TABLE I

CARBETHOXYMETHYL ALKANOATES

The effect of reaction time on yield is illustrated in the case of carbethoxymethyl acetate: 8 hours, 3% yield; 26 hours (with NaI cat.), 69% yield; 48 hours, 44% yield; and for carbethoxymethyl valerate: 1 hour, 14% yield; 24 hours, 82% yield; 48 hours, 55% yield. In this latter 48 hour run, 36.4 g. of a fraction boiling from 114–167° (2 mm.) was obtained. The nature of this higher-boiling fraction was not investigated further as no similar product was observed in any of the other experiments.

R value of acid	Time, hr.	Yield, %	B.p., °C., (60 mm.)	n^{23}_{D}	d^{20}_{20}	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Saponif. equivalent Calcd.	Saponif. equivalent Found	Molecular refract. Calcd.	Molecular refract. Found
Methyl	48	44	108	1.40999	1.0893	49.31	49.05	6.90	6.81	73.1	71.5	33.22	33.24
Ethyl[a]	24	53	119	1.41296	1.0550	52.49	52.74	7.55	7.57	80.1	80.4	37.83	37.85
n-Propyl	49	61	131	1.41677	1.0314	55.16	54.99	8.10	8.08	87.1	86.9	42.40	42.45
Isopropyl	1$^1/_4$	54	123	1.41354	1.0215	55.16	54.99	8.10	8.13	87.1	88.1	42.40	42.57
n-Butyl	24	77	144	1.42049	1.0159	57.43	57.48	8.57	8.58	94.1	94.8	47.07	46.96
Isobutyl	1	60	137	1.41880	1.0093	57.43	57.18	8.57	8.44	94.1	95.2	47.07	47.07
s-Butyl	1	81	136	1.41926	1.0109	57.43	57.28	8.57	8.54	94.1	93.9	47.07	47.05
t-Butyl	6	75	124	1.41507	1.0012	57.43	57.37	8.57	8.53	94.1	94.6	47.07	47.09
n-Amyl	36	70	155	1.42521	1.0011	59.38	59.30	8.97	8.89	101.1	100.3	51.69	51.68
n-Heptyl	2	91	179	1.42911	0.9723	62.58	62.45	9.63	9.67	115.6	113.4	60.92	61.08

[a] In this run 4.0 g. of sodium iodide was used as a catalyst.

stirrer and a thermometer dipping into the reaction mixture. The flask was heated externally with a Glascol heating mantle controlled by a Variac variable transformer. In a typical run, a mixture of from 0.5 to 1.0 mole of the anhydrous sodium salt with a 50–100% excess of ethyl monochloroacetate was added to the reaction flask. The excess ethyl monochloroacetate was used as a solvent to give the mixture sufficient fluidity so that it could be stirred. The mixture was then stirred and heated and began to reflux gently when the temperature of the reaction mixture reached approximately 140°, but it was observed that the mixture became pasty during the heating process and stirring became difficult. Over a period of time the temperature gradually rose to a maximum and then began to drop slowly. At the maximum temperature the gel broke down and stirring became easier. The attainment of the maximum temperature was taken as the end of the reaction. The mixture was cooled, filtered with suction, the salt washed twice with anhydrous ether and the washings added to the filtrate. The ether and excess ethyl monochloroacetate were removed by distillation at atmospheric pressure. The pressure was then lowered and the residue rectified in a 9 mm., 16-inch column packed with $^3/_{32}$-inch stainless steel helices to produce the yields given in Table 1.

The individual esters were further purified by rerectification at 60 mm. pressure using a Unitized Cartesian type manostat[6] to maintain constant pressure. A 9-mm., 16-inch column packed with $^1/_8$-inch Pyrex glass helices was used to produce the pure esters whose physical constants are summarized in the table. The analytical values for carbon and hydrogen given in the table are the averages of two determinations, none of which varied more than ±0.15 unit from the average. The saponification equivalents cited in the table are also averages of two determinations.

Acknowledgment.—The authors are indebted to the Hooker Electrochemical Company, Niagara Falls, N. Y., and to the Applied Research Laboratories of Armour and Company, Chicago, Ill., for generous samples of their chemical products which were used in this investigation.

(6) R. Gilmont, *Anal. Chem.*, **23**, 157 (1951).

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Desulfuration of Thioamides

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Since nitriles are readily converted into thioamides[1] under mild conditions, the reduction of a nitrile to an aldehyde *via* Raney nickel desulfuration of the thioamide would be an attractive process if the yields obtainable in the desulfuration step were satisfactory.

At the time this desulfuration was studied there had been no examples of the reduction of a thioamide to an aldehyde reported in the literature[2,3]; although two N-substituted thiobenzamides had been reduced to benzaldehyde. Ciusa,[4] using zinc and potassium hydroxide, obtained a 42% yield of benzaldehyde from thiobenzanilide and Kindler[1] was able to convert N,N-dimethylthiobenzamide into benzaldehyde in 40% yield by electrolytic reduction.

With thiobenzamide as a model the desulfuration was studied under a variety of conditions. Several types of Raney nickel catalysts were used, W-2, the commercial catalyst,[5] nickel deactivated by acetone at 25°, or at the refluxing temperature for an hour, or by acetone and ammonium hydroxide at 25°. The best results, 32% of benzaldehyde isolated as the 2,4-dinitrophenylhydrazone, were obtained with the last named catalyst in a ratio of 41:1 in ethanol at 25°. Usually, the reaction was complete in 15 minutes or less with yields ranging from 15 to 30%.

No better results were obtained in acetone or *t*-butyl alcohol and higher temperatures and longer reaction times gave less recovered starting thioamide and more reduction of the aldimine to the amine or condensation to hydrobenzamide.

Several thioanilides were treated with Raney nickel since it was expected that the resulting anils would be more stable than the corresponding aldimines. This was found to be the case and a

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(1) A. Cahours, *Compt. rend.*, **27**, 239 (1848); S. Gabriel and P. Heymann, *Ber.*, **23**, 158 (1890); K. Kindler, *Ann.*, **431**, 187 (1923).

(2) After this work had been completed D. Brovet (*Arkiv Kemi*, **20**, 70 (1948); *C. A.*, **44**, 6830 (1950)) reported a 77% yield of benzaldehyde, isolated as the dinitrophenylhydrazone, by the desulfuration of thiobenzamide. There is a possibility that a suitably deactivated nickel might give such a yield, but this is not stated in Brovet's report.

(3) E. C. Kornfeld (*J. Org. Chem.*, **16**, 131 (1951)) has recently described the conversion of thioamides to amines by means of Raney nickel. C. D. Hurd and B. Rudner (THIS JOURNAL, **73**, 5157 (1951)) have also studied the desulfuration of several substituted thioamides.

(4) R. Ciusa, *Atti R. Accad. dei Lincei Roma*, [5] **15**, II, 381 (1906); *Chem. Zentr.*, **78**, I, 28 (1907).

(5) Obtained from the Gilman Paint and Varnish Co., Chattanooga, Tenn.

much higher conversion to the aldehyde was observed. The results are tabulated in Table I. This reaction is not as useful since the thioanilides are less accessible than the thioamides.

The action of lithium aluminum hydride on thiobenzamide was briefly investigated. The products isolated point to an elimination of hydrogen sulfide to give the nitrile followed by reduction of the nitrile to the amine. It has been observed[6] that heating thioacetamide with sodium ethoxide will bring about elimination of hydrogen sulfide to give acetonitrile.

TABLE I

DESULFURATION OF THIOANILIDES[a]

Thioanilide	Conversion, % (DNP)	Aldehyde
Thiobenzanilide[b]	28[c]	
	84	61
p-Methoxythiobenzanilide[b]	96	68
p-Hydroxythiobenzanilide[b]	78[d]	
Thiobutyranilide	32[e]	
Thioisovaleranilide	32[e]	

[a] The solutions were stirred in refluxing acetone for one hour with 15 g. of nickel per gram of thioanilide. After the removal of the nickel and the acetone the anil was hydrolyzed and the aldehyde was steam distilled from an acid solution. The nickel used was deactivated by refluxing in acetone, C. B. Spero, A. V. McIntosh, R. H. Levin, THIS JOURNAL, **70**, 1907 (1948). [b] Prepared from phenyl isocyanate and benzene by the method of A. Friedmann and L. Gattermann, *Ber.*, **35**, 3525 (1892). When the thiobenzanilide was prepared by the action of P_2S_5 on benzanilide it always contained some unreacted benzanilide. [c] Stirred two hours at room temperature, 70% thiobenzanilide recovered. [d] The anil was relatively stable to the refluxing 5% hydrochloric acid and was isolated directly. [e] The crude thioanilide from the reaction of P_2S_5 with the anilide was used. The yield is over-all for the two reactions.

Lithium Aluminum Hydride with Thiobenzamide. a.—To a solution of 5.0 g. of thiobenzamide in 200 ml. of ether cooled in Dry Ice and acetone was added 1.75 g. of lithium aluminum hydride in 25 ml. of ether. The solution gradually warmed to 20° during three hours and upon hydrolysis of the reaction product with sodium potassium tartrate there was obtained 2.5 g. (64%) of benzylamine benzenesulfonamide, m.p. 86–87°.

b.—A mixture of 3.0 g. of thiobenzamide and 0.45 g. of lithium aluminum hydride in 200 ml. of ether was kept at −60° for 15 minutes. The solution was then warmed slowly and at −20 to −10° a solid separated. After coming to room temperature the mixture was worked up as before and there was obtained 1.0 g. (33%) of unreacted thiobenzamide, 0.65 g. (30%) of benzonitrile n^{20}_D 1.5280, and 0.2 g. (8%) of benzylamine.

(6) C. V. Jorgensen, *J. prakt. Chem.*, [2] **66**, 33 (1902).

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The Solubility of Aromatic Hydrocarbons in Water

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In a recent note, Herington[2] has criticized the conclusions drawn by Bohon and Claussen[3] from their data on the solubility of aromatic hydrocarbons in water. He suggests that by the choosing of the vapor as the standard state the abnormalities of the water solution disappear. There is of course no objection to the choice of the vapor as the standard state, but it must be obvious that, since benzene is a normal liquid, no abnormality would be cancelled out by this manipulation.

If one chooses the standard state of the pure hydrocarbon as vapor at 1 mm. pressure and the standard state of the solution when the mole fraction of the dissolved hydrocarbon (N_2) equals unity, then

$$\Delta F^\circ = RT \ln (p_0/N_2) \qquad (1)$$

represents the standard free energy of hydration,[4] where p_0 is the saturated vapor pressure of the liquid hydrocarbon in equilibrium with the saturated water solution and the temperature T is in degrees Kelvin. Then

$$\Delta S^\circ = -(\mathrm{d}\Delta F^\circ/\mathrm{d}T) \qquad (2)$$

represents the standard entropy change for the solution process. Combining equations (1) and (2), one obtains

$$\Delta S^\circ = \frac{\Delta H_{\mathrm{T(sol)}}}{T} - \frac{\Delta H_{\mathrm{T(vap)}}}{T} - R \ln \frac{p_0}{N_2} \qquad (3)$$

where $\Delta H_{\mathrm{T(sol)}}$ is the heat of solution of the liquid hydrocarbon in water as used by Bohon and Claussen and $\Delta H_{\mathrm{T(vap)}}$ is the heat of vaporization of the liquid hydrocarbon. Both of these heats change with temperature and may be subject to an analytical expression of the form

$$\Delta H_{\mathrm{T}} = \Delta H_{298} + \Delta C_{\mathrm{p}}(T - 298^\circ\mathrm{K.}) \qquad (4)$$

by which the heats are referred to a standard temperature of 298°K. and the ΔC_{p} term is the difference between the molar hydrocarbon heat capacities of the solution (or vapor) and the liquid hydrocarbon. Substituting equation (4) in (3) and then differentiating will yield

$$\mathrm{d}\Delta S^\circ/\mathrm{d}T = \Delta C_{\mathrm{p}}/T \qquad (5)$$

where

$$\Delta C_{\mathrm{p}} = \Delta C_{\mathrm{p(sol)}} - \Delta C_{\mathrm{p(vap)}} \qquad (6)$$

$\Delta C_{\mathrm{p(sol)}}$ is the value for the solution of liquid hydrocarbon in water; the average value for all of the aromatics studied by Bohon and Claussen is about 70 cal./mole deg.[5]

The import of these equations is illustrated by the thermochemical changes accompanying the solution of toluene in water. A plot of the standard free energy of solution *versus* T for toluene is shown in Fig. 1. The plot is a *curved* line; the straight line shown in the figure is for comparison. The change in slope with temperature of the curved line which might connect the points in Fig. 1 is equal to $\Delta C_{\mathrm{p}}/T$, by equation 5. ΔC_{p} was approximately calculated using the standard free energy data for three temperatures (316.0, 298.8 and 276.8°K.) and was found to be 91 cal./mole deg. For the vaporization of toluene, ΔC_{p} was found to be about −18 cal./mole deg. Thus, by equation 6, the $\Delta C_{\mathrm{p(sol)}}$ for the liquid toluene in water should be about 73 cal./mole deg., in fairly good agreement with the average value of 70 cal./mole deg.

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(1) Corning Glass Works, Corning, New York.

(2) E. F. G. Herington, THIS JOURNAL, **73**, 5883 (1951).

(3) R. L. Bohon and W. F. Claussen, *ibid.*, **73**, 1571 (1951).

(4) J. A. V. Butler, "Chemical Thermodynamics," 4th ed. (1 Vol), The Macmillan Co., London, 1946, p. 389.

(5) The value of 108 cal./deg. mole given by Bohon and Claussen in their Fig. 4 is in error.