

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

*cis-trans* Isomerizations. II. The Mechanism of the Amine Catalyzed Isomerization of Diethyl Maleate

BY KENZIE NOZAKI

The catalytic effect of amines on *cis-trans* isomerizations has been known for some time. It has been reported that ammonia<sup>1</sup> and pyridine<sup>2</sup> are catalysts for the isomerization of maleic acid to fumaric acid and that ammonia, primary amines and secondary amines<sup>3</sup> are catalysts for the isomerization of dimethyl maleate to dimethyl fumarate. It has generally been assumed<sup>3,4</sup> that the catalysis is due to the formation of an intermediate involving a coordinate link between the hydrogen atom of the base and a carbonyl oxygen of the ethylene derivative. Upon formation of the intermediate, the ethylenic double bond is assumed to shift, leaving an electron-deficient carbon and a single bond around which free rotation is possible. From this mechanism, which attributes the catalytic effect of amines to proton-donating capacity, it might be expected that strong acids such as hydrochloric acid would be much better catalysts for the isomerization than amines. However, it was found from experiments in ether solutions that with identical conditions and concentrations several amines were much better catalysts than hydrochloric acid. The observation<sup>5</sup> that strong bases such as piperidine are the best catalysts is also difficult to interpret by this mechanism.

In an earlier paper<sup>5</sup> a mechanism was proposed for the acid and salt catalyzed isomerization of maleic acid to fumaric acid. The mechanism assumed the formation of an intermediate which involved both a proton donor and an electron donor (anion). Since amines could serve both as proton and electron donors, the possibility that a similar intermediate might be formed in the amine catalyzed isomerization was investigated. In this paper a mechanism involving such an intermediate is presented, together with experimental data in support of it.

## Experimental

**Materials.**—The diethyl maleate was prepared from maleic anhydride and ethyl alcohol, using the method of

Wachholtz,<sup>6</sup> b. p. 106° at 14 mm.,  $n_D^{20}$  1.4412. The diethyl fumarate was prepared from fumaric acid and ethyl alcohol using a similar method.

The amines, Eastman Kodak Co. products, were distilled before use. In addition the tertiary amines were purified by treatment with benzenesulfonyl chloride and aqueous potassium hydroxide. The ether was Baker c. p. "distilled over sodium."

**Procedure.**—The isomerizations were carried out using the following procedure. Solutions containing known concentrations of amine and ester were made up, using diethyl ether as the solvent: 10-cc. portions were pipetted into test-tubes and the stoppered tubes were immersed in a thermostat. At selected intervals the tubes were withdrawn, 2 cc. of 3 *N* sulfuric acid was added and the ether was evaporated at reduced pressure. The ester layer was then separated off, washed with water, and dried over potassium carbonate.

Analysis for percentage conversion was carried out using the method of Kistiakowsky and Smith<sup>7</sup> with the modification that small test-tubes and a mercury thermometer were used. It was found that 0.6 cc. of Nujol and 0.4 cc. of diethyl maleate were completely miscible at 103°. Under the same conditions the fumarate was miscible at 7°.

## Experimental Results

It was found that data from rate measurements conformed best to the rate expression

$$d[F]/dt = k[M][A]^2 \quad (1)$$

where F represents diethyl fumarate, M represents diethyl maleate and A represents the amine. Integration of this expression, assuming that [A] is constant, gives

$$k = \frac{2.303}{[A]^2(t_2 - t_1)} \log \frac{a - x_1}{a - x_2} \quad (2)$$

where the symbols have their usual meanings. The conformity of the data to expressions (1) and (2) is illustrated by the typical example shown in Table I. The isomerizations were generally not carried beyond about 30% because of the simultaneously occurring addition reaction of the amine to the ester. This addition reaction was responsible for a slight dropping off of rate constants during the later stages of the isomerization.

In Table II are summarized the results obtained using diethylamine as the catalyst. From runs 1, 2 and 3, it is apparent that the reaction is of

(1) Tanatar, *J. Russ. Phys.-Chem. Soc.*, **43**, 1742 (1911).

(2) Pfeiffer, *Ber.*, **47**, 1592 (1914).

(3) Clemo and Graham, *J. Chem. Soc.*, 213 (1930).

(4) Mayo and Walling, *Chem. Rev.*, **27**, 403 (1940).

(5) Nozaki and Ogg, *THIS JOURNAL*, **63**, 2583 (1941).

(6) Wachholtz, *Z. physik. Chem.*, **125**, 4 (1927).

(7) Kistiakowsky and Smith, *THIS JOURNAL*, **56**, 638 (1934).

TABLE I

THE ACTION OF DIETHYLAMINE ON DIETHYL MALEATE AT 24.9°

Initial concentrations: diethyl maleate = 0.622 *M*; diethylamine = 0.0923 *M*.

<i>t</i> , sec.	Miscibility temp., °C.	% isomerized	$k \times 10^4$ , $\left(\frac{\text{mole}}{\text{liter}}\right)^{-1} \text{sec.}^{-1}$
0	103	0	
18000	96	7.5	5.09
36000	89	14.8	5.22
54000	83.0	21.0	5.12
90000	72.5	32.0	5.00
126000	64.5	40.5	4.90

first order with respect to diethyl maleate. A fourfold variation in ester concentration has not affected the value of *k* beyond experimental error. Runs 2, 4 and 5, where the concentration of ester was kept constant and the concentration of amine was varied, show clearly that the reaction is of second order with respect to amine. Calculation of the energy of activation for the reaction from the rate constants at 0 and 24.9° gives a value of 9940 calories.

TABLE II

THE DIETHYLAMINE CATALYZED ISOMERIZATION OF DIETHYL MALEATE

Run	Temp., °C.	Initial concn. of diethyl maleate (moles/l.)	<i>c</i> = concn. of catalyst (moles/l.)	<i>kc</i> <sup>2</sup> × 10 <sup>6</sup> , sec. <sup>-1</sup>	$k \times 10^4$ , $\left(\frac{\text{moles}}{\text{liter}}\right)^{-1} \text{sec.}^{-1}$
1	24.9	0.311	0.0923	4.32	5.06
2	24.9	.622	.0923	4.35	5.10
3	24.9	1.244	.0923	4.43	5.20
4	24.9	0.622	.1846	17.1	5.01
5	24.9	.622	.3692	68.9	5.05
6	0.0	.582	.0893	0.894	1.12
7	.0	.582	.1786	3.48	1.07

In Table III are listed the values of the rate constants at 24.9° using various amines as catalysts for the isomerization. It was found, as had been reported earlier,<sup>3</sup> that tertiary amines did not catalyze the isomerization. Even the moderately strong bases, trimethylamine and triethylamine, had no catalytic effect. From the results with primary and secondary amines, it is evident that there is a definite correlation between effectiveness as a catalyst and basic strength. It appears that, in general, the stronger the base, the better it is as a catalyst for the isomerization. The only important exception is diethylamine, which is not as effective a catalyst as would be expected for a base of its strength.

A determination of the relative catalytic effects of hydrochloric acid, diethylamine and piperidine

TABLE III

THE CATALYTIC EFFECT OF VARIOUS AMINES ON THE ISOMERIZATION OF DIETHYL MALEATE AT 24.9°

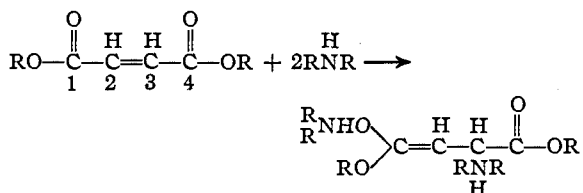
Amine	<i>k</i> , $\left(\frac{\text{mole}}{\text{liter}}\right)^{-1} \text{sec.}^{-1}$	Dissociation constant <sup>a</sup>
Piperidine	$7.66 \times 10^{-2}$	$1.6 \times 10^{-3}$
Dimethylamine	$6.49 \times 10^{-2}$	$7.4 \times 10^{-4}$
Methylamine	$3.84 \times 10^{-2}$	$5.0 \times 10^{-4}$
Ethylamine	$3.13 \times 10^{-2}$	$5.6 \times 10^{-4}$
Benzylamine	$2.36 \times 10^{-2}$	$2.4 \times 10^{-5}$
Diethylamine	$5.10 \times 10^{-4}$	$1.26 \times 10^{-3}$
Aniline	$6.34 \times 10^{-7}$	$4.6 \times 10^{-10}$
Methylaniline	$6.34 \times 10^{-7}$	$4.0 \times 10^{-10}$
Triethylamine	0.00	$6.4 \times 10^{-4}$
Trimethylamine	.00	$7.4 \times 10^{-5}$
Pyridine	.00	$2.3 \times 10^{-9}$
Dimethylaniline	.00	$4.0 \times 10^{-10}$

<sup>a</sup> Landolt-Börnstein, "Physikalisch-chemische Tabellen."

was made. Solutions 0.622 *M* in diethyl maleate and 0.255 *M* in catalyst were made up in diethyl ether, sealed in test-tubes, and immersed in a thermostat at 24.9°. At the end of two hours the diethyl maleate was 5.5% isomerized in tubes containing hydrochloric acid, 21% isomerized in tubes containing diethylamine, and more than 99% isomerized in tubes containing piperidine.

### Discussion

The mechanism proposed for the amine-catalyzed isomerization is similar to that proposed for the isomerization catalyzed by inorganic acids and salts.<sup>5</sup> The rate determining step may be formulated as



As in the other mechanism, the intermediate is assumed to have the same probability of decomposing into the maleate or the fumarate due to the equivalence of the two bonds between carbons 1 and 2 in the complex. The completeness of isomerization is explained, as before, by a difference in the energy of activation of the rate determining step for the maleate and the fumarate. The reaction may involve preliminary association between a molecule of amine and ester before reaction with another molecule of amine. However, since the energy of activation is quite low, the possibility of a truly termolecular reaction is not eliminated.

The mechanism predicts that the isomerization reaction should be of first order with respect to ester and of second order with respect to amine. The kinetic studies reported in this communication show that this is found to be true. Since a proton is necessary for association with the carbonyl oxygen, tertiary amines would not be expected to have any catalytic effect. Such has been found to be the case. According to the mechanism stronger bases, because of their ability to readily donate a pair of electrons, might be expected to be better catalysts for isomerization. Work with different amines has shown that, although other effects are involved, there is a correlation between basic strength and catalytic ability.

The proposed mechanism is applicable to the isomerization of esters of all  $\alpha$ - $\beta$  unsaturated acids.

It is also applicable to the amine-catalyzed isomerization of  $\alpha$ - $\beta$  unsaturated acids. However, in this case the protons would be supplied by the substituted ammonium ions formed by the reaction of the acid with the amine. Thus, even tertiary amines should be catalysts for the isomerization of  $\alpha$ - $\beta$  unsaturated acids. The reported catalysis of the isomerization of maleic acid to fumaric acid by pyridine<sup>2</sup> is thus readily explained.

### Summary

A mechanism has been proposed for the amine catalyzed isomerization of diethyl maleate. Experimental evidence in support of the mechanism has been presented. The applicability of the mechanism to the isomerization of all  $\alpha$ - $\beta$  unsaturated esters and acids has been discussed.

DAVIS, CALIFORNIA

RECEIVED JULY 15, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

## The Reduction of Multiple Carbon-Carbon Bonds. III. Further Studies on the Preparation of Olefins from Acetylenes<sup>1,2</sup>

BY KENNETH N. CAMPBELL AND LAWRENCE T. EBY

The preparation of the pure *trans* isomers of 3-hexene, 3-octene, 4-octene and 5-decene by reduction of the corresponding dialkylacetylenes with sodium in liquid ammonia, and the preparation of the *cis* isomers by catalytic hydrogenation of the acetylenes in the presence of Raney nickel were described in a previous paper.<sup>3</sup> In the present paper data are also recorded for the *cis* and *trans* isomers of 2-hexene and 2-octene, thus completing the series of the *cis* and *trans* isomers of all the straight chain hexenes and octenes.

Since the reduction of dialkylacetylenes with sodium in liquid ammonia led to olefins of a high degree of purity, uncontaminated by any saturated compound, and easily freed from traces of unreduced acetylene, the method was tried with monoalkylacetylenes. It was found to proceed smoothly and gave good yields of 1-alkenes. This method is superior to catalytic hydrogenation of alkylacetylenes for the preparation of such olefins. Lebedev and his co-workers<sup>4</sup> have shown

that terminally unsaturated olefins hydrogenate more rapidly than symmetrically disubstituted ethylenes, and Campbell and O'Connor<sup>5</sup> found that in the catalytic hydrogenation of monoalkylacetylenes there is much less change in velocity at half-reduction than with the dialkylacetylenes. In using catalytic methods with monoalkylacetylenes it is, therefore, harder to stop precisely at the olefin stage, and the olefin obtained may contain traces of saturated hydrocarbon which are hard to remove by fractional distillation. When the sodium-liquid ammonia method is used, however, there is no danger of contaminating the olefin with saturated hydrocarbon, since olefins are not attacked under these conditions.<sup>6</sup> This was confirmed in the present work by treating 1-heptene and the *cis* and *trans* isomers of 5-decene with sodium in liquid ammonia; in every case the olefin was recovered unchanged.

The data in Table I indicate that the 1-alkenes prepared by sodium reduction are purer than those prepared by catalytic hydrogenation. The ones from sodium reduction show the higher freezing points and lower boiling points and densities.

(1) Paper 11, THIS JOURNAL, **63**, 216 (1941).

(2) Paper XLIII on substituted acetylenes and their derivatives; previous paper, THIS JOURNAL, **63**, 1151 (1941). The material in this paper was presented before the Organic Division at the St. Louis meeting of the American Chemical Society, April, 1941.

(3) Campbell and Eby, *ibid.*, **63**, 216 (1941).

(4) Lebedev, Koblinsky and Yakubchik, *J. Chem. Soc.*, **127**, 417 (1925).

(5) Campbell and O'Connor, THIS JOURNAL, **61**, 2897 (1939).

(6) Lebeau and Picon, *Compt. rend.*, **159**, 70 (1914).