

3. The results of the methylation of sodium enol  $\alpha$ -acetyl- $\alpha'$ -carbethoxysuccinic ester is interpreted in the light of the above experiments.

4. The formation of carbomethoxy derivatives from chlorocarbonic methyl ester and sodium enol benzoylacetone in stereomeric forms is proved and its bearing upon the structure of sodium enol benzoylacetone discussed.

5. The products of the reaction between benzoylacetone and semicarbazide are described.

6. The structure of enol benzoylacetone is discussed and an explanation offered of the apparent discrepancy between the results of physical and chemical investigations.

7. The above experiments are interpreted in the light of the partition principle as applied to organic reactions, subject to the reaction velocities and reactivities of the groups involved.

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## NOTES

**Trichloromethylcyclopentanol-1.**—The condensation of chloroform with ketones to give tertiary trichloro alcohols has been limited to acetone<sup>1</sup> and methyl ethyl ketone.<sup>2</sup> Other ketones have been tried but unsatisfactory results have been obtained in every case where a ketone of more than four carbon atoms was used.<sup>3</sup>

In view of the fact that this condensation reaction seemed to be limited to the two lowest members of the series of aliphatic ketones, it was decided to try two of the alicyclic type. Cyclopentanone and cyclohexanone were used and the procedure followed was essentially that described by Willgerodt.

Nine parts of cyclopentanone was mixed with thirteen parts of chloroform and six parts by weight of powdered potassium hydroxide was added over a period of several hours with constant stirring. A vigorous reaction sets in unless the mixture is kept well cooled by surrounding the reaction vessel with ice. When all of the potassium hydroxide had been added, it was allowed to stand for six days at 0–10°, being stirred occasionally. The residue was then filtered off and washed with ether. The combined filtrate and washings, after being neutralized with dilute hydrochloric acid, were washed with water and dried over anhydrous sodium sulfate. Distillation was carried out at atmospheric pressure until all of the ether, unreacted chloroform and cyclopentanone were removed. When the

<sup>1</sup> Willgerodt, *Ber.*, **14**, 2451 (1881).

<sup>2</sup> Ekeley and Klemme, *THIS JOURNAL*, **46**, 1252 (1924).

<sup>3</sup> Howard, *ibid.*, **48**, 774 (1926).

temperature reached  $140^{\circ}$ , decomposition set in so the residual oil was steam distilled. This distillate was then treated with sodium bisulfite solution to remove traces of ketone, taken up in ether and again dried over anhydrous sodium sulfate. On fractional distillation under vacuum no definite product was obtained; it was therefore decided to treat the mixture with bromine water so that the boiling point of unsaturated impurities, formed by condensation of the ketone with itself, would be raised sufficiently to facilitate the separation. A fraction was collected which on further purification distilled at  $102-102.5^{\circ}$  at 10 mm. The yield was about 3.0% based on the total ketone used or 9.1% calculated on the amount reacting. The unsaturated impurity which has a boiling point so near that of the alcohol is cyclopentylidene-cyclopentanone.

Trichloromethylcyclopentanol-1 is a colorless oily liquid, insoluble in water, but soluble in ether, benzene, chloroform, carbon disulfide, carbon tetrachloride and glacial acetic acid; specific gravity,  $1.3690_4^{25}$ ;  $n_D^{25}$  1.5066.

*Anal.* Calcd. for  $C_6H_9OCl_3$ : Cl, 52.29. Found: Cl, 52.03, 51.82. *Mol. wt.* (in benzene). Theoretical, 203.4. Found: 201.0, 205.9.

In an attempt to react chloroform and cyclohexanone by the above method, qualitative tests indicated that a small amount of the alcohol derivative was formed but apparently the tendency for this ketone to condense with itself is somewhat stronger than that of the cyclopentanone. A yield of about 15% of cyclohexylidene-cyclohexanone was obtained which was identified by means of the semicarbazone.<sup>4</sup> Approximately 75% did not react and apparently the remainder formed higher condensation products.

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**Isopropylcyanoacetic Acid.**—Hessler<sup>1</sup> describes pure isopropylcyanoacetic acid as a viscous liquid. The acid obtained by treating with 10% sodium hydroxide solution under Hessler's conditions the mixture of 95% di- and 5% mono-isopropylcyanoacetic esters prepared by the author's modification of Hessler's process<sup>2</sup> was a viscous liquid such as he describes, but after distilling under 15 mm. pressure and keeping for a short time in ice, it developed numerous nuclei from which crystallization proceeded at laboratory temperature till the whole bulk set to a mass of plates.

Freed from traces of oil on a cooled porous plate ( $0^{\circ}$ ), these melted

<sup>4</sup> Garland and Reid, *THIS JOURNAL*, **47**, 2336 (1925).

<sup>1</sup> Hessler, *THIS JOURNAL*, **35**, 990 (1913).

<sup>2</sup> Marshall, *J. Chem. Soc.*, 2754 (1931).

sharply at 31°. Calcd. for  $C_6H_9O_2N$ : C, 56.6; H, 7.1. Found: C, 56.55; H, 7.2.

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## COMMUNICATIONS TO THE EDITOR

### THE CRYSTAL STRUCTURES OF ELECTRODEPOSITED ALLOYS. SILVER-CADMIUM

*Sir:*

The crystal structures of silver-cadmium alloys, ranging in composition from 20% Cd to 96% Cd, have been obtained from x-ray diffraction data. The alloys were deposited at room temperature according to the method of Stout [Preprint No. 29, *Trans. Am. Electrochem. Soc.*, **59** (1931)], using a current density of one ampere.

In general, the structures of the alloys are quite different from those of thermal alloys of corresponding composition which have been brought to equilibrium before examination. The alloys prepared under equilibrium conditions [Astrand and Westgren, *Z. anorg. allgem. Chem.*, **175**, 90 (1928)] show the following phases.

#### Percentage Cd

0-44	$\alpha$ -solid solution of Cd in Ag
44-49	$\alpha + \beta$
49-51	$\beta$ - $C_2Cl$ type cubic lattice. $\beta'$ -close-packed hexagonal lattice, similar to $\epsilon$ , obtained when $\beta$ is heated above 400° and suitably quenched. It differs from $\epsilon$ in axial ratio
51-57	$\beta + \gamma$
57-66	$\gamma$ -body-centered cubic lattice
66-69	$\gamma + \epsilon$
69-83	$\epsilon$ -close-packed hexagonal lattice
83-95	$\epsilon + \eta$
95-100	$\eta$ -solid solution of Ag in Cd

Westgren notes that  $\beta$  should also be formed at high temperatures in the  $\gamma$ -range but his attempts to produce it by heating the  $\gamma$ -phase failed.

The electrodeposited alloys show the following structures: (1) 40% Cd—contains the  $\alpha$ ,  $\beta'$  and  $\gamma$  phases and may contain the  $\beta$  phase; (2) 46-75% Cd—only the  $\epsilon$  phase is deposited. The crystals show a preferred orientation with respect to the base metal, and this orientation differs with the composition; (3) 89-96% Cd—the  $\epsilon$  and  $\eta$  phases are deposited.

Our results do not agree with microscopic data recently published by Fink and Gerapostolou [*Metal Ind.* (N. Y.), **28**, 519, 562 (1930)].

It is evident that under the conditions of deposition used in these experi-