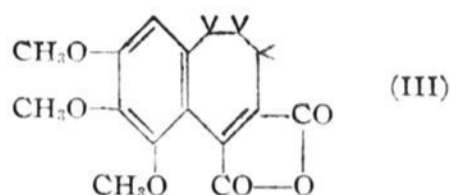
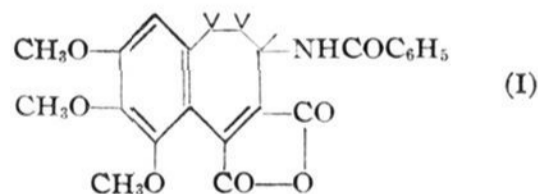


acid anhydride (III). Identity was established by a mixed melting point determination and by comparison of the ultraviolet absorption spectra in chloroform and in aqueous alkali.



2,3,4-Trimethoxybenzuber-5-ene-5,6-dicarboxylic acid anhydride (III) was prepared by the Bougault cyclization of 3,4,5-(CH₃O)₃C₆H₂(CH₂)₃-CH(COOC₂N₅)COCOOC₂H₅ which was obtained by two different routes. (A) Ethyl 3,4,5-trimethoxybenzoylacetate was alkylated with ethyl β-bromopropionate and the resulting ester was hydrolyzed to yield γ-(3,4,5-trimethoxybenzoyl)-butyric acid. The keto-acid was hydrogenated⁵ with a palladium-carbon catalyst to γ-(3,4,5-trimethoxyphenyl)-valeric acid (m. p. 68–69°; reported⁶ m. p. 70°). This acid was converted to the ethyl ester (with ethanol-sulfuric acid) (b. p. 151° at 0.3 mm.). (*Anal.* Calcd. for C₁₆H₂₄O₆: C, 64.59; H, 8.11. Found: C, 64.83; H, 8.32.) Condensation of this ester with ethyl oxalate gave an enolic ester which was cyclized with sulfuric-phosphoric acids to yield the anhydride III (m. p. 119.5–120°). (*Anal.* Calcd. for C₁₆H₁₆O₆: C, 63.15; H, 5.30. Found: C, 63.28; H, 5.59.) (B) A Reformatsky reaction with 3,4,5-trimethoxybenzaldehyde and methyl γ-bromocrotonate yielded an olefinic ester which was hydrogenated (palladium-carbon catalyst) to provide a saturated ester. From this ester, which was not obtained in analytical purity, it was also possible to prepare III by condensation with ethyl oxalate, followed by cyclization.

Degradative,⁷ spectroscopic,⁸ and synthetic⁹ data are now available which show that the conversion of N-acetylcolchinol methyl ether to dihydrodeaminocolchinol methyl ether *via* the de-amino compound does not involve an alteration in the size of the seven-membered B ring. Further, both N-acetylcolchinol and colchicine (the N-acety⁷ analog of N-benzoyltrimethylcolchicine acid) can be oxidized to the same product,⁴ presumably N-acetylcolchicine anhydride. From this it may be concluded (1) that N-benzoylcolchicine anhydride has the structure I, in which the posi-



tion of the benzoylamino group is chosen in accord with the findings of Rapoport, *et al.*,⁹ and (2) that the B-ring of I may be correctly assigned to colchicine itself.

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RECEIVED SEPTEMBER 14, 1950

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EIGHT LIQUID PHASES IN STABLE EQUILIBRIUM *Sir:*

Hildebrand¹ has reported the construction of a system of seven liquid layers in stable equilibrium. This system consisted of heptane, aniline, water, perfluorokerosene, white phosphorus, gallium and mercury. The authors have discovered that an eight-layer system can be constructed by a suitable modification of the Hildebrand system. The eight layers (in order of increasing densities) are paraffin oil, silicone oil, water, aniline, perfluorodimethylcyclohexane, white phosphorus, gallium and mercury. After mixing, the eight layers reappear upon centrifuging. The system is stable indefinitely at 45°. This temperature is required to melt the gallium and phosphorus.

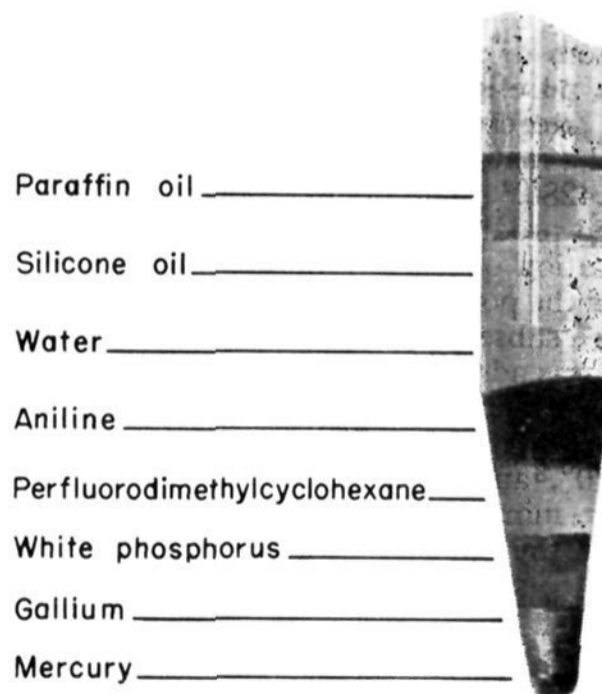


Fig. 1.

The paraffin oil consists of a mixture of paraffin hydrocarbons from C₁₆H₃₄ to C₂₀H₄₂. A Dow Corning silicone oil² was used; it is referred to by

(1) Hildebrand, *J. Phys. Colloid Chem.*, **53**, 944 (1949).

(2) Dow Corning Silicone Notebook, Fluid Series Number 3, 21 (1948).

(5) Horning and Reisner, *THIS JOURNAL*, **71**, 1036 (1949).

(6) Haworth, Moore and Pauson, *J. Chem. Soc.*, 1050 (1948).

(7) Barton, Cook and Loudon, *J. Chem. Soc.*, 176 (1945); Buchanan, Cook, Loudon and MacMillan, *Nature*, **162**, 692 (1948).

(8) Horowitz, Ulliyot, Horning, Horning, Koo, Fish, Parker, and Walker, *THIS JOURNAL*, **72**, 4330 (1950).

(9) Rapoport, Williams and Cisney, *ibid.*, **72**, 3324 (1950).

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-iodooctane 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-iodooctane ($\alpha^{25}_D -45.86^\circ$, 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., $\alpha^{25}_D -0.78 \pm 0.01^\circ$, $l = 0.5$, 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 $\alpha^{25}_D -0.19$, $l = 0.5$ (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

(1) Tarbell and Weiss, *THIS JOURNAL*, **61**, 1203 (1939); Porter, *ibid.*, **67**, 1436 (1935); Schwartz and Johnson, *ibid.*, **53**, 1083 (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.

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 $[\alpha]^{25}_D -2.8^\circ$ (0.0515 g./cc. benzene, $l = 1$). A mixed melting point with an authentic sample showed no depression.

From reported rotations for 2-iodooctane^{3a} and 2-methyloctanoic 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 predominant inversion or retention must be assumed for both the interchange and carbonation reactions.

s-Butyllithium and 2-iodooctane 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.

(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

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

(2) H. Adkins and G. Kraek, *ibid.*, **70**, 393 (1948).