19 g.) were redissolved in ether and the process repeated. The acids (12.5 g.) were digested with about 100 ml. of warm water and after standing for 24 hours, the small amount of isophthalic acid, which had separated, was filtered off. The filtrate was diluted to about 150 ml. with water, 10 ml. of glacial acetic acid added and the solution heated to boiling. While boiling, 100 ml. of an aqueous, 1 *N* solution of calcium acetate was added slowly, with stirring. After digestion for 1 hour on a steam-bath, the solution was cooled and filtered. The filtrate was again heated to boiling and 100 ml. of an aqueous, 1 *N* solution of barium acetate added. Digestion and filtration was carried out as before. The filtrate was acidified with a slight excess of 4 *N* sulfuric acid, evaporated to a volume of about 50 ml. and exhaustively extracted with ether. The extracted acids weighed 7 g. Vacuum drying at 90–95° at 1–2 mm. resulted in the sublimation of small amounts of *o*-phthalic acid. The dried product was dissolved in acetone and the solution treated with benzene until it became turbid. After several days of slow evaporation, the precipitated acid was separated by filtration and dried at 100°. The weight of the product was 5.4 g., corresponding to 16% of the original mixture. The equivalent weight was 72 and the molecular weight, by b.p. in acetone, 220. By heating at 230° a readily volatile anhydride (m.p. 166°) was formed.

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[CONTRIBUTION FROM THE POLYCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., INC.]

Synthesis of Esters from Olefins, Hydrogen, Carbon Monoxide and Acetic Acid

BY RALPH C. SCHREYER

RECEIVED NOVEMBER 2, 1951

Ethylene, propylene, diisobutylene, tetrapropylene, triisobutylene and tetraisobutylene have been treated with hydrogen and carbon monoxide at about 250° in the presence of cobalt acetate and acetic acid to give propyl acetate, butyl acetates, nonyl acetates, tridecyl acetates and heptadecyl acetates, respectively. In the case of ethylene and propylene, 2-methylpentyl acetate and octyl acetates have also been obtained. Similar treatment of cyclopentadiene has given cyclopentylmethyl acetate and the diacetates of the glycols formed from cyclopentadiene dimer. Methyl tetrahydrobenzoate has yielded 3- and 4-acetoxymethylcyclohexanecarboxylic acids. Butanols, 2-ethylhexanol, tridecyl alcohols and heptadecyl alcohols have been obtained by alcoholysis of the corresponding acetate esters.

Recent work[1,2] in this country has shown that aldehydes are obtained in good yields by the reaction of olefins with carbon monoxide, hydrogen and cobalt carbonyls in inert solvents. In this Laboratory, investigation of the reaction of olefins with carbon monoxide and hydrogen in the presence of acetic acid and cobalt acetate has shown that esters are obtained by using more drastic conditions.

$$\begin{aligned}&\mathrm{RCH{=}CH_2 + CO + 2\,H_2 + HOAc} \longrightarrow\\&\qquad \mathrm{RCH_2CH_2CH_2OAc\ (or\ RCH(CH_3)CH_2OAc) + H_2O}\end{aligned}$$

The esters are obtained by processing the olefins and acetic acid with 1:1 carbon monoxide–hydrogen gas mixture at 250° and 700 atm. pressure in a stainless steel shaker tube (325-cc. capacity). A soluble cobalt catalyst, such as cobalt acetate, is generally employed in an excess of acetic acid. However, other cobalt salts are operative. The reaction is very exothermic and rapid. Temperatures less than 200° as well as pressures less than 400 atm. give mainly aldehydes. As the pressure drops, additional quantities of carbon monoxide and hydrogen are injected into the tube to maintain a pressure of 700 atm. The catalyst can be recovered by distilling off most of the acetic acid and water in the product at atmospheric pressure. During this distillation the cobalt carbonyls are decomposed as evidenced by evolution of gases and the precipitation of a solid. This solid, probably cobalt acetate, can be filtered off and reused as the catalyst in the reaction. Ethylene, propylene, diisobutylene, tetrapropylene, triisobutylene and tetraisobutylene have been treated with hydrogen and carbon monoxide in the presence of cobalt acetate and acetic acid to give the acetate esters of the alcohols containing one more carbon than the original olefin by this procedure. Alcoholysis of the acetate esters with methanol gave the corresponding alcohols in quantitative yields.

In the case of ethylene or propylene a side reaction, condensation of the intermediate aldehyde, can be made to predominate by increasing the reaction temperature. Thus, a 40% conversion to octyl acetates and 30% conversion to butyl acetates was obtained by processing propylene and acetic acid at 250–270° and 700 atm.

$$\begin{aligned}&\mathrm{2CH_2{=}CHCH_3 + CH_3CO_2H + 2CO + 4H_2} \longrightarrow\\&\qquad \mathrm{CH_3CH_2CH_2CH_2CH(C_2H_5)CH_2OOCCH_3 + 2H_2O}\end{aligned}$$

Formation of the octyl acetates is believed to occur by aldolization of the intermediate aldehyde, followed by dehydration, hydrogenation and esterification. Alcoholysis of the resulting octyl acetates to octyl alcohols followed by comparison of the mass spectrogram of the octyl alcohols with the mass spectrogram of an authentic sample of 2-ethylhexanol showed that the octyl acetates fraction was essentially 2-ethylhexyl acetate. Ethylene gave propyl acetate and 2-methylpentyl acetate. Higher olefins gave aldehydes that were not as reactive as propionaldehyde or butyraldehyde so that aldolization did not occur as readily. In these cases, the saturated hydrocarbon was the main by-product, conversions being 50–70% to the acetate esters and 20–30% to the hydrocarbon.

Hydroformylation of cyclopentadiene under these conditions yielded cyclopentylmethyl acetate and the diacetates of the glycols formed from the dimerization of cyclopentadiene. A mixture of 3- and 4-acetoxymethylcyclohexanecarboxylic acids was obtained from methyl tetrahydrobenzoate.

Experimental

Acetate Esters.—Hydroformylation of the unsaturated compounds in acetic acid was carried out by processing a 1:2 mole mixture of the unsaturated material and acetic

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(1) W. F. Gresham, R. E. Brooks and W. M. Burner, U. S. Patent 2,437,600.

(2) (a) H. Adkins and G. Krsek, THIS JOURNAL, **70**, 383 (1948), (b) H. Adkins and G. Krsek, *ibid.*, **71**, 3051 (1949).

TABLE I

ACETATE ESTERS

Formula	Yield, %[a]	B.p. °C.	Mm.	n^{25}D	Ester No.[b] Calcd.	Found
$CH_3CH_2CH_2OAc$	10	96–99	...	1.3810	550	516
C_4H_9OAc	33	108–123	...	....	...	...
$CH_3(CH_2)_2CH(CH_3)CH_2OAc$	11	157–159	...	1.4060	389	365
$C_5H_9CH_2OAc$	7	45–50	5	1.4300	395	406
$C_6H_{10}(CO_2H)(CH_2OAc)$[c]	29	150–158	1–2	1.4688	280	274
$C_8H_{17}OAc$	37	60–63	1–2	1.4180	326	283
$C_9H_{19}OAc$	70	55–60	2	1.4225	301	295
$C_{10}H_{14}(CH_2OAc)_2$	19	155–165	2–3	1.4878	401	375
$C_{13}H_{27}OAc$[d]	46	88–90	1–2	1.4350	232	225
$C_{13}H_{27}OAc$[e]	59	88–95	1–2	1.4360	232	232
$C_{17}H_{35}OAc$	54	123–130	1	1.4469	188	183

[a] Yield based on amount of unsaturated material used. [b] The ester, acid or hydroxyl number is the number of milligrams of potassium hydroxide equivalent to the amount of functional group undergoing reaction in one gram of sample. [c] Calculated acid number: 280; found 272. [d] Acetate ester from Sharples triiosbutylene. [e] Acetate ester from Shell tetrapropylene.

acid in the presence of one or two grams of cobalt acetate with a 1:1 gas mixture of carbon monoxide and hydrogen at 225–275° and 700 atm. pressure for one hour in a stainless steel shaker tube (325-cc. capacity). The shaker tube was cooled to room temperature and the pressure released. The resulting liquid products were worked up by distillation. In the case of ethylene and propylene, the propyl acetate and butyl acetates were isolated by steam distillation followed by drying and distillation. Cobalt laurate in the hydroformylation reactions gave comparable results to cobalt acetate. Recycling of the foreshot material (boiling in the range of the olefin) from the hydroformylation of liquid olefins produced substantially no additional acetate esters, indicating that the foreshot material was essentially the saturated hydrocarbon. The yields and properties of the acetate esters are listed in Table I.

Alcohols.—The alcohols were obtained in quantitative yields by methanolysis of the corresponding acetate esters in the presence of traces of sodium methoxide. The properties of the alcohols are given in Table II.

TABLE II

ALCOHOLS

Formula	B.p. °C.	Mm.	n^{25}D	OH No. Calcd.	Found
C_4H_9OH[a]	107–114	...	1.3935	...	...
$C_8H_{17}OH$[b]	177–181	...	1.4281	...	...
$C_{13}H_{27}OH$	95–100	2–3	1.4450	281	277
$C_{13}H_{27}OH$	110–117	2–3	1.4460	281	278
$C_{17}H_{35}OH$	140–145	4–5	1.4571	219	216

[a] Analysis of the butanols by the mass spectrograph showed the following composition in mole %: 24.1 *n*-butyl alcohol, 71.6 isobutyl alcohol, 1.8 *n*-butyl formate, 2.5 *n*-butyl acetate. [b] The mass spectrograms of an authentic sample of 2-ethylhexanol and the $C_8H_{17}OH$ fraction were made and found to be quite similar. However, differences were sufficient to indicate that more than one compound was present in one or both of the samples.

WILMINGTON, DEL.

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

The Structure of the Self-Condensation Product of 1-Phenyl-2-pyrazoline

BY H. R. SNYDER, FRANK VERBANAC AND D. BRUCE BRIGHT[1]

RECEIVED DECEMBER 17, 1951

The product obtained from the self-condensation of 1-phenyl-2-pyrazoline is shown to be 1,1′-diphenyl-3,3′-bi-2-pyrazoline (II). The structure is proved by characterization of oxidation products and by infrared studies. Oxidation of the substance yields 1,1′-diphenyl-3,3′-bipyrazole (V), identified by independent synthesis. 1,1′-Diphenyl-3,4′-bipyrazole (IV) has also been prepared. The reaction of 3-methyl-1-phenylpyrazole with *n*-butyllithium produces the 5-lithium derivative.

Treatment of 1-phenyl-2-pyrazoline with hydrogen chloride yields a self-condensation product which was referred to as bis-N-phenyl-Δ²-pyrazoline by Curtius and Wirsing.[2] In the present work the reaction was accomplished with boron trifluoride and boron trifluoride etherate as well as with dry hydrogen chloride. The product, a yellow solid which exhibits blue fluoresence in ether solution, was reported[2] to have a melting point of 221° and an empirical formula of $C_{18}H_{20}N_4$. However, the product obtained in this Laboratory melted at 235–237° (cor.), and the empirical formula $C_{18}H_{18}N_4$ was required by the analyses and the molecular weight determinations. Thus, the substance is not a simple dimer but rather the product of an oxidative coupling.

The infrared absorption spectrum of the self-condensation product is characterized by the presence of strong bands at 1596 and 1499 cm.$^{-1}$, the absorption being much more intense than that ordinarily attributed to a phenyl group. Similar bands were observed in the spectra of 1-phenyl-2-pyrazoline, 1,5-diphenyl-2-pyrazoline and 1,5-diphenyl-3-*p*-tolyl-2-pyrazoline. The great similarity of the absorption bands indicates that the structural feature common to these known pyrazolines, *i.e.*, the 1-phenyl-2-pyrazoline system, is also present in the self-condensation product. The spectrum of the unknown substance gave no indication of the presence of an –N–H group. Because

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[1] Atomic Energy Commission Fellow, 1951–1952.

[2] Th. Curtius and F. Wirsing, *J. prakt. Chem.*, [2] 50, 531 (1894).