

*Reactivity and Oxidation Kinetics of Cyclic
Ketones by Benzimidazolium Fluorochromate*

K. Anbarasu and A. Samidurai

Research Journal of Agricultural Sciences
An International Journal

P- ISSN: 0976-1675

E- ISSN: 2249-4538

Volume: 13

Issue: 03

Res. Jr. of Agril. Sci. (2022) 13: 589–593

 C A R A S



Reactivity and Oxidation Kinetics of Cyclic Ketones by Benzimidazolium Fluorochromate

K. Anbarasu*¹ and A. Samidurai²

Received: 12 Jan 2022 | Revised accepted: 09 Apr 2022 | Published online: 12 May 2022

© CARAS (Centre for Advanced Research in Agricultural Sciences) 2022

ABSTRACT

The oxidation and mechanistic studies of cyclohexanone by (BIFC) benzimidazolium fluorochromate have been investigated in being of perchloric acid with binary compounds (acetic acid and water). Rate data interpret unit order dependence concerning both BIFC and H⁺ ions and fractional order concerning substrate. The rate of reactions increased with an increase in the portion of acetic acid. The hydrogen ion concentration plays as a catalyst in the chemical reaction mixture. The gain of Mn²⁺ ions retard the reaction rate conforming bi-electron conveyance process in this reaction. The oxidation product 2-hydroxy cyclohexanone was identified. Based on kinetic studies and product analysis; enthalpy, entropy, free energy and energy of activation have been calculated and the probable mechanism was discussed. Furthermore, some of the cyclic ketones were used to check the reactivity. Its reactivity of the cyclic ketones viz., cyclohexanone < cycloheptanone < cyclopentanone < cyclooctanone.

Key words: Kinetics, Oxidation, BIFC, Cyclic ketone, Mechanism, Reactivity

Chromium has frequently and extensively been used as an oxidizing agent for both preparative and analytical chemistry. Benzimidazolium fluorochromate¹ is one of the chromium (VI) oxidants. It is mild, more stable, and easily stored to compare with other chromium (VI) reagents. It is suitable for most oxidation reactions in a kinetic manner. Chromium (VI) is supposed to be highly toxic and hazardous. Whereas, the reduced chromium (III) is biologically active [1]. Chromium (VI) compounds act as irritants of the skin and mucous membranes. On the contrary chromium (III) and chromium (IV) are non-toxic and biologically active. Cyclic ketones are the most widespread and principal raw materials in industrial applications. Cyclic ketones were oxidized by different chromium compounds [2-4] and the reactivity of cyclic ketones by different chromium compounds [5-8]. Few organic substrates were oxidized by benzimidazolium fluorochromate [9-11]. In the present investigation, the oxidation kinetics of cyclanones by BIFC has been done the work in an aqueous acetic acid to propose a suitable mechanism. From this investigation, the reactivity of cyclic ketones has been explained. During this oxidation, the chromium (VI) compound of BIFC is reduced to chromium (IV), i.e., non-toxic and biologically active. Better

understanding the reactivity and oxidation of such compounds to harmless products.

MATERIALS AND METHODS

The oxidant (BIFC) can be prepared from chromium trioxide, benzimidazole and hydrofluoric acid in the calculated molar ratio. It is obtained as crystals with yellow-orange. The compound melted at 195°C (literature m.p. 194 – 196°C). BIFC was prepared with 0.1 molar solution and standardized using a digital spectrometer (ELICO CL 23 MINI SPEC) $\lambda_{\max} = 470$ nm. The structure of Benzimidazolium fluorochromate was shown (Fig 1). Cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone (all Sigma Aldrich) samples were distilled directly and physical constants further checked their purity. The solvent acetic acid (E Merck) was distilled by Orton and Bradfield [13] method. Perchloric acid, sodium perchlorate, acrylonitrile and manganous sulphate (E Merck) were purchased as AnalaR grade and used as such. The blank reaction was checked using these reagents properly. All the reagents were prepared using distilled water.

The oxidation reactions were maintained below the pseudo-first-order system in presence of the perchloric acid. The absorbance was studied using a digital spectrometer (ELICO CL 23 MINI SPEC) $\lambda_{\max} = 470$ nm. The reaction solutions were placed in a thermostat at a stable temperature $\pm 0.5^\circ\text{C}$ accuracies for 15 minutes. The temperature was obsessed using a RAAGAA thermostat to be maintained $\pm 0.5^\circ\text{C}$. In the reaction flask, all the reaction solution mixtures have maintained the temperature and the reaction can be started by adding an oxidant in the known volume. Immediately, the

* K. Anbarasu

✉ arasu007@gmail.com

¹⁻² Department of Chemistry, Arignar Anna Government Arts College, Musiri - 621 211, Tiruchirappalli District, Tamil Nadu, India

minimum volume of the reaction mixture was transferred into the quartz cuvette and again placed in the same reaction flask.

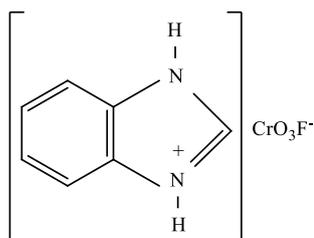


Fig 1 Benzimidazolium fluorochromate

The reactions were monitored spectrometrically for changing the concentration of unreacted oxidants. The rate constant (pseudo-first-order) for each run was determined from this slope values of graph between log Optical Density (OD) and time. The results were reproducible within $\pm 2\%$ error.

Product analysis

From the aforesaid experimental conditions of kinetic determinations, the solutions of oxidant, substrate and perchloric acid were mixed and kept under nitrogen atmosphere for the completion of the reaction at least 24 hours. The product

was filtered with a suitable solvent and the lower layer (organic) was washed with water dehydrated over anhydrous sodium sulphate. The products of oxidation of cyclic ketones were found to be corresponding dibasic acids and they were identified as the corresponding 2-hydroxy cyclic ketones. The products were also detected by spectral studies and their colour reaction with copper-benzidine acetate (spot test [14]).

RESULTS AND DISCUSSION

The oxidation kinetic measurements of some selected cyclic ketones were followed using the same oxidant in an aqueous acetic acid environment.

Oxidant effect: The oxidation of cyclohexanone by BIFC was studied at several concentrations of BIFC, cyclohexanone, perchloric acid, acetic acid, double distilled water and temperature remains constant. The order of BIFC was unity as obtained from the plot between log Optical Density and time. The rate constants k_1 (Table 1) were obtained from the slopes such plots and remain unaffected on changing the concentration of BIFC. Such observations have been reported by several authors [4], [7], [9]. This may be due to the formation of chromium (VI) with acid in the form of acidic chromate [15].

Table 1 Rate data for the oxidation of cyclohexanone by BIFC at 308K

[BIFC] 10^3 (mol dm^{-3})	[Cyclo hexanone] 10^1 (mol dm^{-3})	[H ⁺] (mol dm^{-3})	Percent acetic Acid:Water (v/v)	[NaClO ₄] 10^4 (mol dm^{-3})	[MnSO ₄] 10^4 (mol dm^{-3})	$k_1 10^4$ (s^{-1})
2.0	6.0	0.8	50:50	-	-	4.92
3.0	6.0	0.8	50:50	-	-	4.85
4.0	6.0	0.8	50:50	-	-	4.79
5.0	6.0	0.8	50:50	-	-	4.94
6.0	6.0	0.8	50:50	-	-	4.90
3.0	3.0	0.8	50:50	-	-	3.43
3.0	4.5	0.8	50:50	-	-	4.12
3.0	6.0	0.8	50:50	-	-	4.85
3.0	7.5	0.8	50:50	-	-	5.53
3.0	9.0	0.8	50:50	-	-	6.08
3.0	6.0	0.4	50:50	-	-	2.94
3.0	6.0	0.8	50:50	-	-	4.85
3.0	6.0	1.2	50:50	-	-	7.20
3.0	6.0	1.6	50:50	-	-	9.50
3.0	6.0	2.0	50:50	-	-	12.20

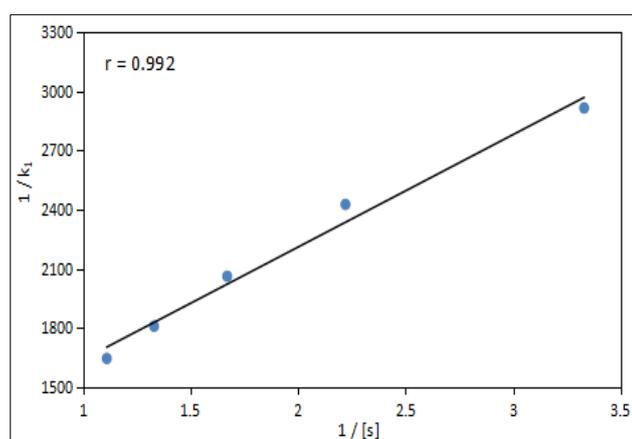


Fig 2 Michaelis-Menton Plot

Substrate effect: The rate constant was linearly related to changing the strength of cyclohexanone (Table 1), the order was calculated from the linear plot of log k_1 against log [s]. It was the slope value 0.528 and treated as fractional order. A plot of $1/k_1$ against $1/[s]$ gave a straight line (Fig 2) which does not

pass-through origin indicating Michaelis-Menten type kinetics of this oxidation reaction. This indicates a complex formation between cyclic ketone with BIFC.

Catalytic effect: At a constant concentration of substrate, oxidant, solvent and temperature was maintained and varying the concentration of perchloric acid; the reaction rates (k_1) were increased with rise in the concentration of perchloric acid [16] (Table 1). The linear plot with fractional slope (0.881) can be obtained between log k_1 and log [H⁺]. The reaction is evidenced to follow fractional-order kinetics since the oxidant is in the protonated form.

Salt and solvent effect: The addition of sodium perchlorate in the oxidation reaction was negligible of rate constants. It indicates the participation of polar species in the rate determining step of the reaction and also not to involve ion-ion type. Five different percentages of acetic acid were modified in the oxidation reaction. The rate of the reactions changed with rise in the percentage of acetic acid (Table 2). The linear plot with a positive slope can be obtained between log k_1 and $1/D$. It may be probably due to ion-dipole interaction [17]

in the slow step of the reaction. This is due to the polar character of the transition state as compared to the reactants.

Electron transfer effect: The nature of electron transfer can be determined by the reaction with changing the dilution of

manganous sulphate (Table 2). It decreases the rate of reaction and the reaction may involve a two-electron process. This is due to the polar character of transition state as compared to the reactants. Also, the absence of free radical mechanism due to nil effect of added acrylonitrile [18].

Table 2 Rate Data for the Oxidation of Cyclohexanone by BIFC at 308K

[BIFC]10 ³ (mol dm ⁻³)	[Cyclo hexanone] 10 ¹ (mol dm ⁻³)	[H ⁺] (mol dm ⁻³)	% Acetic Acid:Water (v/v)	[NaClO ₄] 10 ⁴ (mol dm ⁻³)	[MnSO ₄] 10 ⁴ (mol dm ⁻³)	k ₁ 10 ⁴ (s ⁻¹)
3.0	6.0	0.8	40:60	-	-	3.09
3.0	6.0	0.8	45:55	-	-	3.85
3.0	6.0	0.8	50:50	-	-	4.85
3.0	6.0	0.8	55:45	-	-	5.95
3.0	6.0	0.8	60:40	-	-	7.42
3.0	6.0	0.8	50:50	5.0	-	4.99
3.0	6.0	0.8	50:50	10.0	-	4.92
3.0	6.0	0.8	50:50	15.0	-	4.62
3.0	6.0	0.8	50:50	20.0	-	4.81
3.0	6.0	0.8	50:50	-	5.0	3.67
3.0	6.0	0.8	50:50	-	10.0	3.29
3.0	6.0	0.8	50:50	-	15.0	3.09
3.0	6.0	0.8	50:50	-	20.0	2.84

Temperature effect: At four different temperatures, the rate constants were measured at constant [BIFC], [cyclohexanone] and [perchloric acid]. The result shows to raise the rate of reaction with raising the temperature. Enthalpy, entropy, free energy and energy of activation can be calculated (Table 3) using Eyring's equation [19-20] from the plot between log k₂/T and 1/T. This shows that the Arrhenius equation is valid in this case. It has been pointed out that if the small value of entropy of activation is negative and the reaction will be slow.

Mechanism: The cyclohexanone was oxidized by benzimidazolium fluorochromate to give 2-hydroxy cyclohexanone in presence of perchloric acid. This oxidation reaction shows first-order concerning BIFC, fractional-order concerning cyclohexanone, hydrogen ion concentration. The chromium (VI) concentration was very much lower [21]. From the above kinetic results, the favourable mechanism was projected and desirable rate law was delivered.

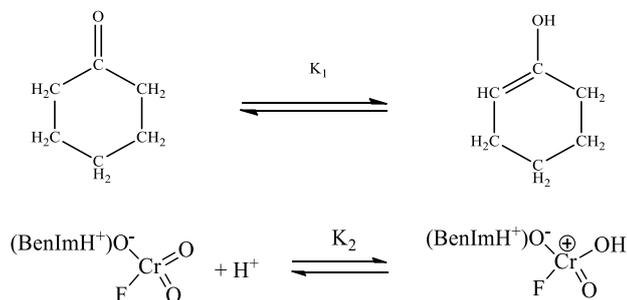
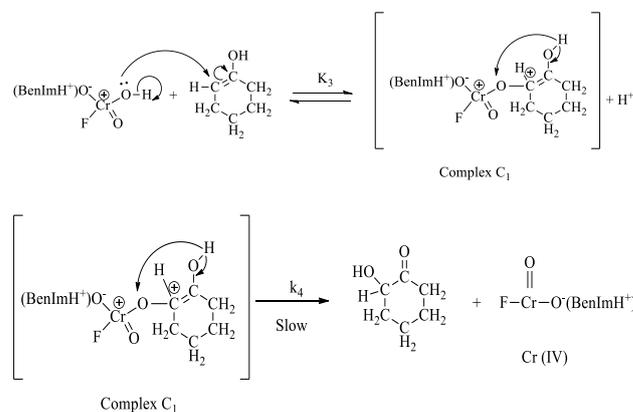


Table 3 Thermodynamic and activation constants for the oxidation of cyclic ketones by BIFC

Cyclic Ketones	Order w.r.to substrate	k ₁ x 10 ⁴ (s ⁻¹)				ΔH [#] (kJmol ⁻¹)	-ΔS [#] (JK ⁻¹ mol ⁻¹)	ΔG [#] (kJmol ⁻¹) at 303 K	E _a (kJmol ⁻¹) at 303 K
		303 K	313 K	323 K	333 K				
Cyclo hexanone	0.528	4.85	8.48	12.80	19.60	31.05	132.96	71.34	33.57
Cyclo heptanone	0.641	12.27	15.88	19.97	25.69	15.97	187.84	72.88	18.49
Cyclo pentanone	0.655	16.47	19.98	24.51	30.09	12.94	196.79	72.57	15.46
Cyclo octanone	0.541	19.45	25.51	31.12	37.74	14.15	192.11	72.36	16.67

$$[\text{BIFC}] = 3.0 \times 10^{-3} \text{ mol dm}^{-3} [\text{Cyclic Ketones}] = 6.0 \times 10^{-1} \text{ mol dm}^{-3} [\text{H}^+] = 0.8 \text{ mol dm}^{-3} \text{ cOH:H}_2\text{O} = 50:50 \text{ (v/v)}$$



$$\begin{aligned} \text{Rate} &= k_4 [\text{Complex}] \\ &= k_4 K_3 [\text{BIFCH}^+] [\text{S}^*] \\ &= k_4 K_3 K_2 [\text{BIFCH}^+] [\text{S}^*] [\text{H}^+] / (1 + K_2 [\text{H}^+]) \\ &= k_4 K_3 K_2 K_1 [\text{BIFCH}^+] [\text{S}] [\text{H}^+] / (1 + K_2 [\text{H}^+]) \end{aligned}$$

The projected mechanism and desirable rate law supports all the kinetic results and including the solvent effect, the negative value of entropy. Rate of reaction has been studied the substrate effect and temperature effect for the cyclic ketones viz., cyclopentanone, cycloheptanone, cyclooctanone (Table 3). All the cyclic ketones have followed the reaction under Michaelis-Menton type kinetics with fractional order and it obeys the linearity of the plot. Thermodynamic and activation parameters were calculated as mentioned above method [19-20].

The activation enthalpies and entropies were linearly related by the following equation [22-24].

$$\Delta H^\ddagger = \Delta H_0^\ddagger + \beta \Delta S^\ddagger \dots\dots\dots (1)$$

A linear plot (Fig 3) between enthalpy and entropy of activation with slope value (β) is 282.45. This slope value is isokinetic temperature from the above-mentioned equation (Equation 1). Since the β value is lower than the experimental temperature, it indicates that this oxidation reaction is an entropy-controlled reaction [25-27] and it follows a common mechanism. The linear Exner's plot with good correlation between different temperatures of the reaction rate constant. This indicates that the four cyclic ketones precede the same mechanism.

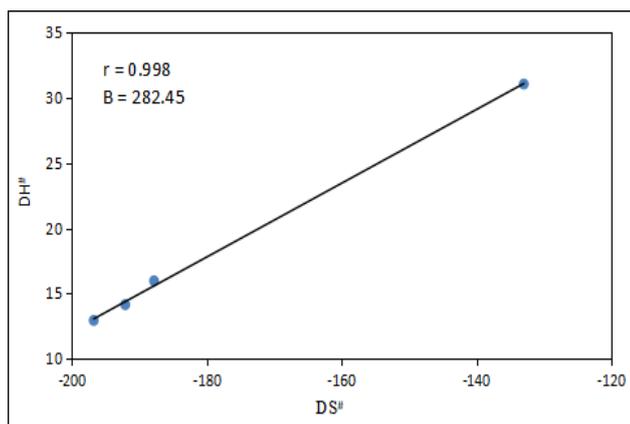


Fig 3 Isokinetic plot

Reactivity: The rate of reaction for the four cyclic ketones were analysed by the changes in strain energy between the ground state and the transition state of the process to be considered [28]. The order of reactivity of the cyclic ketones as

cyclohexanone < cycloheptanone < cyclopentanone < cyclooctanone. This order of reactivity could be rationalized based on a change in the ring system involved in passing from the initial (sp^3) to the transition state (sp^2). In the pentanone, heptanone and octanone ring system, the primary source of strain arises as a result of non-bonded interactions [29]. This type of interaction could not be involved in the hexanone ring system (staggered form). The net result would be the reactions leading to the case of non-bonded interactions in the five, seven and eight-membered ring systems would be facilitated. For a six-membered ring, any deviation from the staggered conformation would be unfavourable, since this would entail high energy of activation. This would be an account of slower in the rate of oxidation of cyclohexanone.

CONCLUSION

Oxidation kinetics of cyclic ketones have been examined in the acetic acid-water medium in being of perchloric acid. The oxidation reaction follows under the Michaelis-Menton type of kinetics and is catalysed by perchloric acid. The observed order of reactivity conforms with the order of their enol-contents, i.e., cyclohexanone < cycloheptanone < cyclopentanone < cyclooctanone.

Acknowledgement

The authors would like to thank Bharathidasan University for permitting me to do the Ph. D. research work. The Department of Chemistry, Arignar Anna Government Arts College, Musiri, is highly appreciated for allowing the research work in the laboratory.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

LITERATURE CITED

- Sivamurugan V, Rajkumar GA, Arabindoo B, Murugesan V. 2005. Selective and clean oxidation of alcohols with benzimidazolium fluorochromate under solvent-free conditions. *Indian Journal of Chemistry* 44B: 144-147.
- Ravishankar M, Sekar KG. 2004. Enhanced reactivity in the oxidation of cyclanones by pyridinium dichromate. *Afinidad* 61(512): 323-327.
- Das S, Rani ER, Mahanti MK. 2007. Kinetics and mechanism of the oxidative cleavage of cyclic ketones by quinolinium dichromate. *Kinetics and Catalysis* 48(3): 381-389.
- Venkatapathy M, Venkatesan M, Anbarasu K. 2019. Oxidation of cyclohexanone by piperidinium chlorochromate - A kinetic mechanistic Aspect. *Infokara Research* 8: 1242-1253.
- Palaniyappan AN, Ravishankar M, Sekar KG. 2008. Structure reactivity in the oxidation of cyclic ketone by quinolinium dichromate. *Asian Journal of Chemistry* 20(2): 1365-1372.
- Sekar KG, Palaniappan AN. 2008. Structural reactivity in the oxidations of cyclic ketones by quinolinium fluorochromate. *Oxidation Communications* 31(3): 606-612.
- Anbarasu K, Chandrasekar S, Venkatapathy M, Suriya S. 2018. Structure and reactivity of oxidation of cyclic ketones by quinoxalinium dichromate. *Journal of Applied Science and Computations* 5(12): 1448-1457.
- Venkatapathy M, Venkatesan M, Anbarasu K. 2020. Mechanistic aspects reactivity of cyclic ketones by piperidinium chlorochromate. *Journal of Xidian University* 14(10): 44-50.
- Mansoor SS, Syed SS, Zahoor AS. 2016. Correlation analysis of reactivity in the oxidation methionine by BIFC in different mole fractions of acetic acid – water mixture. *Arabian Journal of Chemistry* 9(S1): S557-S563.
- Basim H, Asghar Sheik MS, Mohamed HA, Saleem MV, Aswin K, Sudhan SPN 2017. Oxidation of aliphatic aldehydes by bific in non-aqueous medium- A kinetic and mechanistic study. *Arabian Journal of Chemistry* 10(S2): S2115-S2123.
- Sheik MS, Syed SS. 2014. Oxidation of aniline and some p-substituted anilines by BIFC in aqueous acetic acid medium - A kinetic and mechanistic study. *Arabian Journal of Chemistry* 7(2): 171-176.
- Bailer JC. 1973. *Comprehensive Inorganic Chemistry*. 3rd Edition, Pergamon, Oxford.
- Orton KJP, Bradfield AE. 1927. The purification of acetic acid. The estimation of acetic anhydride in acetic acid. *Journal of Chemical Society*. pp 983.
- Fiegel F. 1966. *Spot Tests in Organic Analysis*. 7th Edition, Elsevier Publishing Company, London. pp 66.
- Wiberg KB. 1965. *Oxidation in Organic Chemistry*. Part A, Academic Press, New York. pp 69.

16. Leffler JE. 1955. The enthalpy-entropy relationship and its implications for organic chemistry. *Journal of Organic Chemistry* 20: 1202-1231.
17. Quinlan E, Amis ES. 1955. The alkaline hydrolysis of methyl propionate in acetone-Water mixtures and solutions of different ionic strength. *Journal of American Chemical Society* 77(16): 4187-4440.
18. Walling C. 1957. *Free Radicals in Solution*. John Wiley and Sons, New York.
19. Eyring H. 1955. The activated complex in chemical reactions. *Journal of Chemical Physics* 33: 107-115.
20. Rajalakshmi K, Ramachandramoorthy T, Srinivasan S. 2012. Oxidation of Cyclic Ketones by Benzyl Triethylammonium Chlorochromate by 1, 10-Phenanthroline as Catalyst-Kinetic and mechanistic study. *Journal of Chemical and Pharmaceutical Research* 4: 894-900.
21. Wiberg KB, Mill T. 1958. The kinetics of the chromic acid oxidation of benzaldehyde. *Journal of American Chemical Society* 80(12): 3022-3029.
22. Leffler JE. 1955. The enthalpy-entropy relationship and its implications for organic chemistry. *Journal of Organic Chemistry* 20(9): 1202-1231.
23. Peterson RC. 1964. The linear relationship between enthalpy and entropy of activation. *Journal of Organic Chemistry* 29(11): 3133-3135.
24. Venkatapathy M, Venkatesan M, Anbarasu K. 2021. Hammett plot behaviour of substituted benzaldehydes towards piperidinium chlorochromate oxidation. *Research Journal of Agricultural Sciences* 12(5): 1489-1492.
25. Krishnapillay A, Thirunavukkarasu A. 1981. Kinetics of oxidation of some substituted piperidones by acid permanganate. *Industrial Journal of Chemistry* 20B: 583-585.
26. Khansole SV, Gaikwad DD, Gaikwad SD, Kankariya RD. 2010. Kinetics and mechanism of acid-catalyzed oxidation of phenol and substituted phenols by isoquinolinium bromochromate. *Russian Journal of Physical Chemistry A* 84: 2233-2237.
27. Anbarasu K, Palaniammal N. 2020. Oxidation of thioacids by quinaldinium dichromate - Kinetic and reactivity approach. *Journal of Xidian University* 14(10): 631-636.
28. Saradamani PR, Jegannathan V. 1990. Kinetics and mechanism of the oxidation of aromatic amines by N-Bromoacetamide. *Indian Journal of Chemistry* 29A (1-4): 700-702.
29. Brown HC, Fletcher RS, Johannesen RB. 1951. I-Strain as a factor in the chemistry of ring compounds. *Journal of American Chemical Society* 73(1): 212-221.