TABLE IV

THERMODYNAMIC FUNCTIONS FOR PARAFFINS. TERMS FOR C_p°

$F(\sigma) = 0.$

Temp., °K.	F_0	C–C stretch	C–C bend	I_{rot} skel.	F_{steric} A	F_{steric} B	CH$_3$ I_{rot}	CH$_3$ Vibr.	CH$_2$ vibr.
200	7.949	0.088	1.277	2.207	2.167	0.494	1.757	0.238	0.151
220	7.949	.138	1.400	2.242	1.836	.422	1.857	.364	.242
240	7.949	.198	1.494	2.274	1.571	.362	1.941	.520	.357
260	7.949	.265	1.567	2.301	1.356	.312	2.011	.704	.497
280	7.949	.338	1.625	2.322	1.181	.270	2.067	.913	.657
300	7.949	.413	1.672	2.336	1.037	.236	2.110	1.143	.839
320	7.949	.488	1.710	2.346	0.917	.208	2.145	1.391	1.034
340	7.949	.564	1.742	2.344	.816	.184	2.173	1.653	1.242
360	7.949	.639	1.768	2.338	.731	.165	2.192	1.924	1.458
380	7.949	.710	1.791	2.326	.658	.149	2.200	2.204	1.681
400	7.949	.779	1.810	2.309	.595	.135	2.201	2.485	1.908
420	7.949	.845	1.826	2.288	.541	.123	2.199	2.769	2.136
440	7.949	.907	1.840	2.263	.494	.112	2.189	3.053	2.365
460	7.949	.965	1.853	2.235	.452	.103	2.176	3.335	2.592
480	7.949	1.020	1.864	2.205	.415	.094	2.159	3.614	2.816
500	7.949	1.072	1.874	2.174	.382	.087	2.138	3.890	3.038

vibrational contributions were obtained by linear interpolation in the ONR Einstein function tables[3] and are estimated to be accurate to ±0.001 unit if the given frequencies are accepted. The terms for I_{rot} for the skeleton were obtained by four-point Lagrangean interpolation in the Pitzer and Gwinn[4] tables and are accurate to ±0.001 unit. However, the corresponding terms for I_{rot} for the methyl groups which were obtained in a similar fashion were not as smooth and may deviate from smoothness by ±0.003 unit. (Previous experience has indicated that the body of the Pitzer and Gwinn tables is not smooth to better than ±0.003 to 0.005 unit.)

TABLE V

THERMODYNAMIC FUNCTIONS OF n-HEPTANE. IDEAL GAS STATE

T, °K.	$-F^\circ - H_0^\circ/T$	$H^\circ - H_0^\circ/T$	S°	C_p°
200	67.495	20.937	88.432	30.602
210	68.527	21.416	89.944	31.403
220	69.535	21.889	91.424	32.232
230	70.519	22.357	92.876	33.092
240	71.480	22.823	94.303	33.982
250	72.421	23.288	95.709	34.901
260	73.343	23.752	97.096	35.848
270	74.248	24.218	98.467	36.821
280	75.137	24.686	99.823	37.816
290	76.001	25.156	101.167	38.834
300	76.872	25.629	102.501	39.868
310	77.720	26.105	103.825	40.915
320	78.557	26.584	105.141	41.971
330	79.383	27.066	106.449	43.033
340	80.198	27.552	107.749	44.098
350	81.003	28.040	109.043	45.164
360	81.799	28.530	110.330	46.228
370	82.588	29.023	111.611	47.287
380	83.369	29.517	112.886	48.341
390	84.142	30.013	114.155	49.386
400	84.908	30.511	115.419	50.422
410	85.668	31.009	116.676	51.446
420	86.421	31.508	117.928	52.459
430	87.168	32.007	119.174	53.459
440	87.909	32.505	120.415	54.446
450	88.646	33.003	121.650	55.418
460	89.377	33.501	122.878	56.377
470	90.102	33.998	124.100	57.321
480	90.823	34.494	125.317	58.252
490	91.540	34.988	126.528	59.170
500	92.252	35.481	127.732	60.076

The values in the A column for F_{steric} are for n-heptane and were computed directly; for a = 500 cal./mole they are accurate to ±0.001 unit. The B values corresponding to the CH$_2$ increment above n-heptane were found by calculation of the "steric" functions for n-octane, n-nonane and n-decane at 200 and 300°K. The increment was found to be constant to ±0.0005 unit. The values at the 20° intervals shown were computed by five-point Lagrangean interpolation. These may be uncertain by ±0.010 unit.

The thermodynamic functions for n-heptane presented in Table V were obtained by numerical smoothing of the results obtained by summation of the values in Tables I to IV. The smoothed values at the even 20° intervals do not differ from the direct sums by more than ±0.004, and 83% of the values differ by less than ±0.003. The values at the odd 20° intervals were obtained by three or four point Lagrangean interpolation. The table is self consistent, and the thermodynamic interrelations between the columns are satisfied.

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[3] H. L. Johnston, L. Savedoff and J. Belzer, "Contributions to the Thermodynamic Functions by a Planck-Einstein Oscillator in One Degree of Freedom," Office of Naval Research Report NAVEXOS P-646, July, 1949, Washington, D. C.

[4] K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

The Action of Aluminum Chloride as a Catalyst in Alkylation Reactions

BY C. R. RAHA

RECEIVED AUGUST 11, 1953

Recent communications by this author[1,2] have described the use of aluminum chloride as a catalyst in certain alkylation reactions. The present

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[1] C. Raha, THIS JOURNAL, **75**, 4098 (1953).

[2] C. Raha, *ibid.*, **75**, 4098 (1953).

paper extends this study, reporting the reaction of ethyl chloroacetate with ethyl acetoacetate to give ethyl α-acetosuccinate, of ethylene chlorohydrin with malonic ester to give γ-butyrolactone, and of propylene α-chlorohydrin with malonic ester to give γ-valerolactone, each of these syntheses being catalyzed by aluminum chloride.

The synthesis of ethyl α-acetosuccinate from ethyl chloroacetate and ethyl acetoacetate in the presence of either an acidic or a basic catalyst suggests that ethyl chloroacetate gives the same carbonium ion in both instances. Moreover, the formation of γ-lactones from chlorohydrins and malonic ester in the presence of aluminum chloride indicates that the following type of carbonium ion is present

$$\mathrm{HO{-}CH_2{-}CH_2{-}Cl + AlCl_3 \longrightarrow \overset{\ominus}{AlCl_4} + HO{-}CH_2{-}\overset{\oplus}{CH_2}}$$

Experimental

Diethyl α-Acetosuccinate.—Twenty grams of coarsely powdered anhydrous aluminum chloride (much larger amounts gave tars only) was placed in a standard joint flask fitted with a guard tube and a dropping funnel. A solution of 6.5 g. of ethyl acetoacetate and 6.0 g. of ethyl chloroacetate in 25 ml. of chloroform was added dropwise at room temperature. After the evolution of hydrogen chloride ceased, the mixture was decomposed with ice hydrochloric acid, the chloroform layer was separated and the aqueous layer was extracted with chloroform. The chloroform solution was washed with water, then with very dilute alkali, finally with water, and was then dried over anhydrous sodium sulfate. Removal of the solvent left an oil which was fractionated, giving a fore-run of unreacted starting materials at atmospheric pressure and then 2 to 3 g. of an oil, b.p. 115–120° at 10 mm. pressure. Carbon–hydrogen analysts of this oil indicated that it was ethyl α-acetosuccinate. The phenylhydrazone melted at 155–157°[3] and semicarbazone melted at 164–165°.

Anal. Calcd. for $C_{11}H_{19}N_3O_5$: C, 48.4; H, 6.9. Found: C, 48.6; H, 7.2.

The phenylhydrazone and semicarbazone were also prepared from diethyl α-acetosuccinate synthesized by the base-catalyzed reaction described by Fittig[3] and by Adkins.[4]

α-Acetosuccinic Acid.—Nine and one-half grams of diethyl α-acetosuccinate was placed in a flask cooled externally by ice and 30 ml. of hydrochloric acid (sp. gr. 1.17) was added. After standing for 48 hours at a temperature below 10°, and the subsequent removal of the solvent at 55–60° (25–30 mm.), there was obtained 1.5 g. of white solid, m.p. 181–183°, which melted at 183–184° after two recrystallizations from water.

Anal. Calcd. for $C_6H_8O_5$: C, 45.0; H, 5.0; neut. equiv., 80. Found: C, 45.2; H, 5.3; neut. equiv., 81, 84.

γ-Valerolactone.—To a suspension of 50 g. of coarsely powdered aluminum chloride in 50 ml. of chloroform was added, dropwise, a solution of 16 g. of diethyl malonate and 10 g. of propylene α-chlorohydrin. When the evolution of hydrogen chloride ceased (about 18 hr.), the mixture was decomposed with iced 10% hydrochloric acid and was then refluxed for 40 hours. The product, which smelled like benzaldehyde, was worked up in the usual manner, giving 3.8 g. of an oil, b.p. 100–101° at 8 mm.,[5] which had a neutralization equivalent of 105 (calculated value, 100). Oxidation of 3.3 g. of this oil with 3.0 ml. of concentrated nitric acid (sp. gr. 1.41) gave 1.1 g. of succinic acid, identified by mixed melting point.[6]

γ-Butyrolactone.—The substitution of ethylene chlorohydrin for propylene α-chlorohydrin in the above procedure gave γ-butyrolactone in 60–80% yield. The lactone product, b.p. 85–100° at 12 mm., gave neutralization equivalent values of 81 and 87, and was oxidized to succinic acid by the action of nitric acid.

Acknowledgments.—The author expresses his indebtedness to Dr. D. M. Bose, Director of the Bose Institute, as well as to Dr. D. K. Banerjee, College of Engineering and Technology, Jadavpur, and to Dr. S. K. Mukherjee, Department of Applied Chemistry, University College of Science and Technology, Calcutta, for their valuable help and interest in this work.

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[3] Fittig [*Ann.*, **283**, 67 (1894)] and Emery [*ibid.*, **295**, 94 (1897)] reported a melting point of 155–156°.

[4] H. Adkins, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 262.

[5] Leuchs and co-workers (*Ber.*, **42**, 1228 (1909)) reported a boiling point of 83–84° at 13 mm. for γ-valerolactone.

[6] Fittig and Messerschmidt (*Ann.*, **208**, 97, 107 (1881)) described, but without details, the nitric acid oxidation of γ-valerolactone.

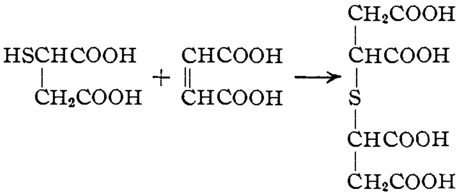
Synthesis of Thiodisuccinic Acid[1,2]

BY A. W. SCHWAB

RECEIVED OCTOBER 2, 1953

Esters of thiodisuccinic acid have been reported,[3,4] but the free acid has not been prepared. Tetrabutyl thiodisuccinate is sold under the trade name "Flexol" Plasticizer TWS. Interest in the use of thiodisuccinic acid as a possible chelating agent has stimulated its preparation. The acid is pentadentate and the sulfur atom may be expected to function as a coördinating atom in the formation of chelate rings especially with the heavy metal ions.

Synthesis of the free acid was accomplished by the addition of mercaptosuccinic acid to the ethylenic bond of maleic acid. Mercaptosuccinic acid adds in the manner



$$\begin{array}{l}\mathrm{HSCHCOOH}\\ \quad|\\ \mathrm{CH_2COOH}\end{array} + \begin{array}{l}\mathrm{CHCOOH}\\ \quad\|\\ \mathrm{CHCOOH}\end{array} \longrightarrow \begin{array}{l}\mathrm{CH_2COOH}\\ |\\ \mathrm{CHCOOH}\\ |\\ \mathrm{S}\\ |\\ \mathrm{CHCOOH}\\ |\\ \mathrm{CH_2COOH}\end{array}$$

Carboxymethylmercaptosuccinic acid has been prepared by the addition of mercaptoacetic acid to maleic acid.[5–7]

Experimental

Mercaptosuccinic acid (15.0 g., 0.1 mole) and maleic acid (11.6 g., 0.1 mole) in 100 ml. of water were heated on the steam-bath for 2 hours. Upon standing overnight, crystals separated. The crystalline product was filtered, washed with cold water, and purified by recrystallization from water. After drying, 11.0 g. of a product was obtained which melted at 196–197°. The neutral equivalent was 67.2 (theory 66.5).

Anal. Calcd. for $C_8H_{10}O_8S$: C, 36.1; H, 3.8; S, 12.0. Found: C, 36.1; H, 3.8; S, 12.1.

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[1] From one of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] Article not copyrighted.

[3] H. F. Smyth, Jr., C. P. Carpenter and C. S. Weil, *Arch. Indus. Hygiene Occup. Med.*, **4**, 119 (1951).

[4] L. W. Newton, U. S. Patent 2,603,616 (July 15, 1952).

[5] E. J. Morgan and E. Friedmann, *Biochem. J.*, **32**, 733 (1938).

[6] E. Larsson, *Trans. Chalmers Univ. Technol., Gothenburg*, No. 47. 3 (1945); *C. A.*, **40**, 2796[5] (1946).

[7] J. F. Mulvaney, J. G. Murphy and R. L. Evans, THIS JOURNAL, **70**, 2428 (1948).