the manufacturer as DC 200 and has a viscosity of 1000 centistokes at 25°. The perfluorodimethylcyclohexane was obtained from Halogen Chemicals, Inc., Columbia, S. C. Its isomeric composition was not specified.

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RECEIVED JULY 21, 1950

FORMATION OF OPTICALLY ACTIVE 1-METHYLHEPTYLLITHIUM

Sir:

The carbonation of the products from a reaction of *s*-butyllithium and (−)2-iodoöctane has led to the isolation of (−)2-methyloctanoic acid. We can interpret this fact only on the basis that (1) optically active 1-methylheptyllithium was formed by a metal-halogen interchange reaction and (2) asymmetry was retained during the carbonation reaction. Previous attempts to prepare asymmetric organometallic compounds of this type have been unsuccessful.[1]

In a typical experiment, a solution of 18.4 g. of 2-iodoöctane (α^{26}_D −45.86°, d^{25}_4 1.3181, n^{25}_D 1.4861) in 100 cc. of petroleum ether (b. p. 28–36°) was added over a two-hour period to a petroleum ether solution of 320 cc. of 1.04 *M* *s*-butyllithium and 25 cc. of peroxide free ether at a temperature of −70°. Two minutes after completion of this addition the mixture was carbonated on Dry Ice. From the acid fraction was isolated 14.84 g. of 2-methylbutyric acid (α^{21}_D 0.00°, $l = 2$) and 0.66 g. of 2-methyloctanoic acid (b. p. 133° at 11 mm., α^{28}_D −0.78 ± 0.01°, $l = 0.5$, n^{25}_D 1.4270). The *p*-chlorophenylisothiuronium salt of 2-methyloctanoic acid melted at 143.5° after recrystallization from dioxane, and the mixed melting point with a pure sample of the racemic salt was the same. Regeneration of the acid from this salt yielded a material with undiminished rotation and n^{25}_D 1.4280.[2] The organic portion from the carbonated products was halogen free, and the highest rotation of any fraction was α^{29}_D −0.19, $l = 0.5$ (for the portion boiling 125–127° at 10 mm.).

Three subsequent reactions differed in that the iodide was added over a period of twenty minutes and the mixture was carbonated (A) after one minute stirring at −70°, (B) after sixty minutes at −70°, and (C) after warming to 0° over a twenty minute period. The results are indicated in the table.

Reaction	α_D iodide ($l = 1$)	α_D acid ($l = 0.5$)
A	−44.36	−1.18
B	−41.00	−0.96
C	−39.85	0.00

It is apparent that the organolithium compound retained its configuration at −70°, but racemized when the temperature was raised to 0°. The *p*-phenylphenacyl ester derivative (from acid A) melted at 59–60° after five recrystallizations and showed a rotation of $[\alpha]^{29}_D$ −2.8° (0.0515 g./cc. benzene, $l = 1$). A mixed melting point with an authentic sample showed no depression.

From reported rotations for 2-iodoöctane[3a] and 2-methyoctanoic acid[3b] it is estimated that about eighty per cent. racemization occurred in the conversion of the iodide to the acid. The configurational relationships are such that either predominate inversion or retention must be assumed for both the interchange and carbonation reactions

s-Butyllithium and 2-iodoöctane in pentane in the absence of ether did not react significantly over a period of forty-two hours at −77°. The fact that ether so facilitates the interconversion suggests that the reaction proceeds by an ionic rather than by a free radical mechanism.

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[1] Tarbell and Weiss, THIS JOURNAL, **61**, 1203 (1939); Porter, *ibid.*, **57**, 1436 (1935); Schwartz and Johnson, *ibid.*, **53**, 1063 (1931); Pickard and Kenyon, *J. Chem. Soc.*, **99**, 65 (1911); Ziegler and Wenz, *Ber.*, **83**, 354 (1950); Wittig, Vidal and Bohnert, *ibid.*, **83**, 359 (1950); Wallis and Adams, THIS JOURNAL, **55**, 3838 (1933). The evidence of Wallis and Adams for an asymmetric carbanion was shown to be erroneous by Wittig, Vidal and Bohnert.

[2] The refractive index of a purified sample of 2-methyloctanoic acid prepared from a Grignard reagent was n^{25}_D 1.4280.

[3a] Pickard and Kenyon, *J. Chem. Soc.*, **99**, 69 (1911).

[3b] Rothen and Levene, *J. Chem. Phys.*, **7**, 975 (1939).

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RECEIVED AUGUST 21, 1950

MECHANISM OF THE OXO AND RELATED REACTIONS. III. EVIDENCE FOR HOMOGENEOUS HYDROGENATION

Sir:

It has been shown that the hydroformylation (oxo) reaction is often accompanied by hydrogenation; indeed, in some instances hydrogenation proceeds to the exclusion of hydroformylation.[1,2] We wish to report evidence strongly supporting the view that the hydrogenation is homogeneous and, in this respect, unique.

Three experiments were performed at 185° with reduced cobalt as catalyst and butyraldehyde as substrate. The catalyst was prepared by treating 9.3 g. of cobaltous formate and 50 ml. of cyclohexane with 2000 p.s.i. of hydrogen at 185° for 2 hours in a stainless-steel autoclave of 500-ml. capacity. An initial partial pressure of 2000 p.s.i. of hydrogen was used in each of the three experiments and the partial pressure of carbon monoxide was varied.

In the first experiment, no carbon monoxide was present. The reduction proceeded smoothly, and the calculated pressure drop was observed. Distillation yielded 57 g. (77%) of butanol-1, b. p. 115.5–117°. In a second experiment, 1000 p.s.i. of carbon monoxide was added (total pressure 3000 p.s.i.). Approximately one mole of gas was again absorbed and 49 g. (66%) of butanol-1, b. p. 116–117.5°, isolated. The reaction was presumably homogeneous with the soluble dicobalt

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[1] Wender, Levine and Orchin, THIS JOURNAL, **72**, 4375 (1950).

[2] H. Adkins and G. Krsek, *ibid.*, **70**, 383 (1948).

octacarbonyl, $[Co(CO)_4]_2$, or cobalt hydrocarbonyl, $HCo(CO)_4$, functioning as the catalyst.[1]

In a third experiment, 300 p.s.i. of carbon monoxide was added ($8H_2{:}1CO$). The mixture was heated at 185° for 2 hours and at 200° for 1 hour, but no gas was absorbed. Distillation gave three fractions: a low-boiling portion containing unchanged butyraldehyde (83%); a middle fraction (1.4 g.) which infrared spectroscopy showed was free of butanol-1; and a residue (6.1 g.), part of which depolymerized to butyraldehyde on heating to 240–270°. In this case, sufficient carbon monoxide was present to poison the cobalt for the heterogeneous catalysis which was successfully conducted in the absence of carbon monoxide (first experiment), but insufficient carbon monoxide was present to permit the formation of $[Co(CO)_4]_2$ or $HCo(CO)_4$, which was a successful catalyst in the second experiment.

In a concluding experiment, butyraldehyde was treated with a clear benzene solution of $[Co(CO)_4]_2$ at 185° and 2000 p.s.i. of hydrogen. No hydrogenation occurred; the carbonyl was reduced to cobalt which did not function as a catalyst because of carbon monoxide poisoning. Distillation gave 39 g. (54%) of butyraldehyde; no butanol-1 was found in the residue (26 g.).

These experiments strongly indicate that the great variety of hydrogenations which occur in the presence of cobalt and a high partial pressure of carbon monoxide[1] probably proceed by homogeneous catalysis in which $[Co(CO)_4]_2$ or $HCo(CO)_4$ functions as the catalyst. Further confirmation was provided by four experiments with compounds containing sulfur. Under the conditions described, thiophenecarboxaldehyde and a solution of butyraldehyde containing small amounts of thiophene reacted rapidly with synthesis gas. With hydrogen alone, both hydrogenations were greatly retarded.

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STUDIES IN THE THEORY OF THE POLAROGRAPHIC DIFFUSION CURRENT. II. THE INSTANTANEOUS DIFFUSION CURRENT AND THE STREHLOW-VON STACKELBERG EQUATION

Sir:

In recent years a considerable body of information on the change of the instantaneous current at a dropping electrode during the life of a drop has become available.[1–4] These data show conclusively that the Ilkovič equation[5] is not an adequate representation of the phenomena occurring during the growth of a drop into a solution containing gelatin.

The subsequent appearance of a new equation for the average diffusion current[6] and its independent derivation by another method[7] have suggested its test with data secured by Taylor, Smith and Cooter[4] during the growth of two drops of $t = 3.4$ sec. into a 3 mM cadmium solution in 0.1 M potassium chloride containing 0.01% gelatin: these conditions are directly comparable with those used by Strehlow and von Stackelberg[6] in their study of the integrated average current.

The equation for the average current during the drop life

$$i_d/Cm^{2/3}t^{1/6} = 607nD^{1/2}[1 + 17D^{1/2}(t^{1/6}/m)^{1/3}] \quad (1)$$

becomes, on differentiation with respect to t

$$i_t = 708nD^{1/2}C[m^{2/3}t^{1/6} + 19.4D^{1/2}(m^{1/3}t^{1/3})] \quad (2)$$

Assuming m to be constant throughout the drop life, for the data of Taylor, Smith and Cooter we have

$$i_t = 7.46 \times 10^3D^{1/2}(t^{1/6} + 14.7D^{1/2}t^{1/3}) \quad (3)$$

or, taking the value of $D = 7.28 \times 10^{-6}$ cm.²/sec.

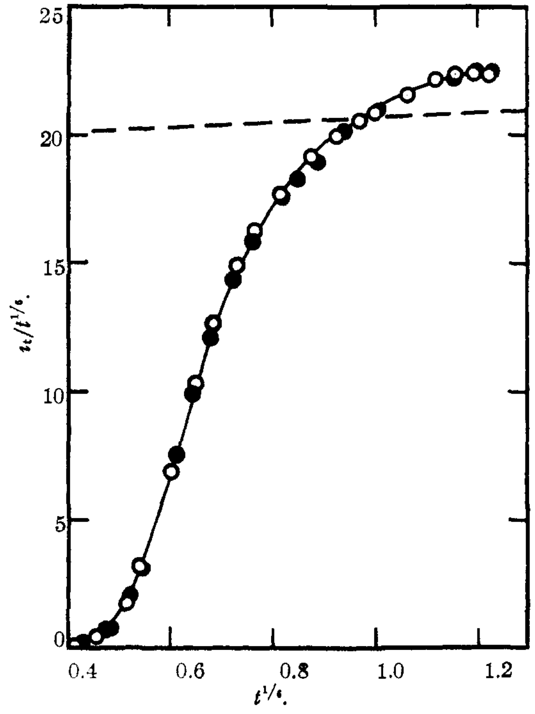

Fig. 1.—Plots of $i_t/t^{1/6}$ against $t^{1/6}$ for "drop one" (open circles) and "drop two" (solid circles): *cf.* ref. 4, p. 391. The dashed line represents the "theoretical" values according to equation (4).

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[1] J. H. Schulman, H. B. Battey and D. G. Jelatis, *Rev. Sci. Instruments*, **18**, 226 (1947).

[2] H. A. McKenzie, THIS JOURNAL, **70**, 3147 (1948).

[3] H. A. McKenzie, quoted by J. J. Lingane, *Anal. Chem.*, **21**, 45 (1949).

[4] J. K. Taylor, R. E. Smith and I. L. Cooter, *J. Res. Natl. Bureau Standards*, **42**, 387 (1949).

[5] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 30–39.

[6] H. Strehlow and M. v. Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

[7] J. J. Lingane and B. A. Loveridge, THIS JOURNAL, **72**, 438 (1950).