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SELECTIVITY IN THE PRODUCT-DISTRIBUTION UPON THE ADDITION OF DICHLOROCARBENE TO OLEFINS BY USE OF TERTIARY AMINES AS CATALYSTS

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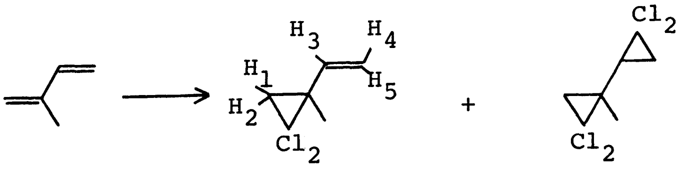
The dichlorocarbene species generated from chloroform and aqueous sodium hydroxide in the presence of tertiary amines exhibits a high selectivity in the product-distribution upon its addition to olefins containing multiple double bonds; the monoadducts was produced in preference to the bisadducts. The selectivity increases with decrease in the reactivity of the dichlorocarbene species.

The generation of dichlorocarbene from chloroform and aqueous sodium hydroxide, which constitute a two-phase system, is facilitated by the addition of a catalytic amount of certain tertiary amines.1) The mechanistic investigations of this reaction have suggested that a nitrogen ylide which is formed from a tertiary amine and dichlorocarbene is involved as an intermediate.2) Therefore, the reactivity of dichlorcarbene generated by this method is supposed to depend on the structure of amines employed and also differs from that of the same species generated by other methods. We report here that the dichlorocarbene species prepared in the presence of tertiary amines exhibits a high selectivity in the product-distribution upon its addition to olefins containing multiple double bonds, and the selectivity can be correlated with the reactivity of the dichlorocarbene species.

In a typical example, a solution of 5 g of NaOH in 10 ml of water was added to a stirred solution of 1 g (14.7 mmol) of 2-methylbutadiene (isoprene)[1] and 83 mg (0.74 mmol) of 1,4-diazabicyclo[2.2.2]octane (DABCO) in 8 ml of $CHCl_3$ at 34°C, and then stirring was continued for 5 h. The mixture was acidified with a dilute HCl solution and extracted with ether. The ethereal extract was dried(Na_2SO_4), concentrated, and distilled to give 0.38 g (20%) of 1,1-dichloro-2-methyl-2-vinylcyclopropane [2]: bp 42°C/16 Torr: NMR (CCl_4)δ=1.47(3H, s, CH_3), 1.29(1H, d, J=7 Hz, H_1 or H_2), 1.58 (1H, d, J= 7 Hz, H_1 or H_2), 5.14(1H, dd, J=17.5 and 2 Hz, H_5), 5.19(1H, dd, J= 9.5 and 2 Hz, H_4), and 5.85 (1H, dd, J=9.5 and 17.5 Hz, H_3).

The reaction of [1] with dichlorocarbene was conducted in the presence of other tertiary amines. The Δ^1-monoadduct [2] and the Δ^1,Δ^3-bisadduct [3] were obtained in



[1] [2] [3]

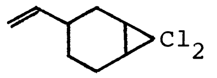
Table 1. Reactions of [1] with Dichlorocarbene in the Presence of Various Catalysts$^{a)}$

Catalyst	Yield of Product,$^{b)}$%	Ratio ([2]:[3]$^{c)}$)
1,4-Diazabicyclo[2.2.2]octane	23	(100: 0)
Tributylamine	47	(82:18)
1-Azabicyclo[2.2.2]octane	49	(73:27)
Dimethyldodecylamine	74	(68:32)
Cetyltrimethylammonium bromide	88	(62:38)

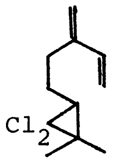
a) The reactions were conducted by stirring a mixture consisting of 14.7 mmol of [1], 0.74 mmol of a catalyst in 8 ml of $CHCl_3$,and 125 mmol of NaOH in 10 ml of water at 34°C for 5 h. b) The yield was determined by GLC. c) A mixture of cis- and trans- Δ^1,Δ^3-bisadducts.

various ratios depending on the amines employed. The results are given in Table 1. When cetyltrimethylammonium bromide (CTABr, a typical phase-transfer catalyst) was used as a catalyst, [2] and [3] were obtained in the ratio of 62:38. The ratio of [2]:[3] increased in the cases of the amine-catalyzed reactions. Specifically, in the DABCO-catalyzed reaction, [2] was obtained as the sole isolable product and no [3] was deteced by GLC analysis of the reaction mixture.

The selectivity in the dichlorocarbene addition to other olefins was then studied using tributylamine as a catalyst. For 4-vinylcyclohexene, only the Δ^1-monoadduct [4] was obtained in 60% yield (99% yield based on the consumed olefin). For 7-methyl-3-methylene-1,6-octadiene (myrcene), only the Δ^6-monoadduct [5] was isolated in 36% yield (88% yield based on the consumed olefin). d-1,8-p-Menthadiene (d-limonene) reacted to give the Δ^1-monoadduct [6] and the Δ^1,Δ^8-bisadduct [7] in the ratio of 57:43 in a total yield of 88%. However, d-limonene was converted into [6] with a very high selectivity (~100%) by the use of DABCO as a catalyst.



[4]



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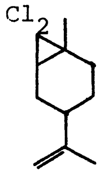
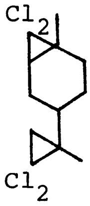


[6]



[7]

A noteworthy feature of the above results is that the dichlorocarbene species generated in the presence of tertiary amines exhibits a higher selectivity in the product-distribution, compared with the selectivity in the addition of dichlorocarbene generated by other methods. For example, when CTABr was employed as a catalyst, the Δ^1-monoadduct and the $\Delta^1,\Delta^{1'}$-bisadduct were obtained in the ratio of 64:36 from 4-vinylcyclohexene$^{3)}$, and only the Δ^1,Δ^8-bisadduct was isolated from dl-limonene.$^{4)}$ These results are in contrast to the results for the amine-catalyzed reactions which produce the monoadducts with a high selectivity.

In order to clarify the catalytic behavior of tertiary amines, kinetic studies were undertaken using [1] as the substrate. The rates of formation of [2] and [3] from [1] in the presence of CTABr and DABCO are shown in Figs. 1 and 2, respectively. In the presence of DABCO, no formation of [3] was observed. Fig. 3 depicts the rates of formation of [3] from [2] in the presence of CTABr, tributylamine, 1-azabicyclo[2.2.2]-

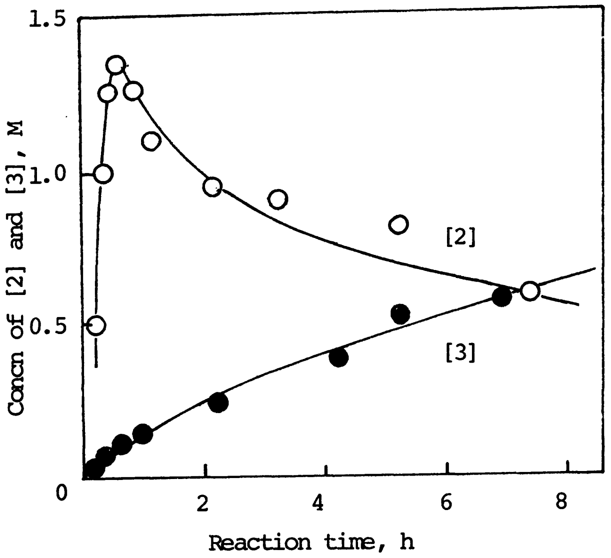


Fig. 1 Plot of the concentrations of [2] and [3] produced from [1] in the presence of CTABr *vs* reaction time.
[1]:1.67 M, CTABr:0.083 M

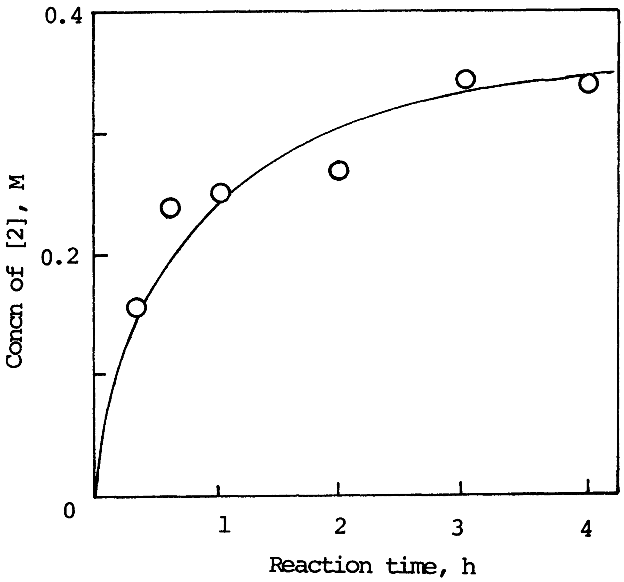


Fig. 2 Plot of the concentration of [2] produced from [1] in the presence of DABCO *vs* reaction time.
[1]:1.67 M, DABCO:0.083 M

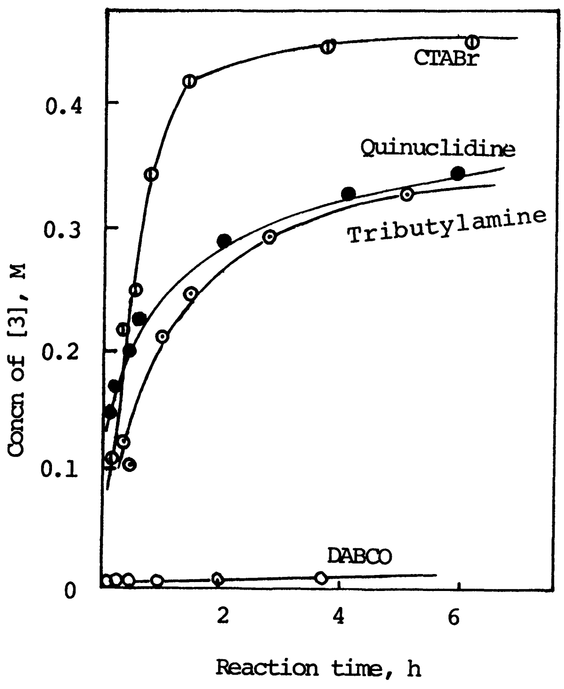


Fig. 3 Plot of the concentration of [3] produced from [2] in the presence of various amines *vs* reaction time.
[2]:1.67 M, amines:0.083 M

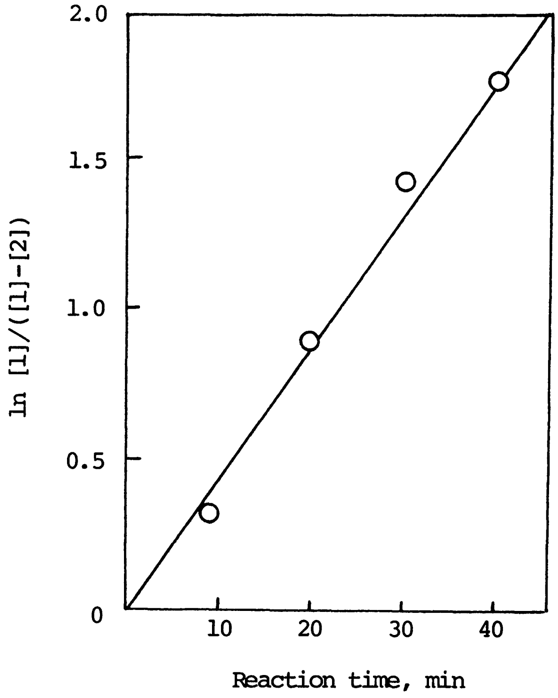


Fig. 4 Pseudo-first-order kinetics for the reaction of [1] with $:CCl_2$ in the presence of CTABr.

$$[1] \xrightarrow{k_1} [2] \xrightarrow{k_2} [3]$$

$$\frac{d[2]}{dt} = k_1[1] \qquad (1) \qquad\qquad \frac{d[3]}{dt} = k_2[2] \qquad (2)$$

Table 2. Pseudo-First-Order Rate Constants (k_1 and k_2) for the Reactions of [1] and [2] with Dichlorocarbene[a)]

Catalyst	$10^4k_1, s^{-1}$	$10^4k_2, s^{-1}$	k_1/k_2
Cetyltrimethylammonium bromide	7.5	0.83	9
1-Azabicyclo[2.2.2]octane	4.3	0.29	15
Tributylamine	1.6	0.10	16
1,4-Diazabicyclo[2.2.2]octane	0.83	0.0025	>300

a) The reactions were conducted by stirring a mixture consisting of 10 mmol of [1] or [2], 0.5 mmol of a catalyst in 5 ml of $CHCl_3$, and 10 ml of 33%(w/w)NaOH at 34°C.

octane (quinuclidine), and DABCO.

The rates of formation of [2] from [1] and also those of [3] from [2] obeyed the pseudo-first-order kinetics as expressed in the form of Eqs. (1) and (2), until 30-40% of the reactant substrates were consumed. A typical experimental result is represented in Fig. 4. The rate constants, k_1 and k_2, measured in the presence of a constant concentration of the amine under the specified reaction conditions are summarized in Table 2. Both of k_1 and k_2 were dependent on the structure of the amines employed, and their magnitude decreased in the order CTABr > quinuclidine > tributylamine > DABCO. However, the ratio k_1/k_2 decreased in the reverse order. Inspection of the results of Tables 1 and 2 reveals that the selectivity in the dichlorocarbene addition increases with decrease in the k_1/k_2 values for the given catalytic reactions. For example, the DABCO-catalyzed reaction which had the highest k_1/k_2 value exhibited the highest selectivity. Moreover, it can be seen that a higher selectivity is attained for the catalysts which produce the lower reactive carbene (the carbene having the smaller k_1 and k_2 values). This feature is consonant with Brown's postulate[5)] for the reactivity-selectivity relationship that in a given reaction, a high reactive species gives rise to a low selectivity, conversely a low reactive species gives rise to a high selectivity.

The reactivity of dichlorocarbene in the amine-catalyzed reactions could be correlated with the stability of a nitrogen ylide which is formed by the interaction between dichlorocarbene and a tertiary amine. The detailed discussion will be reported in a full paper.

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