The picrate is soluble in ethyl and methyl alcohols and very soluble in benzene and acetone. It is slightly soluble in hot but insoluble in cold water.

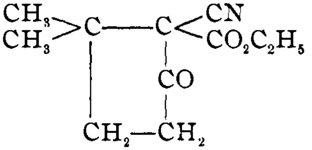
2,5-Dimethyldibenzylamine Mercuric Chloride, $(C_{18}H_{23}N.HCl)_2HgCl_2$.—A concentrated water solution of mercuric chloride was added to a concentrated water solution of the hydrochloride. Upon standing, a white precipitate crystallized out which, upon recrystallizing out of alcohol, crystallized in long, colorless prisms which melted at 157.5°. The crystals are very soluble in ethyl and methyl alcohols and less soluble in benzene. They are very soluble in warm and slightly soluble in cold water.

2,5-Dimethyldibenzylamine Chlorplatinate, $(C_{18}H_{23}HCl)_2.PtCl_4$.—The platinum double salt was prepared by adding to a concentrated water solution of the hydrochloride a concentrated solution of chlorplatinic acid. The salt soon precipitated which recrystallized from alcohol in the form of reddish yellow, prismatic needles which melted at 188°. An analysis gave 21.22 per cent. of platinum, calculated 21.01 per cent. The double salt is soluble in ethyl and methyl alcohols and in acetone. It is insoluble in benzene and in hot and cold water.

SYNTHESIS OF β-METHYLADIPIC ACID.[1]

By William A. Noyes and Irving J. Cox.

Some time ago[2] one of us found that dimethylcyancarboxethylcyclopentanone,



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is decomposed by sodium hydroxide with formation of the sodium salts of malonic and hydroxyisocaproic acids. So far as we are aware, no other similar elimination of a carbon atom, by saponification, from a cyclic compound has been observed, and it seemed of interest to determine whether the reaction is a general one. To throw further light on this question, we have attempted to

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[1] The work here described formed the basis of a thesis for the degree of Bachelor of Science at the Rose Polytechnic Institute.

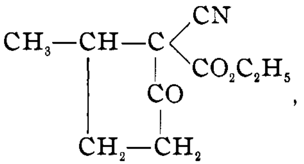
[2] This Journal, **23**, 396.

prepare a similar compound containing one methyl group instead of the two. The amount of the desired compound formed was too small for our original purpose, but some new compounds which seem worthy of a brief description were obtained.

Reduction of Levulinic Acid.—The levulinic acid was prepared from sugar and was purified by one distillation under diminished pressure.[1] From 75 to 80 grams of the acid were obtained from 500 grams of sugar.

For reduction, the acid was divided into portions of 10 grams each, and each portion dissolved in 25 cc. of water. About 225 grams of 3 per cent. sodium amalgam were added slowly to each portion, excessive heating being avoided. After standing for thirty-six hours, the different portions were united, acidified with sulphuric acid, 1 : 1 by volume, and the valerolactone distilled in a current of steam. The distillate was boiled with enough sodium hydroxide to make it alkaline and the solution evaporated nearly to dryness. The residue was acidified, the solution extracted with ether, and, after drying with sodium sulphate and distilling off the ether, the lactone was distilled under atmospheric pressure. Fifty-one grams of the lactone were obtained from 81 grams of the acid. The method is similar to that of Neugebauer,[2] but differs in detail and, especially, in that Neugebauer took fourteen days for the reduction. Our yield was also a little better.

Condensation of γ-Chlorvaleric Ester and of γ-Bromvaleric Ester with Cyanacetic Ester.—γ-Chlorvaleric ester was prepared by treating the lactone with absolute alcohol and hydrochloric acid. By condensing the chlorester with cyanacetic ester by means of sodium ethylate[3] and distilling the resulting products under diminished pressure, a small amount of a crystalline product, which melted at 185°, was obtained from the portion which came over last. It is believed that this compound was 2-methyl-1,1-cyancarboxethylcyclopentanone,



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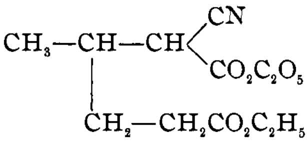
[1] Noyes' "Organic Chemistry for the Laboratory," p. 67.

[2] *Ann. Chem.* (Liebig), **227**, 100.

[3] This Journal, **23**, 397.

but the amount obtained was too small for analysis or for further examination.

β-Methyl-α-cyanadipic Ester,



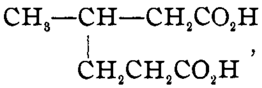
$$\begin{array}{l} CH_3-CH-CH\left\langle\begin{array}{l}CN\\CO_2C_2O_5\end{array}\right. \\ \qquad\quad | \\ \qquad\; CH_2-CH_2CO_2C_2H_5 \end{array}$$

—When γ-bromvaleric ester is condensed with cyanacetic ester, methylcyanadipic ester was formed instead of the cyclic compound, which was desired. This boils at 175°-185° under a pressure of 20 mm. The yield was much greater than with the chlorester. The analysis gave: C, 60.29, 60.09; H, 7.97, 7.99; N, 5.96. Calculated for C, 59.75; H, 7.83; N, 5.81.

3-Methylhexanoic-1,2′,6- Acid.—By saponifying with alcoholic sodium hydroxide, evaporating, dissolving in water, acidifying and extracting with ether, the corresponding tribasic acid was obtained. On slow evaporation of its aqueous solution, the acid crystallizes in plates which melt and decompose at 127°-128°.

The Calcium Salt, $(C_8H_9O_6)_2Ca_3 + 3H_2O$, is sparingly soluble in water. The analysis gave: Ca, 20.92, 20.63; H_2O at 200°, 9.20, 9.36. Calculated for Ca, 20.83; H_2O, 9.37.

β-Methyl Adipic Acid,



$$\begin{array}{l} CH_3-CH-CH_2CO_2H \\ \qquad\quad | \\ \qquad\; CH_2CH_2CO_2H \end{array},$$

if formed when the tribasic acid is heated for a short time to 200°. After crystallization from benzene, the acid melted at 89.2°. On titration with lime-water, 0.0632 gram required the equivalent of 7.73 cc. N/10 alkali. Theory requires 7.90 cc. In a second experiment, 0.0315 took 3.86 cc.; calculated, 3.94 cc.

The melting-point of *active* β-methyladipic acid is given by Manasse and Rupe[1] as 88.5°-89°; by Baeyer[2] as 89°; by Semmler[3] as 84.5°; and by Wagner[4] as 93°-94.5°.

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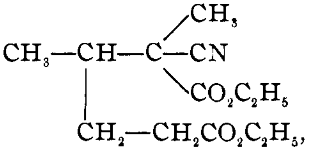
[1] *Ber. d. chem. Ges.*, **27**, 1820.

[2] *Ibid.*, **29**, 30.

[3] *Ibid.*, **25**, 3516.

[4] *Ibid.*, **27**, 1642.

2,3-Dimethyl-2-cyanadipic Ester,



was prepared, as usual, by condensing the monomethyl ester with methyl iodide by means of sodium ethylate in an alcoholic solution. It boils at 181°-194° under a pressure of 29 mm.

The analysis gave:

Calculated for $C_{13}H_{21}O_4N$, C, 61.18; H, 8.24; N, 5.49. Found: C, 61.12, 61.95; H, 8.49, 8.53; N, 5.43.

2,3-Dimethyl-1,2′,6 Acid.—The ester was saponified with much greater difficulty than the corresponding monomethyl ester. It required two days' heating on the water-bath with sodium hydroxide before the evolution of ammonia was complete. The resulting tribasic acid crystallizes in pearly white granules which melt at 159°. On titration with lime-water, 0.0361 gram took the equivalent of 5.07 cc. N/10 alkali, and 0.0407 gram took 5.55 cc.; calculated, 4.97 cc. and 5.60 cc.

α,β-Dimethyladipic Acid.—The dimethyladipic acid, formed by heating the tribasic acid to 200°, could not be induced to crystallize. An analysis of its silver salt gave 55.45 per cent. silver; calculated for $C_8H_{12}O_4Ag_2$, 55.67 per cent.

The copper salt from another preparation gave only 24.90 and 24.98 per cent. copper instead of 27.00 per cent calculated. A salt containing 1 molecule of water would give 24.68 per cent. of copper, and it seems probable that this was the composition of the salt, but such evidence is not altogether satisfactory. We had no time for the further investigation of the salt.

NOTES.

Note on the Avery-Beans Method for the Determination of Arsenious Acid in Paris Green.—This method rests on the principle that arsenious acid may be titrated with iodine in the presence of cupric salts, provided an alkaline tartrate be present. As originally published,[1] the method gives accurate results only when

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[1] This Journal, **23**, 485.