1, 1-Dicyano-2-p-dimethylaminophenyl-2-chloroethylene 의 가수분해 반응메카니즘과 그의 반응속도론적 연구

金 泰 麟・許 泰 聖*

고려대학교 이공대학 화학과

(1974. 9. 7 접수)

The Kinetics and Mechanism of the Hydrolysis of a 1, 1-Dicyano-2-p-dimethylaminophenyl-2-chloroethylene

Tae-Rin Kim and Tae-Seong Huh*

Department of Chemistry, College of Science and Engineering,
Korea University, Seoul, Korea

(Received Sept. 7, 1974)

요 약. 여러 pH 에서 1, 1-dicyano-2-p-dimethylaminophenyl-2-chloroethylene(DPC)의 가수분해 속도상수를 측정하고 넓은 pH 범위에서 잘 맞는 반응 속도로식을 구하였다.

이 식에 의하면 넓은 pH 범위에서 DPC 에 대한 가수분해 반응메카니즘을 잘 설명할 수 있다.

pH 3 이하와 7. 5 이상에서는 속도상수는 hydronium ion 과 hydroxide ion 농도에 각각 비례한다.

또 pH 3~7. 5 사이에서는 물, hydronium ion 과 hydroxide ion 이 DPC 의 가수 분해에 촉매 역활을 함을 알았다.

Abstract. The rate constants of hydrolysis of 1, 1-dicyano-2-p-dimethylaminophenyl-2-chloroethylene(DPC) were determined at various pH and the rate equation which can be applied over wide pH range is obtained. From the rate equation the mechanism of the hydrolysis of a DPC over wide pH range is fully explained; below pH 3 and above pH 7.5, the rate constant is propotional to the concentration of hydronium ion and hydroxide ion, respectively. However, in the range of pH 3 to 7.5, water, hydronium ion and hydroxide ion catalyze the hydrolysis of DPC.

1. Introduction

The addition reaction of the double bond having electron attracting group, unlike ordinary carbon double bonds, are electrophilic. During the past decade a great deal of imformation has appeared in the literature[1~2] concerning the mechanism of nucleophilic addition and qualitative observation to explain a plausible mecha-

nism[3~5] in basic solution, however, it has been the subject only a few kinetic studies.

Kharash[6] and Hurd[7] have suggested a mechanism of the addition of mercaptan to carbonyl compounds in basic media. Stewart[8] pointed out the alkaline scission of 4-hydroxy-3-methexy-β-nitrostyrene. Walker and Young[9] also determined the velocity constants and activation energies for the hydrolytic decomposition of chalcone and six ring substituted mononitro derivatives.
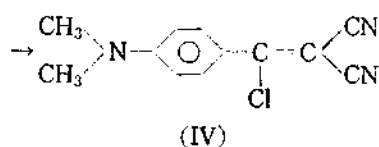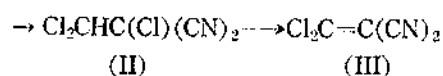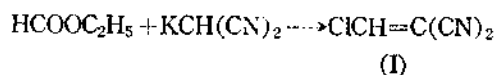
*Department of Chemistry, Song Sim Women College, Choon Chun, Korea

Patai and others[10~12] have studied the elimination of malononitrile from 4,4-dicyano-3-nitrochalcone and malononitrile in methanol. The kinetics of the reaction of barbituric acid with β-nitrostyrene derivatives in non-alkaline media has been reported.[13] In acidic media, the cleavage of β-nitrostyrene was suggested by Crowell[14~15] to take place in a slightly different mechanism. Truce and others[16] have studied the stereochemistry of the mercaptan addition reaction.

The mechanisms of the reaction of mercaptan with maleic anhydride,[17] methylacrylate,[18] β-nitrostyrene,[19] ethylcinnamate,[20] has been reported. But for the DPC, the only vinyllic substitution by aromatic amines in acetonitrile was reported.[21] The purpose of this investigation is to determine each rate constant of hydrolysis over a wide pH range and to reveal the reaction mechanism.

2. Experimental

The DPC(IV) was prepared according to Josey et al.,[22] from ethylformate and potassium malononitrile via 1-chlor-2,2-dicyanoethylene (I), 1,1,2-trichloro-2,2-dicyanoethylene (II) and 1,1-dichloro-2,2-dicyanoethylene (III). Recrystallization of the crude material from methanol yielded orange product, mp. 132 °C (lit[22]., 132~234 °C).

$$HCOOC_2H_5 + KCH(CN)_2 \longrightarrow ClCH=C(CN)_2$$
$$(I)$$

$$\longrightarrow Cl_2CHC(Cl)(CN)_2 \longrightarrow Cl_2C=C(CN)_2$$
$$(II) \qquad\qquad (III)$$

$$\longrightarrow \begin{array}{c} CH_3 \\ CH_3 \end{array}\!\!\!>N-\!\!\!\bigcirc\!\!\!-\overset{\displaystyle}{\underset{\displaystyle Cl}{C}}-C\!\!<\begin{array}{c} CN \\ CN \end{array}$$
$$(IV)$$

All buffer solution were prepared from reagent

grade chemicals(E. Merk) and distilled water. The pH of buffer solutions were confirmed by Zerometric II pH meter(Beckman). The ionic strength was kept constant at 0.1 by adding sodium chloride solution.

The rate vessels used were 100 ml volumetric flasks in the thermostat(25 °C). At zero time, 1 ml of a freshly prepared 0.002 M methanol solution of DPC was pipetted into the 100 ml flask containing 99 ml of buffer solution. The optical density of DPC was determined on a Beckman Model DU spectrophotometer at 445 nm.

3. Result

The logarithmic plots of optical density of DPC vs. times at 445 nm were linear and used to calculate the first-order rate constants(Fig.1). The rate constants calculated from the slope for all runs are given in Table 1. Fig.2. shows the logarithmic plots of k_t against pH. The rate constants for the hydrolysis of DPC at various acetate ion concentration at pH 4.65 are given in Table 2 and Fig.3 and known to be a general base catalysis.
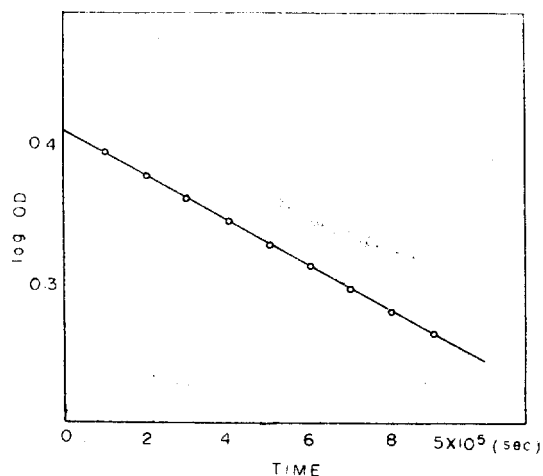

Fig. 1. The plots of log OD of DPC vs. time at pH 4.50 and 25°C.

Table 1. The rate constants for the hydrolysis of DPC at various pH & 25 °C.

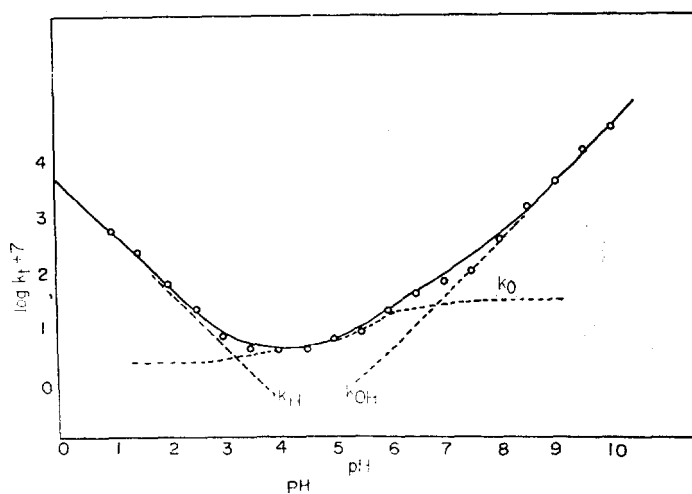| Buffer solution	pH	$k(\text{sec}^{-1})$	
		observed	calculated
HCl	0.00		5.12×10^{-4}
	0.50	2.53×10^{-3}	1.64×10^{-4}
	1.00	5.16×10^{-5}	5.12×10^{-5}
	1.50	2.11×10^{-5}	1.64×10^{-5}
	2.00	5.53×10^{-6}	5.12×10^{-6}
	2.50	$2.01 \times 10^{-}$	1.94×10^{-6}
	3.00	6.14×10^{-7}	8.24×10^{-7}
NAc+NaAc	3.50	3.12×10^{-7}	4.85×10^{-7}
	4.00	4.14×10^{-7}	3.90×10^{-7}
	4.50	3.68×10^{-7}	4.06×10^{-7}
	5.00	5.52×10^{-7}	5.55×10^{-7}
	5.50	5.98×10^{-7}	1.00×10^{-6}
	6.00	1.68×10^{-6}	1.95×10^{-6}
	6.50	3.62×10^{-6}	4.31×10^{-6}
$KH_2PO_4+K_2HPO_4$	7.00	5.89×10^{-6}	7.50×10^{-6}
	7.50	8.00×10^{-6}	1.48×10^{-5}
	8.00	3.20×10^{-5}	3.70×10^{-5}
Boric acid+NaOH	8.50	1.38×10^{-4}	1.05×10^{-4}
	9.00	3.20×10^{-4}	3.25×10^{-4}
	9.50	1.36×10^{-3}	1.00×10^{-3}
	10.00	3.22×10^{-3}	3.20×10^{-3}

Fig. 2. pH-Kate profile for the hydrolysis DPC at 25 °C.

4. Discussion

Analysis of *Fig.* 2 show that the total rate constant k_t is given by an expression of the form

$$k_t = k_0 + k_H a_H + k_{OH} a_{OH}$$

$$= k_0 + k_H a_H + k_{OH} \frac{K_w}{a_H} \quad (1)$$

Where k_0 is the rate constant for the hydrolysis which is insensitive to pH i.e., spontaneous hydrolysis or more accurately, water catalized hydrolysis. While k_{OH} and k_H are the rate constants for hydroxide ion and hydronium ion catalysed hydrolysis respectively.

Below pH 3, the iminonium ion is a likely intermediate since it has been shown to form from the nitrile and hydronium ion. [23~24]

Table 2. The rate constants for the hydrolysis of DPC at various acetate ion concentration at pH 4.65 and 25 °C.

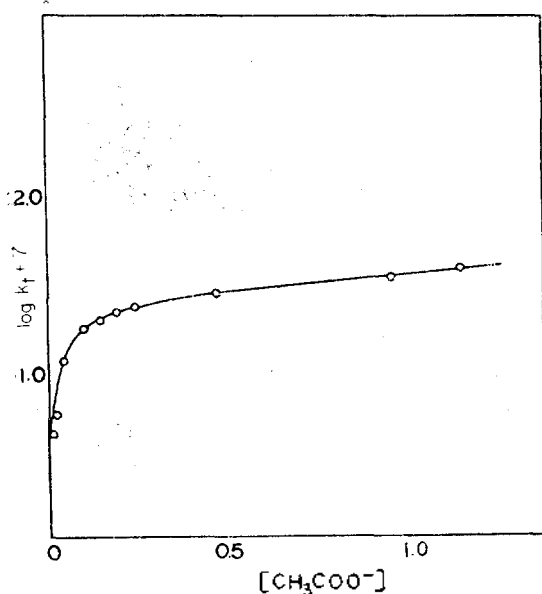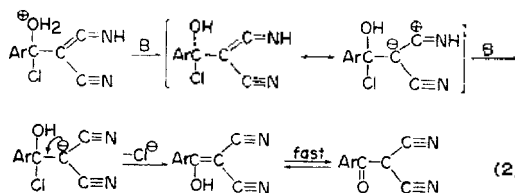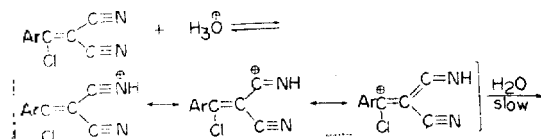| [CH_3COO^-]	$k_{obsd.}$ (sec^{-1})	$k_{calcd.}$ (sec^{-1})
0.01	6.22×10^{-7}	7.00×10^{-7}
0.02	7.44×10^{-7}	9.64×10^{-7}
0.05	1.29×10^{-6}	1.82×10^{-6}
0.10	2.30×10^{-6}	2.52×10^{-6}
0.15	2.70×10^{-6}	2.96×10^{-6}
0.20	3.00×10^{-6}	3.34×10^{-6}
0.25	3.13×10^{-6}	3.58×10^{-6}
0.50	4.06×10^{-6}	4.28×10^{-6}
1.00	4.94×10^{-6}	5.34×10^{-6}
1.20	5.18×10^{-6}	5.44×10^{-6}

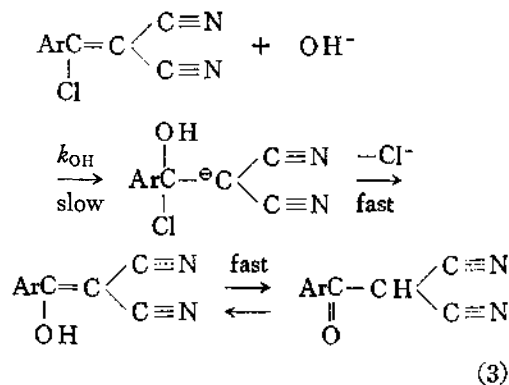Fig. 3. General base catalyzed hydrolysis of DPC at pH 4.65 and 25 °C.

For explaining these rate terms, following addition-eliminaton mechanism is proposed.
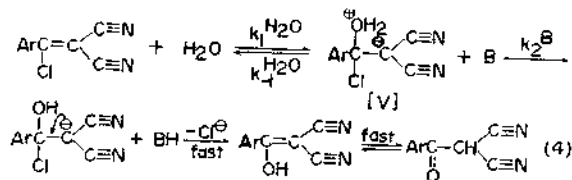
In this mechanism, the first step of the hyd-

(2)

rolysis in acidic media is a protonation of nitrile and second step is the rate-determining step.

Above pH 7.5, as the case of β-nitrostyrene[13] the rate of this reaction is propotional to hydroxide ion concentration. Therefore, the mechanism of hydrolysis in basic media is,

(3)

As shown as Fig. 2 and Table 3, the hydrolysis of DPC is catalized by all base present reaction, however the rate of hydrolysis is not propotional to the concentration of general base. These facts suggest that the reaction mechanism is complicate as the case of β-nitrostyrene[14], and we postulate following reaction mechanism;

(4)

This mechanism was identical with that suggested by Rapoport[21] in the case of vinyllic substitution of DPC by aromatic amines. The final product, ketone, is identified with 2,4-

Table 3. pKa and catalytic constant of bases for hydrolysis of DPC at 25 °C.

Base	pKa	$k_1^{H_2O}k_2^B/k_{-1}^{H_2O}$(1/mole·sec)
H_2O	−1.7	3.10×10^{-9}
$ClCH_2COO^-$	2.82	8.83×10^{-6}
$HCOO^-$	3.78	2.85×10^{-5}
CH_3COO^-	4.65	3.56×10^{-5}
$H_2PO_4^-$	7.21	1.68×10^{-3}
OH^-	15.7	285

dinitrophenylhydrazine. Appling steady-state approximation with respect to(V), k_0 is given as following;

$$\frac{1}{k_0}=\frac{1}{k_1}+\frac{1}{k_1/k_{-1}(k_2^B\Sigma(B))} \qquad (5)$$

If water and hydroxide ion are the only bases present, equation(5) becomes

$$\frac{1}{k_0}=\frac{1}{k_1}+\frac{1}{k_1/k_{-1}(k_2^{H_2O}(H_2O)+k_2^{OH}(OH^-))} \qquad (6)$$

At high general base concentration, k_0 takes 5.18×10^{-6} which is the limiting value of general base catalysis in *Fig.* 3. Since at low pH, $k_2^{OH}(OH^-)$ is negligible compared to the $k_2^{H_2O}$· (H_2O), the value of $k_1/k_{-1}(k_2^{H_2O}(H_2O))$ can be determined from the k_1 and observed rate constant(k_t) and is found to be 3.32×10^{-7} sec^{-1}. The data at pH 5.00 gave the value 2.85×10^{-2} sec^{-1} for $k_1k_2^{OH}/k_{-1}$. This measures the efficiency of hydroxide ion as the base catalyst, B, in our mechanism.

The values of the ratio, $k_1^{H_2O}k_2^B/k_{-1}^{H_2O}$ calculated by equation (5) and the pKa of the bases are given in *Table* 3 and *Fig.* 4 shows the Brфnsted plot. Note that the catalytic constants, k_2 cannot be separated from the hydration equilibrium constant $k_1^{H_2O}/k_{-1}^{H_2O}$.

As the result, if only water and hydroxide ion

are present k_0 becomes

$$\frac{1}{k_0}=\frac{1}{5.18\times10^{-6}}+\frac{1}{3.32\times10^{-7}+2.85\times10^2(OH^-)}$$

$$k_0=\frac{1.72\times10^{-12}+1.47\times10^{-3}(OH^-)}{5.51\times10^{-6}+2.85\times10^{-2}(OH^-)} \qquad (7)$$

The nucleophilic addition constant for hydroxide ion $k_{OH}=3.20\times10$ sec^{-1} is determined from the value of $k_t=3.20\times10^{-4}$ sec^{-1} at pH 9.00 and $k_t=3.22\times10^{-3}$ sec^{-1} at pH 10.00

Similarly, the addition constant for hydronium ion $k_H=5.12\times10^{-4}$ is determined. As a result, over-all rate constant becomes

$$k_t=5.12\times10^{-4}(H^+)+$$
$$\frac{1.72\times10^{-12}+1.47\times10^{-3}(OH^-)}{5.51\times10^{-6}+2.85\times10^2(OH^-)}$$
$$+3.20\times10(OH^-)$$
$$=5.12\times10^{-4}(H^+)+$$
$$\frac{1.72\times10^{-12}+1.47\times10^{-17}/(H^+)}{5.51\times10^{-6}+2.85\times10^{-12}/(H^+)}$$
$$+3.20\times10^{-13}/(H^+) \qquad (8)$$

Fig. 2 and *Table* 1 show that the values of over all rate constant, k_t calculated by equation (8) and the dotted line represents the contribution of each rate constant. The values of calculated k_t are in good agreement with the observed.

From the rate equation, the mechanism of the hydrolsis of a DPC over wide pH range is fully explained; below pH 3 and above pH 7.5, the rate constant is propotional to the concentration of hydronium ion and hydroxide ion, respectively.

However, in the range of pH 3 to 7.5, water, hydronium ion and hydroxide ion catalyze the hydrolysis of DPC. If acetate ion is present as a general base catalyst, equation (5) becomes

$$\frac{1}{k_0}=\frac{1}{k_1}+$$
$$\frac{1}{k_1/k_{-1}(k_2^{H_2O}(H_2O)+k_2^{OH}(OH^-)+k_2^{Ac}(Ac^-))}=$$
$$\frac{k_1+k_1/k_{-1}(k_2^{H_2O}(H_2O)+k_2^{OH}(OH^-)+k_2^{Ac}(Ac^-))}{k_1(k_1/k_{-1}(k_2^{H_2O}(H_2O)+k_2^{OH}(OH^-)+k_2^{Ac}(Ac^-))}$$
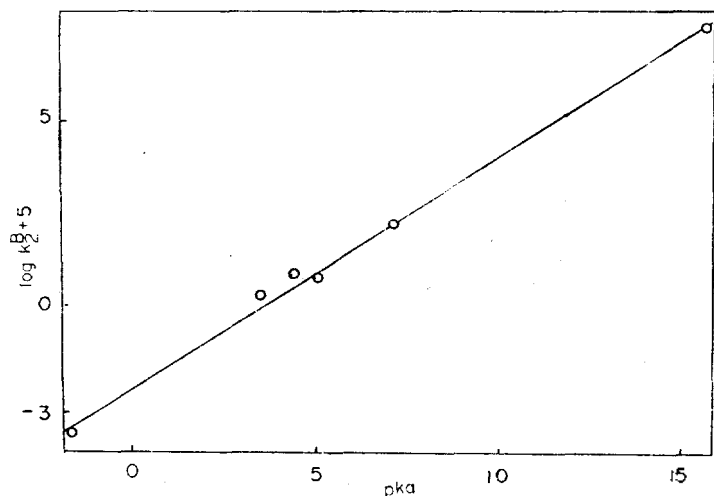$$(9)$$

Fig. 4. Br∅nsted plot for hydrolysis of DPC.

From the values of k_t, $k_1k_2(H_2O)/k_{-1}$, $k_1k_2^{OH}/k_{-1}$, $[Ac^-]=2.0 \ 10^{-2}$, $[OH^-]=4.47 \ 10^{-10}$ mol $/l$(pH=4.65) and observed rate constant k_t, the value of catalytic constant of acetate ion $k_1k_2^{Ac^-}/k_{-1}$ can be determined and is found to be 3.56×10^{-5}.

As the result, equation (9) becomes

$$\frac{1}{k_o} = \frac{1}{5.18 \times 10^{-6}} + \frac{1}{3.32 \times 10^{-7} + 2.85 \times 10^2 \times 4.47} \\ \overline{\times 10^{-10} + 3.65 \times 10^{-5}[Ac^-]}$$

$$k_o = \frac{2.38 \times 10^{-12} + 1.84 \times 10^{-10}[Ac^-]}{5.64 \times 10^{-6} + 3.56 \times 10^{-5} \ [Ac^-]} \quad (10)$$

Therefore, over-all rate constant becomes

$$k_t = 1.13 \times 10^{-8} \\ \therefore \frac{2.38 \times 10^{-12} + 1.84 \times 10^{-10}[Ac^-]}{5.64 \times 10^{-6} + 3.56 \times 10^{-5} \ [Ac^-]} \\ + 1.47 \times 10^{-8} \quad (11)$$

Table 2 and *Fig.* 3 show that the value of over all rate[11] constant, k_t calculated by equation(11) are in good agreement with the observed. At low concentration, proton removal is rate controlling and the rate linear in base concentration. As the amount of base becomes large, hydration becomes rate controlling and k_1 approaches the

limiting values.

5. Conclusion

1) The kinetics of the hydrolysis of a DPC over a wide pH range was presented and analyzed in detail. A following rate equation which can be applied over wide pH range was obtained.

$$k_t = 5.12 \times 10^{-4}[H^+] \\ + \frac{1.72 \times 10^{-12} + 1.47 \times}{5.51 \times 10^{-6} + 2.85 \times} \\ \frac{16^{-17}/[H^+]}{10^{-12}/[H^+]} \\ + 3.20 \times 10^{-13}/[H^+]$$

2) From the rate equation the mechanism of a hydrolysis of a DPC over wide pH range is fully explained; below pH 3 and above pH 7.5, the rate constant is propotional to the concentration of hydronium ion and hydroxide ion, respectively. However, in the range of pH 3 to pH 7.5, water, hydronium ion and hydroxide ion are catalyzed the hydrolysis of DPC. Especially from pH 4 to pH 7.5 the mechanism of hydrolysis is very complicated. In this pH range hydroxide ion acts as a catalyst or a nucleophilic reagent.

Reference.

1. S. Patai, "The Chemistry of Alkene", P. 469, John Willey & Sons, New York, 1964.

2. Z. Rapporort, "Advances in Physical Organic Chemistry. ", Vol. 7, Academic Press, New York, 1969.

3. J. A. Murkiss and J. D. Gettler, *Canad. J. Chem.*, **47**, 1965(1967).

4. M. J. Kamlet and D. J. Glover, *J. Amcr. Chem. Soc.*, **78**, 4556(1956).

5. M. P. Naan and C. P. Hall, *J. Chem. Soc.* (B),

1401(1970).

6. M. Kharash and C. Fuch, *J. Org. Chem.*, **13**, 97(1948).

7) C. D. Hurd and L. L. Geishbein, *J. Amer. Chem. Soc.*, **69**, 2338(1947).

8. R. Stewart, *J. Amer. Chem. Soc.*, **74**, 4531 (1952).

9. E. A. Walker and J. R. Young, *J. Chem. Soc.*, 2045(1957).

10. S. Patai and Z. Rappoport, *J. Chem. Soc.* (B), 377(1962).

11. S. Patai and Z. Rappoport, *ibid.*, 396(1962).

12. S. Patai and Z. Rappoport, *ibid.*, 383(1962).

13. M. J. Kamlet, *J. Amer. Chem. Soc.*, **77**, 4896(1955).

14. T. I. Crowell and A. W. Francis Jr., *J. Amer. Chem. Soc.*, **83**, 591(1961).

15. T. I. Crowell and T. R. Kim, *J. Amer. Chem. Soc.*, **95**, 6781(1973).

16. W. E. Truce & D. L. Goldhamer, *J. Amer. Chem. Soc.*, **81**, 5798(1959).

17. B. Dmuchovsky, B. P. Vinegard and F. B. Zienty, *J. Amer. Chem. Soc.*, **86**, 2875(1964).

18. K. L. Mallik & M. N. Das, *Z. Physik. Chem.*, **41**, 35(1964).

19. T. R. Kim and Y. S. Choi, *This Journal*, **13**, 221(1969).

20. K. S. Kwon and T. R. Kim, *ibid.*, **13**, 289(1969).

21. Z. Rappoport and R. Ta-Shama, *J. Chem. Soc.* (B), 871(1971).

22. A. D. Josey, C. C. Dickinson, K. C. Dewhirst and B. C. Mckusick, *J. Org. Chem.*, **32**, 1941 (1967).

23. H. C. Brown and R. B. Johannson, *J. Amer. Chem. Soc.*, **72**, 2934(1950).

24. M. L. Kilpatrick, *J. Amer. Chem. Soc.*, **69**, 40 (1947).