Preparation of Cyclopropenone.—When a pure sample of IV was added to D_2O, it was immediately hydrolyzed to cyclopropenone and methyl alcohol, nmr (D_2O) τ 1.0 (s). The water solution of cyclopropenone was saturated with sodium chloride and extracted with methylene chloride. This was dried over magnesium sulfate: nmr (CH_2Cl_2) τ 1.0–1.1 (s); ir (CH_2Cl_2) 1870, 1835, and 1730 cm^{-1}. All of these spectral data agree with those reported by Breslow and Ryan.[5]

Preparation of 1,1-Dimethoxy-2-*tert*-butoxycyclopropane (III).—To 30 ml of dry dimethyl sulfoxide in a 50-ml round-bottom flask was added 2.17 g (0.01 mol) of II and 3.36 g (0.03 mol) of KO-*t*-Bu. The solution turned black quickly. It was stirred at room temperature under a drying tube overnight, after which it was poured into water and extracted several times with ether. (Trouble with emulsion formation was experienced). The ethereal solution was dried over anhydrous magnesium sulfate and filtered. The ether was removed by distillation at atmospheric pressure and the residue was distilled bulb-to-bulb at atmospheric pressure. The product was then chromatographed over silica gel using petroleum ether (bp 20–40°) as eluent. III was shown to be pure by vpc. The yield of clear, colorless product was *ca.* 0.8 g (50%): ir (neat) 3110 (w), 2990 (s), 2850 (s), 1450 (s), 1390 (m), 1365 (s), 1295 (s), 1220 (m), 1195 (w), 1150 (s), 1050 (s), 980 (m), and 880 cm^{-1} (m); nmr (CCl_4) τ 8.83–9 (m, 2), 8.74 (s, 9), 6.69 (s, 3), 6.55 (s, 3), and 6.69–6.78 (m, partially hidden, 1). The hidden proton at τ 6.69–6.78 was shown to exist by double resonance at this region while observing the other cyclopropyl protons at τ 8.83–9.30. The double resonance caused the high-field multiplet to collapse to an AB quartet. The mass spectrum did not give a parent peak but did give P − 57 for loss of *tert*-butyl radical. *Anal.* Calcd for $C_9H_{18}O_3$: C, 62.04; H, 10.41. Found: C, 62.20; H, 10.47.

Preparation of an Adduct between 1,3-Diphenylisobenzofuran and IV.—To a CCl_4 solution of IV (prepared from 0.01 mol of II) was added 2.7 g (0.01 mol) of 1,3-diphenylisobenzofuran. The reaction was allowed to continue for 1 week at room temperature. At the end of this time, the solvent was removed under vacuum. The residue was dissolved in hot methanol and allowed to cool. The solution was filtered, and the methanol was allowed to evaporate slowly at room temperature in a crystallization dish. The product (V) was isolated as clear hexagonal crystals: mp 140–141.5°; yield 1.1 g (30%); ir (KBr) 3070 (w), 3040 (w), 2940 (m), 2840 (w), 1600 (w), 1500 (w), 1450 (s), 1375 (s), 1340 (s), 1325 (w), 1305 (s), 1240 (s), 1190 (m), 1120 (s), 1090 (w), 1055 (s), 1015 (m), 995 (m), 975 (w), 900 (w), 860 (m), 800 (m), 760 (s), 700 cm^{-1} (s); nmr (CCl_4) τ 7.90 (s, 2), 7.02 (s, 3), 6.68 (s, 3), and 2.16–3.08 (m, 14). The mass spectrum gave a parent peak at *m/e* 370. *Anal.* Calcd for $C_{25}H_{22}O_3$: C, 81.06; H, 5.99. Found: C, 80.92; H, 6.00.

V was warmed with trifluoroacetic acid, which converted it to 1,4-diphenyl-2-methylnaphthoate. The ester was recrystallized from methanol to give a white crystalline solid: mp 162–162.5°; ir (CCl_4) 3080 (m), 3050 (w), 3005 (w), 2970 (m), 1730 (vs), 1600 (w), 1500 (w), 1440 (m), 1390 (m), 1350 (w), 1255 (s), 1230 (s), 1165 (m), 1130 (m), and 1120 cm^{-1} (m); nmr (CCl_4) τ 6.50 (s, 3), 2.84–2.33 (m, 14), and 2.26 (s, 1). The mass spectrum gave a parent peak at *m/e* 338 (also the base peak) and an intense peak at *m/e* 307 indicative of loss of $CH_3O\cdot$ *Anal.* Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.26; H, 5.42. The hydrazide was prepared from the ester using hydrazine hydrate. The hydrazide had mp 174–176°, compared to the literature value of 179° for the hydrazide of VI.[6]

Dimerization of 3,3-Dimethoxycyclopropene.—A sample of 3,3-dimethoxycyclopropene was placed in a sublimator and left at room temperature for 6 days. During this time white crystals of a new product formed on the condenser and walls of the sublimator. The product was removed from the sublimator and then sublimed twice at 60° (1 mm): ir (CCl_4) 3060 (m), 3005 (m), 2970 and 2950 (s), 2910 (w), 2850 (m), 1440 (m), 1380 (s), 1220 (s), 1180 (m), 1110 (s), 1040 (s), 1010 cm^{-1} (m); nmr (CCl_4) τ 8.27 (s, 2), 6.72 (s, 3), and 6.65 (s, 3). The mass spectrum gave fragments at *m/e* 169, 154, and 126. The parent peak was not observed. These results show the product VII to be 3,3,6,6-tetramethoxytricyclo[3.1.0.0^{2,4}]cyclohexane. *Anal.* Calcd for $C_{10}H_{16}O_4$: C, 59.99; H, 8.06. Found: C, 59.62; H, 7.81.

Preparation of 1,1-Dimethoxy-2-dimethylaminocyclopropane (VIII).—To a small pressure bottle was added 1.0 g (0.01 mol) of IV, and 5 ml of dry dimethylamine was condensed into the bottle. The bottle was sealed and heated at 50° for 3 hr. The next day the dimethylamine was distilled from the product. The residue was then distilled at atmospheric pressure: bp 120–140°; yield 0.9 g (60%); ir (neat) 3100 (w), 3000 (w), 2950 (s), 2920 (w), 2840 (m, doublet), 2780 (m), 1660 (m), 1460 (s), 1280 (s), 1220 (s), 1160 (s), 1090 (s), 1060 and 1040 (s), 995 (m), 925 (m), and 880 cm^{-1} (m); nmr (CCl_4) τ 9.17 (m, 2), 8.28 (m, 1), 7.75 (s, 6), 6.77 (s, 3), and 6.63 (s, 3). The mass spectrum gave fragments at P − 1, *m/e* 144, and a base peak at P − 15, *m/e* 130. The hydrochloride had mp 157–159°; ir (KBr) 2760–2300 (ammonium salt), 3100 cm^{-1} (cyclopropyl). *Anal.* Calcd for $C_7H_{16}NO_2Cl$: C, 46.37; H, 8.71; N, 7.71; Cl, 19.52. Found: C, 46.28; H, 8.88; N, 7.71; Cl, 19.64.

Registry No.—II, 22089-54-9; II 2,4-DNP, 34219-71-1; III, 34219-72-2; IV, 23529-83-1; V, 34219-74-4; VI, 34219-75-5; VII, 34219-76-6; VIII, 34219-77-7; VIII HCl, 34219-78-8.

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The Reaction of Organozinc Compounds with Carbon Monoxide[1]

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Di-*n*-butylzinc and diisopropylzinc react with carbon monoxide at atmospheric pressure in the presence of potassium *tert*-butoxide to furnish, after hydrolysis, the corresponding acyloins. In the absence of the base, the two organozinc compounds are inert to carbon monoxide. Diphenylzinc absorbs only small amounts of carbon monoxide in the presence of potassium *tert*-butoxide and the only identified product is biphenyl. A possible mechanism for the base-promoted carbonylation of dialkylzinc compounds is presented.

The absorption of carbon monoxide by Grignard reagents was first observed by Vinay in 1908.[2] Since that date, the reaction has been studied in detail by a large number of workers using a variety of reaction conditions and catalysts. A host of products has been reported including trialkylcarbinols, ketones, olefins, and acyloins.[3] In contrast, the action of carbon monox-

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ide on the closely related organozinc compounds has been mentioned only once. Fischer[3b] reported that phenylzinc bromide is inert to carbon monoxide at atmospheric pressure. We have completed a survey of the reaction of a variety of simple organozinc compounds with carbon monoxide with the results reported below.

Results

Reaction with Di-*n*-butylzinc.—Di-*n*-butylzinc was prepared by the reaction of activated zinc metal with *n*-butyl iodide. This compound does not absorb carbon monoxide at atmospheric pressure either in the absence of solvents or when dissolved in tetrahydrofuran, diglyme, ether, or benzene. However, the addition of an equivalent amount of potassium *tert*-butoxide to a diglyme solution of di-*n*-butylzinc promotes an absorption of 0.85 equiv of carbon monoxide which is complete in 3 hr at room temperature. Hydrolysis of the reaction mixture with dilute hydrochloric acid produces *n*-butane (1.1 equiv) and *n*-valeroin (0.35 equiv, glpc analysis).

A study of the effect of temperature and amount of base on the reaction of di-*n*-butylzinc with carbon monoxide is shown in Table I. The maximum yield of *n*-valeroin (42%, based on di-*n*-butylzinc) is obtained using 1 equiv of potassium *tert*-butoxide and a reaction temperature of −15°. At this temperature the reaction mixture remains nearly colorless throughout the absorption of carbon monoxide. At room temperature or above, the reaction mixtures usually turn black as absorption proceeds.

TABLE I

REACTION OF DI-*n*-BUTYLZINC (10 MMOL) WITH CARBON MONOXIDE IN DIGLYME SOLUTION (1 *M*) AT ATMOSPHERIC PRESSURE AND 25°

Potassium *tert*-butoxide, mmol	Carbon monoxide, mmol	*n*-Valeroin, mmol[a]	*n*-Butane, mmol[b]
20	9.9	4.0	10.0
10	8.5	3.5	11.0
5	3.6	1.2	16.0
1.5	1.4	0.6	18.5
10[c]	9.0	4.2	10.5

[a] Glpc analysis. [b] Measured by gas buret during acid hydrolysis. [c] Reaction at −15°.

A number of other bases were studied for their effect on the reaction. Triethylamine, pyridine, *N,N,N,N*-tetramethylethylenediamine, and sodium acetate do not promote the reaction with carbon monoxide in either diglyme or benzene solvents. Sodium methoxide promotes a slow uptake of carbon monoxide which stops after the absorption of 0.1 equiv. No products of the reaction could be identified.

Reaction with *n*-Butylzinc Iodide.—*n*-Butylzinc iodide was made by the addition of anhydrous zinc iodide to a solution of di-*n*-butylzinc in diglyme. This compound is inert to carbon monoxide at atmospheric pressure either with or without added potassium *tert*-butoxide.

Reaction with Diisopropylzinc.—Diisopropylzinc behaves similarly to di-*n*-butylzinc. In the absence of potassium *tert*-butoxide the compound is inert to carbon monoxide. In the presence of 1 equiv of the base, the compound absorbs 0.9 equiv of carbon monoxide at −15° and atmospheric pressure. Hydrolysis with dilute hydrochloric acid produces isovaleroin (35%, glpc analysis).

Reaction with Diphenylzinc.—Diphenylzinc is inert to carbon monoxide at atmospheric pressure in the absence of a promoter. In the presence of an equivalent amount of potassium *tert*-butoxide, a slow absorption of 0.25 equiv of carbon monoxide occurs. Hydrolysis of the reaction mixture produces biphenyl (0.3 equiv) as the only identified product. The absence of benzoin in the hydrolyzed reaction mixture was established by glpc.

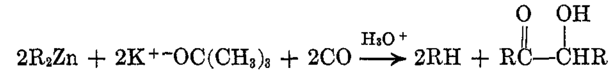
Discussion

In contrast to Grignard reagents, organozinc compounds are unreactive to carbon monoxide in the absence of a promoter. Presumably, this is due to the less polar nature of the zinc–carbon bond. Potassium *tert*-butoxide is an effective promoter for the reaction when present in stoichiometric amounts. It is possible that the function of the base is to coordinate to the zinc compound to furnish a species with greater carbanion character capable of transferring an alkyl group to carbon monoxide. The ability of base to

$$R_2Zn + K^{+-}OC(CH_3)_3 \rightleftharpoons K^+R_2\overset{-}{Zn}-OC(CH_3)_3$$

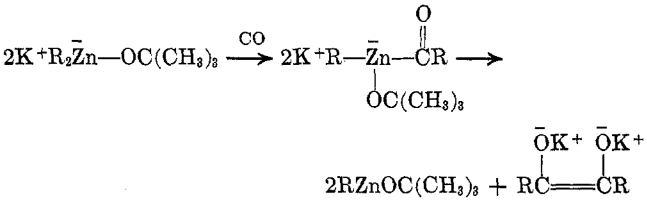
enhance the reactivity of organometallic compounds has been observed in many other cases.[4]

The results in Table I agree reasonably well with the partial stoichiometry shown by the following equation.



$$2R_2Zn + 2K^{+-}OC(CH_3)_3 + 2CO \xrightarrow{H_3O^+} 2RH + R\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{C}}HR$$

The reaction of Grignard reagents with carbon monoxide also produces acyloins,[3a] along with a variety of other products. The intermediacy of an acyl magnesium compound has been postulated to explain the formation of these compounds.[3b] An analogous mechanism for the potassium *tert*-butoxide promoted reaction of organozinc compounds with carbon monoxide is consistent with (although not demanded by) our results. From this mechanism, the dialkylzinc compound could furnish a maximum of 0.5 mol of acyloin.



$$2K^+R_2\overset{-}{Zn}-OC(CH_3)_3 \xrightarrow{CO} 2K^+R-\underset{OC(CH_3)_3}{\underset{|}{\overset{-}{Zn}}}-\overset{O}{\overset{\|}{C}}R \longrightarrow 2RZnOC(CH_3)_3 + R\overset{\bar{O}K^+}{\overset{|}{C}}=\overset{\bar{O}K^+}{\overset{|}{C}}R$$

On this basis, the observed yields of *n*-valeroin and isovaleroin are 84 and 70% of the theoretical maximum, respectively.

The potassium *tert*-butoxide promoted reaction of diphenylzinc with carbon monoxide proceeds differently from that of the dialkylzinc compounds. Benzoin is not formed and the only identified product is biphenyl. Presumably other organic products are

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formed which account for the slight uptake of carbon monoxide.

Experimental Section

Potassium *tert*-butoxide was obtained from MSA Research Corp. Diglyme was distilled from lithium aluminum hydride and stored under nitrogen. Glpc analyses were performed using a 6-ft SE-30 column (5.0% on Chromosorb W, DMCS treated).

Preparation of Di-*n*-butylzinc.—The procedure was essentially that described by Noller[5] except that a specially activated zinc–copper couple,[6] prepared by the treatment of granular zinc (20 mesh) with cupric acetate in glacial acetic acid, was used for the reaction with *n*-butyl iodide. The yield of di-*n*-butylzinc was 75–80%, bp 81–82° (9 mm).

Preparation of Diisopropylzinc.—Reaction of the activated zinc–copper couple with isopropyl iodide produced only modest yields (0–25%) of diisopropylzinc. Yields of 70–75% were obtained by the reaction of isopropylmagnesium bromide with anhydrous zinc iodide in ether solution followed by distillation under reduced pressure.

Preparation of Diphenylzinc.—Diphenylzinc was obtained by the reaction of phenyllithium with zinc iodide.[7]

Reaction of Di-*n*-butylzinc with Carbon Monoxide.—The following procedure is illustrative of the general technique. A dry 50-ml round-bottom flask equipped with magnetic stirring and septum inlet was connected to a gas buret filled with carbon monoxide, the system was flushed with carbon monoxide, and 30 ml (30 mmol) of a solution of potassium *tert*-butoxide in diglyme was injected. The flask was immersed in a cooling bath maintained at a temperature of −15° and stirring was initiated. Di-*n*-butylzinc (30 mmol, 5.28 ml) was injected by means of a syringe and the uptake of carbon monoxide was recorded. Complete absorbance of the gas required 3 hr. A total of 27 mmol of carbon monoxide was absorbed. The reaction mixture was quenched by adding it to 10 ml of cold 5 *M* hydrochloric acid. (Addition of the acid to the reaction mixture results in a lower recovery of the acyloin.) The volume of gas evolved corresponded to 30 mmol of *n*-butane. The clear solution was extracted with 50 ml of pentane and the organic phase was then washed with three 30-mmol portions of *n*-butane. The clear solution was extracted with 50 ml of pentane and the organic phase was then washed with three 30-ml portions of water to remove diglyme. Glpc analysis of an aliquot established the formation of 12.1 mmol of *n*-valeroin. The product was isolated by removal of the solvent and distillation under reduced pressure to obtain 1.77 g (10 mmol) of pure *n*-valeroin, mp 60° (0.5 mm), $n^{24.2}\mathrm{D}$ 1.4312 (lit.[8] $n^{26.6}\mathrm{D}$ 1.4298), mp of phenylosazone 126.5–127.5° (lit.[9] mp 127°).

Reaction of Diisopropylzinc with Carbon Monoxide.—The general procedure was identical with that described above for the reaction with di-*n*-butylzinc. Distillation produced isobutyroin, bp 70° (0.5 mm), $n^{23.8}\mathrm{D}$ 1.4178 (lit.[10] $n^{26.6}\mathrm{D}$ 1.4159), mp of phenylosazone 136–137° (lit.[11] mp 139–140°).

Registry No.—Carbon monoxide, 630-08-0; di-*n*-butylzinc, 1119-90-0; *n*-butylzinc iodide, 34219-54-0; diisopropylzinc, 625-81-0; diphenylzinc, 1078-58-6.

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Reduction of *gem*-Dihalocyclopropanes with Zinc

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Some *gem*-dihalocyclopropanes were reduced to monohalocyclopropanes with zinc powder in ethyl alcohol (or isoamyl alcohol) containing 10% of potassium hydroxide. The reduction of *gem*-dibromocyclopropanes led to a mixture of two geometrical isomers, with the *endo*-bromo (*syn*-bromo) isomer predominating. The reduction of *gem*-bromofluorocyclopropanes proceeded with complete retention of configuration at low temperatures (25–80°) but with some inversion at higher temperatures (130–140°). The extent of stereospecificity observed at higher temperatures was greater than those obtained for the tri-*n*-butyltin hydride reduction. These results were explained by postulating cyclopropyl anion intermediate involved in the proton abstraction step.

The reduction of *gem*-dihalocyclopropanes to monohalocyclopropanes has been effected by various reducing agents such as organotin hydride,[1] methylsulfinyl carbanion,[2] Grignard reagent,[3] chromium sulfate,[4] lithium or sodium in alcohol,[5] alkyllithium in alcohol,[6] and lithium aluminum hydride,[7] by catalytic hydrogenation,[8] or by electrochemical methods.[9]

Zinc in acetic acid has also been used as a means of reducing halocyclopropanes. 3,3-Dibromocyclopropane-*cis*-1,2-diacetic acid was partially dehalogenated to afford the corresponding monobromide in 50% yield.[10] Hodgkins and his coworkers[11] obtained 7-phenylbicyclo[4.1.0]heptane by reducing 7-chloro-7-phenylbicyclo[4.1.0]heptane with zinc in ethanol or in aqueous or glacial acetic acid. Annino and his coworkers[12] showed that the zinc metal reduction of optically active 1-bromo-2,2-diphenylcyclopropanecarboxylic acid or its methyl ester gave products of partially inverted configuration, whereas the reduction of its carboxylate anion or 1-bromo-1-methyl-2,2-

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