

Summary

Improved directions are given for the preparation of mercury dialkyls from organomagnesium halides.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF GRINNELL COLLEGE]

THE SUPPOSED ALPHA,BETA,BETA-TRIMETHYLGLUTARIC ACID OF NOYES AND SKINNER

BY FRANCIS EARL RAY

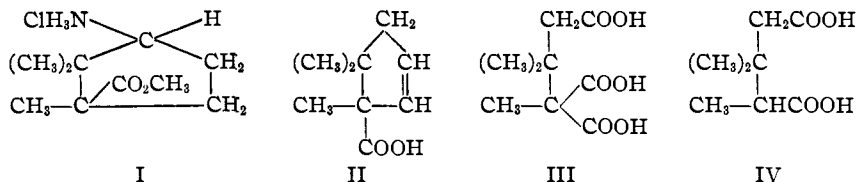
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Introduction

In a previous paper¹ an attempt was made to elucidate the course of the reaction which occurs when the methyl ester of iso-aminocamphanonic acid, I, is decomposed by nitrous acid.

It was thought by Noyes and Skinner² that the reaction gave, in part, the unsaturated compound, II, because on oxidation of this product with alkaline permanganate and decomposition with heat, an acid was obtained which was considered to be α,β,β -trimethylglutaric acid, IV.



It was shown¹ that the acid obtained was not α,β,β -trimethylglutaric acid. The suggestion that α,β,γ -trimethylglutaric acid might be formed by the migration of one of the β -methyl groups was also disproved.

As it then seemed probable that IV was α,α,β -trimethylglutaric acid, Dr. Skinner suggested³ that a methyl group might migrate from the β - to the α -position when carbon dioxide is liberated by heat from III. It is this possibility with which the present investigation deals.

Discussion

Perkin and Thorpe⁴ had obtained α,β,β -trimethylglutaric acid by decomposing the ethyl ester of α,β,β -trimethyl- α -cyanoglutaric acid with hydrochloric acid in a sealed tube at 200° without isolating the intermediate α,β,β -trimethyl- α -carboxyglutaric acid. It seemed possible that this vigorous treatment might prevent a migration that would take place under the influence of heat alone.

¹ Ray, *THIS JOURNAL*, **50**, 558 (1928).

² Noyes and Skinner, *ibid.*, **39**, 2692 (1917).

³ Private communication.

⁴ Perkin and Thorpe, *J. Chem. Soc.*, **75**, 65 (1899).

Accordingly, the α,β,β -trimethyl- α -carboxyglutaric acid was prepared after many attempts and decomposed by heat. It gave, however, the α,β,β -trimethylglutaric acid, showing no evidence of the migration of a methyl group.

An examination of Dr. Skinner's analytical data² for the tricarboxylic acid shows that they correspond to an acid of molecular weight 193 or 194. As trimethylcarboxyglutaric acid has a molecular weight of 218, the explanation of the reaction was based on an error in the interpretation of the analytical data.

The analytical data of Noyes and Skinner seem to indicate that their tribasic acid was a carboxydimethylsuccinic acid, but the melting point of their dibasic acid does not correspond to the melting point of either the unsymmetrical or the fumaroid or maleinoid form of the symmetrical dimethylsuccinic acid. The nature of their acid, and of the unsaturated isomer of lauronic acid from which it was obtained, must be considered uncertain.

Experimental Part

Diethylacrylic Ester.—This ester was prepared from *iso*-amyl alcohol by oxidation with dichromate, bromination, esterification and removal of hydrobromic acid by boiling with quinoline; b. p. 60–65° (5 mm.).

β,β -Dimethyl- α -cyanoglutaric Ester.—Fifty-four g. of dimethylacrylic ester, 60 g. of cyanoacetic ester, 12 g. of sodium and 200 cc. of absolute alcohol dried with magnesium methylate were boiled for fifteen hours; 75 g. of methyl iodide was added and the mixture heated for five hours. In other experiments the mixture with methyl iodide was heated in a pressure flask from six to twenty-four hours. On saponification with potash and decomposition an acid was obtained that melted at 99–100°.⁵ The analysis showed that the third methyl group did not enter the molecule.

Anal. Subs., 0.2002: H₂O, 0.1364; CO₂, 0.3853. Calcd. for C₇H₁₂O₄: H, 7.50; C, 52.50. Found: H, 7.62; C, 52.49.

This difficulty was finally overcome by methylating in an alcohol-free ether or in a benzene solution.

α,β,β -Trimethyl- α -carboxyglutaric Acid.—This acid was not isolated by Perkin and Thorpe.⁴ They obtained only compounds containing nitrogen on heating the ester with potash. In a previous paper¹ it was shown that prolonged boiling with strong potash is necessary to obtain the acids from these esters. In this case, after boiling the ester for twenty hours with 50% potash, the solution was evaporated to dryness and heated to 120° for ten hours. The dry salt was washed with ether, dissolved in water, acidified and extracted with ether. On spontaneous evaporation of the ether the mass crystallized. It was recrystallized, first from hydrochloric acid and then from benzene. After nine recrystallizations it melted at 189–190° with evolution of carbon dioxide.

After heating for thirty minutes at 200°, the mass was recrystallized four times from benzene; m. p. 86°. Perkin and Thorpe⁴ give 86–87° for α,β,β -trimethylglutaric acid.

Anal. Subs., 0.0587: Ag, 0.0325. Calcd. for Ag₂C₈H₁₂O₄: Ag, 55.64. Found: Ag, 55.40.

⁵ Perkin and Goodwin give 101° for β,β -dimethylglutaric acid, *J. Chem. Soc.*, **60**, 1472 (1896).

The writer expresses his thanks to Professor W. A. Noyes for advice and help during the progress of this investigation.

Summary

The explanation given by Noyes and Skinner for the formation of the unsaturated acid obtained by the decomposition of iso-aminocamphonic acid with nitrous acid is shown to be based on an erroneous interpretation of the analytical data.

No member of the trimethylglutaric acid series is formed on oxidation of this unsaturated acid.

The decomposition of α,β,β -trimethyl- α -carboxyglutaric acid proceeds normally, giving α,β,β -trimethylglutaric acid whether decomposition is effected by heat alone or by heating the ester with hydrochloric acid in a sealed tube at 200°.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

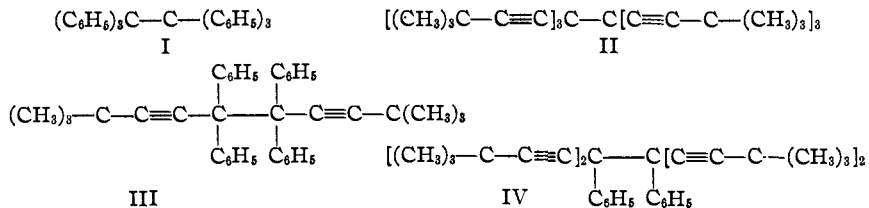
SYMMETRICAL DIPHENYL-TETRA-TERTIARY-BUTYLETHYNYLETHANE

BY S. S. ROSSANDER AND C. S. MARVEL

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As the first step in a study of the effect of acetylenic groups on the stability of the ethane linkage in a hexa-substituted ethane, Salzberg and Marvel¹ have prepared hexa-*tert.*-butylethynylethane (II). This hydrocarbon was found to be stable toward oxygen and in this respect to differ very markedly from the hexa-aryl ethanes. However, it did react with 1% sodium amalgam to give tri-*tert.*-butylethynylmethyl sodium. This reaction indicates that this hexa-substituted ethane has a central linkage that is about as easily ruptured with metals as that in hexaphenylethane (I).



For further information concerning these acetylenic derivatives a study of the compounds intermediate between hexaphenylethane and hexa-*tert.*-butylethynylethane has been made. A hydrocarbon $\text{C}_{38}\text{H}_{38}$, which may be *sym.*-tetraphenyl-di-*tert.*-butylethynylethane (III), was described

¹ Salzberg and Marvel, THIS JOURNAL, 50, 1737 (1928).