the temperature range for which data are available and is more soluble in cyclohexane than in *n*-butane throughout much of the lower temperature range.

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RECEIVED MARCH 2, 1948

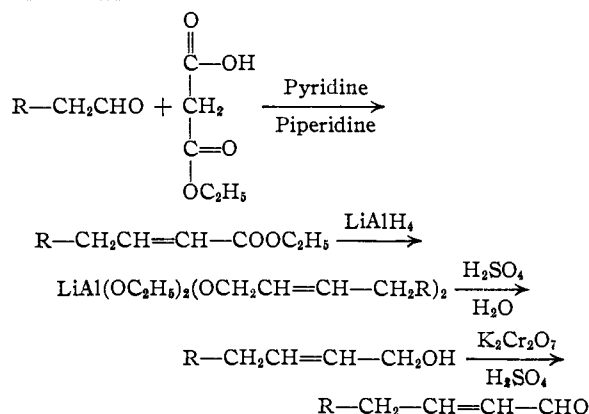
(3) Heldman and Thurmond, *ibid.*, **66**, 427 (1944).
(4) Boedeker and Oblad, *ibid.*, **69**, 2036 (1947).

The Preparation of 2-Heptenal and 2-Nonenal

By C. J. MARTIN, A. I. SCHEPARTZ AND B. F. DAUBERT¹

Recent work in this Laboratory on the isolation and identification of flavor components in "reverted" soybean oil has necessitated the preparation of a number of α,β -unsaturated aldehydes of a high degree of purity. The recent availability of lithium aluminum hydride as a reducing agent² led to the development of a suitable method for the preparation of such aldehydes free of their saturated isomers.

The general scheme of reaction may be outlined as follows



Experimental

Preparation of 2-Heptenal.—Ethyl hydrogen malonate (256 g.) was condensed with *n*-valeraldehyde (83.3 g.) in pyridine (469 g.) with piperidine (1.2 ml.) as a catalyst, according to the method of Galat.³ After removal of the pyridine and piperidine, the ethyl 2-heptenoate was distilled *in vacuo* under nitrogen: yield, 118 g. (78.2%), b. p. 58–58.8° (3 mm.), n_D^{20} 1.4355.

To a solution of lithium aluminum hydride (10.9 g., 14% excess) in absolute ether (450 ml.) there was added ethyl 2-heptenoate (78 g.) according to the method of Nystrom and Brown.² Although the crude yield of 2-heptenol was 45 g. (79%), distillation, under nitrogen, through a Vigreux column, resulted in a loss of approximately 50% because of partial polymerization of the alcohol. The 2-heptenol had a boiling point of 75–75.5° at 15 mm.

The 2-heptenol (21.7 g.) was oxidized by the low-temperature oxidation procedure of Delaby and Guillot-Allègre,⁴ yielding 2-heptenal, 15.9 g. (74.6%).

The product was stabilized with hydroquinone and distilled in a glass helix-packed column; b. p. 80–85° at 14 mm., n_D^{20} 1.4314. The aldehyde was identified by preparation of the following derivatives: semicarbazone, m. p. 168–168.4° (Delaby, *et al.*,⁴ 169°); *p*-nitrophenylhydrazone, m. p. 115.5–116° (Delaby, *et al.*,⁴ 110–112°); 2,4-dinitrophenylhydrazone, m. p. 131.5–132°.

Anal. Calcd. for C₁₃H₁₆N₄O₄: C, 53.41; H, 5.52; N, 19.17. Found: C, 53.17; H, 5.23; N, 19.03.

Preparation of 2-Nonenal.—Ethyl hydrogen malonate (143.6 g.) was condensed with heptaldehyde (63 g.) in the manner described above: yield of ethyl 2-nonenoate, 79.4 g. (78.2%); b. p. 104° at 8 mm.

The ethyl 2-nonenoate (79.4 g.) was reduced with

(1) The financial assistance of the National Association of Margarine Manufacturers is gratefully acknowledged.
(2) Nystrom and Brown, *THIS JOURNAL*, **69**, 1197 (1947).
(3) Galat, *ibid.*, **68**, 376 (1946).
(4) Delaby and Guillot-Allègre, *Bull. soc. chim.*, **53**, 301 (1933).