which partly crystallized from ethanol; yield, 3.3 g. It was purified from isopropyl alcohol, m. p. 213.5–214.5° (corr.).

Anal. Calcd. for $C_{19}H_{23}O_3N$: C, 72.82; H, 7.40. Found: C, 72.96, 72.48; H, 7.62, 7.49.

Methyldihydropseudocodeinone was unaffected by treatment with sodium in alcohol or in boiling cyclohexanol, by catalytic hydrogenation in alcohol, acidified alcohol or glacial acetic acid, by zinc and hydrochloric acid (seven hours under reflux), or by hydroxylamine or semicarbazide under various conditions.

The use of ethylmagnesium iodide in the above reaction gave non-crystalline products.

Summary

1. Pseudocodeinone can be reduced under proper conditions to a non-phenolic dihydropseudocodeinone. The relationship of this to dihydropseudocodeine-A establishes its structure.

2. Demethylation of dihydropseudocodeinone results in dihydroisomorphinone, the 8-keto analog of Dilaudid.

3. Dihydropseudocodeinone is indifferent to methylmagnesium iodide, but pseudocodeinone reacts to give a phenolic dihydromethylpseudocodeinone. This product is remarkable in the complete passivity of its carbonyl group and double linkage toward the usual reagents affecting such structures.

4. Comparison of the physiological action of dihydropseudocodeinone and dihydroisomorphinone with that of Dicodid and Dilaudid, and that of the codeine and morphine isomers indicates that morphine derivatives with the functional group at C-6 are more effective than those with the same group at C-8, but that spatial relationships are also very important.

UNIVERSITY, VIRGINIA

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Vinyldiazomethane

BY CHARLES D. HURD AND S. C. LUI

Recently, Adamson and Kenner[1] described vinyldiazomethane as if it were new. Nirdlinger and Acree,[2] however, prepared it in 1910. They synthesized it from allylnitrosourethan whereas Kenner employed allyl (acetyl-*t*-butyl)-nitrosamine. In the present work, done in 1933–1934, it was studied to learn whether allyl, cyclopropyl or propenyl esters would be formed during reaction with acids. Actually, it was the ally ester which resulted: $C_6H_5COOH + CH_2{=}CHCHN_2 \longrightarrow N_2 + C_6H_5COOCH_2CH{=}CH_2$. The isomerization of vinyldiazomethane to pyrazole, reported by Adamson and Kenner, was observed. In fact, it was found to isomerize appreciably even during the distillation of the diazo compound.

Vinyldiazomethane was prepared by Nirdlinger and Acree's method, namely, by adding a solution (20%) of potassium hydroxide in methanol to a solution of the nitroso compound (A) in ether (B). When a 1:15 or 1:20 ratio of A:B was maintained, a 22–25% yield of vinyldiazomethane resulted. With a 1:9 ratio, the yield dropped to 13%.

Allylurethan and allylnitrosourethan were prepared by methods closely adapted from those given for methylurethan and methylnitrosourethan in "Organic Syntheses" [Vol. XII, p. 38; XIII. p. 84], the difference being that allylamine was taken instead of methylamine. The yields, respectively, were 81 and 94%. This preparation of allylnitrosourethan is new. Nirdlinger and Acree, who made it from nitrogen trioxide and allylurethan, mentioned no yield and gave no analysis. In the present work, the nitroso compound was analyzed after being thoroughly washed, dried and freed from solvent ether: d^{15}_{15} 1.051 d^{20}_{20} 1.047, d^{25}_{25} 1.044. Decomposition attended efforts to distil it (a red oil) at 3 mm.

Anal. Calcd. for $C_6H_{10}O_3N_2$: N, 17.7. Found: N, 17.4.

To estimate the yields, 10.00 cc. of the ether solution of vinyldiazomethane was mixed in a stoppered flask with a solution of 0.500 g. of *p*-nitrobenzoic acid in 25 cc. of dry ether. When the solution became colorless in 15–25 minutes it was back-titrated with 0.1 *N* barium hydroxide. When the reaction period was extended to twenty-four hours the results were but slightly higher; *e. g.*, a 22.3% value changed to 23.1%. With 2,4,6-trinitrobenzoic acid decolorization occurred immediately and gave quantitative values (23.0% in the case cited) if back-titrated at once.

For comparison of *p*-nitrobenzoic acid and benzoic acid, duplicate experiments were performed with reaction times of one-half, one and twenty-four hours. The yields, respectively, from *p*-nitrobenzoic acid were 22.3, 22.8, 23.1%; from benzoic acid, 12.1, 15.2, 16.2%.

Allyl Benzoate.—Vinyldiazomethane (1.855 g.) and benzoic acid (10 g.) were mixed in 360 cc. of dry ether and left for two days. Then the ether and excess acid were removed. The ester which remained distilled at 228°; yield, 2.90 g. or 65.7%. Two grams of this ester was hy-

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(1) Adamson and Kenner, *J. Chem. Soc.*, 286 (1935).

(2) Nirdlinger and Acree, *Am. Chem. J.*, **43**, 381 (1910).

drolyzed by sodium hydroxide, the alcohol portion ether extracted and a part of it treated with α-naphthyl isocyanate. The allyl α-naphthylcarbamate[3] thus obtained, after two recrystallizations from ligroin, melted at 108°.

Pyrazole.—A vinyldiazomethane solution (0.53 g. in 100 cc. of ether) was set aside for two days, then evaporated. The crystalline residue of pyrazole weighed 0.72 g. This indicates that an appreciable isomerization of the vinyldiazomethane occurs during synthesis in the distillation process. After being twice recrystallized from ether, it melted at 68°. It was identified as pyrazole by converting 0.1 g. of it to pyrazole picrate, m. p. 160°.

Summary

The synthesis and some of the properties of allylnitrosourethan and vinyldiazomethane are discussed.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 21, 1935

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(3) Neuberg and Kansky, *Biochem. Z.*, **20**, 446 (1909), reported m. p. of 109°.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

The Constitution of Liquid Zinc Amalgams

BY HERMAN A. LIEBHAFSKY

Cells in which the electrodes are zinc amalgams of different concentrations, and the electrolyte is an aqueous solution of a zinc salt, have been investigated frequently during the past fifty years.[1] In three of these investigations,[1,2,3] exceptional care has been employed and the accuracy consequently attained has been so great that the problem of determining the electromotive forces of such cells near room temperature appears to be closed, with these two experimental results definitely established. First, dilute zinc amalgams, even in the absence of oxygen, tend increasingly to lose zinc as they become more dilute,[2a] so that the resulting uncertainties in composition constitute the chief stumbling blocks in obtaining the electromotive forces of zinc amalgam cells to within, say, 0.001 millivolt. And, second, these electromotive forces are actually smaller than the ideal values corresponding to the Nernst equation, so that[4]

$$E_{\text{act}} + \Delta E = E_{\text{id}} = 0.09922T \log[\Sigma(\text{Zn})_1/\Sigma(\text{Zn})_2] \quad (1)$$

ΔE, the departure from ideality, is positive and decreases with the concentration of the more concentrated amalgam in the cell. Richards and Forbes[1] pointed out that this departure from ideality qualitatively indicated a partial polymerization of the zinc. Hildebrand[5] contributed greatly to the problem from the experimental side[5b] when he proved that the vapor pressures of zinc amalgams at 300° exhibit deviations from ideality corresponding to ΔE; and from the theoretical side when he showed, in accord with the ideas of Dolezalek,[6] that both types of deviations could, within certain limits, be *quantitatively* explained on the assumption that

$$\text{Zn}_2 \overset{K_2}{\rightleftharpoons} 2\text{Zn};\ K_2 = (\text{Zn})^2/(\text{Zn}_2) \quad (2)$$

was the only equilibrium existing in these amalgams. More recently the *activities* of zinc amalgams have been calculated from the electromotive force data[2b,3] and the interpretation of ΔE in terms of molecular species (a *concentration* treatment) has lost ground—a state of affairs easy to comprehend if, as Crenshaw[2b] states, the best experimental results for these amalgams agree better with each other than they do with Hildebrand's equation

$$E = 0.19834\,\frac{T}{n}\log\frac{1 + N_2 + \sqrt{N_2{}^2 + 2AN_2 + A}}{1 + N_1 + \sqrt{N_1{}^2 + 2AN_1 + A}} \quad (4)$$

where $n = 2$, the N's are the number of moles of mercury for one mole of zinc in amalgams 1 and 2, and $A = 4/(K_2^N + 1)$(see Footnote 4).

It is our purpose here to show that the positive values of ΔE for the zinc amalgams can be quantitatively accounted for without recourse to an activity treatment if we assume the equilibrium

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(1) Richards and Forbes, *Z. physik. Chem.*, **58**, 683 (1907).

(2) Crenshaw, (a) *J. Phys. Chem.*, **14**, 158 (1910); (b) *ibid.*, **34**, 863 (1930).

(3) Pearce and Eversole, *ibid.*, **32**, 209 (1928). For a complete historical summary and additional references, see Ref. 1.

(4) The summation sign, Σ, prefixed to a concentration term indicates that all the zinc in an amalgam is meant; thus, $\Sigma(\text{Zn}) = (\text{Zn}) + (\text{Zn}_2) + (\text{Zn}_3) + \ldots$. Four concentration units have been employed in the investigations referred to above: *viz.*, (1) g. Zn/100 g. Hg, here denoted (as it has just been) by ( ); (2) g. Zn/100 g. amalgam; (3) the units of Richards and Forbes, which we shall designate by $(\text{Zn})^v$—namely, g. Zn/100 g. amalgam for the most concentrated amalgam only; for any other amalgam, this unit with the density change compensated which occurs when the amalgam is prepared by dilution from the most concentrated; (4) the mole fraction of zinc, equal to $1/(1 + N)$, where N is the number of moles of mercury for one mole of zinc; equilibrium constants expressed in this unit will be distinguished by a superscript; thus K_2^N. Electromotive forces will usually be expressed in *millivolts*.

(5) Hildebrand, (a) THIS JOURNAL, **35**, 501 (1913); (b) *Trans. Am. Electrochem. Soc.*, **22**, 335 (1913).

(6) Dolezalek, *Z. physik. Chem.*, (a) **64**, 727 (1908); (b) **71**, 191 (1910).