BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 928—931 (1968)

Reactions of Triethylaluminum with α,β-Unsaturated Carbonyl Compounds

Yoshio Baba

Resources Research Institute, Kawaguchi, Saitama

(Received April 17, 1967)

The reactions of triethylaluminum and its various ether adducts with α,β-unsaturated ketone, aldehyde, ester, and methyleneanthrone have shown that the addition occurs mainly at the 1,2-positions of the carbonyl function, and not at the 1,4-positions as has been observed in the Grignard reaction. The mode of addition was discussed in view of the reactivity of the organometallic compound and the steric factor of the unsaturated carbonyl compounds.

A possible mode of the addition of organometallic compounds to unsaturated carbonyl compounds has been studied by many investigators.

Cologe[1] has proposed correlations between the structure of α,β-unsaturated ketones and the mode of addition in the reaction of a simple Grignard reagent.

$$\left.\begin{array}{l} \mathrm{RHC{=}\overset{R'}{\overset{|}{C}}\text{-}COR''} \\ \mathrm{RR'C{=}\overset{R''}{\overset{|}{C}}\text{-}COR'''} \end{array}\right\}\ \text{1,2-addition}$$

$$\mathrm{RR'C{=}CHCOR''}\qquad \text{1,4-addition}$$

Gilman,[2] however, has reported that the reactivity of the organometallic compounds determines the direction of the addition. The relatively less reactive phenyl metallic compounds add to benzalacetophenone at the 1,4-positions, while the reactions with more reactive members afford 1,2-addition products.

Recently, Wittig[3-5] has proposed a mechanism of the addition reaction of organometallic compounds in which the mode of addition is effected by the ability of ate-complex formation. Thus, even though difficulty is encountered in the reaction of benzophenone with triphenylaluminum, the reaction of benzalacetophenone with triphenylaluminum proceeds readily to give the 1,4-addition product. The facile reaction of benzalacetophenone is interpreted as being due to the ability of ate-complex (I) formation, as is shown in Eq. (1):

---

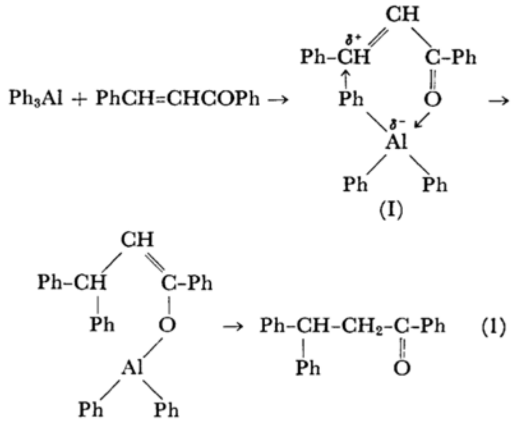
[1] J. Colonge, *Bull. Soc. Chim.*, (5), **2**, 754 (1935).

[2] H. Gilman and R. H. Kirby, *J. Am. Chem. Soc.*, **63**, 2046 (1941).

[3] G. Wittig, *Angew. Chem.*, **70**, 65 (1958).

[4] G. Wittig and O. Bub, *Ann.*, **566**, 113 (1950).

[5] A. Luettringhaus and K. Scholtis, *ibid.*, **557**, 70 (1941).



Phenylsodium or phenyllithium, however, reacts with the same α,β-unsaturated ketone to give the 1,2-addition product because of its lack of the ability to make an ate-complex intermediate.

The present work was undertaken to study the possible modes of addition in the reaction of triethylaluminum with unsaturated carbonyl compounds.

Experimental

All the reactions were carried out in an atmosphere of dry nitrogen. The melting points were measured on a micro hot stage and were not corrected.

Materials. Triethylaluminum purchased from the Ethyl Corp. was used without further purification. Commercial di-*n*-propyl ether (bp 90°C), diisopropyl ether (bp 68°C), di-*n*-butyl ether (bp 142°C), di-*n*-amyl ether (bp 186°C), diisoamyl ether (bp 172°C), cinnamaldehyde (bp 93—94°C/5 mmHg), benzalacetone (bp 112—113°C/5 mmHg, mp 41—42°C), ethyl cinnamate (bp 127—128°C/7 mmHg), crotonaldehyde (bp 102°C), mesityl oxide (bp 129°C), methyl crotonate (bp 127°C), and benzophenone (bp 150—151°C/5 mmHg) were purified by distillation. Methyleneanthrone (mp 146—147°C) was prepared from anthraquinone *via* anthrone.[6] Ethyl ethylenetetracarboxylate (mp 52.0—52.5°C) was synthesized from diethyl malonate *via* diethyl bromomalonate.[7]

Analytical Procedure. The C=C double bond and carbonyl group were analyzed according to the Lucas[8] and Iddles[9] methods respectively.

Reactions of Benzalacetone with Triethylaluminum and Its Various Ether Adducts. A 30-weight-percent solution of an aluminum compound in dry benzene containing 0.1 mol of triethylaluminum or its ether adducts was added drop by drop, to an ice-cooled solution of benzalacetone (0.05 mol) in dry benzene. The reaction mixture was, after standing for 0.5 hr in an ice-bath, refluxed for 1 hr. The crude product obtained by the usual method was distilled under reduced pressure. The carbonyl component in the distillate was extracted with a Girard reagent $(C_5H_5N\text{-}\overset{+}{C}H_2CONHNH_2)Cl^-$. The amounts of unchanged ketone and 1,4-addition product were then determined by C=C double bond and carbonyl group analysis in the carbonyl fraction by the methods described in the "analytical procedure" section, while the amounts of alcohol produced by the 1,2-addition reaction and its dehydrated product produced in the course of the distillation were determined by active-hydrogen and C=C double bond analysis of the non-carbonyl fraction.

Reaction of Benzophenone with Triethylaluminum. The reaction of benzophenone (9.1 g, 0.05 mol) with 0.075 mol of triethylaluminum in a benzene solution (refluxed for 1 hr) yielded 9.2 g of an oily product distilled at 143—150°C/5 mmHg. The above product was mixed with phthalic anhydride (6.0 g) and 24 g of dry pyridine. After a 3 hrs' refluxing of the reaction solution, the pyridine was removed by distillation and the residue was dissolved in 30 m*l* of benzene. From the benzene solution, the mono ester of the phthalic acid of secondary alcohol was extracted with a 10% potassium hydroxide solution, while the benzene solution, after drying over calcium chloride, was evaporated to give 4.3 g (42%) of crystals (mp 90—92°C). The recrystallization of the crude crystal from petroleum ether gave plates, mp 93—94°C, which showed no depression in melting point upon the admixture of diphenylethylcarbinol (mp 93—94°C), prepared from ethylmagnesium bromide and benzophenone. The alkaline solution containing the mono ester of phthalic acid of the secondary alcohol was boiled for 5—10 min, and then the separated oil was extracted with benzene. The benzene solution was dried over calcium chloride and the benzene was evaporated. The crude crystals (mp 65—66°C, 4.7 g, 51%) were recrystallized from ethanol, mp 66—67°C, needles, the melting point was undepressed by admixture with benzhydrol.

Reaction of Methyleneanthrone with Triethylaluminum. A powdered methyleneanthrone (5.2 g, 0.025 mol) was added to a stirred solution of triethylaluminum (0.076 mol) in dry petroleum ether. The solid methyleneanthrone dissolved readily, and a faint-yellow-colored solution resulted. The reaction solution was stirred for 4 hr at room temperature and then treated by the usual method. The faintly-yellow-colored oily product (7.0 g) was mixed with a small amount of ethanol and then allowed to stand for several days at room temperature. The crystals which separated were collected by filtration and washed with ethanol. The crude crystal (1.7 g, 33.0%) was recrystallized from ethanol; mp 283—284°C, undepressed by admixture with anthraquinone. The chromic acid oxidation of the oily product yielded 9-ethylanthrol (mp 106—107°C, from ethanol).

Found: C, 80.39; H, 6.35%. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92%.

Reaction of Ethyl Ethylenetetracarboxylate with Triethylaluminum. The reaction of ethyl ethylenetetracarboxylate (12.9 g, 0.041 mol) with 0.184 mol of triethylaluminum yielded 5.5 g (42.2%) of crystals, mp 75—76°C, from ethanol; the crystals were identified as ethyl ethanetetracarboxylate by a mixed melting point determination with a sample prepared from

---

[6] E. Barnett, *Ber.*, **59**, 767 (1926); "Organic Syntheses," Coll. Vol. I, p. 60 (1956).

[7] "Organic Syntheses," Coll. Vol I, p. 245; II, p. 273 (1956).

[8] H. Lucas and D. Pressman, *Ind. Eng. Chem., Anal. Ed.*, **10**, 140 (1938).

[9] H. Iddles and C. Jackson, *ibid.*, **6**, 454 (1934).

ethylmagnesium bromide and ethyl ethylenetetracarboxylate according to the procedure reported by Hsing.[10]

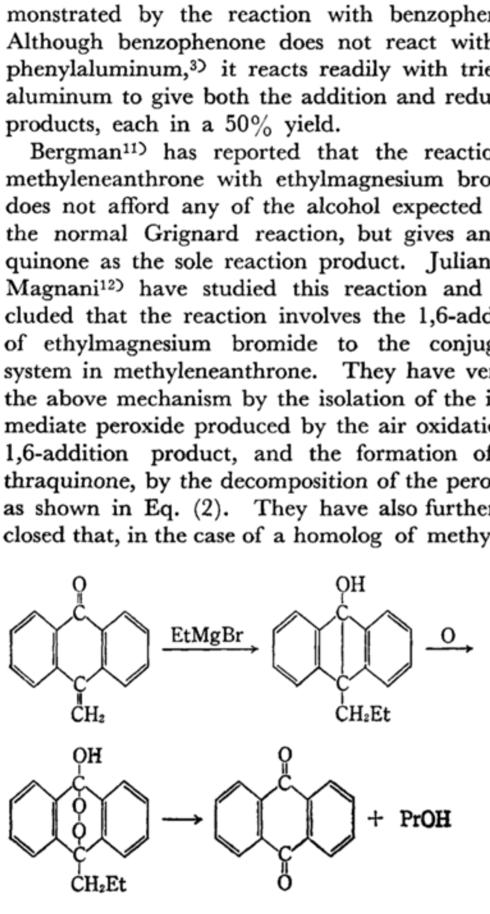
Results and Discussion

The results of the experiments of benzalacetone with triethylaluminum and its various ether adducts shows that, as Table 1 indicates, in every case the 1,2-addition reaction constituted the principal reaction, whether the free triethylaluminum or its ether adducts, which are considered to have some influence on the ate-complex formation, were employed. On the basis of these data, it seems reasonable to infer that the mode of addition in the reaction of triethylaluminum with α,β-unsaturated ketone is not influenced by the ability of ate-complex formation, but is rather defined by the reactivity of organometallic compounds.

Thus, even in the reaction of organometallic compounds with the same metal atom, such as triethylaluminum and triphenylaluminum, the highly reactive member permits the 1,2-addition, while the compound with a lower reactivity gives the 1,4-addition product.

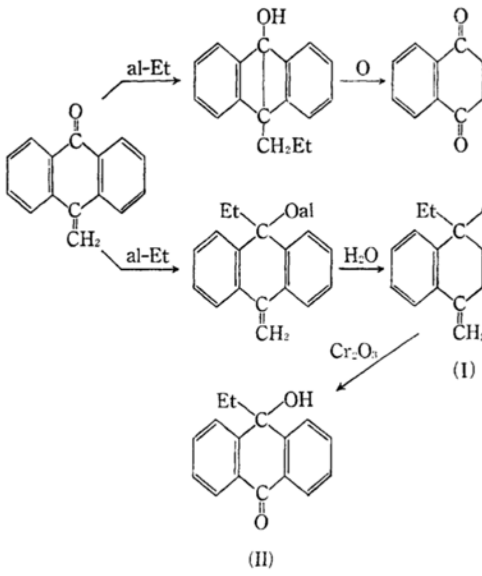
A higher reactivity of triethylaluminum as compared with triphenylaluminum was demonstrated by the reaction with benzophenone. Although benzophenone does not react with triphenylaluminum,[3] it reacts readily with triethylaluminum to give both the addition and reduction products, each in a 50% yield.

Bergman[11] has reported that the reaction of methyleneanthrone with ethylmagnesium bromide does not afford any of the alcohol expected from the normal Grignard reaction, but gives anthraquinone as the sole reaction product. Julian and Magnani[12] have studied this reaction and concluded that the reaction involves the 1,6-addition of ethylmagnesium bromide to the conjugated system in methyleneanthrone. They have verified the above mechanism by the isolation of the intermediate peroxide produced by the air oxidation of 1,6-addition product, and the formation of anthraquinone, by the decomposition of the peroxide, as shown in Eq. (2). They have also further disclosed that, in the case of a homolog of methyleneanthrone carrying a bulky group at the γ-position, benzalanthrone for example, the 1,6-addition is inhibited and the 1,2-addition is realized.



(2)

Methyleneanthrone reacted with triethylaluminum to give anthraquinone, an oxidative degradation product of the 1,6-addition product, in a 33% yield, but a substance carrying a hydroxyl group was obtained in a 32% yield as another product. A postulation that the alcohol (I) formation can be attributed to the 1,2-addition of al-Et to the conjugated system of methyleneanthrone was verified by the chromic acid oxidation of this alcohol to yield 9-ethylanthrol (II) (*cf.* Eq. (3)).



(3)

Thus it was found that triethylaluminum tends to add more readily to the carbonyl group of the conjugated system in methyleneanthrone than the corresponding magnesium compound, and that the mode of addition is defined both by the reactivity of the organometallic compound and by the steric factor of the unsaturated ketones.

The facile addition of trialkylaluminum to the carbonyl group in the unsaturated carbonyl compound could be verified from the reaction of triethylaluminum with the six α,β-unsaturated carbonyl compounds listed in Table 2; the 1,2-addition products were obtained as the major products.

A difficulty of the 1,2-addition of al-Et group to a carbonyl group in the unsaturated carbonyl compound was encountered in the reaction with ethyl ethylenetetracarboxylate. Hsing[10] has found that the reaction of ethyl ethylenetetracarboxylate with a large excess of ethylmagnesium bromide

---

[10] C.-Y. Hsing and L.-T. Li, *J. Am. Chem. Soc.*, **71**, 774 (1949).

[11] E. Bergman, *Ber.*, **63**, 1041 (1930).

[12] P. L. Julian and A. Magnani, *J. Am. Chem. Soc.*, **56**, 2174 (1934).

TABLE 1. REACTIONS OF BENZALACETONE WITH TRIETHYLALUMINUM AND ITS ETHER ADDUCTS

Aluminum compd.	Ketone recovered (b)	Condensation product (a)	1,4-Addition product (b)	1,2-Addition product (b)
$AlEt_3$	1.9	17.8	8.1	69.2
$AlEt_3$-Et_2O	5.5	29.5	15.5	47.5
$AlEt_3$-Pr_2O-*n*	2.9	9.5	23.6	60.8
$AlEt_3Pr_2O$-*i*	1.5	11.5	2.9	81.9
$AlEt_3$-Bu_2O-*n*	1.8	13.2	24.7	57.2
$AlEt_3$-Am_2O-*n*	1.9	13.4	27.4	53.1
$AlEt_3$-Am_2O-*i*	3.1	14.1	20.6	58.1

(a) Weight percent (b) Theor. yield %

TABLE 2. REACTION OF TRIETHYLALUMINUM WITH UNSATURATED CARBONYL COMPOUNDS

Unsaturated carbonyl compd.	Unchanged compd. (b)	Condensation product (a)	1,2-Addition product (b)	1,4-Addition product (b)
$C_6H_5CH{=}CH{-}CHO$	0	2.5	99.3	0
$C_6H_5CH{=}CHCOOC_2H_5$	20.0	3.4	65.7	4.0
$C_6H_5CH{=}CHCOCH_3$	10.9	17.8	65.2	1.1
$CH_3CH{=}CHCHO$	0	4.8	91.6	1.0
$(CH_3)_2C{=}CHCOCH_3$	4.0	26.1	65.6	0.3
$CH_3CH{=}CHCOOCH_3$	20.0	6.7	58.4	10.9

(a) Weight percent (b) Theor. yield %

does not cause the addition of metalalkyl linkage to the carbonyl group of the ester, but yields the reduction product of the C=C double bond and the product derived from the addition of the metal-ethyl linkage to the C=C double bond in yield of 43% and 56% respectively. The reaction of this unsaturated ester with eight moles of triethylaluminum was found to give the same product as expected from the analogy of the corresponding Grignard reaction.

The author wishes to thank Dr. J. Yoshimura, Professor of Tokyo Institute of Technology, for his many helpful discussions and suggestions during this work, and Y. Koenuma for his assistance in the experimental work.