

in ethanol (83 ml.). 1-Chloromethylnaphthalene (83.1 g., 0.47 mole) (prepared by the method of Fuson and McKeever<sup>8</sup>) was added rapidly from a separatory funnel to the vigorously stirred refluxing mixture. The product precipitated instantly. The mixture was stirred under reflux for an hour, cooled to 0°, filtered, pressed, and the crude product rinsed with cold ethanol and air-dried. The crude product weighed 95.9 g. (81%) and had m.p. 226–228°. One recrystallization from ethanol raised the m.p. to 232°. The highest m.p. obtained on further recrystallization was 233°.

*Anal.* (By a semi-micro Kjeldahl determination) Calcd. for C<sub>12</sub>H<sub>11</sub>N<sub>2</sub>SCl: N, 11.09. Found: N, 11.10.

**S-1-Naphthylmethylthiuronium Salts of Organic Acids.**—Derivatives of aliphatic and aromatic carboxylic acids were most readily prepared in the following manner. The acid (0.10 g.) was dissolved in ethanol (about 1 ml.) using heat if necessary. A drop of 1% phenolphthalein solution was added and the mixture titrated to a faint pink with a 10% solution of sodium ethoxide prepared by dissolving sodium in the correct amount of ethanol. The suspension of the sodium salt of the acid was warmed and treated at once with a boiling solution consisting of a 10% excess of S-1-naphthylmethylthiuronium chloride dissolved

in a minimum quantity of boiling ethanol. The product usually crystallized immediately, and the suspension was boiled gently for a minute or so under vigorous stirring, permitted to cool slowly, chilled, collected, and rinsed with cold ethanol. The crude products were recrystallized twice from ethanol with the aid of a centrifuge, air dried and the melting points and analyses conducted. Nitrogen analyses by a semi-micro Kjeldahl procedure agreed acceptably with calculated values. Yields in the majority of cases were close to quantitative, and the melting points of the first seven crude products listed were not raised materially by the two succeeding recrystallizations. Melting points of the remaining products were not determined before recrystallization. The preparation of sulfonic acid derivatives was similar to that described above, except that aqueous media were employed throughout. Yields of sulfonic acid derivatives were considerably lower when alcoholic media were employed. Corrected melting points of the S-1-naphthylmethylthiuronium salts of the acids studied are listed in Table I.

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TABLE I

S-1-NAPHTHYLMETHYLTHIURONIUM SALTS OF ORGANIC ACIDS

No.	Acid	M. p., °C., of salt	% Nitrogen	
			Calcd.	Found <sup>b</sup>
1	Formic	183.5	10.71	10.95
2	Acetic	160.5	10.13	10.13
3	Propionic	142.5	9.64	9.85
4	Butyric	160.0	9.20	9.30
5	Valeric	167.0	8.80	9.02
6	Isovaleric	153.0	8.80	8.39
7	Caproic	152.5	8.42	8.40
8	Isocaproic	163.5	8.42	8.09
9	Heptylic	156.5	8.13	8.22
10	Caprylic	165.0	7.78	7.24
11	Pelargonic	159.5	7.48	7.66
12	Capric	163.0	7.19	7.14
13	Undecylic	160.5	6.96	6.95
14	Lauric	155.0	6.72	6.70
15	Myristic	152.5	6.30	6.42
16	Palmitic	150.5	5.92	5.70
17	Stearic	150.0	5.59	5.45
18	Crotonic	180.5	9.26	9.31
19	Levulinic	146.5	8.42	8.23
20	Trichloroacetic	143.0	7.36	7.24
21	Phenylacetic	166.5	7.94	8.05
22	Furoic	220.0	8.52	8.42
23	Benzoic	181.5	8.27	8.33
24	<i>o</i> -Benzoylbenzoic	193.5	6.32	6.39
25	$\beta$ -Naphthoic	186.5	7.20	7.03
26	Cinnamic	179.5	7.67	7.71
27	Anisic	189.0	7.59	7.20
28	Salicylic	170.0	7.88	7.81
29	Benzenesulfonic <sup>a</sup>	186.0	7.48	7.54
30	<i>p</i> -Toluenesulfonic	178.0	7.20	7.76
31	$\beta$ -Naphthalenesulfonic <sup>a</sup>	179.5	6.59	6.50
32	<i>p</i> -Phenolsulfonic <sup>a</sup>	106.0	7.16	6.84
33	Benzenesulfonic <sup>a</sup>	177 (dec.)	7.83	7.36

<sup>a</sup> Made directly from sodium salt.

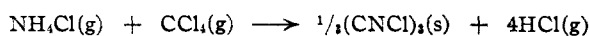
<sup>b</sup> By semi-micro Kjeldahl method.

(8) Fuson and McKeever in "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 70.

## A Reaction between Carbon Tetrachloride and Ammonium Chloride

BY D. D. CUBICCIOTTI AND WENDELL M. LATIMER

From thermodynamic considerations it would appear that ammonium chloride should react with carbon tetrachloride. The reaction



has a favorable free energy change. The  $\Delta H$  of the reaction is  $-20$  kcal.,<sup>1</sup> and the  $\Delta S$  must be positive because of the increase in number of moles of gas on reaction. It seemed reasonable, therefore, to investigate the possible reaction experimentally.

The first experiments involved passing a mixture of carbon tetrachloride and nitrogen (to carry the vapor) over a container of ammonium chloride heated to 350–400°. Although varying pressures of carbon tetrachloride vapor (up to one atmosphere) and varying temperatures (up to 400°) were applied, no apparent reaction occurred.

In order to attain more extreme conditions a closed system was tried. The reactants were sealed into an evacuated Pyrex "bomb" tube and heated to 450–475° for an hour or longer. This treatment yielded a yellow solid and hydrogen chloride gas together with traces of hydrogen cyanide and possibly other compounds. From the amount of hydrogen chloride gas formed in one experiment it was estimated that the pressures in the containers reached about twenty atmospheres.

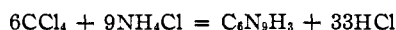
The yellow solid was insoluble in water, alcohol, ether and hydrocarbons, but dissolved after long treatment with hot, concentrated alkali. It did not melt at 300° but does darken slightly at this temperature. For analysis a sample of the yellow solid was prepared as above and washed with water and heated *in vacuo* to 300° (to remove all the ammonium chloride). The sample gained in

(1) Heat of formation of (CNCl) from Lemault, *Ann. chim.*, [7] 18, 344 (1899).

weight on exposure to air (presumably absorbing water vapor) but did not appear otherwise altered. The analysis of this sample showed: C, 33.40; H, 2.08; N, 56.68; Cl, 0.0; total, 92.16. Assuming the difference from 100% to be oxygen from absorbed water, the analysis on a dry basis becomes: C, 36.6; H, 1.2; N, 62.2. This percentage composition corresponds very well to that given by Franklin<sup>2</sup> and Laurent and Gerhardt<sup>3</sup> for the compound melon. In fact, the color, solubility, and non-melting of the compound fit the data on melon<sup>4</sup> quite well.

The formula assigned to melon<sup>4</sup> is  $C_6N_9H_3$ . From the amount of water absorbed by the sample analyzed one calculates the formula of the water containing substance to be  $C_6N_9H_3 \cdot 1.01H_2O$ —or closely one water molecule per molecule of melon.

The equation for the formation of melon is



It is striking in that almost all of the bonds in the initial compounds are eventually broken to be replaced by carbon-nitrogen bonds. Most probably there is a series of intermediates involved in this extensive rupture and reconstitution of bonds. It is further of interest to note that when chloroform and ammonium chloride were heated together no reaction occurred, except decomposition of the chloroform.

(2) E. C. Franklin, *THIS JOURNAL*, **44**, 506 (1922).

(3) Laurent and Gerhardt, *Ann. chim.*, [3] **19**, 89 (1847).

(4) Beilstein, "Handbuch der organischen Chemie," 4th ed., Vol. III, 1921, p. 169.

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## Cyclobutane Derivatives. V. Ziegler Bromination of Cyclobutene<sup>1</sup>

BY E. R. BUCHMAN AND D. R. HOWTON

Our interest in the cyclobutadiene problem<sup>2</sup> has led us to investigate the Ziegler bromination<sup>3</sup> of cyclobutene. Orienting experiments carried out according to Ziegler<sup>4</sup> gave only traces of allylic bromide. The optimum conditions<sup>5</sup> for bromination of the related methylenecyclobutane, when applied to cyclobutene, yielded about 1%<sup>6</sup> of 3-bromocyclobutene-1; a major product was 1,2-dibromocyclobutane<sup>7</sup> (48%<sup>6</sup>). This reaction is

(1) This study was aided by a grant from the Research Corporation.

(2) Cf. Buchman, Schlatter and Reims, *THIS JOURNAL*, **64**, 2701 (1942).

(3) Ziegler<sup>4</sup> recommended his method as a general tool for preparing cyclic conjugated diolefin from the corresponding monoolefins. When the work reported here was already in progress, W. Baker in a Tilden Lecture (*J. Chem. Soc.*, 258 (1945)) suggested the Ziegler bromination of cyclobutene as a step in the synthesis of cyclobutadiene.

(4) Cf. Ziegler, *et al.*, *Ann.*, **551**, 80 (1942).

(5) Buchman and Howton, *THIS JOURNAL*, **70**, 2517 (1948).

(6) Based on cyclobutene consumed.

thus of doubtful value in connection with the synthesis of cyclobutadiene.

### Experimental<sup>8</sup>

The glass liner of a 1-l. high pressure hydrogenation bomb was charged with 52.2 g. (0.293 mole) of N-bromosuccinimide (NBS), 1.14 g. (1.6 mole per cent.) of dibenzoyl peroxide and a solution of 22.8 g. (0.422 mole) of cyclobutene<sup>9</sup> in 211 ml. of dry c.p. benzene. The bomb was assembled, set rocking, heated to about 80° during forty-five minutes and maintained at 75–80° for seven hours; it was then allowed to cool to 4°. Working at this latter temperature to avoid losses, the contents of the bomb were washed out with 100 ml. of c.p. toluene and the suspended white crystalline solid (23.7 g., m.p. 100–119°, principally succinimide) was filtered off. Careful fractional distillation of the filtrate led to the recovery of 11.9 g. (0.22 mole) of cyclobutene. Then benzene, bromocyclobutene and some toluene were removed through a short column, collecting material of b.p. up to 48° at 100 mm.

This material, except for about 200 ml. of the most volatile part (which gave only a very weak positive test with alcoholic silver nitrate), was carefully refractionated at atmospheric pressure through a 75-cm. helix-packed heated column topped by a total reflux, variable take-off head. There was no appreciable amount of a constant-boiling bromide component. The portions (total ca. 12 g.) collected in the interval between benzene and toluene, which gave strong positive tests with alcoholic silver nitrate (fractions immediately before and after these gave weak tests), were treated with 20 g. of an 18% solution of trimethylamine in benzene. A cloudiness developed at once; overnight partially crystalline oil was deposited which was extracted with water; further prolonged treatment of the benzene phase with trimethylamine gave a smaller additional amount of oily salt. The aqueous extracts were evaporated to dryness *in vacuo*; total yield of crude residue 0.42 g. (1.08%<sup>8</sup>). To an ethanolic solution of the residue, after purification with Norit, ether was added dropwise; a colored oil precipitated and then a gummy crystalline hygroscopic solid. This latter was converted<sup>10</sup> to the picrate (0.30 g. = 0.43%<sup>8</sup>), crude m.p. 191.5–194°; recrystallization from ethanol-water gave deep-yellow, rough blades in sparse latticed clusters, m.p. 197.0–197.5°; the mixed m.p. with authentic 2-cyclobutenyltrimethylammonium picrate<sup>11</sup> showed no depression.

*Anal.* Calcd. for  $C_{11}H_{16}N_4O_7$ : C, 45.88; H, 4.74; N, 16.47. Found: C, 45.92; H, 4.93; N, 16.42.

On standing for four days, the residual clear brown oil (left after removing benzene and toluene from the reaction mixture) deposited 6.25 g. of massive rhombic crystals, m.p. 147–152°, identified after recrystallization as N-phenylsuccinimide<sup>12</sup> (mixed m.p.), yield 12.1% based on NBS. The filtrate from these crystals was distilled through a short column, first at 100 mm., then at 10 mm. A colorless oil (21.14 g.), b.p. 52.8–53.7° at 10 mm. was collected (the last portions of this fraction were removed at 3.5 mm., b.p. up to 35.3°). The oil was identified as 1,2-dibromocyclobutane<sup>7</sup> (48.8%<sup>6</sup>; 67.3% based on NBS); it solidified on cooling, melted at 3.5–4.5° and boiled at 174.5° (cor.) at 748 mm. (Erich micro method); when mixed with authentic dibromide<sup>13</sup> no depression of the m.p. was noted. The further distillation (from a flask with a low side arm) of the viscous material (13.2 g.) re-

(7) See ref. 5, footnote 7.

(8) All melting points are corrected; microanalyses by Dr. G. Oppenheimer and Mr. G. A. Swinehart of this Institute.

(9) Willstätter and Bruce, *Ber.*, **40**, 3979 (1907); cf. Heisig, *THIS JOURNAL*, **63**, 1698 (1941).

(10) Cf. Howton, *ibid.*, **69**, 2555 (1947), footnote 5.

(11) Buchman and Howton, to be published.

(12) Cf. Howton, *ibid.*, **69**, 2060 (1947); cf. ref. 5.

(13) Prepared by bromination of cyclobutene, m. p. 4.7–5.7°, Erich b. p. 176.2° (cor.) at 741 mm.; Willstätter and von Schmaedel, *Ber.*, **38**, 1992 (1905), reported m. p. 1–4°, b. p. 171–174°.