steam distillation). The residue was dissolved in 750 ml. petroleum ether at room temperature and washed with 300 ml. 50% ethyl alcohol to remove traces of soap, after which the petroleum ether solution was dried and filtered. The solvent was removed, the residue distilled at 10 mm. pressure, and the fraction boiling at 161–165° collected. The yield of crude alcohol was 11 g. (40%).

After two crystallizations from acetone at −60° and vacuum distillation (b. p. 134°, 2 mm.) the 2-methyltetradecanol-1 melted at 32.0–32.2°. The alcohol is soluble in all common organic solvents.

*Anal.* Calcd. for $C_{15}H_{32}O$: C, 78.86; H, 14.13. Found: C, 78.90; H, 14.21.

INSTITUTE OF MEDICAL CHEMISTRY KARIN LINDBLAD
UNIVERSITY OF UPPSALA, SWEDEN EINAR STENHAGEN
RECEIVED OCTOBER 6, 1941

# COMMUNICATIONS TO THE EDITOR

## THE DECOMPOSITION OF OZONIDES WITH RANEY NICKEL

*Sir:*

We find that ozonides react with Raney nickel to give aldehydes or ketones and nickel oxide. The reaction is vigorous at 35° when a pentane solution of ozonide is slowly added to a suspension of the nickel in pentane. It appears to be the only reaction taking place and the yield of aldehydes and ketones is comparable with that obtained in the less convenient method of F. G. H. Fischer [Long, *Chem. Rev.*, **27**, 437 (1940)], and at least twice that obtained by the earlier procedures. The simple manipulation and the absence of water improve the value of the ozonolysis reaction as an analytical method.

A solution of 200 cc. of pentane and 75 g. (0.6 mole) of the nonenes from the dehydration of methylethylneopentyl carbinol was ozonized during fifteen hours with about 5% ozone at salt and ice temperature. The ozonide was then slowly added to 48 g. (0.8 g. atom, *i. e.*, 100% excess) of Raney nickel suspended in 100 cc. of pentane in a 500-cc. 3-necked flask. The flask was equipped with a mercury-seal stirrer, condenser and dropping funnel. The reaction was vigorous at first, boiling the pentane as the ozonide was added, but slowed down considerably before all the ozonide was added. Then a further 20 g. of Raney nickel was added. The mixture showed no test for ozonide after stirring overnight with the nickel. To be sure of the decomposition of the ozonide, the pentane was stripped and the mixture was refluxed for an hour over the nickel at 115–120°.

The nickel was allowed to settle and the product was decanted. The residue was extracted three times with 50-cc. portions of pentane and finally centrifuged to remove the last solid.

The pentane strippings from the decomposition which had been caught in a dry-ice trap were fractionated through a small 15-plate column using a dry-ice trap to catch most of the low-boiling products. About 5 g. of acetaldehyde was collected in the first pentane fractions. The dry-ice trap contents weighed 20 g. This was acetaldehyde with a trace of formaldehyde. These were identified as usual. The pentane extract was then fractionated and found to contain 46 g. of a mixture of methyl neopentyl ketone, ethyl neopentyl ketone and traces of trimethylacetaldehyde and methyl ethyl ketone. There was about three times as much of the first ketone as of the second. About 10 g. of higher boiling material was present which has not been identified. The yield of aldehydes and ketones from the reaction was about 75%. This new method is being studied intensively in all of its ramifications.

It is not as yet known that all ozonides in various solvents will react with Raney nickel or that the reaction is complete. Consequently the usual care and precautions should be used to avoid the danger of explosions. In this Laboratory wire glass screens are used in front of all apparatus even during the final distillation of the probably ozonide-free products.

DEPARTMENT OF CHEMISTRY
THE PENNSYLVANIA STATE COLLEGE NEWELL C. COOK
STATE COLLEGE, PENNSYLVANIA FRANK C. WHITMORE
RECEIVED NOVEMBER 21, 1941

## IN REFERENCE TO THE CATALYTIC REDUCTION OF ESTERS USING NICKEL ALONE AS A CATALYST

*Sir:*

In February, 1940, there appeared an article by Peter L. de Benneville and Ralph Connor,[1] concerning which I wish to make several comments.

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[1] De Benneville and Connor, THIS JOURNAL, **62**, 283 (1940).

I. Referring to a publication by H. Adkins, the authors establish a comparison between the catalytic activity of nickel and that of copper chromite. In conclusion, they add: "these seem to be the only known examples ... of the attack of an ester group in the presence of a nickel catalyst," an attack which is, on the contrary, normal in the presence of copper chromite.

However, in 1935 my collaborator, S. Sabetay, and I showed that over nickel alone as a catalyst, the high pressure hydrogenation of certain essential oils brought about a lowering of the index of saponification and an elevation of the index of acetylation; in other words, there was some transformation of the ester function to the alcohol function, catalytically, by a true Bouveault–Blanc reaction.[2]

We have confirmed these preliminary results by the hydrogenation of pure esters. Ethyl laurate and butyl stearate have furnished the corresponding alcohols, lauryl and stearyl, free from impurity, with yields up to 62%. We think that we were the first to have realized the direct conversion of esters to alcohols under the action of nickel alone as a catalyst.

II. Since it is coumarin which constituted the principal object of the article by de Benneville and Connor, we recall at this time that the preparation of dihydrocoumarin is very easily carried out over Raney nickel.[3]

The hydrogenation begins at about 40° and becomes very rapid in the neighborhood of 80°. At the end of an hour a charge of 1300 g. is converted to a product which distills entirely at 145° (13 mm.) and freezes at 24°; that is to say, the product is free from impurity and the yield quantitative. Simultaneous recording of temperature and pressure on the same graph, using the apparatus which we have devised, permits the operation to be followed in detail.

LABORATOIRE DE CHIMIE ORGANIQUE
DE L'INSTITUT CATHOLIQUE DE PARIS
PARIS, FRANCE CHANOINE L. PALFRAY[4]

RECEIVED JUNE 26, 1940

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[2] (a) Palfray and Sabetay, *Chemie et Industrie, numero special* (Congrès de Bruxelles), 1935, p. 746; (b) *Bull. soc. chim.*, **3**, 682 (1936); (c) **5**, 1424 (1938).

[3] A more complete account may be found in two of our articles; one, chiefly technical, Palfray, *Science et Industrie*, **284** (bis), 53 (1937); the other, chiefly chemical, *Bull. soc. chim.*, in press, to appear in the April–June issue.

[4] All attempts to communicate with Professor Palfray have been in vain and we have not, therefore, been able either to submit to him Dr. Connor's reply or to secure his approval of the translation of his own manuscript.—THE EDITOR.

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## THE BEHAVIOR OF ESTERS OVER RANEY NICKEL

*Sir:*

The statement from our paper[1] quoted above was intended to apply to results with Raney nickel and the nickel on kieselguhr catalysts described by Adkins.[2,3] We are sorry if our failure to make clear this limitation has seemed to detract from the work of Palfray and Sabetay. The results of these workers indicate that their method differs considerably from the one we used. Over their catalyst they obtained alcohols from esters, while we have observed that ethyl $\beta$-cyclohexylpropionate and cyclohexyl $n$-butyrate were unchanged[4] after treatment at 250° over Raney nickel at pressures of 100–150 atmospheres. Furthermore, they report the formation of hydrocarbons having the same number of carbon atoms as the alcohols, while under the conditions we used, primary alcohols may be converted to hydrocarbons with one less carbon atom.[5] It was these indications of differences in conditions which led us to omit the citation of the work of Palfray and Sabetay, and we are glad to acknowledge their contributions using nickel alone as a catalyst. Their work has been cited in our subsequent papers.[4,6]

We should also like to call attention to the hydrogenation[7] of ethyl laurate over another type of nickel catalyst. This constitutes, so far as we are aware, the earliest report of hydrogenation of the ester group over a catalyst containing nickel.

The formation of dihydrocoumarin by the catalytic hydrogenation of coumarin is in line with the usual behavior of $\alpha,\beta$-unsaturated esters and it had been carried out previously.[8] We did not regard our result as novel or original but reported the isolation of dihydrocoumarin to show that it was the precursor of the other hydrogenation products.

We should like to make clear the fact that, in

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[1] De Benneville and Connor, THIS JOURNAL, **62**, 283 (1940).

[2] Adkins, "Reactions of Hydrogen, etc.," University of Wisconsin Press, Madison, Wis., 1937.

[3] Our original statement suggested that other functional groups might alter the ease of hydrogenation of the ester group. This was based on the report of Raney and Adkins [THIS JOURNAL, **61**, 1107 (1939)] that a hydroxymethylpyrrolidine was formed by the hydrogenation of 2-carbethoxypyrrole over Raney nickel. Ovakimian, Kuna and Levene [THIS JOURNAL, **62**, 677 (1940)] have since found that other $\alpha$-amino esters behave similarly.

[4] McClellan and Connor, THIS JOURNAL, **63**, 484 (1941). However, this paper reports the formation of glycols from substituted coumarins and of alcohols from esters of phenols over Raney nickel.

[5] Wojcik and Adkins, *ibid.*, **55**, 1293 (1933).

[6] De Benneville and Connor, *ibid.*, **62**, 3067 (1940).

[7] Folkers and Adkins, *ibid.*, **53**, 1097 (1931).

[8] Adkins, private communication (1937); Späth and Galinowsky, *Ber.*, **70B**, 235 (1937); Palfray and Sabetay, *Bull. soc. chim.*, **5**, 1424 (1938).