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OXIDATIVE DEGRADATION OF SOME KETONES BY N-CHLOROSACCHARIN

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Abstract

The oxidative degradation of 2-propanone and 3-pentanone have been carried out kinetically with N-chlorosaccharin in aqueous acetic acid medium. The study indicated that rate of reaction is proportional to first power of concentration of, oxidant, and one to zero order for substrates and perchloric acid at higher concentration. The retardation in reaction velocity was observed with rise in percentage composition of acetic acid and concentration of saccharin. Added the sodium perchlorate slightly increases the rate of oxidation. H_2O^+ Cl and HOCl, the remote reacting species have been postulated that react with 1:8 and 1:2 mole of enolic ketones to form the diones as end-products. Various thermodynamic parameters were determined and mechanism was proposed with consistent of derived rate law.

Key words: Degradation, composition, vessel, consonance, conformity.

INTRODUCTION

N-chlorosaccharin is a halo oxidant with potential + 1.201 V. This industrial oxidant is non-hazardous and easy to handle. Bacchawat[1] reported that >N-Cl bond undergoes heterolytic fission in polar medium producing chloronium (Cl^+), a strong electrophile than bromonium ion (Br^+). The anion of saccharin can be stabilized by resonance to acyl and sulphonyl group which provide large orbital for electron delocalisation.[2]

The ketones (2-propanone and 3-pentanone) comprise a group of organic compounds possessing the reactive carbonyl group, exhibit a well known phenomenon of tautomerism. This involves a shift of α–H atom to the carbonyl oxygen producing a reactive enol depending on the structural alternation of the compound in presence of electron donating and electron attracting groups. This makes the mechanism of oxidation somewhat complicated and interesting.

The survey of literature pertaining to the oxidation involving N-halo-oxidant (NCSA) reveals that alcohols[3], hydroxy acids[4], aldehyde[5], 2-alkanones[6], have been studied. The kinetics studies of ketones have also been acclaimed by employing different oxidants such as CAT[7], BAT[8], NBSA[9], $KMnO_4$[10], H_2CrO_4 [11], SeO_2 [12], Ce(IV)[13] etc.

The present work is a modest attempt to incorporate the oxidation of wide range of ketones with NCSA. Owing to presence of reactive carbonyl group, enolic content and profile H_2O^+Cl reacting species and to throw light insight the reaction paths and its vital activity the author has undertaken this task of kinetic probe.

EXPERIMENTAL

All the chemicals employed in the study were of either G.R.S. Merck, k-light and B.D.H. grade. The oxidant's solution was prepared as suggested by Chattway[14] in 100% acetic acid (B.D.H.) and kept either amber coloured flask or black paper wrapped around it to save it from the action of diffused day light which alters appreciably its concentrations. The preliminary experiments were preformed for the oxidation of 2-propanone and 3-pentanone with NCSA to choose the appropriate conditions separately. The requisite volume of oxidant and substrate were taken in a separate glass stoppered flasks with other required reagents were placed in a thermostat maintained at experimental temperature of sensitivity $\pm$ 0.1^0C. When both the solutions attained the temperature of the thermostat the solutions were mixed in reaction vessel and aliquot was withdrawn immediately and the amount of un-reacted NCSA was estimated iodometrically[15] with the help of standard solution of sodium thiosulphate using starch as an indicator. The titre value 'a' at zero time and (a-x) after regular intervals of time't' were fed in integrated form of rate equation, to evaluate rate constant.

The variation of concentrations of oxidant, substrates, $HClO_4$, salt, saccharin and different compositions of binary solvent polarity of acetic acid-water were studied. The thermodynamic parameters and stoichiometry were also determined. The product analysis was carried out chromatographically and by other existing methods.

RESULTS AND DISCUSSION

The results obtained for kinetic investigation of ketones indicate that order with respect to [NCSA] is one, while order falls from 1 to 0 at higher concentration of substrates (Fig. 1). The double reciprocal plot suggested the formation of intermediate complex between enolic ketones and active species (H_2O^+Cl) of N-chlorosaccharin (Fig. 2). The addition of $HClO_4$ accelerates the reaction velocity and attains limiting value at its higher concentration indicating that order falls from one to zero. The slope of lg-lg plot (Fig. 3) is nearly lies between 1 to 0. This may be attributed due to the protonated species of NCSA which may exist in the solution in presence of $HClO_4$[16]. Similar observations have also been reported by oxidation of ketones by V(V)[17], NCSA[6] etc.

It has been found that the reaction velocity of ketones under probe decreases with dielectric constant of the medium (Table: 1). Similar pattern of kinetic features has also been reported in oxidation of ketones by NBSA[9], this probably involve ion-dipole or dipole-dipole in the slow rate determining step. The primary salt ($NaClO_4$) effect is almost negligible suggested that one of the reactants involved in the slow step should be a neutral molecule. The rate of oxidative degradation of ketones was found to diminish by adding varying concentration of saccharin showed that it is a pre-equilibrium product.

The mole ratio 1:8 and 1:2 have been determined for 2-propanone and 3-pentanone stoichiometrically. Carbon dioxide and 2:3 diones were reported as the oxidation products of 2-propanone and 3-pentanone besides saccharin, which were qualitatively identified by existing conventional methods[18,19]. The study completely rules out the formation free radicals. Unlike other researcher, the author postulates H_2O^+Cl and HOCl as the active species. The rate of enolisation determined by bromination method was found to be much faster than the rate of oxidation. Hence enol was considered to be involved in the rate determining steps.

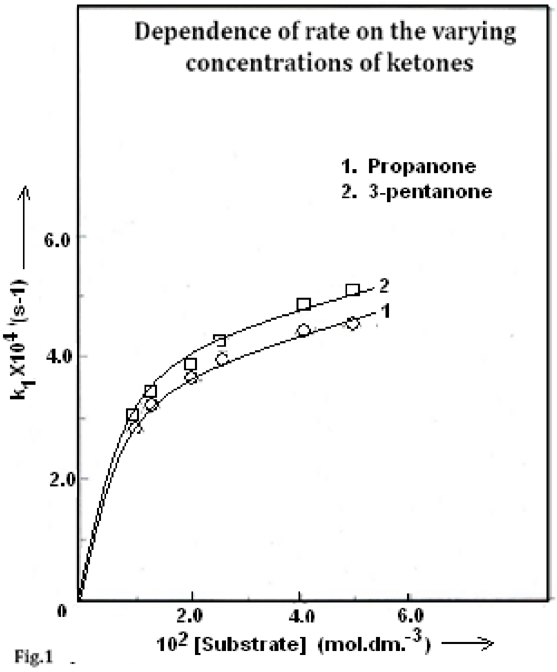


Fig.1

[NCSA]10^3 (mol.dm.$^{-3}$)=2.50(1,2);
[H +](mol.dm.$^{-3}$) =0.005(1,2);
HOAc-H_2O % (v/v) =30(1,2);
Temp. K =328(1,2)

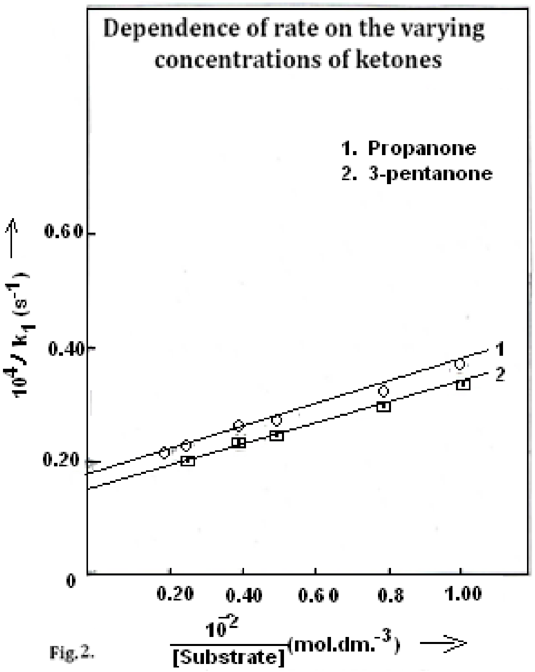


Fig.2.

[NCSA]10^3 (mol.dm.$^{-3}$)=2.50(1,2);
[H +](mol.dm.$^{-3}$) =0.005(1,2);
HOAc-H_2O % (v/v) =30(1,2);
Temp. K =328(1,2)

Table: 1

Dependence of rate on Dielectric constant of the medium

10^3 [NCSA] (mol dm^{-3}) = 2.50 (1, 2) ; 10^2 [substrate] (mol dm^{-3}) = 1.25 (1, 2) ;
[H^+] (mol dm^{-3}) = 0.005 (1, 2) ; Temperature K = 328 (1,2).

r. No.	[HOAc-H_2O] % (v/v)	$\frac{10^3}{D}$	2-propanone	3-pentanone
			← 10^4 k_1 (s^{-1}) →	
			(1)	(2)
1.	10	15.50	3.62	3.80
2.	20	17.17	3.39	3.60
3.	30	19.15	3.25	3.40
4.	40	21.98	2.81	3.12
5.	50	25.64	2.39	2.78
6.	60	30.36	1.92	2.37

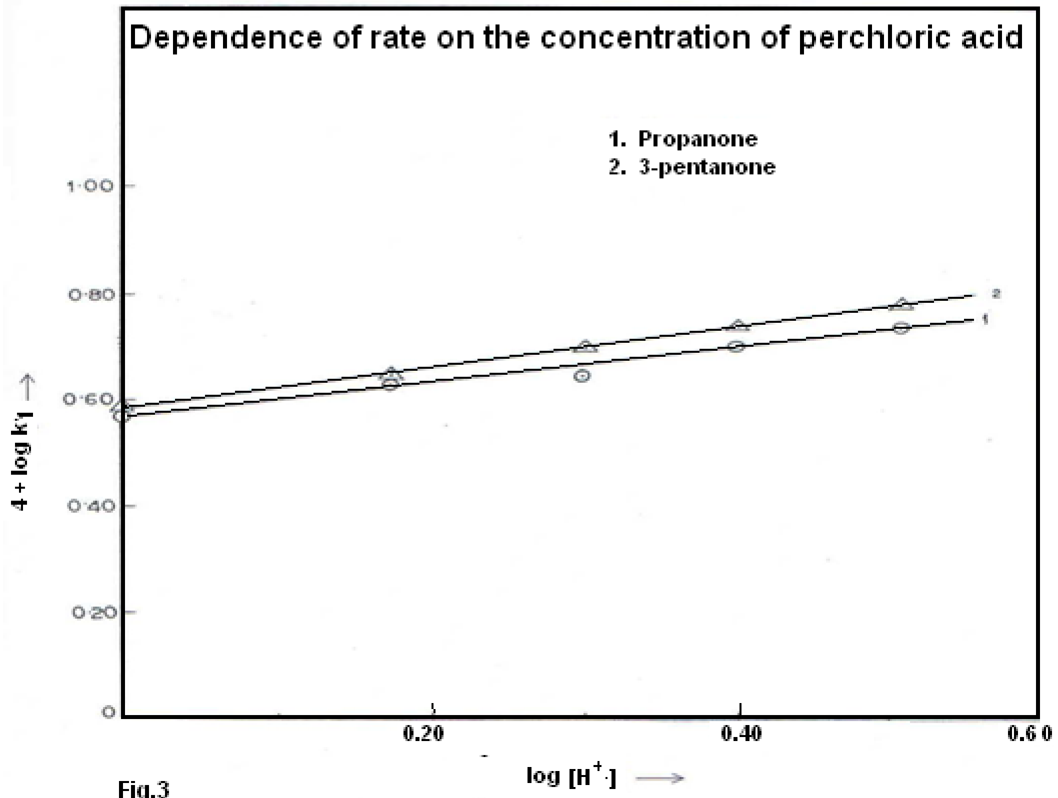


Fig.3

[NCSA]10^3 (mol.dm.$^{-3}$)=2.50(1.2):
10^2 [Substrate] =1.25(1,2)
HOAc-H_2O % (v/v) =30(1,2);
Temp. K =328(1,2)

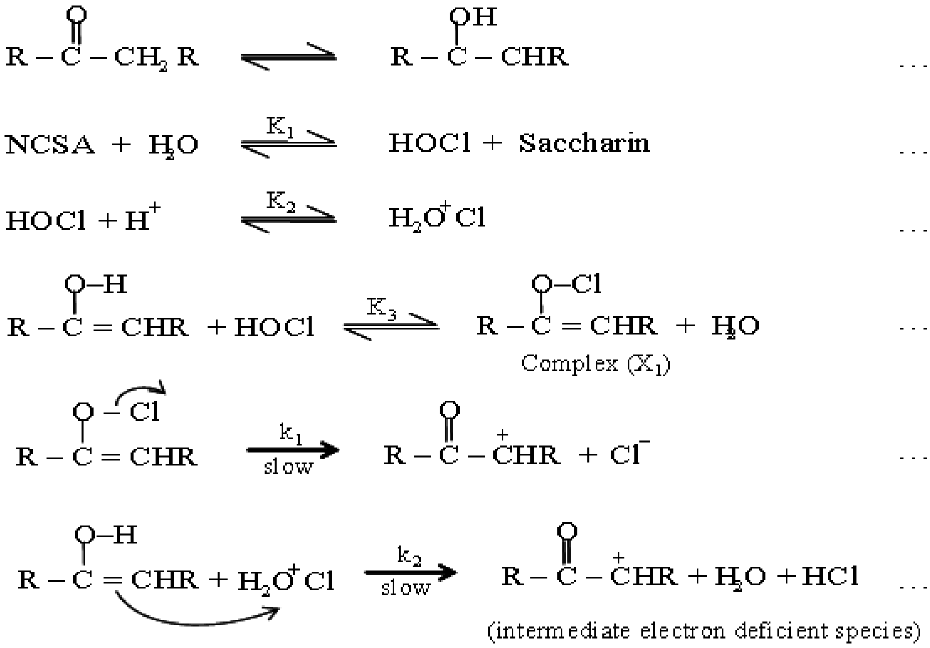
Table: 2

Thermodynamic parameters for ketone – NCSA system

Sr. No.	Substrate	Ea kJ mol^{-1}	A (s^{-1})	$\Delta H^\#$ kJ mol^{-1}	$\Delta G^\#$ kJ mol^{-1}	$-\Delta S^\#$ JK^{-1} mol^{-1}
1.	2- propanone	86.78 $\pm$ 0.70	1.99×10^{10} $\pm$ 0.20	85.80 $\pm$ 0.91	90.59 $\pm$ 0.19	14.51 $\pm$ 0.03
2.	3-pentanone	55.32 $\pm$ 0.40	2.33×10^5 $\pm$ 0.14	$\pm$ 54.26 $\pm$ 0.53	91.16 $\pm$ 0.87	110.24 $\pm$ 0.02

MECHANISM

On the basis of the kinetic findings the general mechanism may be proposed as:



$$\mathrm{R-\overset{\overset{O}{\|}}{C}-CH_2R \rightleftharpoons R-\overset{\overset{OH}{|}}{C}-CHR} \quad \text{...........} \tag{1}$$

$$\mathrm{NCSA + H_2O \overset{K_1}{\rightleftharpoons} HOCl + Saccharin} \quad \text{...........} \tag{2}$$

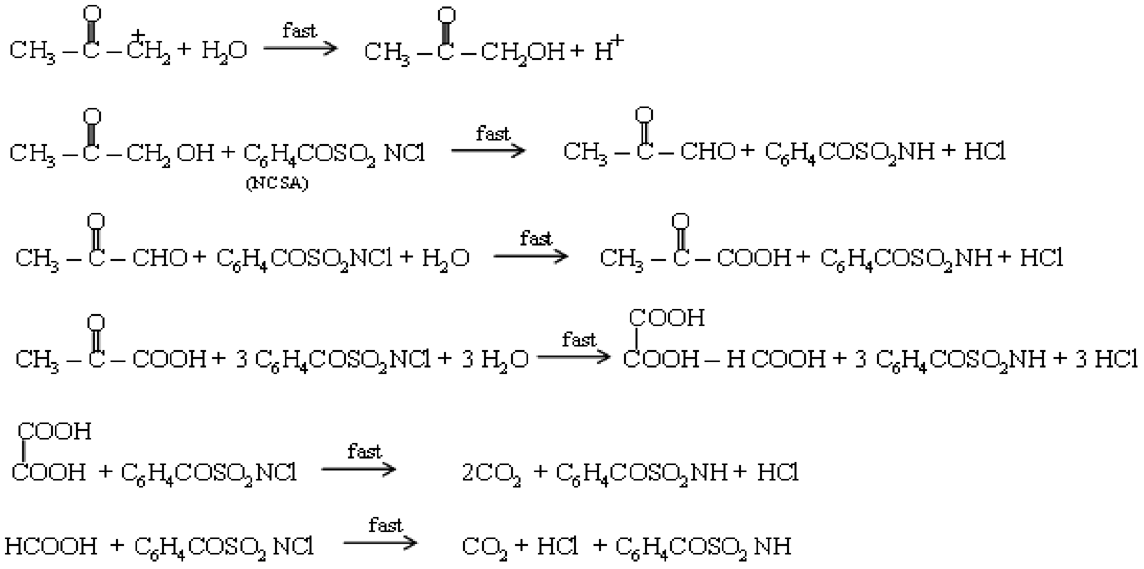
$$\mathrm{HOCl + H^+ \overset{K_2}{\rightleftharpoons} H_2O^+Cl} \quad \text{...........} \tag{3}$$

$$\mathrm{R-\overset{\overset{O-H}{|}}{C}=CHR + HOCl \overset{K_3}{\rightleftharpoons} \underset{\text{Complex }(X_1)}{R-\overset{\overset{O-Cl}{|}}{C}=CHR} + H_2O} \quad \text{...........} \tag{4}$$

$$\mathrm{R-\overset{\overset{O-Cl}{|}}{C}=CHR \xrightarrow[\text{slow}]{k_1} R-\overset{\overset{O}{\|}}{C}-\overset{+}{C}HR + Cl^-} \quad \text{...........} \tag{5}$$

$$\mathrm{R-\overset{\overset{O-H}{|}}{C}=CHR + H_2O^+Cl \xrightarrow[\text{slow}]{k_2} \underset{\text{(intermediate electron deficient species)}}{R-\overset{\overset{O}{\|}}{C}-\overset{+}{C}HR} + H_2O + HCl} \quad \text{...........} \tag{6}$$

For 2-propanone



$$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-\overset{+}{C}H_2 + H_2O \xrightarrow{fast} CH_3-\overset{\overset{O}{\|}}{C}-CH_2OH + H^+}$$

$$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-CH_2OH + \underset{(NCSA)}{C_6H_4COSO_2NCl} \xrightarrow{fast} CH_3-\overset{\overset{O}{\|}}{C}-CHO + C_6H_4COSO_2NH + HCl}$$

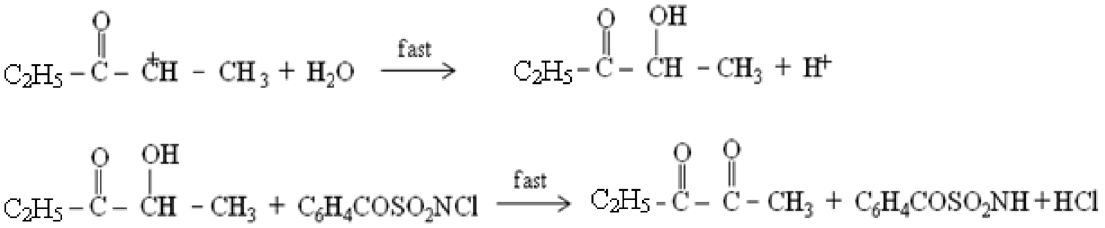
$$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-CHO + C_6H_4COSO_2NCl + H_2O \xrightarrow{fast} CH_3-\overset{\overset{O}{\|}}{C}-COOH + C_6H_4COSO_2NH + HCl}$$

$$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-COOH + 3\,C_6H_4COSO_2NCl + 3\,H_2O \xrightarrow{fast} \overset{\overset{COOH}{|}}{COOH} - HCOOH + 3\,C_6H_4COSO_2NH + 3\,HCl}$$

$$\mathrm{\overset{\overset{COOH}{|}}{COOH} + C_6H_4COSO_2NCl \xrightarrow{fast} 2CO_2 + C_6H_4COSO_2NH + HCl}$$

$$\mathrm{HCOOH + C_6H_4COSO_2NCl \xrightarrow{fast} CO_2 + HCl + C_6H_4COSO_2NH}$$

For 3-pentanone



$$\mathrm{C_2H_5-\overset{\overset{O}{\|}}{C}-\overset{+}{C}H-CH_3 + H_2O \xrightarrow{fast} C_2H_5-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{C}H-CH_3 + H^+}$$

$$\mathrm{C_2H_5-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{C}H-CH_3 + C_6H_4COSO_2NCl \xrightarrow{fast} C_2H_5-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3 + C_6H_4COSO_2NH + HCl}$$

Rate law

$$\text{Keto} \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \text{Enol}$$

$$\text{NCSA} + H_2O \overset{K_1}{\rightleftharpoons} \text{HOCl} + \text{Saccharin (s)}$$

$$\text{HOCl} + H^+ \overset{K_2}{\rightleftharpoons} H_2O^+Cl$$

$$\text{Enol} + \text{HOCl} \overset{K_3}{\rightleftharpoons} \underset{\text{complex}}{X_1} + H_2O$$

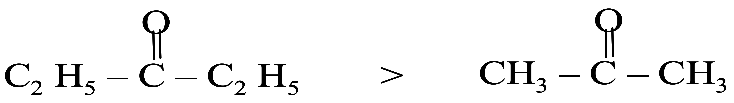
$$X_1 \xrightarrow[\text{slow}]{k_1} \text{products}$$

Applying steady state condition, the final derived rate law is

$$k_{obs} = \frac{[\text{Enol}]\{(K_1 K_3 k_1 + K_1 K_2 k_2 [H^+]\}}{[S] + K_1 + K_1 K_2 [H^+] + K_1 K_3 [\text{Enol}]}$$

The proposed reaction mechanism is in good conformity with rate expression.

In the present study the observed order of reactivity is



$$C_2H_5 - \overset{\overset{\displaystyle O}{\|}}{C} - C_2H_5 \quad > \quad CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3$$

(3-pentanone) (2-propanone)

The above order of reactivity is in consonance with the number of alkyl group, which increases the rate of oxidation indicating a dominating hyper conjugative effect in the enol content. No such hyper conjugation could occur in the intermediate from 2-propanone due to lack of β-H atom. This may account for the slow oxidation of 2-propanone.

Generally, the high value of energy of activation (Table: 2) suggests the reaction to be slow. The values of $\Delta S^{\#}$ for 2-propanone and 3-pentanone lies between 14.51 to 110.24 JK mol^{-1} suggested C-H bond fission in the rate determining step. The isokinetic temperature 352 K was evaluated well above the experimental temperature suggested that reactions are enthalpy controlled.

References

1. Bachhawat, J.M. and Matur, N.C. : Indian J. Chem., 9, 1335, (1971).
2. Zabicky, Jacob : “The chemistry of Amides” Inter Science Publishers, John Wiley and Sons, 374, (1970).
3. Khan, M.U., Tiwari, R.K., Verma, J.K. and Gupta, H.D. : Oxid. Commun. 20, No.1, 117-123, (1997).
4. Singh, V.P., Khan, M.U., and Chauhan, D.B.S. : Oxid. Commun,. 20, No.1, 124-131, (1997).
5. Nigam, S.K., Khan, M.U., Tiwari, Saras, Dwivedi, H.P. and Singh, P.K. : Asian J. Chem., 16, No.2, 761-766, (2004).
6. Khan, Shahnaz, Nigam, S.K., Dwivedi, H.P. and Singh, P.K. : Asian J. Chem., 16, No.2, 761-766, (2004).
7. Bose, A.K., Sanehi, R. and Mushran, S.P. : J. Indian Chem., Soc., 50, 197, (1973).
8. Singh, Bharat, Singh (Miss) Deepika, Rajendra Chand, and Singh, A.K. : J. Indian Chem. Soc., 64, 56, (1987).
9. Vijay Mohan, K., RaghuNath Rao, P., and Sundaram, E.V. : J. Indian Chem., 61, 225, (1984).
10. Pillai, M.K. and Thirunavukkarasu, A. : Indian J. Chem., 20, 583, (1981).
11. Khandual, N.C., Nayak, P.L., and Sathpathy, K.K. : J. Chem. Soc., 11, 328, (1974).
12. Riley, H.L., Morley, J.F. and Friend, N.A.C. : J. Chem. Soc., 1875, (1932).
13. Shorter, J. and Hinshelwood, C.N. : J. Chem. Soc., 3276, (1950).
14. Chattaway : J. Chem. Soc. 87, 1884, (1905).
15. Barkat, M.A., and Abdel Wahab, M.F. : Analyst, Chem., 26, 1973, (1954).
16. Murthy, G.S.S., Sethuram, B. and Rao, T.N. : Indian J. Chem., 15A, 880, (1977).
17. Chithambarathanu Pillai, G., Rajaram, J. and Kuricose, J.C. : Indian J. Chem., 19A, 585, (1980).
18. Treibs, W. and Vogt, R. : Ber, 94, 1739, (1961).
19. Vogel, A.I. : “Elementary practical organic chemistry” Part, Qualitative organic analysis, IInd Edn. 113, (1974).

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