[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ACTION OF SODIUM-POTASSIUM ALLOY ON CERTAIN HYDROCARBONS[1]

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We have found that sodium-potassium alloy reacts with various samples of petroleum forming highly colored organometallic compounds. These on treatment with carbon dioxide yield the salts of a mixture of acids.[4] In order to throw more light on this interesting reaction we have studied the action of the alloy on certain pure hydrocarbons which have not been hitherto investigated from this standpoint. The analysis of the mixture of acids obtained from petroleum indicated the presence of one aryl group per carboxyl group. We have therefore turned our attention to two classes of hydrocarbons which might conceivably react with the alloy and carbon dioxide with the formation of acids similar to those obtained by us from petroleum.

Derivatives of Dibenzyl

The first class of substances prepared and investigated were derivatives of dibenzyl which may be represented by the general formula I. We prepared dimethyldiphenylethane ($R = CH_3$), di-*iso*propyldiphenylethane, ($R = (CH_3)_2CH-$), di-*n*-butyldiphenylethane ($R = C_4H_9$) and di-*tert.*-butyldiphenylethane ($R = (CH_3)_3C-$).

$$\begin{array}{c} C_6H_5\underset{\displaystyle R}{\underset{|}{C}}H\underset{\displaystyle R}{\underset{|}{C}}HC_6H_5 \end{array}$$

I

Ziegler has shown[5] that tetraphenylethane ($R = C_6H_5$, Formula I) reacts with sodium-potassium alloy in ether forming the metallic derivative of diphenylmethane [$(C_6H_5)_2CHK$]. Dibenzyl itself does not undergo this reaction.[6] It was, therefore, a matter of considerable theoretical interest, quite aside from the petroleum problem, to see whether or not the derivatives containing alkyl groups would behave like dibenzyl or like tetraphenylethane.

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[1] This paper contains results obtained in an investigation on "Isolation and Investigation of Thermo-Labile Hydrocarbons Present in Petroleum" listed as Project 16 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by the Universal Oil Products Company. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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[4] Conant and Blatt, THIS JOURNAL, 50, 542 (1928).

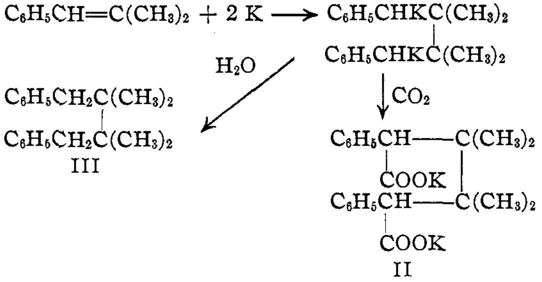
[5] Ziegler and Thielmann, *Ber.*, 56B, 1743 (1923).

[6] Conant and Garvey, THIS JOURNAL, 49, 2599 (1927).

The results were all negative. After shaking the ethane with the alloy in ether in the usual way, more than 90% of the compound was recovered unchanged; there was no color produced and no evidence of a reaction. Even boiling the di-*iso*propyl and the di-*tert.*-butyl compounds, with the alloy in dioxane was without effect. It may be concluded, therefore, that the metallic compounds formed in the petroleum reaction were not produced as a result of the cleavage of di-aryl-di-alkyl ethanes. It is also evident that even the *iso*propyl and *tert.*-butyl groups are not equivalent to a phenyl group in increasing the reactivity of tetra-substituted ethanes toward sodium-potassium alloy. Considering the effectiveness of the branched alkyl groups in promoting dissociation in the dixanthyl series,[7] this is somewhat surprising. Since, however, even a tetra-aryl ethane reacts with sodium-potassium alloy and not with 40 per cent. sodium amalgam we are obviously dealing with about the limits of reactivity which can be estimated by the methods developed in this Laboratory.[6] Even if the dissociating influence of *sec.* and *tert.*-alkyl groups (as indicated by studies in the dixanthyl series)[7] is exerted in the tetra-substituted ethanes, a di-aryl di-*tert.*-alkyl ethane might just fall short of reacting with the alloy.

Derivatives of Styrene

Schlenk[8] has shown that unsymmetrical diphenylethylene $(C_6H_5)_2C{=}CH_2$ reacts with the alkali metals with the formation of the compound $(C_6H_5)_2CKCH_2CH_2CK(C_6H_5)_2$, (written as the potassium compound). A similar reaction has not been reported with unsaturated hydrocarbons containing one phenyl group, although Schlenk found that styrene $(C_6H_5CH{=}CH_2)$ reacts very slightly and then polymerizes. Using sodium-potassium alloy in ether we have found that propylstyrene $(C_6H_5CH{=}CHC_3H_6)$ and dimethylstyrene $(C_6H_5CH{=}C(CH_3)_2)$ yield metallic derivatives corresponding to the reaction characteristic of unsymmetrical diphenylethylene. On treatment with carbon dioxide, the salt of a dibasic acid is formed (II); with water a saturated hydrocarbon (III) is produced.



$$C_6H_5CH{=}C(CH_3)_2 + 2\,K \longrightarrow \begin{array}{l} C_6H_5CHKC(CH_3)_2 \\ \quad\quad\quad\;\; | \\ C_6H_5CHKC(CH_3)_2 \end{array}$$

$$\begin{array}{l} C_6H_5CHKC(CH_3)_2 \\ \quad\quad\quad\;\; | \\ C_6H_5CHKC(CH_3)_2 \end{array} \xrightarrow{H_2O} \begin{array}{l} C_6H_5CH_2C(CH_3)_2 \\ \quad\quad\quad\;\; | \\ C_6H_5CH_2C(CH_3)_2 \end{array}\ \text{III}$$

$$\begin{array}{l} C_6H_5CHKC(CH_3)_2 \\ \quad\quad\quad\;\; | \\ C_6H_5CHKC(CH_3)_2 \end{array} \xrightarrow{CO_2} \begin{array}{l} C_6H_5CH{-}{-}C(CH_3)_2 \\ \quad\;\; |\quad\quad\;\; | \\ \quad COOK\;\; | \\ C_6H_5CH{-}{-}C(CH_3)_2 \\ \quad\;\; | \\ \quad COOK \end{array}\ \text{II}$$

III

II

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[7] Conant, Small and Sloan, This Journal, **48**, 1743 (1926).

[8] Schlenk, *et al.*, *Ber.*, **47**, 473 (1914).

The composition of the resulting acids, which have one phenyl group per carboxyl group, is similar to the composition of our petroleum acid. This reaction must, therefore, be considered among the possibilities. It might be noted in this connection that the color of the metallic derivatives is bright red while the compounds from petroleum are nearly black; the only dark metallic derivative that we have met in working with hydrocarbons of known structure is from stilbene. This is an indication (but not proof) that the organometallic compounds from petroleum are of the type

$$\text{Aryl-}\underset{\text{R}}{\underset{|}{\text{C}}}\text{K}\ \ \underset{\text{R}}{\underset{|}{\text{C}}}\text{K-aryl}$$

The hydrocarbon formed by the action of water on the reaction mixture from dimethylstyrene is tetramethyldibenzylethane (III above). It is a representative of a class of substances—the hexa-alkyl-ethanes—of which very few representatives are known. (The benzyl group is essentially a primary alkyl group.) We have been very anxious to prepare members of this class as we believe that if the alkyl groups are branched the hydrocarbons will be reactive and tend to disproportionate on heating. We are now investigating the action of the alloy on di-*iso*propylstyrene with the hope of preparing dibenzyl-tetra-*iso*propylethane.

Sodium potassium alloy is without action on di benzyl-tetramethylethane (III) as would be expected since there are only primary groups attached to the ethane carbon atoms.

The results of the analyses of the hydrocarbons and certain of the acids were very irregular when the combustion was performed in the usual way. The percentages of both carbon and hydrogen were low. That the difficulty lay with the analysis and not with the purity of the compounds was shown by the irregularities with a given sample and by the fact that repeated crystallization from varied solvents was without effect. After repeated trials it was found possible to obtain results which were only 1 to 1.5% low in carbon. This was accomplished by burning the sample mixed with a large amount of copper oxide wire much as a Dumas nitrogen determination is carried out. In spite of these somewhat unsatisfactory analyses, the formulas of the compounds have been established without doubt. The hydrocarbons were shown to contain no nitrogen, sulfur or halogen and were not changed by boiling with zinc and acetic acid. The molecular weights of all the substances were determined by the micro method using camphor. The formulas we have assigned are the only ones possible on the basis of these molecular weights and the analytical data. Our difficulties with the analyses seem to be connected with predominance of methyl groups in the compounds. It seems probable that methane (or formaldehyde) was formed in the combustion tube and escaped further oxidation.

Experimental

Preparation of the Carbinols

The phenyl alkyl carbinols were prepared by a uniform procedure. Benzaldehyde (in one case acetaldehyde) was added to an excess of the appropriate Grignard reagent, cold and free from excess magnesium. After standing overnight the reaction mixture was decomposed with ice and a slight excess of sulfuric acid, the ether layer separated and the aqueous layer extracted once with ether. The combined ether layers were washed with water, sodium carbonate, then water and dried over sodium sulfate. After removing the ether on the steam-bath, the residual material was distilled under reduced pressure. The yields given are based on the amount of aldehyde employed.

Phenylmethylcarbinol.[9]—Forty-four grams (1.0 mole) of acetaldehyde was added to the Grignard reagent (1.2 moles) prepared from 28.8 g. of magnesium, 190 g. of bromobenzene and 600 cc. of ether. The product boiled at 110–111° at 28 mm.; yield, 97 g. or 80%.

Phenyl*iso*propylcarbinol.[10]—Seventy-four grams (0.7 mole) of benzaldehyde was added to the reagent (1.0 mole) from 24 g. of magnesium, 130 g. of *iso*propyl bromide and 500 cc. of ether. The resulting carbinol boiled at 101–104° at 7 mm.; yield, 87 g. or 83%.

Phenylbutylcarbinol.[11]—Eighty-five grams (0.8 mole) of benzaldehyde was added to the reagent from 24 g. of magnesium, 100 g. of butyl chloride and 500 cc. of ether. The product boiled at 129–130° at 13 mm.; yield, 112 g. or 85%.

Phenyl-*tert.*-butylcarbinol.[12]—One hundred and twenty-seven grams (1.2 moles) of benzaldehyde was added to the reagent prepared from 72 g. of magnesium and 324 g. of *tert.*-butyl chloride and 1 liter of ether. On distillation the product boiled over a wide range but all the material which came over above 95° at 7 mm. solidified promptly in the receiving flasks. The yield was 118 g.; 60%. There was considerable residue which did not distil at a pressure of 7 mm. and bath temperature of 220°.

Preparation of the Bromides

The bromides were obtained by passing dry hydrogen bromide into the carbinols, which were kept cold by means of an ice-bath. Two layers soon formed: an upper one of organic bromide, a lower one of saturated aqueous hydrobromic acid. The reaction mixture was transferred to a separatory funnel, the lower layer drawn off, the organic bromide then placed in a beaker containing fused sodium sulfate and left in a desiccator over potassium hydroxide until free from hydrogen bromide. Finally, the product was distilled *in vacuo*.

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[9] Grignard, *Ann. chim.*, [7] **24**, 466 (1901), from benzaldehyde and methylmagnesium iodide.

[10] Grignard, ref. 9, p. 467.

[11] (a) Puyal and Montagne, *Bull. soc. chim.*, [4] **27**, 860 (1920); (b) Fourneau, Puyal and Montagne, *Anales soc. españ. fís. quím.*, **18**, 323 (1920); *C. A.*, **16**, 240 (1922).

[12] (a) Lepin, *J. Russ. Phys.-Chem. Soc.*, **44**, 1165 (1912); *Chem. Centr.*, **1912**, II, 2080; (b) Ramart Lucas, *Compt. rend.*, **150**, 1061 (1910); (c) *Ann. chim.*, [8] **30**, 361 (1913).

The purity of the bromides was controlled by Volhard analyses for bromine. A weighed sample of bromide was boiled for two hours with an excess of halogen-free sodium methylate then acidified with nitric acid. From this stage the regular Volhard procedure was followed.

All of the bromides were lachrymators.

Phenylmethylbromomethane.[13]—From 63 g. of carbinol there was obtained 70 g. of bromide, boiling at 92–94° under 8 mm.; yield, 74%.

Phenyl-*iso*propylbromomethane, $C_6H_5CHBrCH(CH_3)_2$.—Seventy-five grams of carbinol gave 68 g. of bromide, boiling at 116–119° at 17 mm.; yield, 64%. Calcd. for $C_{10}H_{13}Br$: Br, 37.6. Found: Br, 37.9.

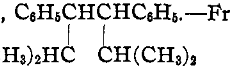
Phenylbutylbromomethane, $C_6H_5CHBrC_4H_9$.—From 96 g. of phenylbutylcarbinol was obtained 96 g. of the bromide; boiling point 120–123° at 10 mm.; yield, 70%. Calcd. for $C_{11}H_{15}Br$: Br, 35.2. Found: Br, 34.2.

Phenyl-*tert*.-butylbromomethane.[12a]—From 65.6 g. of carbinol there was obtained 50 g. of the bromide, boiling point 106–112° at 9 mm.; yield, 55%.

Preparation of the Ethanes

The ethanes were prepared by adding a solution of the bromide in anhydrous ether (500 cc. ether per mole of bromide) to magnesium turnings, in the usual fashion of preparing a Grignard reagent. After the addition the solution was boiled for one and one-half hours, then cooled in an ice-bath while anhydrous cupric chloride (one mole per mole of bromide) was added. At this stage a vigorous reaction took place. The reaction mixture was left overnight, then decomposed with ice and hydrochloric acid, the ether layer separated, the aqueous layer extracted once with ether and the combined ether extracts were washed with water, carbonate solution, then water and dried over calcium chloride. On concentrating the ether the ethane was obtained.

Diphenyldimethylethane.[12a,13a]—From 74 g. of phenylmethylbromomethane, 9.6 g. of magnesium, 200 cc. of ether and 53 g. of anhydrous cupric chloride there was obtained 8.3 g. of ethane; yield, 20%. Considerable amounts of the oily isomer were formed at the same time. For use in the cleavage tests the ethane was crystallized four times from alcohol; m. p. 124–125°.

Diphenyl-di-isopropylethane,  $\underset{(CH_3)_2HC}{C_6H_5CH}\underset{CH(CH_3)_2}{CHC_6H_5}$.—From 42.6 g. of phenyl-*iso*propylbromomethane, 4.8 g. magnesium, 100 cc. of ether and 27 g. of cupric chloride there was obtained 8 g. of the ethane; yield, 30%. The material is moderately soluble in cold ether and ethyl acetate, only slightly soluble in cold ethanol and acetic acid. It was purified by two crystallizations from glacial acetic acid, followed by a final crystallization from ethanol. From all of these solvents the ethane separates in very fine, white needles which melt at 150–150.5°.

Anal. Calcd. for $C_{20}H_{26}$: C, 90.2; H, 9.8. Found: C, 88.1; H, 9.7.

Mol. wt.: subs., 0.0138: camphor, 0.1359; depression, 15.5°. $K = 40{,}000$. Calcd. for $C_{20}H_{26}$: mol. wt., 266. Found: 262.

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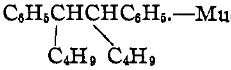
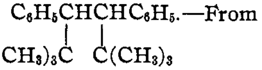
[13] (a) Radziszewski, *Ber.*, 7, 142 (1874); (b) Engler and Bethge, *Ber.*, 7, 1126 (1874).

Diphenyl-di-*n*-butylethane,  $C_6H_5\underset{C_4H_9}{CH}\underset{C_4H_9}{CH}C_6H_5$.—Much difficulty was encountered in securing this ethane as a solid since small amounts of phenylamylene formed in the course of its preparation prevented crystallization. On evaporation of the ether after working up the reaction mixture an oil was invariably obtained. This was subjected to steam distillation, which removed the phenylamylene. The residue from the steam distillation when taken up in petroleum ether (20–40°) and repeatedly evaporated gave a mushy solid mixed with oil. The solid and oil were separated by means of a sintered glass filter and the solid was then left on a porous plate. Finally it was crystallized from ethanol until it had a sharp and constant melting point at 80°. The yield of crude material dried on porous plate is small, about 10%. Once free from oil the ethane is only slightly soluble in alcohol, moderately soluble in ethyl acetate and quite soluble in ether.

Anal. Calcd. for $C_{22}H_{30}$: C, 89.8; H, 10.2. Found: C, 88.4; H, 10.6.

Mol. wt.: subs., 0.0280; camphor, 0.2838; depression, 13°. Calcd. for $C_{22}H_{30}$: mol. wt., 294. Found: 305.

Diphenyl-di-*tert.*-butylethane,  $C_6H_5\underset{(CH_3)_3C}{CH}\underset{C(CH_3)_3}{CH}C_6H_5$.—From 45.4 g. of phenyl-*tert.*-butylbromomethane, 4.8 g. of magnesium, 125 cc. of ether and 27 g. of cupric chloride there was obtained 7 g. of the ethane, a yield of 24%. The ethane is moderately soluble in ether, only slightly soluble cold in ethanol, acetic acid and ethyl acetate. For use in the cleavage tests it was twice crystallized from glacial acetic acid, then once from ethyl acetate: stout prisms, on very slow crystallization rectangular plates; m. p. 180–181°.

Anal. Calcd. for $C_{22}H_{30}$: C, 89.8; H, 10.2. Found: C, 88.7; H, 10.2.

Mol. wt.: subs., 0.0171; camphor, 0.1588; depression, 14°. Calcd. for $C_{22}H_{30}$: mol. wt., 294. Found: 308.

Treatment of the Ethanes with Alloy

In each experiment 0.0005 mole of purified ethane, 10 cc. of ether ("absolute" ether dried over phosphorus pentoxide, then sodium potassium alloy) and 1 cc. of alloy were sealed in glass tubes under nitrogen. After shaking for forty-eight hours and then standing for an additional 120 hours there was no evidence of reaction. The tubes were opened in an atmosphere of carbon dioxide, moist ether was added and the excess alloy removed. After the addition of water, the resulting ether layer and alkaline aqueous layer were worked up separately. In each case the ethane was recovered and its identity proved by a melting point and mixed melting point. With the dimethylethane 75% of the material was recovered, with the di-*iso*propylethane, 80%. In the cases of the di-*n*-butyl- and di-*tert.*-butylethanes, the recovery was over 90%. There were no acidic products formed.

Finally the di-*iso*propyl- and the di-*tert.*-butylethane were heated with alloy in dioxane at the boiling point of the solvent for ten minutes. No color developed and over 90% of the ethanes were recovered unchanged.

Action of Sodium-Potassium Alloy on Mono- and Di-alkyl Substituted Styrenes

α-Phenylamylene (7-Propylstyrene).[14]—The ethylene was prepared from phenylbutylbromomethane by boiling with sodium methylate solution. From 100 g. of crude bromide there was obtained 50 g. of α-phenylamylene, b. p. 212–215°.

α,α′-Diphenyl-β,β′-dipropyladipic Acid.—When the alloy (5 cc.) is added to the phenylamylene (7.3 g.) there is no reaction. On addition of dry ether, 150 cc., there is immediate formation of a thin film of cherry-red metallic derivative over the surface of the alloy. The reaction mixture was sealed off under an atmosphere of purified nitrogen and shaken for twenty-four hours, then dry carbon dioxide admitted until the color of the metallic derivative disappeared.

Moist ether was next added and the excess of alloy removed. Finally water was added and the alkaline solution thus obtained was extracted twice with ether and heated on the steam-bath to remove dissolved ether. On cooling and acidifying with hydrochloric acid the organic acid separated as a white, slimy mass. It was dissolved in ether, the ether dried, concentrated and petroleum ether added. From this mixture the acid crystallized in small white cubes. These were purified by crystallization from alcohol. The melting point of the acid is 278°, uncorrected.

Anal. Calcd. for $C_{24}H_{30}O_4$: C, 75.4; H, 7.85. Found: C, 74.9; H, 8.0.

Phenyldimethylethylene and Alloy.—The ethylene was first prepared according to the procedure of Tiffeneau.[15] It is more convenient to heat the alcohol and oxalic acid in a flask fitted with a wide glass tube, 50 cm. long, at such a temperature that the water formed distils out of the top of the condenser. After the water has been removed, the temperature rises and anhydrous oxalic acid begins to sublime into the condenser. At this point the dehydration is complete.

α,α′ - Diphenyl - β,β,β′,β′ - tetramethyladipic Acid, $C_6H_5CH(COOH)C(CH_3)_2$-$C(CH_3)_2CH(COOH)C_6H_5$.—When the alloy (2 cc.) is added to 3.2 g. of the ethylene there is no reaction. Upon the addition of ether the formation of a cherry-red metallic derivative starts at once. The reaction mixture was shaken under nitrogen for thirty-six hours, then decomposed with dry carbon dioxide and worked up in the usual manner. From the alkaline layer over 2 g. of acid was obtained. The ether layer yielded a *small amount of neutral material (see below—decomposition with water).*

The acid was purified by crystallization from ether-petroleum ether, when it was obtained as white crystals melting at 238–240° with evolution of gas. For analysis it was vacuum dried at 80°.

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.6; H, 7.34. Found: C, 73.6; H, 7.5.

Mol. wt.: subs. 0.0101; camphor, 0.1113; depression, 10.5°. Calcd. for $C_{22}H_{26}O_4$: mol. wt., 354. Found: 346.

Dibenzyltetramethylethane, $C_6H_5CH_2C(CH_3)_2C(CH_3)_2CH_2C_6H_5$.—A mixture of 3.2 g. of ethylene, 3 cc. of alloy and 150 cc. of dry ether was shaken in an atmosphere of nitrogen for seventy-two hours, then decomposed with moist ether. On working up the ether layer there was obtained 2.2 g. of neutral material, identical with that found in small amounts in the carbon dioxide run. The neutral material was purified by crystallization from alcohol, from which it separated in fern-shaped aggregates of very fine, white needles, melting at 131–132°. For analysis it was dried *in vacuo* at 80°.

Anal. Calcd. for $C_{20}H_{26}$: C, 90.2; H, 9.8. Found: C, 89.0; H, 9.85.

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[14] (a) Schramm, *Ann.*, **218**, 392 (1883); (b) Klages, *Ber.*, **39**, 2592 (1906).

[15] Tiffeneau, *Ann. chim.*, [8] **10**, 365 (1907).

Mol. wt.: subs., 0.0090; camphor, 0.0893; depression, 15°. Calcd. for $C_{20}H_{26}$: mol. wt., 264. Found: 263.

Dibenzyltetramethylethane is very soluble in ether, moderately soluble in alcohol and ethyl acetate. It is unaffected by treatment with sodium-potassium alloy in dioxane at 100°. On heating 0.133 g. of the substance with alloy in dioxane at the boiling point for ten minutes no color was developed and on working up the products over 90% of the ethane was recovered unchanged.

Summary

1. Sodium-potassium alloy was found to be without action on diphenyldimethylethane, diphenyldibutylethane, diphenyl-di-*iso*propylethane and diphenyl-di-*tert.*-butylethane. The last three hydrocarbons are new.

2. Propylstyrene and dimethylstyrene add sodium and potassium alloy and undergo condensation. By the action of carbon dioxide derivatives of adipic acid were formed. The action of water on the metallic compound from dimethylstyrene yielded a hexa-alkyl ethane (dibenzyltetramethylethane).

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

THE SYNTHESIS OF α,β,γ-TRIMETHYLGLUTARIC ACID

BY FRANCIS EARL RAY

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Introduction

In 1913 Noyes and Littleton[1] studied the decomposition of the methyl ester of *iso*-aminocamphonanic acid with nitrous acid. The only product isolated was the *cis*-camphonololactone. Later Noyes and Skinner[2] studied the same reaction and fractionated the decomposition products under reduced pressure. The fraction boiling at 86–88° (21 mm.) contained unsaturated acids. It was saponified and submitted to oxidation with alkaline permanganate, giving an acid which lost carbon dioxide at its melting point and supposedly formed α,β,β-trimethylglutaric acid.

Dr. Friedrich Richter in revising Beilstein's "Handbuch" found that α,β,β-trimethylglutaric acid had been previously obtained by Balbiano[3] and synthesized by Perkin and Thorpe[4] and kindly called Professor Noyes' attention to the oversight. The α,β,β-trimethylglutaric acid had a melting point of 88–89°. In view of this discrepancy, it seems evident that the acid melting at 111° obtained by Noyes and Skinner was not the α,β,β-trimethylglutaric acid.

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[1] Noyes and Littleton, THIS JOURNAL, **35**, 75 (1913).

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

[3] Balbiano, *Ber.*, **27**, 2136 (1894); **28**, 1508 (1895).

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