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REACTIONS OF ORGANOALUMINATES WITH COPPER(II) ACETATE IN THE ABSENCE OR IN THE PRESENCE OF CARBON MONOXIDE. A CONVENIENT METHOD FOR CONVERSION OF OLEFINS INTO THEIR SATURATED DIMERS OR KETONES

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Hydroalumination of olefins with lithium aluminum hydride followed by treatment with copper(II) acetate results in the formation of the coupled products. When the reaction of organoaluminates with copper(II) acetate is carried out under a carbon monoxide atmosphere, ketones are obtained, suggesting the formation of an alkylcopper intermediate in this reaction. This new development provides a convenient method for the conversion of olefin derivatives into their dimers or ketones.

Recently, Y. Otsuji and his collaborators have found that $LiAlR_2H_2$, which is obtained by hydroalumination of olefins with $LiAlH_4$ with catalysis by $(\eta^5\text{-}C_5H_5)_2Ti\text{-}(AlH_3)_2$,[1] reacts with copper(II) acetate to give the coupling products.[2,3] However, as olefin-based yields were relatively low (32-49%) in this reaction, presumably due to the presence of the remaining hydrides in the organoaluminum compound, its applicability in organic syntheses appears to be limited.

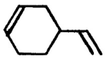
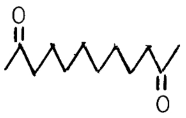
During the course of our exploration of new reactions of $LiAlR_4$, which is prepared by $TiCl_4$-catalyzed hydroalumination of olefins with $LiAlH_4$,[4] it was found that organoaluminates react with copper(II) halide or lead(IV) acetate to afford terminal alkyl halides[5] or acetates,[6] respectively, in excellent yields. Our subsequent studies on the reactions of organoaluminates with inorganic compounds have revealed that $LiAlR_4$ reacts with copper(II) acetate to give coupling products in excellent yield, which is an improvement on Otsuji's reaction. We also report here that by carring out the coupling reaction under a carbon monoxide atmosphere, the corresponding ketone (RCOR) is obtained in fair yield.

As shown in Table 1, various olefins including nonconjugated diolefins were converted to their saturated dimers via hydroalumination followed by treatment with copper(II) acetate. (Eq. 1)

$$\mathrm{LiAlH_4} + 4\ \mathrm{RCH{=}CH_2} \xrightarrow{\mathrm{TiCl_4}} \mathrm{LiAl(CH_2CH_2R)_4} \xrightarrow{+\ 4\ \mathrm{Cu(OAc)_2}} 2\ \mathrm{RCH_2CH_2CH_2CH_2R} \tag{1}$$

Study of the reaction of mixed organoaluminates, prepared by simultaneous hydroalumination of two different olefins, with Cu(OAc)$_2$ revealed that the yields of the three possible products were nearly statistical, and the yield of a desired cross-coupled dimer can be improved by using an excess of the more readily-available olefin as is shown in entry 2 of Table 1.

TABLE 1.
YIELDS AND PRODUCTS OF THE COUPLING REACTION

Entry	Olefin	Product^a	Yield^b %
1			84 (70)^c
2			
	1 : 1	1 : 2 : 1	93
	1 : 3	1 : 6.5 : 10	73
3			69
4			72
5			92 (70)^c
6		 ^{d}	(64)^c

^{a}The products were identified by GLC, ^{1}H NMR and mass spectra. ^{b}By GLC analysis and based on olefin. ^{c}Isolated yield. ^{d}After hydrolysis of ketal with dil. H_2SO_4.

These reactions appear to be similar to the coupling reactions of the organoboranes, as the hydroboration of olefins followed by treatment with $AgNO_3$ also results in formation of coupling products.7) However, in the case of the organoboranes from 1-olefins, the product contains a by-product arising from a secondary boron derivative. Also, it seems to be impossible to prepare from diolefins such coupled products as are shown in entrys 3-5 of Table 1 by hydroboration methods.

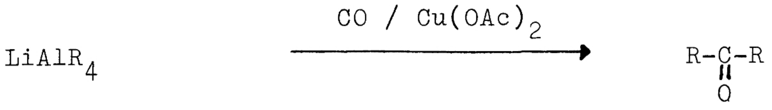
This coupling reaction seems to be characteristic of copper(II) acetate. Reaction of $LiAlR_4$ with copper(I) compounds, such as CuCl or CuBr, gave coupling products only in less than 10% yields,8) while reaction with $CuCl_2$ or $CuBr_2$ gave alkyl halides as main product.5)

It is assumed that the reaction involves formation of an organocopper compound formed by the reaction of copper(II) acetate and the organoaluminum compound. To clarify whether the organocopper(II) intermediate is present or not, we carried out the above reaction under a carbon monoxide atmosphere, since it has been shown that alkylcopper compounds, though these are copper(I) compounds, react with carbon monoxide giving ketones.[11)] The results of the coupling reaction affording ketones in fair yields (Table 2) strongly suggest the formation of alkylcopper(II) intermediates in these reactions.

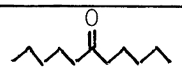
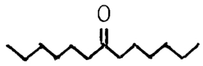
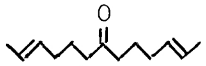
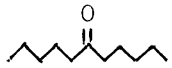
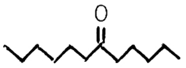
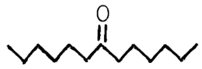
Though the yields of ketone with regard to the olefin are not so high, such reactions may be useful as a preparative method for ketones, especially for unsaturated ketones, since the corresponding alkenylaluminum compounds can be obtained readily from diolefins.

TABLE 2

PRODUCTS OF THE COUPLING REACTION IN THE PRESENCE OF CARBON MONOXIDE AND THEIR YIELDS



$$\mathrm{LiAlR_4} \xrightarrow{\mathrm{CO\ /\ Cu(OAc)_2}} \mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}R}$$

Olefin	Product^a	Yield (%)^b
		34 (22)^c
		47 (31)^c
		46
 	  	29
1 : 1	1 : 2 : 1	

^{a}Identified by IR, GLC, ^{1}H NMR and mass spectra. Other products are mainly the saturated dimers. ^{b}GLC analysis, based on olefin. ^{c}Isolated yield.

The following description of the preparation of n-dodecane is representative. To a clear solution of $\mathrm{LiAlH_4}$ in THF (38 ml of 0.26 molar, 10 mmol) was added 1-hexene (3.0 g, 36 mmol) and $\mathrm{TiCl_4}$ (86 mg, 0.45 mmol). After 2h under nitrogen at room temperature, the temperature was cooled to -30°C and $\mathrm{Cu(OAc)_2}$ (7.9 g, 43 mmol) was added. After 2h at -30°C with stirring, the mixture was brought to room temperature over about one hour. GLC analysis showed 84% yield of n-dodecane with less than 1% of by-product if any. After the usual workup 2.1 g of n-dodecane (70%) was isolated by distillation.

The reaction of organoaluminates with carbon monoxide in the presence of $Cu(OAc)_2$ was carried out as follows in the case of 1-hexene : After hydroalumination of 1-hexene (36 mmol) with $LiAlH_4$ (10 mmol) as described above, the solution was saturated with carbon monoxide by evacuation and introduction of the gas. The reaction mixture was cooled to -78°C and $Cu(OAc)_2$ (43 mmol) was added. The mixture was then warmed to -50°C and maintained at that temperature for 4h with vigorous stirring under the carbon monoxide atmosphere. GLC analysis showed the presence of a 47% yield of 7-tridecanone and a 27% yield of n-dodecane (based on 1-hexene).

The present procedures are so simple and so general that they should provide a major new preparative method for conversion of olefin derivatives into their dimers or ketones.

References and Notes

1) K. Isagawa, K. Tatsumi, H. Kosugi, and Y. Otsuji, Chem. Lett., 1017(1977) ; in this method $LiAlR_4$ can not be obtained even by using excess olefin.
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