Alcohol	Acid, g.	Alc., g.	Time, hrs.	% ester	B. p. 756 mm. °C.	B. p., °C.	B. p., Mm.	Sp. gr. 20°/20°	Chlorine, % Calcd.	Chlorine, % Found
				Esters of Acetic Acid						
n-Butyl	240	300	3	90	124–126					
				Esters of Monochloroacetic Acid						
n-Butyl	47	50	1.5	97		94	38			
n-Amyl	100	120	3	88	196	105	35	1.0514	21.59	21.81
s-Amyl	47	50	3	89	185	93	27	1.0475	21.59	21.65
Diethyl methyl	94	100	4	85	184	93	30	1.0469	21.59	21.62
t-Amyl	94	100	2	65	168	88	43	1.0627	21.59	21.61
				Esters of Dichloroacetic Acid						
n-Butyl	64	50	3	98		102	37			
n-Amyl	65	60	1.5	94	207	124	48	1.1455	35.63	35.52
s-Amyl	65	60	4	93	198	93	20	1.1210	35.63	35.29
Diethyl methyl	65	60	7	95	197[a]	105	40	1.1225	35.63	35.35
t-Amyl	65	60	2	75	180[a]	93	30	1.1230	35.63	35.72
				Esters of Trichloroacetic Acid						
n-Butyl	82	50	3	98		111	40			
n-Amyl	61	38	3	91	218	118	30	1.2475	45.59	45.90
s-Amyl	81	60	2.5	95	206	108	30	1.2084	45.59	45.55
Diethyl methyl	163	100	5	80	201[a]	105	25	1.2081	45.59	45.71
t-Amyl	81	60	1.5	84	191[a]	105	30	1.2505	45.59	45.73

[a] These tend to decompose partly into olefin and acid.

new; some old esters are given for comparisons of yields.

Chemistry Laboratory
University of Washington
Seattle, Washington

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The Relative Partial Molal Heat Content of Sodium Bromide in Aqueous Solutions at 25°

By A. L. Robinson

Harned and Crawford[1] have measured recently the electromotive forces of the cells

$$\mathrm{Ag{-}AgBr/NaBr}(m)\mathrm{/Na_xHg}(m<0.1)\mathrm{/NaBr(0.1)/AgBr{-}Ag}$$

at temperatures from 0 to 40° and from these have calculated values for the relative partial molal heat contents of sodium bromide. Their $\bar{L}_2$ values at 25° may be compared with values determined from calorimetric measurements extending to 0.00016 *m*.[2]

m	$\bar{L}_2$, e. m. f.	$\bar{L}_2$, cal.
0.1	101	76
.2	79	56
.5	55	− 32
1.0	−211	−208
1.5	−421	−384
2.0	−587	−540
2.5	−719	−656
3.0	−819	−753
3.5	−857	−834
4.0	−887	−899

The agreement is fair although the differences are somewhat larger than the usual estimates of precision of the two methods.

Department of Chemistry
University of Pittsburgh
Pittsburgh, Penna.

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(1) H. S. Harned and C. C. Crawford, This Journal, **59**, 1903 (1937).

(2) H. Hammerschmid and A. L. Robinson, *ibid.*, **54**, 3120 (1932).

A Sensitive Manostat for Low Gas Pressures. A Correction

By Theodore Soller, Seymore Goldwasser and Ralph A. Beebe

We are indebted to Professor Earl B. Working for calling our attention to the fact that the diagram of the photoelectric relay circuit given in our paper: "A Sensitive Manostat for Low Pressures and its Application to the Adsorption of Hydrogen and Deuterium on Copper,"[1] should contain a grid leak, that is, a high resistance of the order of 10^8 ohms, between the grid and the cathode of the 6C6 tube. With infinite resistance in the grid circuit, this tube would block.

We have found that under ordinary conditions of humidity, the leakage resistance of the condenser and the sockets is sufficient to prevent blocking, so it has not been necessary for us to introduce a separate resistor. But under conditions of extremely good insulation it would be necessary to introduce a separate high resistance of this order of magnitude.

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(1) This Journal, **58**, 1703 (1936).

We thank Professor Working for calling this to our attention.

MOORE LABORATORY OF CHEMISTRY
AMHERST COLLEGE
AMHERST, MASS.
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The Action of Sodium Phenylacetylene on α,β-Unsaturated Esters

BY DAVID E. WORRALL

It has been reported[1] that esters of formic acid react with sodium phenylacetylene producing an unsaturated aldehyde. Nef,[2] however, was unable to obtain even a trace of the corresponding ketone from ethyl acetate or benzoate, although the acid chloride and anhydride gave positive results. Because of these contradictory results and because little is known concerning the activity of acetylenic salts with unsaturated systems, an investigation was made with several unsaturated esters.

It was found that phenylcinnamylacetylene is obtained readily by the interaction of sodium phenylacetylene and ethyl cinnamate the result probably of 1,2-addition followed by the elimination of sodium alcoholate. This ketone, containing as it does a double and triple bond conjugated with a carbonyl group, has interesting possibilities as a vehicle for testing the selective reactivity of reagents for such conjugate systems. Actually the accumulation of unsaturated groups appears to hinder rather than promote the normal reactivity of the carbonyl group. Attempts to force a reaction result in the formation of nontractable tars, while more powerful reagents such as the Grignard cause the ketone to act as an enol.

Experimental

Cinnamylphenylacetylene.—To 0.2 gram mole of sodium phenylacetylene suspended in dry ether and connected to a reflux condenser was added the equivalent of ethyl or methyl cinnamate. Heat sufficient to cause gentle boiling was evidenced for a few minutes. A slow but steady evolution of hydrogen took place even after long standing, due to secondary reactions. The deeply colored mixture was allowed to evaporate in a stream of air after addition to cracked ice containing a slight excess of acetic acid. The resulting oil quickly became crystalline if seeded: yield, after washing with a small volume of cold alcohol, 21 g. It separated from benzene–petroleum ether mixtures in the form of small lustrous needles melting at 140–141°.

Anal. Calcd. for $C_{17}H_{12}O$: C, 88.0; H, 5.1. Found: C, 87.9; H, 5.3.

It responded to the usual tests for unsaturation, but the addition products, with bromine for example, were obtained only as intractable mixtures. The original substance was sensitive to acids and even dilute acetic acid caused tar formation on long standing at room temperature. A purple color formed when a trace of the ketone was dissolved in cold sulfuric acid, subsequently becoming greenish-fluorescent in appearance. While more stable toward alkaline reagents, hot solutions eventually caused resinification. Traces of phenylacetylene and benzaldehyde were detected. No reactions were observed with hydroxylamine or hydrazine even after long heating. The use of higher temperatures with sealed tubes produced tars. A crystalline product quickly formed with both methyl- and phenylmagnesium halide, but on decomposition with dilute acid the original ketone was recovered. It liberated hydrogen on contact with sodium and displaced sodium from sodium phenylacetylene, thus explaining the secondary reactions observed in the original preparation. Benzoic acid and benzaldehyde were identified among the oxidation products of the ketone with permanganate. Ethyl crotonate reacted even more vigorously with sodium phenylacetylene, but the product was obtained only as a thick oil. Benzoyl methyl acrylate yielded an amorphous powder that was not further examined.

PEARSON MEMORIAL LABORATORY
TUFTS COLLEGE
MEDFORD, MASS.
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[1] Moureu and Delage, *Compt. rend.*, **133**, 105 (1901).

[2] *Ann.*, **308**, 279 (1899).