ml. of 96% ethanol gave a solution whose qualitative and quantitative composition could easily be determined on a Beckman Spectrophotometer.

The adsorbent can be recovered by placing in a chromatographic tube, washing with enough 96% ethanol to wet the entire column, then washing with three times this volume of petroleum ether, and finally drying in the air at room temperature. Silica–zinc sulfide mixture so recovered showed slightly weaker adsorptive properties than fresh adsorbent, but was its equivalent for all practical purposes. Both fresh and recovered mixtures were used in this work.

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Osmotic and Activity Coefficients of Lithium Bromide and Calcium Bromide Solutions

BY R. A. ROBINSON AND H. J. MCCOACH

The osmotic and activity coefficients of lithium chloride and calcium chloride solutions have been determined recently[1,2] up to the highest concentrations. Similar measurements on the bromides have now been made to extend the concentration range beyond that of earlier measurements.[3,4]

Isopiestic determinations were made using platinum dishes as it has been found that some corrosion of silver dishes occurs with concentrated bromide solutions. Calcium chloride and sulfuric acid were used as reference electrolytes. The molalities of pairs of solutions of equal vapor pressure are given in Table I. From these measurements the osmotic and activity coefficients given in Table II were evaluated. This table contains values at low concentrations, the earlier data having been recalculated to conform with more recent reference data.[5]

TABLE I

MOLALITIES OF ISOPIESTIC SOLUTIONS AT 25°

LiBr	$CaCl_2$	LiBr	$CaCl_2$	LiBr	$CaCl_2$	LiBr	$CaCl_2$
4.837	3.110	5.937	3.756	6.913	4.345	7.942	4.984
9.388	5.980	10.12	6.553	11.02	7.426	11.87	8.342

LiBr	H_2SO_4	LiBr	H_2SO_4	LiBr	H_2SO_4	LiBr	H_2SO_4
11.95	12.85	13.61	15.29	14.33	16.32	15.46	17.88
16.14	18.80	16.47	19.20	16.58	19.35	17.09	20.04
18.39	21.64	18.99	22.35	19.85	23.21		

$CaBr_2$	$CaCl_2$	$CaBr_2$	$CaCl_2$	$CaBr_2$	$CaCl_2$	$CaBr_2$	$CaCl_2$
1.422	1.524	1.766	1.897	2.140	2.309	2.152	2.321
2.554	2.764	2.584	2.801	2.791	3.026	3.116	3.387
3.565	3.888	3.785	4.158	3.922	4.312	4.435	4.965
5.144	5.952	5.595	6.655	5.726	6.893	5.984	7.470
6.170	7.831	6.286	8.067	6.406	8.375	6.583	8.730
6.630	8.838	6.863	9.498	6.965	9.815	7.216	10.41

$CaBr_2$	H_2SO_4	$CaBr_2$	H_2SO_4	$CaBr_2$	H_2SO_4	$CaBr_2$	H_2SO_4
7.636	16.10	7.922	16.81	8.406	17.97	9.210	19.61

TABLE II

OSMOTIC AND ACTIVITY COEFFICIENTS OF LITHIUM AND CALCIUM BROMIDE AT 25°

	LiBr		$CaBr_2$	
m	φ	γ	φ	γ
0.1	0.943	0.796	0.863	0.532
.2	.944	.766	.878	.492
.3	.952	.756	.900	.482
.4	.960	.752	.927	.483
.5	.970	.753	.958	.491
.6	.981	.758	.990	.505
.7	.993	.767	1.022	.522
.8	1.007	.777	1.057	.543
.9	1.021	.789	1.093	.568
1.0	1.035	.803	1.131	.597
1.2	1.067	.837	1.207	.665
1.4	1.098	.874	1.286	.747
1.6	1.130	.917	1.370	.848
1.8	1.163	.964	1.455	.970
2.0	1.196	1.015	1.547	1.121
2.5	1.278	1.161	1.790	1.657
3.0	1.364	1.341	2.048	2.54
3.5	1.467	1.584	2.297	3.89
4.0	1.578	1.897	2.584	6.28
4.5	1.687	2.28	2.908	10.66
5.0	1.793	2.74	3.239	18.47
6.0	1.989	3.92	3.880	55.8
7.0	2.206	5.76	4.463	163.0
8.0	2.432	8.61	4.809	375
9.0	2.656	12.92	4.969	696
10.0	2.902	19.92	...	.....
11.0	3.150	31.0	...	.....
12.0	3.356	46.3	...	.....
13.0	3.581	70.6	...	.....
14.0	3.776	104.7	...	.....
15.0	3.912	146.0	...	.....
16.0	4.025	198.0	...	.....
17.0	4.110	260	...	.....
18.0	4.173	331	...	.....
19.0	4.216	411	...	.....
20.0	4.217	485	...	.....

CHEMISTRY DEPARTMENT
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(1) R. A. Robinson, *Trans. Faraday Soc.*, **41**, 756 (1945).

(2) R. H. Stokes, *ibid.*, **41**, 637 (1945).

(3) R. A. Robinson, THIS JOURNAL, **57**, 1161 (1935).

(4) R. A. Robinson, *Trans. Faraday Soc.*, **38**, 445 (1942).

(5) (a) S. Shankman and A. R. Gordon, THIS JOURNAL, **61**, 2370 (1939); (b) R. H. Stokes and B. J. Levien, *ibid.*, **68**, 333 (1946); (c) R. H. Stokes, *ibid.*, **69**, 1291 (1947).

A Claisen Condensation by a Primary Grignard Reagent

BY S. B. SOLOWAY AND F. B. LAFORGE

The abnormal reactions of the Grignard reagents have been frequently reported in the literature. In the majority of such reactions the Grignard reagent has been prepared from either a secondary or a tertiary halide. Recently the Claisen condensation of esters by the agency of *t*-butylmagnesium chloride has been reported.[1] In this note we describe a mixed ketone–ester condensation by means of a Grignard reagent prepared from a primary halide.

The reaction between ethyl levulinate and the Grignard reagent is known to give low yields of

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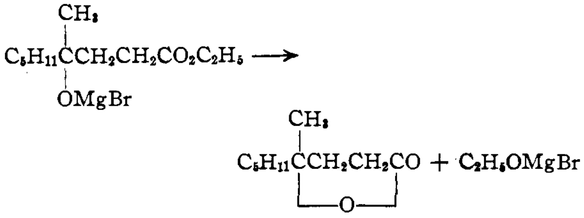
(1) Zook, McAleer and Horwin, *ibid.*, **68**, 2404 (1946).

lactone: 28% for hexyl chloride, 31% for hexyl bromide,[2] 29% for amyl chloride[3] and 38% (based on crude product) for β-bromonaphthalene.[4]

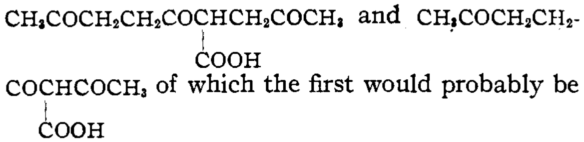
We have treated ethyl levulinate with amylmagnesium bromide and have increased the yield of lactone to 41% based on the halide, by employing a 50% excess of the ester. After the lactone had been distilled off, a large amount of material remained, which has been investigated. From this by-product a tri-keto acid, probably 4,6,9-trioxocapric acid, m. p. 118°, was the only compound that could be isolated. This acid evidently resulted from the hydrolysis of the ester arising from the condensation of the ester group of one molecule of ethyl levulinate with the methyl group of another molecule.

$$2CH_3COC\;\;CH_2COOC_2H_5 \xrightarrow{C_5H_{11}MgBr} CH_3COCH_2CH_2COCH_2COCH_2CH_2COOC_2H_5$$

It is quite possible that the actual condensation agent is ethoxymagnesium bromide which would be present by the reaction of the Grignard reagent with the ester grouping as well as by the reaction which occurs after addition of the reagent to the carbonyl group.[5]



Other possible structures for the acid include



$CH_3COCH_2CH_2COCH(COOH)CH_2COCH_3$ and $CH_3COCH_2CH_2COCH(COOH)COCH_3$ of which the first would probably be unstable.

That the condensation resulted in a straight-chain compound containing only one acetyl group seems highly probable from the terminal methyl determination.[6] The results show that on an average 66% of one acetyl group was converted to acetic acid. This figure is in agreement with the terminal methyl value observed for the semicarbazone of ethyl methyl ketone (67%).[5]

Experimental

The Grignard reaction was carried out by the inverse addition of the reagent, prepared from 302 g. (2 moles) of amyl bromide and 48 g. (2 g. atoms) of magnesium in 500 ml. of ether, to 432 g. (3 moles) of ethyl levulinate in 600 ml. of benzene. The reaction proceeded in the usual manner, and the product was distilled, yielding 140 g. (41% based on halide) of γ-methyl-γ-pelargonolactone, b. p. 110° (0.5 mm.), n^{25}_D 1.4468. The higher boiling fraction, which was not distilled, amounted to 205 g.

4,6,9-Trioxocapric Acid.—Twenty-five grams of the undistilled fraction was treated with 100 ml. of 10% sodium hydroxide and allowed to stand overnight at room temperature. After about 1 g. of neutral material had been removed by ether extraction, the solution was acidified with dilute hydrochloric acid, saturated with sodium chloride, and extracted with ether. The ether solution was washed free of acid with salt solution and dried, and the solvent was removed. The residue, 15.6 g., was subjected to high-vacuum distillation and yielded 2 g. of uncharacterized material. The residue was then poured into a beaker and, after about a week, crystals formed in the dark-brown mass. Trituration with cold ethyl acetate yielded 2.6 g. of crystals, which upon recrystallization from ethyl acetate melted at 118°.

Anal. Calcd. for $C_{10}H_{14}O_5$: C, 56.07; H, 6.59; neut. equiv., 214; 1 CH_3, 7.0. Found: C, 56.09; H, 6.53; neut. equiv., 215; CH_3, 4.4, 4.8.

The acid yielded a monosemicarbazone, m. p. 193°.

Anal. Calcd. for $C_{11}H_{17}O_5N_3$: C, 48.70; H, 6.32. Found: C, 49.02; H, 6.29.

BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
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Heats of Polymerization of Some Unsaturates

BY L. K. J. TONG AND W. O. KENYON

The heats of polymerization of certain unsaturates have been measured and found to be: methyl acrylate 18.7 ± 0.2, vinyl acetate 21.3 ± 0.2, acrylonitrile 17.3 ± 0.5, and vinylidene chloride 14.4 ± 0.5 kcal./mole of monomeric unit. The unsaturates used were highly purified for these measurements. The calorimeter and the technique of its operation have been described previously.[1] With the exception of methyl acrylate, corrections have been made for unreacted monomers. The heat of polymerization value for methyl acrylate was determined using 0.01% of benzoyl peroxide catalyst, while vinyl acetate was determined with 0.018% and 0.035% of the catalyst. These latter values did not vary significantly. Measurements with acrylonitrile were made using catalyst concentrations of 0.05 to 0.20%, and with vinylidene chloride using 0.25 to 0.86%. The final values given above for the two latter monomers were determined by extrapolation to zero catalyst concentration. All determinations reported were at 76.8°. The $-\Delta H$ of 21.3 kcal./mole for vinyl acetate is quite different from the value of 28.0 reported by Houwink[2] and 8.0 ± 0.4 by Mark, *et al.*[3] Based on considerations of the stability of the polymerizable double bond, vinyl acetate should show a larger value of $-\Delta H$ than do methyl acrylate or styrene, wherein the double bond is conjugated. Our value of 21.3 is close to those calculated by

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[2] Frank and co-workers, *ibid.*, **66**, 4 (1944).

[3] LaForge and Barthel, *J. Org. Chem.*, **10**, 222 (1945).

[4] Robinson and Slater, *J. Chem. Soc.*, 376 (1941).

[5] Grignard, *Compt. rend.*, **135**, 627 (1902).

[6] Barthel and LaForge, *Ind. Eng. Chem., Anal. Ed.*, **16**, 434 (1944).

[1] Tong and Kenyon, THIS JOURNAL, **67**, 1278 (1945); **68**, 1335 (1946); **69**, 1402 (1947).

[2] Houwink, "Chemie und Tech. der Kunststoff," Vol. I, Akad. Verlags., Leipzig, 1940, p. 60.

[3] Goldfinger, Josefowitz and Mark, THIS JOURNAL, **65**, 1432 (1943).