recrystallized from ethanol to give white, needle-like crystals. The ether solution from the hydrochloride was washed with 100 cc. of 5% hydrochloric acid, dried over anhydrous sodium sulfate and finally distilled to yield 8.1 g. of dodecanol.

Transalkylation of Triethylamine with Dodecanol.—A mixture of 37.2 g. (0.2 mole) of dodecanol, 73 g. (0.73 mole) of triethylamine and 10 g. of copper-chromium-barium oxide was heated for 10 hours under 380 atmospheres of hydrogen. On cooling, the catalyst was washed with triethylamine and dried; 10 g. of black catalyst was recovered. The triethylamine-water-ethanol azeotrope (22 g.) was separated by distillation through a 30-cm. Vigreux column. This and a similar fraction (28 g.) from another reaction were combined, neutralized to congo red with dilute sulfuric acid, distilled and the fraction, b.p. 77-83°, collected. The ethanol was salted out with anhydrous potassium carbonate, separated and distilled to give 4.3 g., b.p. 77-78°, $n^{25}\text{D}$ 1.3620. The N-phenyl- and N-α-naphthylurethans were prepared and showed no depression with the same derivatives prepared from ethanol. After removal of the remaining triethylamine from the reaction products, the residue was fractionated at 2 mm. into the following fractions: (1) 11.8 g., b.p. 109-121°, $n^{25}\text{D}$ 1.4420, consisting of 52.5% diethyldodecylamine in dodecanol, (2) 26.3 g., b.p. 121-123°, $n^{25}\text{D}$ 1.4393, and (3) 5.3 g. holdup, $n^{25}\text{D}$ 1.4505. Fraction (2) was redistilled to give 20 g. of pure diethyldodecylamine. Fraction (3) was combined with similar material from other experiments. From 11 g. of such material, distilled in a modified Claisen flask, 7.7 g. of didodecylethylamine was obtained as a colorless oil.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE RESEARCH DIVISION OF ARMOUR AND COMPANY]

The Polymorphic Behavior of Dodecylammonium Chloride with Organic Solvents

BY C. W. HOERR AND H. J. HARWOOD

RECEIVED JANUARY 28, 1952

The solubility of dodecylammonium chloride has been determined in carbon tetrachloride, carbon tetrabromide, chloroform, bromoform, ethyl acetate, "absolute" ethanol, *n*-butanol and acetonitrile. The behavior in these solvents is similar to that previously reported for the benzene system. Dodecylammonium chloride exhibits two enantiotropic forms and a monotropic variation of the lower-temperature enantiotrope.

Recent investigations[1,2] of the behavior of dodecylammonium chloride have demonstrated that this salt exists in two crystalline modifications having an enantiotropic transition at 57.5°. Among the fatty acids and their derivatives, this enantiotropy appears to be almost unique. With very few exceptions, the aliphatic compounds exhibit monotropic polymorphism.

This transition between the two stable forms of dodecylammonium chloride has been established by determination of the respective solubility curves[1] in benzene and 95% ethanol, by the configuration of the phase diagram[2] of this salt with water, and by visual observation[1,2] of the change in crystalline structure upon heating under the microscope. In both the previous investigations, it was found that the N-methyl derivatives of this salt do not exhibit enantiotropic polymorphism. Under certain conditions, the mono-, di- and trimethyldodecylammonium chlorides reveal monotropic modifications.

In connection with studies of the solubility of dodecylammonium chloride in benzene and aqueous ethanol, it was found[1] that several discontinuities in the curves occur at temperatures other than the enantiotropic transition point at 57.5°. In the benzene system there is a break in the unstable region, whereas in aqueous ethanol a break appears in the curve representing the stable system above the transition temperature. In order to ascertain whether these breaks are consequences of solvent-solute interaction, or are attributable to other factors, investigation of the behavior of dodecylammonium chloride has been extended by determination of its solubility in carbon tetrachloride, carbon tetrabromide, chloroform, bromoform, ethyl acetate, "absolute" ethanol, *n*-butanol and acetonitrile.

Experimental

The dodecylammonium chloride employed herein was the material used in the previous investigations.[1,2]

The solvents were of the best grade available and were freshly distilled in a Stedman-packed column before use, with the exception of carbon tetrabromide (Eastman Kodak Co. white-label) which was used without further treatment. The "absolute" ethanol employed herein was obtained by azeotropic distillation of 190-proof neutral grain spirits with benzene in a Stedman-packed column. The final product was estimated to be at least 99.8% ethanol by comparison of its density with values in the "International Critical Tables."[3]

The procedures for determining the solubilities of both the stable and metastable forms of the solute have been described in recent publications.[1,2] Weighed portions of salt and solvent were sealed in small glass tubes, dissolved by heating, thoroughly mixed, and then cooled below the crystallization point. Solution temperatures were observed during slow heating of these samples as they were rotated in a regulated, electrically-heated water-bath (silicone-bath above 100°). Temperatures were measured by means of thermometers which were graduated in 0.1° intervals and were calibrated by the National Bureau of Standards. The solution temperatures obtained are considered accurate within ±0.1°.

The solution temperatures of the metastable polymorphs were determined by observing in addition the behavior upon cooling. Homogeneous samples were cooled gradually below temperatures on the higher liquidus curve and the temperature at which precipitation occurred was noted. Solution could usually be effected by heating the samples immediately to temperatures just above the precipitation point. By repetition of this procedure it was readily possible to locate the metastable solution temperatures within ±0.1°. Upon maintaining samples for a time at temperatures below their precipitation points, the metastable form converted to the stable form, the transformation being more rapid at the lower concentrations, particularly in the nonpolar solvents and in those of low polarity. To effect transformation in some cases, it was necessary to chill samples for several hours.

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(1) F. K. Broome and H. J. Harwood, THIS JOURNAL, **72**, 3257 (1950).

(2) F. K. Broome, C. W. Hoerr and H. J. Harwood, *ibid.*, **73**, 3350 (1951).

(3) "International Critical Tables," 1929, Vol. III, p. 117.

Results and Discussion

The solution temperatures of dodecylammonium chloride in carbon tetrachloride, carbon tetrabromide, chloroform, bromoform, ethyl acetate, 99.8% ethanol and *n*-butanol are listed in Table I. The solubility of this salt in acetonitrile was found to be quite limited. Although not determined accurately, the solubility in this solvent is less than 0.39% at 80°. This value indicates that the solubility of dodecylammonium chloride in acetonitrile, a highly polar solvent, approximates the solubility (<0.35% at 95°) of this salt in the non-polar solvent *n*-hexane.

TABLE I

SOLUBILITY OF DODECYLAMMONIUM CHLORIDE IN ORGANIC SOLVENTS

Wt. % salt	Solution temperature Metastable	Solution temperature Stable
In carbon tetrachloride		
1.50	39.0	43.8
2.96	43.1	47.0
5.74	47.2	50.6
9.10	50.8	53.5
11.72	53.0	55.2
13.46	54.0 54.4	56.3
13.8	54.6^a	....
14.89	56.2	57.1
15.8	..	57.5^a
16.62	..	58.7
21.98	..	66.5
26.60	..	73.3
31.72	..	81.1
35.48	..	87.2
In carbon tetrabromide		
0.00	..	91.6
2.24	..	89.4
4.44	..	87.4
6.67	..	85.2
7.21	..	84.6
10.85	..	80.1
16.74	..	72.5
18.7 (Eutectic)		69.8
19.90	..	71.8
24.85	..	79.6
32.76	..	92.0
39.54	..	102.8
50.80	..	120.4
In ethyl acetate		
0.28	53.8	56.3
0.51	54.2	56.7
0.80	54.5	57.1
1.00	54.7^a	....
1.10	55.6	57.4
1.18	..	57.5^a
1.36	..	57.6
1.78	..	60.6
2.56	..	65.2
3.11	..	67.5
3.48	..	69.0
5.08	..	74.1
6.72	..	78.2
In 99.8% ethanol		
10.97	12.7	22.3
19.12	23.2	31.9
30.40	34.1	40.9
41.35	42.4	47.9
49.68	48.4	52.3
55.24	52.3	55.2
57.32	53.7	56.2
58.50	54.4	56.8
59.0	54.7^a	....
59.58	56.4^a	57.3
60.0	..	57.5^a
60.30	..	58.5
60.80	..	60.1
61.45	..	61.8
62.20	..	63.8
62.88	..	66.0
63.75	..	68.2
64.81	..	71.1
65.55	..	73.3
66.35	..	75.4
68.40	..	78.5
In chloroform		
0.82	..	15.0
2.02	..	22.0
4.05	17.0	28.0
6.95	23.5	31.6
12.18	31.0	36.4
18.20	36.5	40.2
25.72	42.0	45.2
30.80	45.1	48.2
34.19	47.1	50.1
38.39	49.5	52.3
43.32	52.2	54.8
43.48	52.3	55.1
45.73	53.5	56.0
46.21	53.9	56.4
47.14	53.4 54.4	56.8
47.6	54.6^a	....
47.70	55.0	57.1
48.22	56.5	57.3
48.58	..	57.5
48.6	..	57.5^a
48.79	..	58.2
49.18	..	59.4
50.11	..	62.1
50.73	..	63.9
53.42	..	68.8
53.95	..	73.5
59.92	..	90.5
66.58	..	110.0
In bromoform		
0.90	24.6	39.8
1.27	25.2	40.4
3.04	34.5	45.4
5.00	39.2	48.3
8.05	43.7	50.4
13.74	49.5	53.9
18.23	52.9	55.8
20.26	53.4	56.6
20.59	53.5	56.7
21.2	54.8^a	....
21.92	56.1	57.2
22.7	..	57.5^a
23.40	..	58.7
24.63	..	60.7
28.96	..	68.3
32.23	..	74.4
40.77	..	93.1
45.96	..	104.0
54.54	..	122.5
In *n*-butanol		
7.98	22.5	28.0
13.30	29.2	34.1
19.96	35.4	39.6
24.96	39.3	43.0
33.29	45.0	48.1
39.94	49.2	52.1
44.40	52.0	54.7
46.45	53.4	55.9
47.57	54.2	56.6
48.2	54.6^a	....
48.71	55.9	57.3
49.3	..	57.6^a
49.92	..	59.2
53.26	..	68.8
57.08	..	79.5
66.60	..	106.0

[a] Invariant points, estimated graphically.

Dodecylammonium chloride exhibits similar systems with all the organic solvents investigated with the exception of carbon tetrabromide. The behavior is illustrated by the chloroform system shown in Fig. 1. This system presents the same general configuration as that with benzene.[1] It is characterized by the solubilities of the stable forms of dodecylammonium chloride, alpha and beta, represented by points on the curves AT and TB, respec-

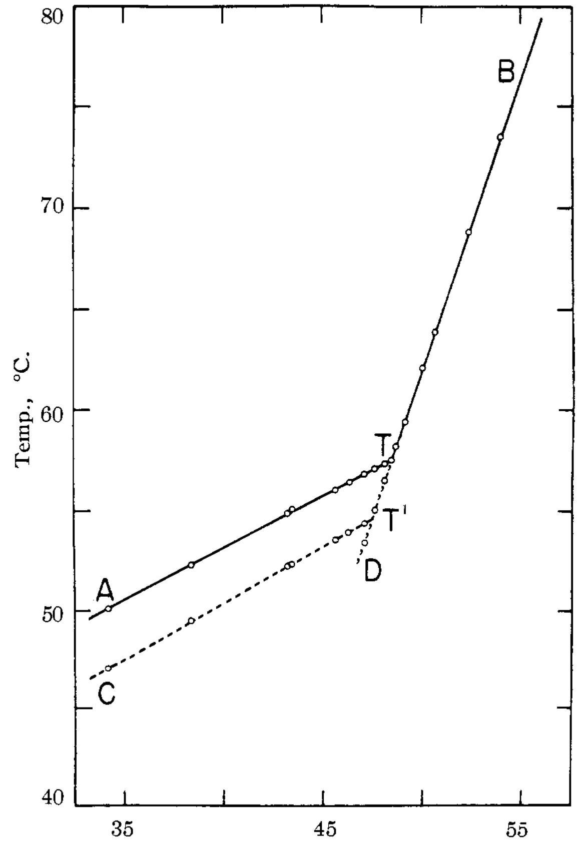


Fig. 1.—Solubility of dodecylammonium chloride in chloroform.

tively. These curves intersect at the enantiotropic transition point *T*. In the mestastable region, the solubility of the α'-form is represented by points on the curve CT′. This curve intersects the metastable solubility curve of the β-modification (shown by points on DT′T) at the metastable enantiotropic transition point T′.

The locations of the intersections of the solubility curves of dodecylammonium chloride with reference to temperature and concentration have been inserted in Table I. These data establish the transition temperature *T* quite definitely at 57.5 ± 0.1°, which is the value obtained by microscopic observations.[1,2] The change of slope in the metastable region at T′ occurs consistently at 54.7 ± 0.1°. Re-examination of the data[1] for the solubility in 95% ethanol shows a slight hint of a similar (unreported) intersection in the metastable region of this region of this system in the neighborhood of 54.5°, but too few experimental points have been recorded to demonstrate the point conclusively. The changes in slope of the solubility curves[4] of dodecylammonium bromide and iodide in benzene and 95% ethanol suggest that these substances may possess transitions similar to those of dodecylammonium chloride.

The data for the anhydrous ethanol show no "break" in the solubility curve above the transition temperature.[2]

The system of dodecylammonium chloride with carbon tetrabromide, with a eutectic at 69.8°, involves only the higher-temperature form, beta.

[4] C. W. Hoerr and A. W. Ralston, THIS JOURNAL, **64**, 2824 (1942).

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE GLIDDEN COMPANY—NAVAL STORES DIVISION]

Nopol. III. Thermal Isomerization in the Liquid Phase

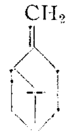
BY JOSEPH P. BAIN, ALBERT H. BEST AND ROBERT L. WEBB

RECEIVED JANUARY 31, 1952

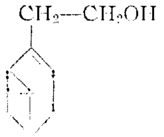
Upon being heated in the liquid phase, nopol showly racemizes and undergoes loss of formaldehyde to form a partly racemic β-pinene through reversal of the β-pinene–formaldehyde condensation. Simultaneously, the isomeric alcohols, dipentene-7-carbinol and alloöcimenecarbinol are formed. Infrared and ultraviolet absorption spectral data are presented in support of the suggested course of the reaction.

β-Pinene (I) and formaldehyde condense to form nopol[1] (II) (6,6-dimethylbicyclo[3,1,1]hept-2-ene-2-ethanol), a structural derivative of α-pinene (III). Infrared spectra are shown in Fig. 1 for the two pinenes and for nopol.

The products of pyrolysis of α-pinene ordinarily[2] recovered are dipentene and the triene alloöcimene although it was recently shown[3] that ocimene can be recovered from the pyrolysis products when a suitable method is employed to avoid its isomerization. Ocimene is so readily isomerized to alloöcimene that the latter is usually the sole acyclic product isolated. Two geometric isomers of alloöcimene have been described.[4] Alloöcimene may be recyclized[5,6] in the vapor phase to a complex mixture consisting chiefly of alkyl cyclohexadienes in which α- and β-pyronene and 1,3-dimethyl-1-ethyl-3,5-cyclohexadiene predominate. At lower temperatures and in the liquid phase, alloöcimene may be converted[7] in high yields to a dimer or mixture of dimers.

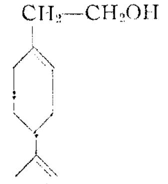


I

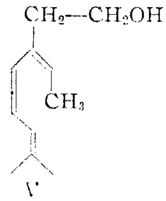


II

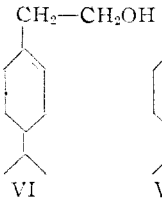
III



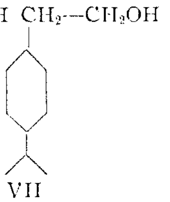
IV



V



VI



VII

Nopol behaves similarly in the vapor phase since there were isolated products described as menthadiene-7-carbinol[1] and alloöcimenecarbinol[8] from nopol pyrolysis mixtures, but structures were not proved nor were secondary products of pyrolysis described.

It is the purpose of this paper to report that thermal isomerization of nopol is analogous to that of α-pinene and to show that the products of pyrolysis are dipentene-7-carbinol (IV), the allo-ocimenecarbinol (V) and partly racemized nopol. Simultaneously, a partly racemic β-pinene is formed by loss of formaldehyde from the partly racemized nopol. Secondary products of pyrolysis will be referred to, but will be more fully described in a forthcoming paper.

Initial experiments showed that as nopol was heated at reflux at atmospheric pressure, the boiling point gradually rose, small amounts of paraformaldehyde appeared in the condenser and, as shown in Fig. 2, absorptions in the ultraviolet region of the spectrum developed at about λ_{max} 278 mμ. After about 2.5 hours of refluxing, the absorption maxi-

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[1] J. P. Bain, THIS JOURNAL, **68**, 638 (1946).

[2] B. Arbuzov, *J. Gen. Chem.* (*U.S.S.R.*), **3**, 21 (1933); *Ber.*, **67B**, 563 (1934).

[3] J. E. Hawkins and H. G. Hunt, THIS JOURNAL, **73**, 5379 (1951).

[4] J. J. Hopfield, S. A. Hall and L. A. Goldblatt, *ibid.*, **66**, 115 (1944).

[5] L. A. Goldblatt and S. Palkin, *ibid.*, **66**, 655 (1944).

[6] E. E. Parker and L. A. Goldblatt, *ibid.*, **72**, 2151 (1950).

[7] R. E. Fuguitt and J. E. Hawkins, *ibid.*, **67**, 242 (1945); **69**, 319 (1947).

[8] J. P. Bain and A. H. Best, U. S. Patent 2,453,110 (November 9, (1948).