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REACTIONS OF ORGANOLITHIUM COMPOUNDS WITH COBALTOUS CHLORIDE*

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SUMMARY

The reactions of *cis*- and *trans*-2-lithio-2-butenes with cobaltous ion yield 3,4-dimethyl-2,4-hexadienes. The products are formed with essentially complete retention of stereochemistry. Neopentyl- and neophyllithium [(β,β-dimethylphenethyl)lithium] react with cobaltous ion to give unrearranged monomeric and dimeric products. n-Butyllithium reacts with cobaltous ion to give butane and butenes in very nearly equal quantities. Small amounts of n-octane are also formed. The mechanisms of these reactions are discussed in terms of intermediate organocobalt compounds.

INTRODUCTION

The reactions of various organometallics *i.e.* Grignard reagents and organolithium compounds with transition metal complex ions can often lead to stable substances containing σ-alkyl or σ-aryl bonds***. Further reactions of the intermediates have received increasing attention. Reaction of transition metal cations, where chloride was the anion, with methyllithium and ethylmagnesium bromide yielded hydrocarbon products which varied with the nature of the metal ion. For example, methyllithium reacted with titanium tetrachloride to give an 84% yield of methane. Iron(II) chloride gave both methane and ethane. Copper(I) chloride yielded only ethane[2]. The intermediacy of organometallics in these reactions is entirely reasonable, however the mechanisms of the decompositions of these intermediates must vary with the nature of the transition metal. For example the production of methane when titanium is a reactant clearly indicates a different mode of decomposition from that found with copper(I) which yields ethane as the major product.

The present study has been aimed at determining the nature of the products obtained when cobalt(II) chloride is allowed to react with a variety of organolithium compounds. The major focus has been to determine whether free radicals are important intermediates in these reactions.

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** NASA Fellow, 1965–1968.

*** For a recent review see ref. 1.

RESULTS

Reaction of 0.8–1.3 *M* solutions of either *trans*-rich or *cis*-rich 2-lithio-2-butenes in diethyl ether with an equivalent amount of anhydrous cobaltous chloride at 0–25° yielded 10–15% normal butenes and 30–55% of isomeric 3,4-dimethyl-2,4-hexadienes. The ratios of these isomers, *trans,trans*, (I), *cis,trans*, (II), and *cis.cis*, (III), are collected in Table 1. The ratio of isomers is essentially that which is predicted if coupling occurs in a statistical manner without loss of the stereochemistry present in the starting 2-lithio-2-butenes.

TABLE 1

ISOMERIC COMPOSITION OF 3,4-DIMETHYL-2,4-HEXADIENES FORMED IN THE REACTION OF 2-LITHIO-2-BUTENES WITH COBALTOUS CHLORIDE

Composition of 2-lithio-2-butene (%)		Composition of 3,4-dimethyl-2,4-hexadienes found (calcd.[a]) (%)		
cis	*trans*	*trans.trans* (I)	*cis,trans* (II)	*cis,cis* (III)
18	82	63(67)	30 (29.5)	7 (3.5)
8	92	89(84.5)	8.5(14.7)	2.5(0.8)
86	14	4(2)	23 (24)	73 (74)

[a] Calcd. if coupling occurs in a statistical manner without loss of the stereochemistry present in the starting 2-lithio-2-butenes.

The stereochemistry of the butenes was determined, however no conclusions can be drawn because isomerization of butenes occurs under the reaction condition. By a series of control experiments it was demonstrated that about half of the total butenes were formed by a reaction which is not due to traces of moisture or other spurious proton sources*.

When the reaction of 2-lithio-2-butene was carried out in benzene only a trace of 2-phenyl-2-butene was found, similarly essentially no 2,3-dimethyl-2,3-diphenylbutane was formed when the reaction was conducted in cumene.

Reaction of neopentyllithium in hexane with a slurry of cobaltous chloride in diethyl ether yielded 9% neopentane and 53% 2,2,5,5-tetramethylhexane as the only detectable hydrocarbon products. A similar reaction in cyclohexane afforded 14% neopentane and 57% 2,2,5,5-tetramethylhexane. No traces of isopentane, 2-methyl-1-butene or 2-methyl-2-butene could be detected.

Neophyllithium [(β,β-dimethylphenethyl)lithium] in hexane reacted with an equivalent amount of anhydrous cobaltous chloride to give 18% tert-butylbenzene and 64% 2,5-dimethyl-2,5-diphenylhexane. An unidentified material, ca. 5%, was also formed. This substance had a GLC retention time on a non-polar column slightly greater than 2,5-dimethyl-2,5-diphenylhexane. Its NMR spectrum was inconsistent with those of the three possible dimers which could be obtained by combination of neophyl (β,β-dimethylphenethyl) radicals and the rearranged tert-butylphenyl radical[4].

Reaction of n-butyllithium with cobaltous chloride in hexane gave 40–50%

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* A detailed description of the control experiments can be found in ref. 3.

n-butane, 30–35% butenes, and 3–7% n-octane. Typically, the composition of the butenes was 8% 1-butene, 72% *trans*-2-butene, and 20% *cis*-2-butene. A series of reactions under scrupulously anhydrous conditions yielded nearly equimolar amounts of n-butane and n-butenes. The average composition from four reactions was 50.6 mole % n-butane and 49.4 mole % n-butene.

The butene composition was found to vary with the ratio of n-butyllithium to cobaltous chloride. When a five-fold excess of n-butyllithium was used, the typical butene composition was 49% 1-butene, 33% *trans*-2-butene and 18% *cis*-2-butene.

The relative yield of n-butane to butenes was reduced when equimolar amounts of methyllithium and butyllithium were mixed and allowed to react with half an equivalent of cobaltous chloride. The composition of C_4 hydrocarbons obtained from this reaction was 40% n-butane, 23% 1-butene, 25% *trans*-2-butene, and 12% *cis*-2-butene.

Reaction mixtures of n-butyllithium, cobaltous chloride and an olefin led to reduction of the olefin. For example when a 2/1/1 molar ratio of n-butyllithium, cobaltous chloride, and *trans*-2-heptene was allowed to react, n-heptane was formed in 10% yield. Isomerization of the heptene occurred under the reaction conditions. Similarly 2-methylpropene (isobutene) was reduced to isobutane. The hydrogen source need not be an alkyllithium. Lithium aluminum hydride, cobaltous chloride and *trans*-2-heptene reacted to give a 95% yield of n-heptane[5].

DISCUSSION

The reactions of the organolithium compounds with stoichiometric amounts of cobaltous chloride divide themselves into two types. One yields as the major products dimers formed by combination of two of the groups bonded to lithium. This path is followed when an alkenyllithium is used or when an alkyllithium which does not contain β-hydrogens is allowed to react with cobaltous ion.

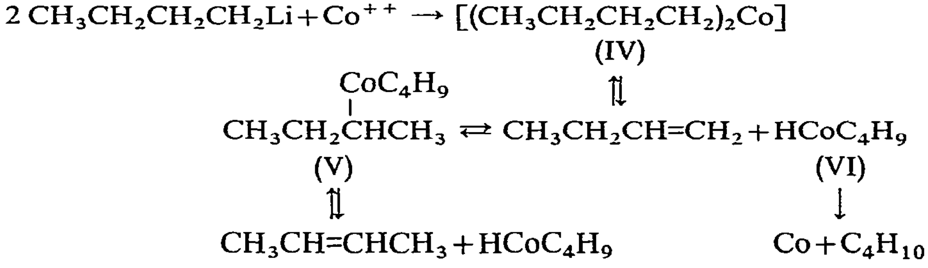
The dimerization reactions do not appear to involve the combination of "non-caged" free radicals. If free 2-butenyl radicals had been formed from the 2-lithio-2-butenes they would have undergone extensive isomerization and the ratio of hexadienes should have reflected the extent of isomerization. Reduction of either *trans*- or *cis*-2-bromo-2-butene with tri-n-butyltin hydride at ambient temperature yielded 65% *trans*-2-butene and 35% *cis*-2-butene[6]. Under these conditions complete isomerization of the butenyl radicals occurred. Other workers have observed extensive isomerization of vinyl radicals[7].

The formation of only very small amounts of dicumyl and *trans*-2-phenyl-2-butene also argue against any extensive production of free 2-butenyl radicals. The exact details of dimer formation are not known, however formation of a carbon–cobalt bond seems to be a requisite. Subsequent decomposition yields the dimer and cobalt metal. Recently Whitesides and Casey[6] have studied the thermal decomposition of the tri-n-butylphosphine complexes of the isomeric 1-propenyl- and (1-methyl-1-propenyl)silver(I) and -copper(I) compounds. The products, dienes, were obtained in quantitative yield and with complete retention of configuration. Their results are in essential agreement with those obtained in this work.

The formation of monomer *i.e.* butenes during these reactions can be attributed in part to normal decomposition reactions of the alkenyl lithiums. The control experiments suggest that not all of the butenes arise in this manner. There may be some free radical decomposition of intermediate organocobalt compounds. The level of free radical production may be low enough so that attempts to detect them by formation of 2,3-dimethyl-2,3-diphenylbutane (from cumene) or 2-phenyl-2-butene is not sufficiently sensitive.

The large amount of dimer relative to monomer that results when neopentyl and neophyllithium are allowed to react with cobaltous ion is also indicative of a reaction path for dimer formation which does not involve "non-caged" free radicals. The lack of rearrangement in the neophyl system indicates that if tert-butylbenzene is formed from the neophyl radical, the radical must be destroyed very efficiently. Usually rearrangement products are found when the neophyl radical is an intermediate[8], however only small amounts of rearranged products were found[9] from the electrolysis of 3-methyl-3-phenylbutanoic acid at 60°. The neophyl radical is undoubtedly an intermediate in the electrolysis reaction and if it can react to give nonrearranged products at 60° there is no reason for its not being able to do so at 25°. Clearly more work is required before the mechanism for monomer formation can be understood.

The reaction of n-butyllithium and cobaltous ion most certainly involves an intermediate organocobalt. It has been established that cobalt hydride complexes such as, $Co(CN)_5H^{3-}$, will add to olefins to give substances with carbon–cobalt bonds[10]. These are reversible reactions and olefins can be isomerized by use of these and similar catalysts[1]. A general scheme which accounts for the results obtained in this study involves addition of butyl groups to cobalt to give an intermediate, (IV).



$$2\,CH_3CH_2CH_2CH_2Li + Co^{++} \rightarrow [(CH_3CH_2CH_2CH_2)_2Co] \quad \text{(IV)}$$

$$\text{(IV)} \rightleftharpoons CH_3CH_2CH{=}CH_2 + HCoC_4H_9 \quad \text{(VI)}$$

$$\underset{\text{(V)}}{CH_3CH_2\overset{CoC_4H_9}{\overset{|}{C}}HCH_3} \rightleftharpoons CH_3CH_2CH{=}CH_2 + \underset{\text{(VI)}}{HCoC_4H_9}$$

$$\text{(V)} \rightleftharpoons CH_3CH{=}CHCH_3 + HCoC_4H_9$$

$$\text{(VI)} \rightarrow Co + C_4H_{10}$$

For convenience (IV) is represented as having two butyl groups bonded to cobalt. It should be recognized that there is no evidence as to the structures of the intermediate cobalt compounds. Loss of 1-butene from (IV) yields a cobalt hydride which can add to 1-butene to give (IV) or the isomer (V) which will dissociate to 2-butenes and thus the olefin isomerization can be accounted for. Addition to added olefin *e.g. trans*-2-heptene can account for its isomerization. The clean stoichiometry of the reaction under carefully controlled conditions suggests that the products are formed by a relatively simple reaction sequence, that is, that there are not a multiplicity of paths to the products. One possible mode for the generation of saturated hydrocarbon would be by an intramolecular decomposition of a compound such as (VI), or by attack of the hydride on (IV). Such a decomposition can account for the formation of heptane when *trans*-2-heptene is incorporated in the reaction mixture. In fact good evidence has been provided for the intermolecular decomposition of alkyl copper compounds. The suggested mechanism involves elimination of olefin with formation of a copper hydride which reduces alkyl copper to hydrocarbon[11]. Clearly a similar mechanism can be operating with the cobalt reaction.

There is some evidence that the alkyllithium may be able to attack on a cobalt hydride to give hydrocarbon and reduction of the cobalt. The lessening of olefin isomerization when an excess of n-butyllithium was used indicates that the cobalt hydride was not as effective as an isomerization catalyst. This could be due to its more rapid destruction under these reaction conditions. Similarly the lowering in butane yield when methyllithium was included in the reaction mixture might be accounted for by attack by methyllithium on a cobalt hydride, however it can also be accounted for by decomposition of a mixed cobalt compound, (VII). The reduction of added olefin cannot be accounted for by a mechanism which only allows saturated hydrocarbon to be produced by attack of alkyllithium on cobalt hydride.

$$\underset{\text{(VII)}}{C_4H_9CoCH_3} \rightarrow CH_3CH_2CH{=}CH_2 + CH_3CoH \rightarrow Co + CH_4$$

The bulk of the evidence in the reactions of n-butyllithium with cobaltous ion argues against the production of free radicals as important intermediates in these reactions. The 1/1 ratio of butenes to butanes is not in accord with free radical intermediates. For example the ethane to ethylene ratio obtained from the photolysis of azoethane at 25° is 3.3/1[12]. In fact the evidence for the production of radicals from any of these reactions is vanishingly small, and although they cannot be completely excluded, mechanisms involving reactions of organocobalt compounds seem to be most favorable at this time.

EXPERIMENTAL

All NMR spectra were run on a Varian Model A-60 spectrometer unless otherwise noted. All chemical shifts are reported in ppm downfield from internal standard tetramethylsilane unless otherwise noted. IR spectra were obtained with a Perkin–Elmer Model 21, and UV spectra were obtained with a Cary Model 14 spectrometer. The majority of the GLC analyses were performed with an F and M Model 500 gas chromatograph. Other instruments were used occasionally and they are specified in the text. The gas chromatographic columns used are listed with code letters: Column A: $15' \times \frac{1}{4}''$, 20% 2,5-hexanedione on 35/80 Chromosorb P; column B: $15' \times \frac{1}{4}''$, 10% dinonyl phthalate on 35/80 Chromosorb P; column C: $12' \times \frac{1}{4}''$, 10% silicone gum rubber on 35/80 Chromosorb P; column D: $12' \times \frac{1}{4}''$, 1.5% silicone gum rubber on Chromosorb WHMDS; column E: $6' \times \frac{1}{8}''$, 10% silicone rubber Sc-30 on 80/100 Chromosorb P.

Elemental analyses were performed by George I. Robertson, Jr., Florham Park, N.J.

Reagents

Anhydrous cobaltous chloride was prepared by a standard technique[13]. It was stored in a desiccator over phosphorus pentoxide.

trans-2-Bromo-2-butene was isolated by fractional distillation of a commercial mixture of 80% *trans*- and 20% *cis*-2-bromo-2-butene*. The distillate, b.p. 41.7–

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* Columbia Organic Co., Columbia, S.C.

42.0° (160 mm) [lit.[14] 41.7–42.0° (160 mm)] was stored at 0–5° in a blackened flask. The *trans/cis* composition was determined by GLC, column B, 100°, 60 ml/min. There was no isomerization over a 5 months period.

cis-2-Bromo-2-butene was prepared by the procedure of Bordwell and Landis[15]. It had b.p. 48.5–49.8° (160 mm) [lit.[17] 49.0–49.5° (160 mm)].

Neopentyl chloride was obtained from Matheson, Coleman and Bell. It was distilled from calcium hydride and stored over molecular sieve, 5A.

Neophyl chloride [(2-chloro-1,1-dimethylethyl)benzene] was prepared by a previously described procedure[16]. GLC analysis, column D, 80° showed only one component.

Butyllithium, methyllithium and lithium metal dispersion, 200 μ 50 wt.% in hexane, were purchased from Foote Mineral Co.

Preparation and stereochemistry of trans- and cis-2-lithio-2-butenes

Dry ether, 200 ml, was added to a three necked flask equipped with a reflux condenser, stirrer and pressure equalized dropping funnel all in an atmosphere of argon. Lithium, 4.0 g (0.57 g-atom), which had been hammered into a thin sheet and cut into small pieces was added. *trans*-2-Bromo-2-butene (96% *trans*, 4% *cis*, 30.0 g, 0.24 mole) was added to the dropping funnel; thirty drops were added to the rapidly stirred mixture of ether and lithium. After the reaction had started (the ethereal solution became cloudy and bright spots appeared on the surface of the lithium metal), the reaction flask was cooled in an ice bath and the remaining bromide was added dropwise over a period of 1 h. Stirring was continued $\frac{1}{2}$ h after the addition was complete. A 2 ml aliquot of the reaction mixture was hydrolyzed and analyzed by GLC. If the analysis showed more than 1% unreacted 2-bromo-2-butene, stirring was continued until a hydrolyzed aliquot showed less than 1% 2-bromo-2-butene. The organolithium solution was filtered into a dry bottle by pressure-filtration with argon through a gas-dispersion tube. The bottle was sealed with a rubber serum cap, sealed in a plastic bag, and stored in a refrigerator at 0–5° between use.

Determination of molarity and stereochemistry of trans- and cis-2-lithio-2-butenes

The molarity of the organolithium solutions was determined by (I) direct titration of a hydrolyzed aliquot with 0.1 *N* hydrochloric acid (II) Gilman double titration using 1,2-dibromoethane[17], and (3) by reaction with chlorotrimethylsilane in the presence of an internal standard followed by GLC[18]. Representive values, 0.91 *M*, direct titration, 0.87 *M* Gilman double titration, and 0.86 *M* silane method, were obtained on a solution prepared from 95% *cis*- and 5% *trans*-2-bromo-2-butene. Direct titration gave 1.33 *M* and the silane method, 1.3 *M*, on a solution prepared from 96% *trans*- and 4% *cis*-2-bromo-2-butene.

The stereochemistry was determined by allowing 1–2 ml aliquots to react with water. The resulting gasses were collected over water and analyzed by GLC. The relative areas of the isomeric (1-methyl-1-propenyl)trimethylsilanes were also measured. The results of these analyses agreed well with each other. For example *cis*-2-lithio-2-butene prepared from 95% *cis*- and 5% *trans*-2-bromo-2-butene gave 85% *cis*- and 15% *trans*-2-butenes on hydrolysis and 86% *cis*- and 14% *trans*-trimethylsilyl derivatives. The two methods never differed by more than 1%.

Reaction of isomeric 2-lithio-2-butenes with cobaltous chloride

A 1000 ml three-necked flask equipped with a magnetic stirring bar, condenser, two gas inlet adapters, and a powder addition adapter was assembled in an argon filled dry box. *trans*-2-Lithio-2-butene (82% *trans*- and 18% *cis*) 300 ml of a 0.85 *M* solution was added and 16.5 g (0.127 mole) of anhydrous cobaltous chloride was added to the powder addition adapter. The apparatus was sealed and removed from the dry box. An argon filled balloon was connected to a gas-inlet adapter; stirring was started and the cobaltous chloride was added in small portions over 1 h. The reaction mixture was stirred for an additional h.

The gas above the reaction mixture was analyzed by GLC, column A, room temp., 30 ml/min. The chromatogram showed a trace of n-butane, 1-butene, 3%, *trans*-2-butene, 74%, and *cis*-2-butene, 23%.

The reaction flask was cooled in a dry ice bath and attached to a high vacuum system. The volatiles were distilled at 10^{-5} mm and collected in a liquid nitrogen cooled trap. This procedure was followed because it was found that solids could not be separated by filtration.

The cooled distillate was allowed to warm and to distill through a glass-helice packed distillation column, 50 × 1.5 cm. The following fractions were collected: 7 ml in a dry ice cooled trap connected to the head of the distillation column; 35 ml b.p. up to 34.5°; 34.5–35° 180 ml; residue 40 g.

The material in the trap and the material boiling up to 34.5° were allowed to react with excess 10% bromine in carbon tetrachloride, combined, washed with aqueous sodium thiosulfate, water, and dried over calcium chloride. The solution was analyzed for dibromobutanes by GLC using n-decane as a standard. All three possible dibromobutanes were observed. The total yield of butenes was 2.1 g.

The residue from the distillation was analyzed by GLC, column B, 100°, 75 ml/min. It had *trans,trans*-, *cis,trans*-, and *cis,cis*-3,4-dimethylhexadienes in a ratio of 63/30/7. The total yield of the three isomers was obtained by adding ethylcyclohexane as an internal standard. The yield by this method was 5.8 g (61%).

The structures of the three isomeric 3,4-dimethyl-2,4-hexadienes were determined by isolating each by preparative GLC on a 16′ × $\frac{3}{8}$″ column, 20% Carbowax 20M on 35/80 Chromosorb P; column temp. 70° for 8 min, then heated at 10°/min for 7 min; helium flow 400 ml/min.

The first material, ret.time 5.7 min, showed no absorbance between 205–250 mμ. The NMR spectrum (500 Hz sweep width) consisted of a complex doublet, *J* 6.4 Hz, centered at 1.41 ppm, a complex singlet at 1.63 ppm, and a complex quartet ppm *J* 6.4 Hz, at 5.20. The relative areas of the absorption were 3/3/1. The NMR (100 Hz sweep width) resolved the doublet at 1.41 ppm into a pair of quartets. The lines of the quartets were separated by 1.46 Hz. The quartet at 5.2 ppm was resolved into a quartet of quartets. The long range splitting was 1.26 Hz. The singlet at 1.63 ppm was resolved into a quintet. The quintet pattern matches the pattern calculated from coupling with one proton by 1.26 Hz to give a doublet which is further split 1.46 Hz by three protons. (Found: C, 86.69; H, 13.29. C_8H_{14} calcd.: C, 87.19; H, 12.81%.)

This material is assigned the *trans,trans*-structure on the basis of the NMR evidence which shows that there are only two kinds of methyl groups present in the molecule. The various couplings are also in agreement with this structure as is the lack of absorption in the UV.

The second material, ret.time 7.5 min, showed no absorbance between 205–250 mμ. The NMR spectrum had three absorptions in the methyl region at 1.49, 1.58 and 1.67 ppm. There was also a complex multiplet centered at 4.95 ppm. Integration showed these were in the ratio 6/1. The NMR spectrum in benzene had absorptions at 1.53, 1.62, 1.72 and 5.25 ppm. This material is assigned the *cis,trans*-structure because there are at least three different methyl groups present and there is no UV absorption*.

The third material, ret.time 13.9 min, had an absorption at 231.5 mμ with an extinction coefficient of 1.7×10^4. The NMR spectrum had two peaks in the methyl region at 1.60 and 1.68 ppm and a quartet centered at 5.49 ppm. This material is assigned *cis,cis*-stereochemistry on the basis of its UV and NMR spectra.

Reaction of 92% *trans-2-lithio-2-butene with cobaltous chloride in benzene*

An ethereal solution of the 2-lithio-2-butenes, 55 ml 1.3 *M*, was evaporated to dryness; 10 ml of benzene was added and it was evaporated. Benzene, 55 ml, was added followed by the addition of 4.92 g (0.038 mole) of cobaltous chloride. The mixture was stirred for 3 h and then evaporated to give 53 g of distillate. GLC analysis showed the usual products plus a material with a retention time of 7.5 min which was identical with that of *trans*-2-phenyl-2-butene. The total amount was estimated to be 0.1 g *i.e.* ca. 1 mmole from 74 mmoles of 2-lithio-2-butenes. The UV spectrum of a sample isolated by GLC was identical to that of *trans*-2-phenyl-2-butene.

Reaction of 2-lithio-2-butene with cobaltous chloride in cumene

The ether from 400 ml of 0.85 *M* 2-lithio-2-butene was evaporated and replaced by 150 ml of cumene. Cobaltous chloride, 30 g (0.23 mole) was added with stirring over 30 min. After stirring 3 h the total volatiles were distilled. Redistillation yielded 0.65 g of high boiling material. The solid from the original distillation was extracted with two 500-ml portions of benzene. Evaporation yielded 7.3 g of material; a 2 g portion was chromatographed on alumina. GLC analysis showed that one fraction contained a small amount of 2,2-dimethyl-2,2-diphenylbutane.

Reaction of neopentyllithium with cobaltous chloride

Solutions of neopentyllithium were prepared in hexane and cyclohexane by allowing lithium metal dispersion** to react with neopentyl chloride. The solutions were added to cobaltous chloride and also to a completely similar apparatus[3] which served as a control. The results are collected in Table 2.

Reaction of neophyllithium with cobaltous chloride

Neophyllithium was prepared from neophyl chloride and lithium dispersion as a solution in hexane. A solution, 530 ml, of 0.19 *M* neophyllithium was added with stirring to 7.05 g (0.054 mole) of cobaltous chloride in 25 ml of diethyl ether. After stirring for 19 h the reaction mixture was passed through a column containing 150 g of 80–200 mesh alumina. Various fractions were collected and concentrated. The first fraction which was obtained by elution with 1100 ml of pentane contained 2.4 g of

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* R. Criegee and N. Klaus[19] have prepared the *cis,trans* and *cis,cis* isomers. They report that the *cis,cis* has λ_{max} 230 mμ, log ε 4.1 while the *cis,trans* isomer shows no absorbance between 200–250 mμ.

** Lithium metal dispersion, 200 μ, 50 wt.% in hexane containing 1% sodium metal was purchased from Foote Mineral Co., Exton, Penn.

TABLE 2

REACTIONS OF NEOPENTYLLITHIUM WITH COBALTOUS CHLORIDE
Reaction conditions: temp. 0°, time 105 min.

Run no.	Starting materials			Reaction products	
	$C_5H_{11}Li$[a]		$CoCl_2$ (mmole)	C_5H_{12}[b] (mmole)	$C_{10}H_{22}$[c] (mmole)
	(ml)	(*M*)			
1[d]	20[d]	0.55	6	1	2.9
Control (1)[d]	20[d]	0.55	0	0.4	0.2
2[e]	25[e]	0.7	9.3	3.2	5.6
Control (2)[e]	25[e]	0.7	0	0.8	0.6

[a] Neopentyllithium. [b] Neopentane. [c] 2,2,5,5-Tetramethylhexane. [d] Hexane as solvent. [e] Cyclohexane as solvent.

tert-butylbenzene and a trace of isobutylbenzene. Evaporation of the pentane gave a residue which was distilled to give 7.7 g of material b.p. 100–110° (0.2 mm). This material crystallized from methanol, m.p. 62.5–63° (lit.[20] 62–63°). The NMR spectrum agreed with that reported[4a]. Extensive investigation of mother liquors and residues did not reveal any of the possible dimeric rearrangement products.

Reactions of n-butyllithium with cobaltous chloride

n-Butyllithium in hexane, 17.3 ml, 1.6 *M*, was added dropwise to a stirred slurry of 3.63 g (0.0279 mole) of cobaltous chloride in 8 ml of hexane over a period of 90 min in a closed system under helium. The gas above the reaction mixture was analyzed after 1 h. The composition was 58% n-butene, 4% 1-butene, 28% *trans*-2-butene and 10% *cis*-2-butene. The total volatiles were distilled at 10^{-4} mm and allowed to react with a slight excess of 10% bromine in carbon tetrachloride at −10°. The total dibromobutanes were determined by GLC as was the amount of n-octane.

In other experiments the butyllithium solution was added directly to powdered cobaltous chloride and only the composition of the C_4 products was determined. The results are (1) 2 h at 0°, 49% n-butane, 25% 1-butene, 17% *trans*-2-butene and 9% *cis*-2-butene (2) 4 h at −78°, 52% n-butane, 21% 1-butene, 19% *trans*-2-butene and 8% *cis*-2-butene (3) 9 h at 0°, 51% n-butane, 4% 1-butene, 33% *trans*-2-butene and 12% *cis*-2-butene (4) 4 h at −78°, 53% n-butane, 3% 1-butene, 30% *trans*-2-butene and 14% *cis*-2-butene.

Reaction of an equimolar mixture of methyllithium and n-butyllithium with cobaltous chloride

A solution of methyllithium, 10 ml, 1.6 *M* in diethyl ether and 10 ml of 1.6 *M* n-butyllithium in hexane were mixed and added to a stirred slurry of 1.0 g (0.0077 mole) of cobaltous chloride in 3 ml of ether. GLC analysis showed 42% n-butane, 22% 1-butene, 24% *trans*-2-butene and 12% *cis*-2-butene. Two other materials were noted and these may have been methane and ethane.

Reaction of n-butyllithium with cobaltous chloride in the presence of trans-2-heptene

n-Butyllithium, 10 ml, 1.6 *M*, 1.06 g (0.0082 mole) of cobaltous chloride, 0.83 g

(0.0085 mole) of *trans*-2-heptene were allowed to react in 3 ml of ether. GLC analysis of the gas above the reaction mixture showed 46% n-butane, 5% 1-butene, 35% *trans*-2-butene, and 14% *cis*-2-butene.

The reaction mixture was distilled and the distillate was analyzed by GLC; peaks with retention times identical to those of n-heptane and *trans*-2-heptene were found.

A 5 ml aliquot of the reaction distillate was stirred with 10 ml of concentrated sulfuric acid at 0° for 30 min. The organic layer showed only n-heptane by GLC and IR analysis.

REFERENCES

1 G. W. Parshall and J. J. Mrowca, *Advan. Organometal. Chem.*, 7 (1968) 157.
2 H. Gilman, G. Jones and L. Woods, *J. Amer. Chem. Soc.*, 76 (1954) 3615.
3 W. R. Davis, Ph.D. Thesis, Rutgers University, New Brunswick, N.J., 1968.
4 (a) C. Rüchardt and H. Trautwein, *Chem. Ber.*, 95 (1962) 1197;
(b) G. M. Whitesides, private communication.
5 Y. Takegumi, T. Ueno and T. Fujii, *Bull. Chem. Soc. Jap.*, 38 (1965) 1279.
6 G. M. Whitesides and C. P. Casey, *J. Amer. Chem. Soc.*, 88 (1966) 4541.
7 J. A. Kampmeir and R. M. Fantazier, *J. Amer. Chem. Soc.*, 88 (1966) 1959; L. A. Singer and N. P. Kong, *Tetrahedron Lett.*, (1966) 2089; G. D. Sargent and M. W. Browne, *J. Amer. Chem. Soc.*, 89 (1967) 2788.
8 C. Walling, *Molecular Rearrangements*, Part 1, Interscience, New York, 1963, Chap. 7.
9 H. Breederveld and E. C. Kooyman, *Rect. Trav. Chim. Pays-Bas*, 76 (1957) 297.
10 J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.*, 3 (1965) 421.
11 G. M. Whitesides, E. R. Stedronsky, C. P. Casey and J. San Filippo, Jr., *J. Amer. Chem. Soc.*, 92 (1970) 1426.
12 P. S. Dixon, A. P. Stefani and M. Sywarc, *J. Amer. Chem. Soc.*, 85 (1963) 2551.
13 *Inorg. Syn.*, 7 (1963) 113.
14 H. L. Goering and D. W. Larsen, *J. Amer. Chem. Soc.*, 81 (1959) 5937.
15 F. G. Bordwell and P. S. Landis, *J. Amer. Chem. Soc.*, 79 (1957) 1593.
16 *Organic Syntheses*, Coll. Vol. IV, Wiley, New York, 1963, p. 702.
17 H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, 2 (1964) 447.
18 H. O. House and W. L. Respess, *J. Organometal. Chem.*, 4 (1965) 95.
19 R. Criegee and N. Klaus, *Justus Liebigs Ann. Chem.*, 627 (1959) 1.
20 H. Pines and L. Schaap, *J. Amer. Chem. Soc.*, 80 (1958) 4378.