but it was difficult to obtain consistent results because of the ready racemization of the acid in solution. The best sample had $[\alpha]^{26}\text{D}$ 2.4 ± 0.5° (0.0538 g. in 2 ml. of ethyl acetate, 2-dm. tube). It melted at the same temperature as the racemic acid and the mixed melting point was not depressed. Further studies of the racemization of the salt and the acid will be made and a full description of this work and of the synthesis of 1,4,5-trimethylphenanthrene, m. p. 62.6–63.0°, will be published soon.

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RECEIVED MARCH 17, 1947

HYDROGEN CHLORIDE AS A CONDENSING AGENT

Sir:

Mr. S. H. McAllister has kindly pointed out to us an error in our paper "Hydrogen Chloride as a Condensing Agent", in THIS JOURNAL, **66,** 1309 (1944), in the statement that the alkylation of toluene with isopropyl chloride using hydrogen chloride as the catalyst resulted in the exclusive formation of the para substituted product. In a duplication of this experiment in the laboratories of the Shell Development Company by Mr. Edwin F. Bullard, it was found by infrared spectral analysis that the monosubstituted product contained 25% ortho, 22% meta, and 53% para. As we do not have the expensive equipment available in the industrial laboratory, our products were kindly analyzed by Mr. F. S. Mortimer of the above mentioned company with the following results: 31 ± 1% ortho, 27 ± 1% meta, and 42 ± 1% para. These analyses have been confirmed by Dr. R. V. Weigand at The Pennsylvania State College by raman spectra with the following results: 38% ortho, 25% meta, and 37% para.

This illustrates the need of caution in giving the ratio of isomers in a product when adequate methods of analysis are not available.

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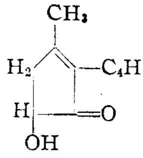
RECEIVED MARCH 29, 1947

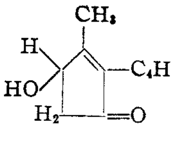
THE SYNTHESIS OF DIHYDROCINEROLONE

Sir:

In a previous communication[1] we reported the synthesis of 1-butyl-5-hydroxy-3-methyl-2-cyclopenten-1-one (I), the structure previously ascribed to dihydrocinerolone.[2] As the α-hydroxyketone (I) was not identical with the dihydro derivative of natural cinerolone, the revised formula 2-butyl-4-hydroxy-3-methyl-2-cyclopenten-1-one (II) was suggested.

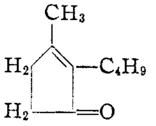


I



II

We have now synthesized the hydroxy ketone identical with dihydrocinerolone. The synthesis was accomplished by the bromination of dihydrocinerone (III) with the employment of N-bromosuccinimide and subsequent hydrolysis of the bromo derivative.



III

Equimolecular quantities of dihydrocinerone and N-bromosuccinimide in carbon tetrachloride were heated under reflux for eighteen hours and, after removal of the insoluble succinimide and the solvent, the crude bromo derivative was hydrolyzed by refluxing with an aqueous suspension of calcium carbonate. This hydrolysis procedure has been employed for the conversion of chlorocinerone to cinerolone. The product had properties in agreement with those of dihydrocinerolone (Table I).

TABLE I

COMPARISON OF THE PROPERTIES OF DIHYDROCINEROLONES

Dihydro-cinerolone	B. p. °C.	Mm.	n_D	Semi-carba-zone m.p., °C.	3,5-Di-nitro-benzo-ate m. p., °C.
From cinerolone	115–117	1[2]	1.4958 (22°)[2]	185[2]	111
Synthetic	110–114	0.3	1.4955 (25°)	187	111

The slight difference in melting points of the semicarbazones is probably due to impurities in the natural materials (mixed m. p. 185–187°). A similar difference in the melting points of the 3,5-dinitrobenzoates was initially observed. However, after several recrystallizations the derivative from the natural material melted at the same point as that of the synthetic compound (mixed m. p. 111°).

The substitution of bromine into the 4-position of dihydrocinerone (III) is not unexpected, as Ziegler and co-workers[3] have shown that N-bromosuccinimide characteristically brominates in the allyl position. These results, then, support structure II for dihydrocinerolone.

The action of N-bromosuccinimide is being

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[1] LaForge and Soloway, THIS JOURNAL, **69**, 186 (1947). In column 1, line 8, the position of the hydroxyl group in the name of the compound should read "5" in place of "4."

[2] LaForge and Barthel, *J. Org. Chem.*, **10**, 222 (1945).

[3] Ziegler and co-workers, *Ann.*, **551**, 80 (1942).