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Preliminary communication

THE REACTION BETWEEN METHYLENE DIALUMINUM TETRABROMIDE AND CARBONYL COMPOUNDS, SYNTHESIS OF OLEFINS

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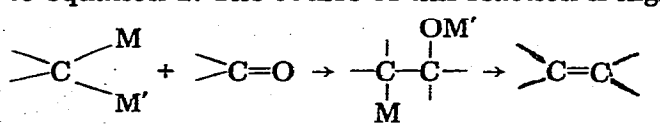
Summary

The reaction between carbonyl compounds and methylenedialuminum tetrabromide or methylenelithium aluminum dibromide in dry THF gives the corresponding methylenic olefins in satisfactory yields.

Many *gem*-dimetallic derivatives (I, M = M′ or M ≠ M′) are known to react with carbonyl compounds (II) to give the corresponding olefins (III), according to equation 1. The course of this reaction is highly dependent on the nature of

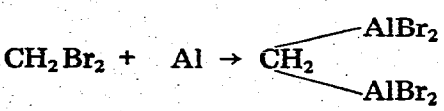


(1)

(I) (II) (III)

the metals present in the organometallic species. *gem*-Dimagnesium dihalide derivatives [1], magnesium silicon [2] and lithium phosphorus [3] compounds are especially reactive toward carbonyl compounds, giving olefins in high yields, while *gem*-diboron [4], dimercury [5], ditin [6], and disilicon [7] compounds are completely unreactive.

We have examined the conversion of carbonyl compounds into olefins by methylenedialuminum tetrabromide* (IV); IV is easily obtained in the solid state



(2)

(IV)

*The NMR spectrum in THF-d_8 of (IV) shows two signals (δ, —0.46; δ, —0.86). The principal signal at δ, —0.86 is attributable to (IV). We are studying the temperature dependence of the NMR spectrum of this organometallic species.

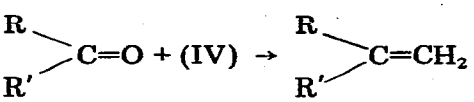
TABLE 1

OLEFINS OBTAINED FROM REACTIONS OF METHYLENEDIALUMINUM TETRABROMIDE WITH ALDEHYDES

Aldehyde	Olefin	Yield [a] (%)
Benzaldehyde	Styrene	65 [b]
p-Chlorobenzaldehyde	*p*-Chlorostyrene	50 [b]
p-Nitrobenzaldehyde	*p*-Nitrostyrene	60 [b]
p-Methylbenzaldehyde	*p*-Methylstyrene	60 [b]
2-Naphthaldehyde	2-Vinylnaphthalene	80 [b]
9-Fluorenone	9-Methylenefluorene	35 [c]
Decanal	1-Undecene	25 [c]

[a] Yield determined by GLC or on isolated purified compounds. [b] From methylenedialuminum tetrabromide (IV). [c] From methylenelithium aluminum dibromide (VI).

by treatment of an excess of dibromomethane with aluminum [8], eqn. 2, followed by vacuum distillation of the residual dibromomethane. It reacts with aldehydes (II, R′ = H) in tetrahydrofuran to give the expected methylenic olefins (V) in satisfactory yields (eqn. 3).



(3)

(II) (V)

The results are summarized in Table 1. Products were identified either by direct comparison with authentic material or by NMR and mass spectra.

The yields of olefins are generally of the order of 60%. The reaction seems general for aldehydes without α-hydrogen; with other aldehydes self-condensation products are obtained.

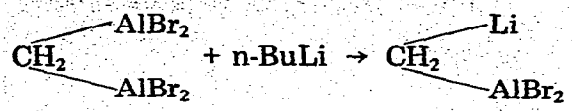
The conversion of *p*-methylbenzaldehyde into *p*-methylstyrene illustrates a typical procedure. A dry reaction vessel was flushed with argon, and 1.08 g (40 mmole) of aluminum foil (in about 3 mm squares) and 24 ml of dibromomethane were added. An exothermic reaction was induced by brief heating, and was controlled by cooling. After all the aluminum had reacted, the excess of dibromomethane was distilled off under high-vacuum at low temperature. To the solid residue of (IV), 40 ml of dry tetrahydrofuran were added. The clear solution was placed in a 3-necked flask equipped with magnetic stirrer, dropping funnel and reflux condenser under argon. A solution of 15 mmoles of the *p*-methylbenzaldehyde in 20 ml of dry tetrahydrofuran was added dropwise. The reaction mixture was refluxed for 2 h, then poured into ice-water and extracted with ether. After washing with water, drying and evaporating, the *p*-methylstyrene was isolated by chromatography on silica gel.

Under similar conditions bezophenone, cyclohexanone and fluorenone did not give the corresponding olefins.

It is known that the reactivity of *gem*-dimetallic compounds toward carbonyl compounds can be enhanced by a suitable transmetallation reaction,for instance with n-butyllithium [4] in dry THF gives a new organometallic species (probably a *gem*-lithium-aluminum derivative* (VI))which reacts with fluorenone

*When two moles of n-butyllithium per mole of (IV) were added the yield of 9-methylenefluorene was not increased.

and with decanal to yield the corresponding methylenic olefins.



(IV) (VI)

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References

1 F. Bertini, P. Grasselli, G. Zubiani and G. Cainelli, Tetrahedron, 26 (1970) 1281; V. Pascali, N. Tangari and A. Umani-Ronchi, J. Chem. Soc. Perkin I, (1973) 1166.
2 T.H. Chan, E. Chang and E. Vinokur, Tetrahedron Lett., (1970) 1137.
3 G. Wittig, Pure Appl. Chem., 9 (1964) 245.
4 G. Cainelli, G. Dal Bello and G. Zubiani, Tetrahedron Lett., (1966) 4315.
5 D.S. Matteson and J.G. Shdo, J. Org. Chem., 29 (1964) 2742.
6 C.A. Kraus and A.M. Neal, J. Amer. Chem. Soc., 52 (1930) 695; D. Seyferth, F.M. Armbrecht Jr. and B. Schneider, J. Amer. Chem. Soc., 91 (1969) 1954.
7 P.D. George, M. Prober and J.R. Elliot, Chem. Rev., 56 (1956) 1065.
8 M.R. Ort and E.H. Mottus, J. Organometal. Chem., 50 (1973) 47.