was obtained in 21% yield. It crystallized from a benzene-ligroin mixture in colorless needles, m.p. 98–99° (dec.).

Anal. Calcd. for $C_{14}H_{10}Cl_2O_2S$: C, 53.7; H, 3.3; Cl, 22.6; S, 10.2. Found: C, 53.7; H, 3.2; Cl, 23.0; S, 10.1.

2,2-Di-(*p*-bromophenyl)-ethene-1-sulfinic Acid.—This acid was obtained from 1,1-di-(*p*-bromophenyl)-ethylene[10] as above, but without solvent, after 51 hours at room temperature, in 20% yield, m.p. 102°.

Anal. Calcd. for $C_{14}H_{10}Br_2O_2S$: C, 41.8; H, 2.6; S, 8.0. Found: C, 41.6; H, 2.7; S, 7.8.

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[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, POLYTECHNIC INSTITUTE OF MILAN]

Hydrogen Transfer Reactions Accompanying the Cobalt-catalyzed Addition of Carbon Monoxide to Olefinic Compounds

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The cobalt-catalyzed reaction of carbon monoxide and olefins with alcohols and with amines normally yields esters and amides. In some instances, however, products containing added hydrogen are formed. The hydrogen is furnished by the reactants, possibly *via* the formation and decomposition of cobalt hydrocarbonyl.

During the oxo synthesis, some reduction of aldehydes to alcohols occurs and indeed if the reaction temperature is kept at 185–220°, alcohols are formed as principal products. Table I shows that the extent of hydrogenation depends mostly on time and is not greatly influenced by the nature of the solvent.

TABLE I

Cyclohexene, moles	Solvent	Solvent, g.	Time, minutes	Ratio alcohol/alcohol + aldehyde
0.5	None	..	120	0.95
.5	Benzene	50	120	.93
.5	Cyclohexane	50	120	.96
.5	Cyclohexane	50	50	.29
.5	*n*-Hexane	50	50	.38

The one-step synthesis of alcohols, however, does not give as good yields as can be secured by the isolation of the intermediate aldehyde and subsequent hydrogenation.

The hydrogen consumed in the oxo synthesis is unquestionably furnished by the synthesis gas present in the system. In the closely related reactions of olefins and pure carbon monoxide with alcohols and with amines, products containing added hydrogen are isolated. The hydrogen must be furnished by the reactants in some type of transfer process: in fact products from dehydrogenation of reactants are often detected. In all the experiments described below either Raney cobalt or cobalt-on-kieselguhr was employed as catalyst.

Reaction of Carbon Monoxide and Olefins with Alcohols.—The reaction of olefins having *n* carbon atoms with carbon monoxide and alcohols in addition to providing esters, can lead to the formation of aldehydes and alcohols with *n* + 1 carbon atoms and of ketones having 2*n* + 1 carbon atoms. The four possible reactions are illustrated with cyclohexene and isopropyl alcohol as examples

$$C_6H_{10} + CO + CH_3CHOHCH_3 \longrightarrow C_6H_{11}COOCH(CH_3)_2 \quad (1)$$

$$C_6H_{10} + CO + CH_3CHOHCH_3 \longrightarrow C_6H_{11}COC_6H_{11} + CH_3COCH_3 \quad (2)$$

$$C_6H_{10} + CO + CH_3CHOHCH_3 \longrightarrow C_6H_{11}CHO + CH_3COCH_3 \quad (3)$$

$$C_6H_{10} + CO + 2CH_3CHOHCH_3 \longrightarrow C_6H_{11}CH_2OH + 2CH_3COCH_3 \quad (4)$$

It is apparent that the hydrogen required for reactions 2, 3 and 4 is furnished by dehydrogenation of the isopropyl alcohol to acetone. The competition between the various possible reactions is influenced by the ratio of reactants and as shown in Table II the carbinol is found in largest amount when a large excess of hydrogen donor is present.

TABLE II

Ratio alcohol/cyclohexene	Yield, mole %[a]		
	Dicyclohexyl ketone	Cyclohexylcarbinol	Ester
0.5	12	4	15
1.3	6	14	30
10	Traces	40	31

[a] Based on the initial concentration of cyclohexene.

When methanol is used in the reaction some aldehydes and ketones are produced according to type reactions 2 and 3. It might therefore be expected that formaldehyde would be formed as a result of a hydrogen transfer process but no appreciable quantity was detected. However, dimethyl ether was found in the gaseous reaction products and it is possible that the required hydrogen was formed *via* the reactions

$$2CH_3OH \longrightarrow CH_3OCH_3 + H_2O$$

$$H_2O + CO \longrightarrow H_2 + CO_2$$

The competition between the various possible type reactions (1–4) when methanol is used is influenced by the olefin. Table III shows that the yield of esters increases and the yield of ketone decreases with increased size of the olefin. When ethylene is the olefinic substrate, diethyl ketone appears to be the principal product regardless of what alcohol is present. Thus, in the presence of butanol-2 and pentanol-3 the yield of diethyl ketone was 64.5 and 60%, respectively, compared to 57% with methanol.

TABLE III

Olefin	Moles, % esters	Moles, % dialkyl ketone	Moles, % aldehyde
Ethylene	21.5	57	5
Propylene	33.2	26	3
Isobutylene	56.0	Traces	3

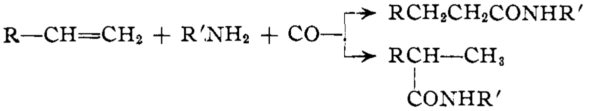
TABLE IV

SYNTHESIS OF SUBSTITUTED AMIDES

Olefin	Amine	Chief reaction products	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found	Yield on introduced olefin, %
Ethylene	Aniline	Propionanilide	103–104	9.40	9.47	75
Propylene	Aniline	*n*-Butyranilide	93–94	8.60	8.97	
		Isobutyranilide	102			80–95
Isobutylene	Aniline	Isovaleranilide	108–110	7.90	7.93	..
Styrene	Aniline	Phenylpropionanilide	97	6.22	6.48	14
Cyclohexene	Aniline	Cyclohexanecarboxanilide	138–140	6.90	7.15	70
Cyclohexene	1-Naphthylamine	N-1-naphthylcyclohexanecarboxamide	184–185[a]	5.54	5.59	..
Cyclohexene	Cyclohexylamine	N-Cyclohexylcyclohexane carboxamide	163–165[b]	6.73	6.63	..
Cyclohexene	Stearylamine	N-Stearylcyclohexane carboxamide	84–87[c]	3.69	3.81	..
Methyl crotonate	Aniline	Methylsuccinanilide	214–217	10	9.97	..

[a] The amide obtained from 1-naphthylamine and cyclohexanecarbonyl chloride melted at 183–185°. [b] The amide obtained from cyclohexylamine and cyclohexanecarbonyl chloride melted at 164°. [c] The amide obtained from stearylamine and cyclohexanecarbonyl chloride melted at 88–89°.

Reaction of Carbon Monoxide and Olefins with Amines.—The synthesis of substituted amides from olefins, carbon monoxide and amines usually proceeds according to the equation



$$R{-}CH{=}CH_2 + R'NH_2 + CO \rightarrow \begin{cases} RCH_2CH_2CONHR' \\ RCH{-}CH_3 \\ \quad | \\ \quad CONHR' \end{cases}$$

In contrast to the ester synthesis large amounts of secondary products are seldom formed.[1]

Using pressures of 150–400 atm. and temperature of 150–200°, the amines react smoothly, while ammonia does not react at all or reacts with very great difficulty. Primary amines react more easily than secondary amines, while aromatic amines react more quickly than aliphatic and alicyclic amines.

The influence of the type of olefinic compound used on the structure and composition of the reaction products is analogous to that observed in the oxo synthesis. Thus, the use of asymmetric olefins leads usually to the formation of two isomeric amides. Also in this case the addition of the carbon monoxide molecule occurs predominantly at the least substituted carbon atom of the olefinic group. Table IV shows the principal products obtained in experiments with different olefins and amines. The yields of amides with respect to the amount of olefins used are determined in some cases and are found fairly high.

An unusual and interesting example of hydrogen transfer was observed also in this series. In the most part of our experiments diphenylurea was isolated as by-product in very different amount. In the reaction between styrene, aniline and carbon monoxide, the amount of diphenylurea is abnormally high and a portion of the styrene is reduced to ethylbenzene

$$2C_6H_5NH_2 + CO + C_6H_5CH{=}CH_2 \longrightarrow C_6H_5NHCONHC_6H_5 + C_6H_5CH_2CH_3$$

It is of our belief that in the hydrogen transfer reactions, cobalt carbonyl acts as a hydrogen-transfer agent by formation and decomposition of the hydrocarbonyl

$$1/2H_2 + 1/2[Co(CO)_4]_2 \rightleftarrows Co(CO)_3COH$$

In the absence of gaseous hydrogen, the hydrocarbonyl may be formed[2] from hydrogen supplied from one of the reactants, for example, water from the dehydration of methanol or hydrogen from the dehydrogenation of either isopropyl alcohol or amines.

Experimental

All b.ps. and m.ps. are uncorrected.

The liquid products employed were accurately rectified and their purity was tested by refractive index.

The technique and the apparatus used were identical with those described in previous works.[3]

When not otherwise specified the rectifications were made in a Fenske column 90 cm. high. The aldehydes were determined by the hydroxylamine method[4]; the alcohols by the phthalic anhydride method[5]; the esters by saponification by $N/2$ alcoholic KOH.

Cyclohexylcarbinol.—Fifty grams of cyclohexane, 41 g. of cyclohexene and 1 g. of Raney cobalt are put into a 435-ml. autoclave, and 1:1 CO and H_2 is compressed to 20 atm. The agitation is started and the reaction vessel is heated to about 210°. Then 1:1 CO and H_2 is compressed up to a pressure of 450 atm. After two hours of continuous agitation the pressure falls to 220 atm. After cooling, 105 g. of a yellowish-brown liquid and suspended metallic cobalt are let out. After decantation, 100 g. of clear liquid is distilled first over a boiling water-bath and then under reduced pressure, obtaining four fractions. The quantitative determinations of the carbonyl compounds and alcohols give the results reported in Table V.

TABLE V

Fraction	Boiling points °C.	Boiling points Mm.	Cyclohexanecarboxaldehyde, g.	Cyclohexylcarbinol, g.
1	70–95	755	1	..
2	65–80	15	0.5	4
3	80–90	15	...	32
4	90–150	15	...	3

Cyclohexylcarbinol from Cyclohexene, CO and Isopropyl Alcohol.—Sixty-eight grams of cyclohexene, 1.5 g. of Raney cobalt and 480 g. of isopropyl alcohol are put into a 1700-ml. reaction vessel and carbon monoxide is pumped to a pressure of 250 atm. The agitation is started and the vessel is heated to 210°. In the course of 3.5 hr. the pressure drops from 505 to 470 atm. After cooling, the gases are let out and 562 g. of liquid is taken out. After settling, 520 g. of clear liquid is rectified, obtaining six fractions. The identification and analysis lead to the conclusion that fraction (50 g.), b.p. 54–60° at 761 mm. consists pre-

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(1) P. Pino and C. Paleari, *Gazz. chim. ital.*, **81**, 646 (1951).

(2) W. Hieber, H. Schulten and R. Martin, *Z. anorg. allgem. Chem.*, **240**, 263 (1939).

(3) G. Natta, P. Pino and E. Mantica, *Gazz. chim. ital.*, **80**, 680 (1950).

(4) W. M. D. Bryant and L. M. Smith, THIS JOURNAL, **57**, 57 (1935).

(5) P. J. Elving and B. Warshowsky, *Ind. Eng. Chem.*, *Anal. Ed.*, **19**, 1006 (1947).

dominantly of acetone and that fraction (56 g.), b.p. 79–83° at 20 mm., contains 38 g. of cyclohexylcarbinol and 16 g. of isopropyl ester of cyclohexanecarboxylic acid.

Reaction between Ethylene, CO and Methanol.—One hundred and twenty-eight grams of methanol, 4 g. of Raney cobalt, 43 g. of ethylene and carbon monoxide up to a pressure of 250 atm. are charged into a rocking autoclave of 1700-ml. capacity. The agitation is started and the autoclave is heated to 200°. The temperature is held at 200–205° for 8 hr., during which time the pressure drops from 470 to 405 atm. After cooling, 250 l. of gas (ethylene 2.5%) and 181 g. of liquid containing suspended metallic cobalt are obtained. By fractional distillation, 3 g. of propionaldehyde, 21 g. of methyl propionate and 27.5 g. of diethyl ketone are obtained.

Reaction between Ethylene, CO and 2-Butanol.—Two hundred and ten grams of 2-butanol, 4 g. of Raney cobalt, 110 g. of ethylene and carbon monoxide up to a pressure of 170 atm. are charged to the autoclave described above. The agitation is started and the autoclave is heated to 210°. The temperature is held at 207–210° for 9 hr., during which time the pressure drops from 355 to 275 atm. After cooling, 195 l. of gas (ethylene 18%) and 306 g. of liquid containing metallic cobalt in suspension are taken off. Fractional distillation of 299 g. of decanted liquid, followed by analytical determination shows that 55 g. of methyl ethyl ketone and 68 g. of diethyl ketone are obtained.

Reaction between Propylene, CO and Aniline.—Three hundred and ten grams of aniline, 13 g. of propylene and 3 g. of Raney cobalt are introduced in an autoclave of 435 ml. capacity. Carbon monoxide is then introduced up to a pressure of 250 atm. The agitation is started and the autoclave is heated to 170° and held at this temperature for 5 hr. After cooling, 335 g. of products are discharged, and, after filtration, the unaltered aniline (250 g.) is distilled at 20 mm. The remaining products are distilled at 0.8 mm. 28 g. of aniline and 41 g. of a mixture of *n*- and isobutyranilide are obtained.

Reaction between Styrene, CO and Aniline.—Sixty-nine grams of aniline, 61.6 g. of freshly redistilled styrene and 2.4 g. of Raney cobalt are put into a 435-ml. autoclave. Carbon monoxide is then introduced up to a pressure of 250 atm. The agitation is started and the autoclave is heated to 200° and held at this temperature for 6 hr. After cooling, 127 g. of a mixture of solid and liquid compounds are discharged. The products are filtered and 45 g. of diphenylurea separated as a white precipitate. The precipitate is washed with ether and the washing liquid is added to the filtrate. After removal of ether by rectification, the liquid products are distilled and two fractions are collected. The first fraction (24 g.), b.p. 112–160°, is accurately rectified and yields 13 g. of ethylbenzene, $n^{20}\text{D}$ 1.4960. The second fraction (16 g.), b.p. 75–80° at 20 mm., is mostly aniline. The residue (50 g.) is then distilled at 0.5 mm.: the fraction boiling at 180–210° (19.4 g.), after several recrystallizations from ligroin, yields pure β-phenylpropionanilide, m.p. 97–98°.

Reaction between Methyl Crotonate, CO and Aniline.—Ninety-three grams of aniline, 60 g. of methyl crotonate and 1 g. of cobalt on kieselguhr are put into a 435-ml. autoclave. Carbon monoxide is then introduced to a pressure of 180 atm. The agitation is started and the autoclave is heated to 200° and held at this temperature for 6 hr. After cooling, 165 g. of liquid products is discharged. The catalyst is separated by filtration and the unreacted aniline (64 g.) and methyl crotonate (40 g.) are distilled off under reduced pressure, the residue dissolved in ligroin, the solution decolorized with bone charcoal and concentrated. On standing, methylsuccinic acid dianilide (30 g.) crystallizes.

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Reactions of Haloalkyl Ethers with Phenyllithium[1]

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Phenyllithium may react with haloalkyl ethers to cause displacement of halogen by phenyl, dehydrohalogenation, or halogen-metal interconversion. The nature and position of the halogen atom determine which type of reaction will predominate. With γ-haloalkyl ethers, the yield of the product of displacement of halogen by phenyl increased in the order Cl < Br < I, and the amount of dehydrohalogenation decreased in the order Cl > Br or I. With the β-halogen compounds, halogen–metal interconversion occurred with iodine or bromine (I ≫ Br), but the γ-halogen ethers gave essentially no halogen–metal interconversion, even when the halogen was iodine. In the case of α-chloroalkyl ethers the expected displacement of halogen by phenyl occurred.

The reactions which have been reported in the literature as occurring with halogen-substituted alkyl ethers and active organometallic compounds (usually Grignard reagents) are of three types; (1) displacement of halogen on carbon, (2) elimination of the elements of HX or (3) displacement of carbon on halogen ("halogen–metal interconversion"). Besides these, reactions involving cleavage of C–O bonds by the RM compound may occur, either simultaneously or subsequently. This paper reports some experiments which indicate that when the organometallic compound is phenyllithium all three of the above types of reactions can be realized, and that the nature and position of the halogen atom determine which type of reaction will predominate. The results obtained are shown in Table I.

The reaction of α-haloalkyl ethers with Grignard reagents[2] has been applied extensively in the past. A similar reaction for organolithium compounds has not been reported, perhaps because the use of a lithium compound offers no apparent advantages for preparative purposes. This type of reaction was found to proceed satisfactorily with phenyllithium and α-chloroalkyl ethers at room temperature.

Although reactions of type 1 are quite broad in scope, they cannot be used to prepare ethers such as 1-methoxy-2-phenylethane from benzylmagnesium halides and chloromethyl ethers, because of the occurrence of rearrangement.[3] It was thought possible that organolithium compounds, which are sometimes more active in displacement reactions than are Grignard reagents, might react well enough with β-haloalkyl ethers to make the synthesis of such β-substituted ethers in this fashion practical. The reaction of phenyllithium with one equivalent of 1-methoxy-2-chloroethane, however, gave 74% of benzene and only a trace of

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[1] This work was supported in part by a Frederick Gardner Cottrell grant from the Research Corporation.

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