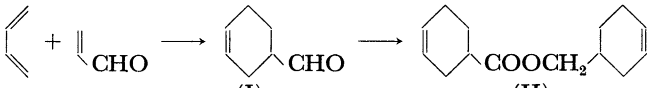
BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1553—1554(1972)

The Reaction of α,β-Unsaturated Aldehydes with 1,3-Dienes in the Presence of Alkylaluminums

Shingo MIYAJIMA and Takashi INUKAI
The Central Research Laboratories, Chisso Corporation, Kamariya, Kanazawa-ku, Yokohama

(Received September 18, 1971)

The reaction mixture in suspension form, prepared from 3 $AlEt_3$–$TiCl_4$ in heptane, is known to catalyze the Diels-Alder reactions of α,β-unsaturated aldehydes with 1,3-dienes followed by the Tishchenko condensation of the resulting 3-cyclohexenecarboxaldehyde (I) to give the bicyclic ester (II).[1]



(I) (II)

On the other hand the solid catalyst, prepared from 2 $AlEt_2Cl$–$TiCl_4$ and washed with octane, was reported to be useful for preparation of I.[2] Although the question as to the chemical species of the catalytic activity is left open, these catalyzed Diels-Alder reactions are regarded as those related to general Lewis acid catalyzed reactions of dienophiles carrying carbonyl functions.[3] We now tried $AlEt_3$, $AlEt_2Cl$, and $AlEtCl_2$ as the catalysts for the reactions of acrolein, methacrolein, and crotonaldehyde with dienes in search of a more satisfactory catalyst than those so far known.[1,2,3c]

Results

The reactions between acroleins and dienes proceed with moderate rates at normal temperature and pressure in benzene solution in the presence of suitable aluminum compounds. The reaction conditions and results are summarized in Table 1.

It appears that $AlEt_3$ is too weak as a Lewis acid to catalyze the reaction and that the catalytic activity

TABLE 1. REACTIONS OF α, β-UNSATURATED ALDEHYDES WITH 1,3-DIENES[a]

Diene	Dienophile	Catalyst	Yield[b], %
Butadiene	Acrolein	$AlEt_3$	none
		$AlEt_2Cl$	(19.4)[c]
		$AlEtCl_2$	41.4
—	Methacrolein	$AlEtCl_2$	42.9
		$AlCl_3$	19.8
—	Crotonaldehyde	$AlEt_2Cl$	3.5
		$AlEtCl_2$	48.0
		$AlCl_3$	47.0
Isoprene	Crotonaldehyde	$AlEtCl_2$	26.9

a) Reaction in benzene solution at room temperature for *ca.* 20 hr.
b) Yield of the isolated Diels-Alder adduct based on the dienophile charged.
c) Yield of the isolated Tishchenko ester II based on the dienophile charged.

---

[1] E. F. Lutz, *J. Org. Chem.*, **28**, 912 (1963).

[2] R. Robinson and G. I. Fray, Brit. 835840 (1960).

[3] a) P. Yates and P. Eaton, *J. Amer. Chem. Soc.*, **82**, 4436 (1960); b) G. I. Fray and R. Robinson, *ibid.*, **83**, 249 (1961); c) E. F. Lutz and G. M. Bailey, *ibid.*, **86**, 3899 (1964); d) T. Inukai and M. Kasai, *J. Org. Chem.*, **30**, 3567 (1965).

increases as the acidity of catalysts increases by substitution with chlorine atoms. For acid sensitive acrolein and methacrolein, however, aluminum chloride seems to be too drastic, and brings about much tar formation, as in the cases with $SnCl_4 \cdot 5H_2O$.[3c,4] So far as we have experienced $AlEtCl_2$ is the generally recommendable catalyst for aldehyde dienophiles.[5]

$AlEt_2Cl$ is unique in that it leads to the Tishchenko condensation product II leaving not more than trace of I. An aluminum alkoxide compound, that is active in catalyzing Tishchenko condensation, is naturally assumed to form *in situ*.[6]

The reaction product formed from crotonaldehyde and butadiene by the present method is pure *trans*-6-methyl-3-cyclohexenecarboxaldehyde at the initial stage of the reaction, conforming to the well-known stereochemistry of the Diels-Alder reactions, but it undergoes acid-catalyzed transformation to a *ca.* 2.7: 1 mixture of the *trans* and *cis* isomers before synthetically acceptable yield is attained.

Experimental

General Procedure. Under exclusion of oxygen and moisture, an aldehyde (0.5 mol) solution in benzene (100 m*l*) was added dropwise into a solution or suspension (in the case of $AlCl_3$) of catalyst (0.05 mol) in benzene (500 m*l*) with stirring in 5 hr, and concurrently a slight excess of a diene was slowly bubbled into the reaction mixture which was kept at 20±1°C by external cooling. After standing overnight at room temperature the mixture was treated with water (250 m*l*), the benzene layer dried with anhydrous magnesium sulfate, and the reaction product isolated by fractional distillation under reduced pressure.

Reaction Products. 3-Cyclohexenecarboxaldehyde, 1-methyl-3-cyclohexenecarboxaldehyde, and 4,6-dimethyl-3-cyclohexenecarboxaldehyde were identified by agreement of physical properties of themselves and their crystalline derivatives with those of the authentic samples: semicarbazone of 1-methyl-3-cyclohexenecarboxaldehyde, mp 174°C, (Found: C, 59.7; H, 8.3; N, 23.1%. Calcd for $C_9H_{15}N_3O$: C, 59.64; H, 8.34; N, 23.18%.). 3-Methyl-3-cyclohexenecarboxaldehyde (III) obtained by the catalytic reaction showed the same bp (59.5—61°C/12 mmHg) and IR spectrum as the authentic sample,[7] but the glpc analysis with a tricresyl phosphate column showed two peaks in an area ratio of *ca.* 2.7: 1. The major peak coincided with that of pure *trans*-III[7] in the retention time, and the minor peak with that of *cis*-III formed by thermal isomerization[8] of *trans*-III. The identification was further supported by the fact that both the reaction product and *trans*-III gave the identical *trans* to *cis* peak ratio of 1.4: 1 after thermal isomerization at 240°C. 3-Cyclohexenylmethyl 3-cyclohexenecarboxylate (II), bp 109—112°C/0.56 mmHg (lit,[1] 108—109°C/0.6 mmHg), was identified by hydrolyzing it into 3-cyclohexenylcarbinol and 3-cyclohexenecarboxylic acid: *p*-nitrobenzoate of the carbinol, mp 60—61°C (lit,[9] 60—62°C); *p*-bromophenacyl ester of the acid, mp 81.5—82.5°C (lit,[1] 81.5—82°C).

---

[4] Unpublished work.

[5] $AlEtCl_2$ was recently reported to catalyze the Diels-Alder reaction of acrylonitrile too [J. Furukawa, E. Kobayashi, K. Haga, and Y. Iseda, *Polymer Journal*, **2**, 475 (1971)].

[6] We are not in a position to study the reaction of alkylaluminums with acrolein, but it may be worth noting that $AlEt_2Cl$ reacts with acrolein to give off ethylene and from acid hydrolysis of the reaction mixture was isolated 0.3 mol of allyl alcohol per mol of $AlEt_2Cl$, indicating the formation of $CH_2{=}CH{-}CH_2OAl(Et)Cl$.

[7] O. Diels and K. Alder, *Ann.*, **470**, 62 (1929).

[8] G. P. Kugatova-Shemyakina and Yu. A. Ovchinnikov, *Tetrahedron*, **18**, 697 (1962).

[9] E. G. E. Hawkins, D. J. G. Long, and F. W. Major, *J. Chem. Soc.*, **1955**, 1465.