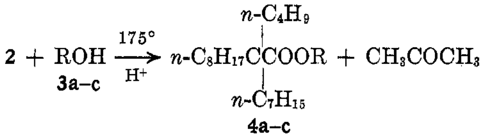
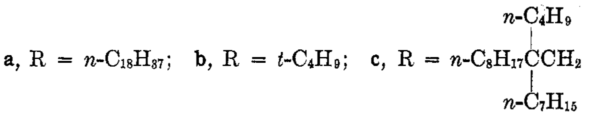
lowing representative alcohols—*n*-octadecanol (**3a**), 2-methyl-2-propanol (**3b**), and 2-butyl-2-heptyldecanol (**3c**) (obtained by sodium in alcohol reduction of **2**)—to the corresponding esters **4a**, **4b**, and **4c** in good



$$\mathbf{2} + \underset{\mathbf{3a\text{–}c}}{\mathrm{ROH}} \xrightarrow[\mathrm{H^+}]{175°} \underset{\mathbf{4a\text{–}c}}{n\text{-}C_8H_{17}\overset{n\text{-}C_4H_9}{\underset{n\text{-}C_7H_{15}}{C}}COOR} + CH_3COCH_3 \qquad (2)$$



$$\mathbf{a},\ R = n\text{-}C_{18}H_{37};\quad \mathbf{b},\ R = t\text{-}C_4H_9;\quad \mathbf{c},\ R = n\text{-}C_8H_{17}\overset{n\text{-}C_4H_9}{\underset{n\text{-}C_7H_{15}}{C}}CH_2$$

yields. The acylations when carried out neat at 175° with a trace of acid catalyst were complete in 5–10 min.

The mechanism of the acylation is uncertain, but it is evident that a ketene intermediate cannot be involved with trialkylacetic acid derivatives. Our previous work with isopropenyl stearate indicated the formation of hexadecylketene as the probable intermediate in the acylation reaction.[7] Apparently, there is more than one pathway available in isopropenyl ester acylations.

Experimental Section

The carboxylic acid starting material was of higher purity than 99% as estimated by glc. Products described below were of a similar order of purity as assayed by the same method.

Isopropenyl 2-Butyl-2-heptyldecanoate (2).—The carboxylic acid **1** (9.5 g, 0.029 mol) and ZnO (61 mg) were heated in an autoclave[5] with propyne under N_2 (auxiliary pressure 400 psi) for 70 hr. Zinc salts were removed by chromatography on Florisil and the liquid ester **2** (9.5 g, 90%) was eluted with pentane: ir (CS_2) 1740 (C=O), 1670 (C=C), 838 ($C=CH_2$) cm^{-1}; nmr (CCl_4) δ 4.58 (s, 1, C=CH), 4.53 (s, 1, C=CH), 1.90 (s, 3, $C=CCH_3$), 1.75–0.70 (m, 41); mass spectrum, *m/e* (rel intensity) 309 (1.24), 281 (92.8), 85 (58), 57 (100).

Anal. Calcd for $C_{24}H_{46}O_2$: C, 78.62; H, 12.65. Found: C, 78.81; H, 12.75.

Octadecyl 2-Butyl-2-heptyldecanoate (4a).—A mixture of enol ester **2** (406 mg, 1.11 mmol) and *n*-octadecanol (300 mg, 1.11 mmol) was melted, treated with *p*-toluenesulfonic acid (5 mg), and heated for 6 min at 180° (Woods metal bath). The ir of the crude product was similar to the ir of the analytical sample. Purification for removal of catalyst was effected by dissolving in pentane and filtering through a small plug of Florisil in a microcolumn to give the ester **4a** (591 mg, 92%): ir (CS_2) 1727 cm^{-1} (C=O); nmr δ 4.00 (t, 2, OCH_2) 1.70–0.70 (m, 76); mass spectrum, *m/e* (rel intensity) 57 (100, butyl), 99 (17.5, heptyl), 113 (12, octyl), 253 (0.9, octadecyl), 269 (1.33, octadecyloxy), 281 (48, trialkylmethyl), 309 (1.19, trialky acetyl). The gaseous product of the reaction was acetone al confirmed by conversion to the 2,4-dinitrophenylhydrazone derivative, mp 125° (lit.[8] mp 126°). Prolonged hydrolysis of **4a** with aqueous alcoholic potassium hydroxide under vigorous conditions gave a single acid identical with the starting acid **1** in glc retention time (single peak) and ir. The ester **4a** is a liquid.

Anal. Calcd for $C_{39}H_{78}O_2$: C, 80.89; H, 13.58. Found: C, 80.93; H, 13.74.

***tert*-Butyl 2-Butyl-2-heptyldecanoate (4b).**—The enol ester **2** (200 mg, 0.55 mmol) and *p*-toluenesulfonic acid (2 mg) were heated to 200° (Woods metal bath) and an excess of dry 2-methyl-2-propanol was added as rapidly as possible through a reflux condenser (caution); this was followed by a 3-min reaction time. (The procedural modification was necessary owing to the low boiling point of the alcohol.) The product was contaminated with a little anhydride[9] removable by a pass in pentane solution through a microcolumn of mildly alkaline alumina (Florisil was unsuitable since the anhydride impurity eluted easily and with the same R_f value as the ester). The *tert*-butyl ester **4b** (156 mg, 75%) gave ir (CS_2) 1721 cm^{-1} (C=O); nmr (CCl_4) δ 1.42 [s, 9, $C(CH_3)_3$], 1.40–0.70 (m, 41); mass spectrum (*m/e*, rel intensity), 281 (31), 57 (100).

Anal. Calcd for $C_{25}H_{50}O_2$: C, 78.47; H, 13.17. Found: C, 78.52; H, 13.15.

2-Butyl-2-heptyldecanol (3c).—A sample of the enol ester **2** (700 mg, 1.9 mmol) was dissolved in dry ethanol and treated with an excess of sodium metal until the rate of metal dissolution became very sluggish. Dilution with water, extraction of the organic material with ether, drying ($MgSO_4$), and solvent removal gave the carbinol **3c**. To prepare the analytically pure material, small amounts of impurities[10] were removed by chromatography on Florisil. The product (475 mg, 85%) was eluted with CH_2Cl_2: ir (CS_2) 3620 (OH), 1193 cm^{-1} (CO); nmr (CCl_4) δ 3.25 (s, 2, CH_2OH) 1.62 (s, 1, OH) 1.50–0.70 (m, 41); mass spectrum (*m/e*, rel intensity) 281 (100).

Anal. Calcd for $C_{21}H_{44}O$: C, 80.69; H, 14.19. Found: C, 81.02; H, 14.02.

2′-Butyl-2′-heptyldecyl 2-Butyl-2-heptyldecanoate (4c).—The alcohol **3c** (105 mg, 0.34 mmol) and the enol ester **2** (123 mg, 0.34 mmol) were heated to 195° for 6 min in the presence of *p*-toluenesulfonic acid (2 mg). Gas evolution (acetone vapor) was immediate. The product was freed of catalyst by passing its pentane solution through a Florisil column to yield ester **4c** (199 mg, 95%): ir (CS_2) 1720 (C=O), 1190 cm^{-1} (CO); nmr ($CDCl_3$) δ 3.76 (s, 2, OCH_2) 1.70–0.70 (m, 82); mass spectrum (*m/e*, rel intensity) 57 (100, butyl), 99 (39, heptyl), 113 (0.4, octyl), 281 (100, trialkylmethyl), 295 (9.7, RCH_2).

Anal. Calcd for $C_{42}H_{84}O_2$: C, 81.22; H, 13.63. Found: C, 81.28; H, 13.66.

Registry No.—**2**, 35341-91-4; **3c**, 35341-92-5; **4a**, 35341-93-6; **4b**, 35341-94-7; **4c**, 35341-95-8.

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[7] Such indications in the case of isopropenyl stearate include (a) isolation of tetrameric hexadecylketene as the sole product when no acylatable substrate was provided [see E. Rothman, *J. Amer. Oil Chem. Soc.*, **45**, 189 (1968)], (b) loss of half the deuterium label when the isopropenyl ester of α-deuteriostearic acid was used as the acylation agent (unpublished data), and (c) formation of stearic *anhydride* or *tert*-butyl stearate *from addition of water* or 2-methyl-2-propanol, respectively, to an isopropenyl stearate–acid catalyst mixture which had been heated to 200° and cooled to room temperature prior to addition of reagent (unpublished data).

[8] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, Ed., "Systematic Identification of Organic Compounds," 4th ed, Wiley, New York, N. Y., 1962, p 221.

[9] The anhydride of acid **1** [ir (CS_2) 1803, 1737 cm^{-1}] may arise *via* the following sequence: dehydration of 2-methyl-2-propanol liberating water, hydrolysis of **2** to acid **1**, and reaction of **1** with **2**.

[10] The impurities were essentially traces of acid **1**, its ethyl ester, and a nonpolar fraction, apparently the ether corresponding to alcohol **3c**.

A Facile Reduction of Unsaturated Compounds Containing Nitrogen[1]

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Catalytic hydrogenation reactions involving compounds containing nitrogen have been reported to give a variety of products depending on reaction condi-

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[1] Presented at the 27th Southwest Regional Meeting of the American Chemical Society, San Antonio, Texas, Dec 1–3, 1971.

tions. Maxted,[2] in a series of papers, has described the poisoning of platinum catalysts by free amines. Rylander,[3] in summarizing the catalytic reductions of nitriles, lists primary, secondary, and tertiary amines, imines, hydrocarbons, aldehydes, amides, and alcohols among the products, the major product depending on the catalyst, substrate and reaction conditions. Hartung and Simonoff[4] have summarized the hydrogenolyses of some benzylamines, employing platinum, palladium, and nickel catalysts. Southard[5] has employed the catalytic hydrogenolysis of a urethane group as a major step in a general peptide synthesis.

We have found that nickel boride exhibits a high proficiency for catalyzing the addition of hydrogen to unsaturated compounds containing nitrogen. First reported over twenty years ago,[6] the catalyst has been found to cause no rearrangements of unsaturated hydrocarbons during catalytic hydrogenation reactions.[7] The catalyst is also highly selective for the reduction of unsaturated compounds containing oxygen,[8] causing neither hydrogenation nor hydrogenolysis of oxygen functions.

A representative selection of the nitrogen-containing unsaturated compounds studied by us appear in Table I. The reaction products of the compounds listed were isolated and identified by spectral comparisons.

TABLE I

TIMES OF HYDROGENATION OVER NICKEL BORIDE

Compd	Time,[a] min
Allylamine	10
Diallylamine	25[b]
Acrylamide	8
Methacrylamide	15
3-Butenenitrile	30
2-Butenenitrile	30[c]
Cinnamonitrile	16 hr[c]

[a] Time required for the uptake of 1 equiv of hydrogen, 100 mmol of substrate, 5 mmol of catalyst, 50 ml of solvent. [b] Time required for the uptake of 2 equiv of hydrogen. [c] 20 mmol of catalyst.

The amines and amides gave quantitative yields of single compounds from reduction of the carbon–carbon π bonds. No products resulting from hydrogenation or hydrogenolysis of the functional groups were detected by gas chromatography. Also, no further uptake of hydrogen was observed following the uptake of the calculated amount for the carbon–carbon π bonds.

However, the carbon–nitrogen π bonds of the nitriles could be reduced, yielding primary amines. While not unique, nickel boride does exhibit a high selectivity for the carbon–carbon π bond. For example, butyronitrile, formed quantitatively in 30 min from either 2- or 3-butenenitrile, gives a 56% yield of butylamine in 6 days with 5 mmol of catalyst or 2 days with 20 mmol of catalyst. No products from the coupling reactions listed by Rylander[3] were detected in the reaction mixture.

From the short reaction times, it is apparent that the poisoning by amines of palladium catalysts reported by Maxted[2] does not extend to the nickel of nickel boride.

The catalyst is exceedingly simple to prepare. The reaction of nickel(II) salts (dissolved in water or suspended in ethanol) and sodium borohydride yields the black precipitate of interest. It may be used directly or stored for future use.

The physical appearance of the catalyst changes with the preparation medium, but this change does not appear to affect the selectivity of the catalyst. It does, however, effect the times of reduction. The granular material from water solvent exhibits longer hydrogenation times than the colloidial material from alcohol.

These findings, coupled with the earlier results on oxygen-containing compounds,[8] indicate the potential applications of nickel boride in the synthesis of complex organic molecules. Work on further applications of nickel boride on compounds containing π-bonded nitrogen, halogen, and small rings is currently underway.

Experimental Section

Chemicals.—All chemicals were used directly from the bottles with no further purification. Nitriles were Eastman practical grade. Other chemicals were reagent grade.

Catalyst Preparation.—For a single hydrogenation, 5 mmol of powdered nickel(II) salt, 50 ml of liquid, and a short magnetic spinbar are placed in a Parr hydrogenation flask. Stirring is begun and the flask flushed with hydrogen. Addition of 5 mmol of sodium borohydride (5 ml of 1.0 M solution in water or alcohol or 185 mg of solid) to the flask produces the catalyst.

Nickel salts used are acetate, chloride, nitrate, and sulfate. Liquids include water as a solvent and absolute and 95% ethanol as suspension media.

For a bulk preparation, the above procedure is followed using larger amounts of nickel(II) salts and sodium borohydride. The catalyst can be isolated by either filtering or centrifuging, depending on particle size. The isolated catalyst can be stored indefinitely under nitrogen, either dry or under alcohol.

Hydrogenation Procedure.—To the catalyst and preparatory solution in a Parr hydrogenation flask is added the compound to be hydrogenated, neat if liquid or dissolved in a minimum amount of solvent if solid. If the preprepared catalyst is used, the compound to be hydrogenated is added to ~50 mg of the catalyst in 50 ml of the solvent. The flask is then attached to the hydrogenator and shaken until the theoretical pressure drop for hydrogen is observed. Initial pressure was 30 psi and temperature was ambient with no external cooling in all experiments.

The contents of the hydrogenation flask were centrifuged to separate the catalyst, the decantate being analyzed by gas chromatography. All reaction products were isolated and identified by comparisons of infrared spectra with authentic samples. Yields of the amines and nitriles were determined by gas chromatographic methods employing external standards. The yields of the amides were estimated from the melting points of the reaction products following evaporation of the hydrogenation solvent.

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(8) T. W. Russell and R. C. Hoy, *ibid.*, **36**, 2018 (1971).