

NOTES.

Substituted cycloHexyl Nitrites. By LOUIS HUNTER and JOHN A. MARRIOTT.

cycloHexyl nitrite decomposes spontaneously, giving adipic acid, crystals of which begin to be deposited about a week after preparation. Substituted *cyclohexyl nitrites*, with the few exceptions noted below, are stable for long periods.

The nitrites were prepared by treating the requisite alcohol with a slight excess of aqueous sodium nitrite, followed by the theoretical quantity of sulphuric acid (about 50%), the mixture being thoroughly shaken and cooled. After dilution the nitrite layer (usually at the top) was separated, washed, dried over calcium chloride, and distilled under reduced pressure, the

first fraction being the nitrite. The yield was usually practically theoretical. There was no indication of any separation of 2-, 3-, and 4-substituted *cyclohexyl nitrites* by fractional distillation into geometrical isomerides.

cycloHexyl nitrite was a pale yellow liquid with the characteristic odour of organic nitrites; b. p. 31°/10 mm., d_4^{25} 0.9840, n_D^{18} 1.4372 (Found: C, 55.7; H, 8.6; N, 10.9; *M* in benzene, 131. $C_6H_{11}O_2N$ requires C, 55.8; H, 8.5; N, 10.8%; *M*, 129). Adipic acid (Equiv., 74.0. Calc., 73.0) separated after 1—4 weeks. Decomposition was most rapid and complete in open vessels, but was not prevented in sealed tubes: these ultimately burst owing to the gaseous pressure generated.

The following nitrites were stable for at least 6 months: *2-Methylcyclohexyl nitrite*, b. p. 42°/10 mm., d_4^{25} 0.9607, n_D^{14} 1.4402 (Found: C, 58.6; H, 9.3; N, 10.0. $C_7H_{13}O_2N$ requires C, 58.75; H, 9.1; N, 9.8%). *3-Methylcyclohexyl nitrite*, b. p. 45°/12 mm., d_4^{25} 0.9510, n_D^{15} 1.4416 (Found: C, 58.5; H, 9.3; N, 9.7%). *4-Methylcyclohexyl nitrite*, b. p. 45°/14 mm., d_4^{25} 0.9645, $n_D^{14.5}$ 1.4427 (Found: C, 58.6; H, 9.2; N, 10.0%). *2-Chlorocyclohexyl nitrite*, b. p. 71°/12 mm., d_4^{25} 1.1550, $n_D^{15.5}$ 1.4739 (Found: Cl, 22.6. $C_6H_{10}O_2NCl$ requires Cl, 21.7%). The 1-methyl-, b. p. 46°/12 mm., 2-bromo-, b. p. 87°/10 mm., and 1-ethyl-, b. p. 63°/15 mm., derivatives.

2-Iodocyclohexyl nitrite, b. p. 110—117° (decomp.)/20—25 mm., rapidly darkened and decomposed after about 7 days into oxides of nitrogen and a black residue free from adipic acid. 1-Phenylcyclohexyl nitrite decomposed profoundly on distilling at 10 mm.

2-Bromocyclohexanol.—Freshly precipitated mercuric oxide was added (240 g. in 30 g. lots) alternately with bromine (80 g. in 10 g. lots) to well-shaken ice-cold water (800 c.c.) during 90 minutes. The pale yellow solution of hypobromous acid was rapidly filtered, and added in small quantities, with cooling and shaking, to cyclohexene (about 40 g.) until a positive starch-iodide test was obtained. 2-Bromocyclohexanol was isolated by steam-distillation, dried over anhydrous sodium sulphate, and fractionated under reduced pressure, giving a heavy colourless liquid, b. p. 103—104°/18 mm. (Found: Br, 44.0. Calc.: Br, 44.7%), which, even in the dark, rapidly became pink, red, purple, and finally black. The colour was not removed by washing with thiosulphate. Yield, 30%.

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The Electrolytic Separation of Deuterium. By A. J. EDWARDS, H. F. WALTON, R. P. BELL, and J. H. WOLFENDEN.

ONE of the characteristic features of the electrolytic separation of the hydrogen isotopes is its lack of reproducibility, which is also reflected in the frequent discrepancies between the results of different investigators. It has not, however, always been clear whether the appropriate correction for loss by evaporation has been applied, or whether the experimental conditions of different workers were truly comparable. Preparatory to a detailed study of the mechanism of the electrolytic separation, we have therefore made experiments to determine whether the minimisation of, and correction for, evaporation loss, together with a general standardisation of the conditions of electrolysis, would eliminate these fluctuations.

Electrolyses of 2% solutions of sodium hydroxide containing 0.5—1% of deuterium oxide were carried out at a variety of cathodes at a *C.D.* of ca. 0.25 amp./cm.², the temperature of the electrolyte being maintained between 25° and 30°. Loss by evaporation and spray was minimised by fitting each cell with an effective condenser, and measured by placing each group of cells in series with a voltmeter consisting of an electrolytic cell fitted with drying tubes so that the loss of weight of this cell was due to electrolysis only. The deuterium content of the electrolyte after electrolysis was measured by the flotation-temperature method, the density error being about two parts per million. The resultant error in α , the separation coefficient, is estimated at about 3%.

Various cathodes, specified in the table, were used, and the values of α obtained are tabulated: results with the same series number (denoted by Roman numerals) refer to the same group of cells in series, using identical electrolyte and undergoing the same (minor) fluctuations in temperature and *C.D.*; values of α within the same series therefore correspond to closely comparable conditions.

Cathode.	Electrolytic separation coefficient.	Mean.
Nickel	(I) 4.3, 4.0; (II) 4.8, 4.3, 5.5, 6.2, 6.4	5.1
Copper	(III) 5.9, 6.3, 5.7, 7.0, 5.1, 6.65, 5.8, 7.0	6.2
Arc carbon	(IV) 6.85, 6.3; (V) 4.85, 5.2, 5.7	5.8
Iron	(VI) 10.1, 9.6, 9.2, 8.6, 11.0, 10.2, 10.9	9.9
Nickel coated with sulphide	(VII) 6.3, 6.3, 7.2, 6.7, 6.0, 5.9	6.4
Iron coated with sulphide	(VIII) 8.9, 8.4, 10.9	9.4
Graphite (pure)	(IX) 3.1, 8.9, 4.7, 8.7, 4.7, 3.6	6.7

The variations in α are in every case greater than the most unfavourable estimate of the experimental error. It seems that, in protracted electrolyses under apparently identical conditions, serious fluctuations in the separation coefficient cannot be eliminated. The contrast between iron and the other cathode materials, the extreme variability of α at a graphite cathode, and the effect of a sulphide film on nickel are of interest.

The principal inference to be drawn from these results is that protracted electrolysis experiments are likely to throw very little light on the nature of the electrolytic separation of the isotopes. The observed separation coefficient is likely to be the resultant of several processes, in all of which isotopic discrimination may play a part, and to be further complicated by the partial establishment of the $H_2 + DOH = HD + H_2O$ equilibrium. The most hopeful approach would seem to be electrolyses on a much smaller scale under rigorously controlled conditions, such as have been used in recent studies of overvoltage, together with micro-methods for the analysis of the cathode gas. Such experiments are now in progress in this laboratory.—BALLIOL COLLEGE AND TRINITY COLLEGE LABORATORY, OXFORD. [Received, November 18th, 1935.]

Phenyl-ψ-pelletierine. By B. K. BLOUNT.

DURING the search for suitable dialdehydes to condense to aromatic tropinones (cf. J., 1933, 553) attention was turned to the substituted glutardialdehydes described by Meerwein (*J. pr. Chem.*, 1918, **97**, 225; *Ber.*, 1920, **53**, 1829). Meerwein found that phenylacetaldehyde readily undergoes a sort of Michael addition to Δ^{α} -aldehydes. The primary product, a dialdehyde, was in no case isolated, but was identified after internal disproportioning to the isomeric lactone.

Phenylacetaldehyde and acraldehyde were condensed to α -phenylglutardialdehyde (I), and this was used in the tropinone synthesis, 6-phenylgranatan-3-one (phenyl-ψ-pelletierine) (II) being ultimately obtained and isolated as the *dipiperonylidene* derivative. It is of interest that this complicated tropinone can be built up of *four* substituents by reactions occurring in solution at or below the ordinary temperature. When cinnamaldehyde was substituted for acraldehyde, no trace of a tropinone could be identified.

Meerwein (*loc. cit.*) has shown that certain aliphatic aldehydes also can add on to Δ^{α} -aldehydes. It seemed possible, therefore, that ψ-pelletierine might be synthesised in an analogous way, starting from acetaldehyde and acraldehyde. The reaction gave a basic oil, from which, however, no trace of the characteristic and insoluble dipiperonylidene derivative of ψ-pelletierine could be isolated.



6-Phenylgranatan-3-one.—A solution of phenylacetaldehyde and acraldehyde (3 c.c. of each, both freshly distilled) in methyl alcohol (20 c.c.) was cooled to -18° and treated drop by drop with a solution of sodium methoxide in methyl alcohol. The first few drops caused no reaction; then reaction suddenly took place and the temperature rose to 15° . After the temperature had again fallen below 0° , the mixture was removed from the freezing-bath and kept at 0° for 16 hours. The solution, containing α -phenylglutardialdehyde, was condensed in the usual way with acetonedicarboxylic acid (5 g.), chalk (6 g.) in water (30 c.c.) and methyl alcohol (20 c.c.) being used, and methylamine (15 c.c. of a 33% aqueous solution) added. After isolation in the usual manner, the mixture of bases was distilled to give an orange-coloured oil (1.5 g.), b. p. $130\text{--}210^{\circ}/15$ mm. This was mixed with piperonal (2.5 g.), ethyl alcohol (30 c.c.), and 40% potash solution (0.5 c.c.), and heated on the water-bath for an hour. After cooling, the dark-coloured sticky solid was collected, stirred with acetone, and washed with the same solvent. *2:4-Dipiperonylidene-6-phenylgranatan-3-one* remained as a bright yellow powder, which crystallised from amyl alcohol in spherical aggregates of small yellow needles (0.1 g.), m. p. 210°

(Found : C, 75.3; H, 5.7; N, 3.3. $C_{31}H_{27}O_5N$ requires C, 75.5; H, 5.5; N, 2.8%). The substance gave with concentrated sulphuric acid the intense royal-blue colour reaction characteristic of dipiperonylidene tropinones.

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