

TABLE I

Ketones	Amines (as form- amides)	Secondary amine obtained	Yield, %	Hydrochloride	
				M. p., °C.	Cl analyses, % Calcd. Found
Acetophenone	Methyl	<i>dl</i> -Methyl- α -phenethyl ^a	60	178-179	20.69 20.59
<i>p</i> -Methylacetophenone	Methyl	<i>dl</i> -Methyl- α - <i>p</i> -methylphenethyl	50	159-160	19.13 19.17
<i>p</i> -Chloroacetophenone	Methyl	<i>dl</i> -Methyl- α - <i>p</i> -chlorophenethyl	70	199-200	17.39 17.23
<i>p</i> -Bromoacetophenone	Methyl	<i>dl</i> -Methyl- α - <i>p</i> -bromophenethyl	70	196-197	14.20 14.17
Acetophenone	Ethyl	<i>dl</i> -Ethyl- α -phenethyl ^b	70	199-200	19.13 19.17
<i>p</i> -Methylacetophenone	Ethyl	<i>dl</i> -Ethyl- α - <i>p</i> -methylphenethyl	60	217-218	17.77 17.75
<i>p</i> -Chloroacetophenone	Ethyl	<i>dl</i> -Ethyl- α - <i>p</i> -chlorophenethyl	80	<250	16.13 15.97
<i>p</i> -Bromoacetophenone	Ethyl	<i>dl</i> -Ethyl- α - <i>p</i> -bromophenethyl	60	<250	14.20 14.17
Acetophenone	Butyl	<i>dl</i> -Butyl- α -phenethyl	70	154-155	16.62 16.68
<i>p</i> -Methylacetophenone	Butyl	<i>dl</i> -Butyl- α - <i>p</i> -methylphenethyl	50	159-160	15.62 15.62
<i>p</i> -Chloroacetophenone	Butyl	<i>dl</i> -Butyl- α - <i>p</i> -chlorophenethyl	80	174-175	14.31 14.20
<i>p</i> -Bromoacetophenone	Butyl	<i>dl</i> -Butyl- α - <i>p</i> -bromophenethyl	70	174-175	12.42 12.30

^a Busch and Lefhelm, *loc. cit.*, 173°. ^b *Ibid.*, 201°.

cold formic acid. The temperature is raised slowly to 180-190° and this temperature maintained as long as water distills. After cooling, 1 mole of ketone is added and the mixture heated until boiling begins; water, carbon dioxide, and amine distil and are collected in concentrated hydrochloric acid. In case any ketone distils over, it is returned to the flask at intervals. The temperature of the boiling mixture is 190-230°, which is maintained for four to eight hours, after which the mixture is cooled and diluted with 3-4 volumes of water, giving oily and aqueous layers. The aqueous layer, mixed with the hydrochloric acid used in collecting the distilled amine, is concentrated to give the hydrochloride of the excess of amine used. The oil is refluxed for several hours with 150-200 cc. of hydrochloric acid per mole of ketone taken, and after the hydrolysis is complete water is added, the solution filtered

through moist paper to separate resinified material and the filtrate, if not clear, extracted once or twice with ether. In some experiments the amine hydrochloride crystallizes on cooling. The aqueous solution is made alkaline with ammonia, extracted with ether, the ether solution dried with sodium sulfate and saturated with hydrogen chloride to give the amine hydrochloride. The product is purified further by dissolving in absolute alcohol and precipitating with absolute ether.

Table I summarizes the melting points and analyses of the various hydrochlorides.

Summary

A new method of obtaining secondary amines, based on the Leuckart synthesis, is described. It has been applied to the preparation of several old and new amines.

LA PLATA, R. ARGENTINA RECEIVED AUGUST 12, 1938

NOTES

β -Nitrostyrene in the Diene Synthesis

BY C. F. H. ALLEN AND ALAN BELL

In view of a recent paper,¹ we wish to place on record our work on the addition of β -nitrostyrene to dienes. This unsaturated nitro compound added readily to the hydrocarbons listed in Table I, and to the unsaturated ketones, methyleneanthrone and tetraphenylcyclopentadienone; it did not react with furan, sylvan, or 2,5-dimethyl-

furan. In some instances, the products could be distilled *in vacuo* unchanged, whereas in others oxides of nitrogen were evolved even during the addition; thus with methyleneanthrone the principal product was *Bz*-1-phenylbenzanthrone. With the tetracyclone, carbon monoxide was also eliminated and the sole product was the known pentaphenylbenzene.

The addition products are undoubtedly aliphatic nitro compounds (I) since as long as there is an available hydrogen atom in the alpha posi-

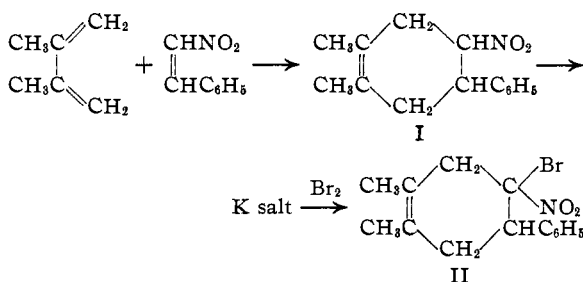
(1) Alder, Richert and Windemuth, *Ber.*, **71**, 2451 (1938).

TABLE I
PROPERTIES OF THE (ADDITION) PRODUCTS

Addend	Yield, %	M. p., °C.	Formula	Calcd., %			Found, %		
				C	H	N	C	H	N
2,3-Dimethylbutadiene	82	96	C ₁₄ H ₁₇ O ₂ N	73.2	7.4		72.9	7.4	
Isoprene	7	52	C ₁₈ H ₁₆ O ₂ N	71.9	7.0	6.5	72.4	7.1	6.2
2,3-Diphenylbutadiene ^{a,b}	9	175	C ₂₄ H ₂₁ O ₂ N	81.1	5.9	3.9	81.2	6.0	3.8
1,4-Diphenylbutadiene	40	130	C ₂₄ H ₂₁ O ₂ N	81.1	5.9	3.9	80.9	5.8	4.2
Methyleneanthrone ^{a,c,d}	3	255	C ₂₈ H ₁₈ O ₃ N	78.6	3.7	4.0	78.6	3.7	4.1
Tetracyclone ^{a,e}									
		B. p.							
Phellandrene	45	190/1 mm.	C ₁₈ H ₂₈ O ₂ N	75.8	8.4	4.9	76.3	8.1	4.5
Cyclopentadiene	95	145/1 mm.	C ₁₈ H ₁₆ O ₂ N	72.6	6.1	6.5	72.6	6.1	6.4
Cyclohexadiene	20	138-142/1 mm.	C ₁₄ H ₁₆ O ₂ N	73.3	6.6	6.1	72.9	6.1	6.4

^a Oxides of nitrogen evolved. ^b 5% yield of a hydrocarbon, C₂₄H₂₀, m. p. 77°. Calcd. C, 93.5; H, 6.5. Found: C, 93.0; H, 6.7. ^c 25% yield of *Bz*-1-phenylbenzanthrone. ^d On oxidation, the product yielded α -benzoylanthraquinone, hence it is *Bz*-1-phenyl-*bz*-2-nitrobenzanthrone. ^e Gave only pentaphenylbenzene, m. p. 246°, mixed m. p. 246°.

tion, they dissolve in alkaline solutions, and the latter take up bromine. Substance I does not decolorize bromine.



Anal. Calcd. for C₁₄H₁₆O₂NBr (II): C, 54.2; H, 5.2; N, 4.5. Found: C, 54.2; H, 5.1; N, 4.3.

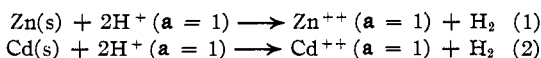
EASTMAN KODAK COMPANY
ROCHESTER, N. Y.

RECEIVED JANUARY 6, 1939

The Entropies of Aqueous Zinc and Cadmium Ions. The Heat Capacity of Zinc Ion

BY ROGER G. BATES¹

Recent studies by the writer have shown² that the standard electromotive forces, E^0 , of the reactions



may be expressed by the equations

$$E_{\text{Zn}}^0 = 0.76274 - 0.0001(t - 25) - 0.00000031(t - 25)^2 \quad (3)$$

$$E_{\text{Cd}}^0 = 0.40178 + 0.000089(t - 25) + 0.00000081(t - 25)^2 + 0.00000075(t - 25)^3 \quad (4)$$

(1) Sterling Fellow.

(2) Bates, *THIS JOURNAL*, **60**, 2983 (1938); **61**, 308 (1939).

(3) Precise measurements of this cell between 0 and 30° were made by Parks and La Mer, *ibid.*, **56**, 90 (1934). The result of Getman, *ibid.*, **39**, 1806 (1917), at 35° does not agree sufficiently well with the value calculated from the equation of Parks and La Mer to justify extending the range of validity of equation (4) to that temperature.

where t is the temperature in degrees C.

Equation (3) is valid over the temperature range 5 to 40°, but the upper temperature limit for equation (4) must be set at 30°, above which consistent measurements of the cell³ Cd(Hg)/Cd⁺⁺/Cd(s) have not been made.

By the application of the usual thermodynamic relationships to equations (3) and (4), ΔF^0 , ΔH^0 , ΔS^0 and ΔC_p^0 for reactions (1) and (2) may be computed. The values of these quantities for reaction (1) at 15, 25 and 35° and for reaction (2) at 15 and 25° are summarized in Table I. Uncertainties in d^2E^0/dT^2 from equation (4) are sufficiently large to render ΔC_p^0 for reaction (2) useless for the calculation of ionic heat capacities; ΔC_p^0 for this reaction has therefore been omitted from Table I.

TABLE I
THERMODYNAMIC QUANTITIES FOR REACTIONS (1) AND (2)

t	E^0	ΔF^0	ΔH^0	ΔS^0	ΔC_p^0
Reaction (1)					
15	0.76371	-35,244	-36,491	-4.34	-8.24
25	.76274	-35,199	-36,575	-4.61	-8.53
35	.76171	-35,151	-36,661	-4.90	-8.82
Reaction (2)					
15	0.40089	-18,500	-17,233	4.40	
25	.40178	-18,541	-17,317	4.11	

Standard entropies and heat capacities of hydrogen and zinc and the entropy of cadmium are listed in Table II. Values at 25° for zinc and cadmium and for the entropy of hydrogen were taken from the summary of Kelley.⁴ The heat capacity of hydrogen at all three temperatures and the temperature coefficient of the heat ca-

(4) Kelley, Bureau of Mines, Bull. 394, U. S. Government Printing Office, Washington, D. C., 1936.