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A Stereochemical and Kinetic Study of the Conversion of Methyl Cyclopropyl Ketones to 4,5-Dihydrofurans¹

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The thermal and photochemical conversion of $(1R^*, 2R^*, 3S^*)$, $(1S^*, 2R^*, 3S^*)$, and $(1S^*, 2R^*, 3R^*)$ -1acetyl-1,2-dimethyl-3-phenylcyclopropane (1, 2, and 3) to *cis*- and *trans*-2,3,4-trimethyl-5-phenyl-4,5dihydrofurans has been studied. Concurrent with this reaction is an equilibration of 1, 2, and 3, a thermal ring opening of 1 by a 1,5-hydrogen shift, and a cyclopropane-to-propene type reaction under the photochemical conditions. The dihydrofuran from 1 and 2 by the thermal and photochemical conditions is 97% *trans*- and 3% *cis*- corresponding to predominant retention at the migrating carbon. The dihydrofuran formed from 3 by the thermal and photochemical reaction is 85% *cis*- and 15% *trans*- again corresponding to predominant retention. A kinetic study of the rearrangement of 1-acetyl-1-methyl-2-phenylcyclopropane to 1,2-dimethyl-5-phenyl-4,5-dihydrofuran provides E_a of 48.1 kcal/mol and log A of 14.9 for this first order reaction in the temperature range of 255–288 °C.

It is concluded that the thermal and photochemical reactions occur by a non-concerted process through a common 1,3-diradical intermediate in which bond rotation and ring closure steps are competitive.

La transformation thermique et photochimique du $(1R^*, 2R^*, 3S^*)$, $(1S^*, 2R^*, 3S^*)$, et $(1S^*, 2R^*, 3R^*)$ acétyl-1 diméthyl-1,2 phényl-3 cyclopropane (1, 2, et 3) en *cis* et *trans* triméthyl-2,3,4 phényl-5 dihydro-4,5 furanes, a été étudiée. Entrent en compétion avec cette réaction, une équilibration de 1, 2, et 3, une ouverture thermique de cycle de 1 par transfert-1,5 d'hydrogène et une réaction du type cycloprane-propène dans les conditions photochimiques. Le dihydrofurane issu de 1 et 2 dans les conditions thermique et photochimique est à 97% *trans* et 3% *cis* avec rétention prédominante sur le carbone qui migre. Le dihydrofurane formé à partir de 3 par réaction thermique et photochimique est à 85% *cis* et 15% *trans* avec encore rétention prédominante. Une étude cinétique du réarrangement thermique de l'acétyl-1 méthyl-1 phényl-2 cyclopropane en diméthyl-1,2 phényl-5 dihydro-4,5 furane conduit à un E_a de 48.1 kcal/mol et à un log A de 14.9 pour cette réaction de premier ordre dans l'intervalle de température de 255-288 °C.

Il a été conclu que les réactions thermique et photochimique se produisent selon un processus non concerté, par l'intermédiaire d'un diradical-1,3 dans lequel les étapes de rotation autour de la liaison et de fermeture de cycle sont en compétition. [Traduit par le journal]

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The non-catalyzed conversion of cyclopropyl ketones to dihydrofurans formally resembles the conversion of vinylcyclopropanes to cyclopentenes. This latter reaction has been studied extensively by kinetic and stereochemical means;

¹Taken in part from the Ph.D. thesis of J.W.M., University of British Columbia, Vancouver, B.C., May 1972. however, the former reaction has been discussed in only a few notes. The thermally induced reaction was first noted by Wilson and Armitage (1, 2) and a photochemically induced reaction has been reported by Dauben and Shaffer (3). The reverse reaction of dihydrofurans to cyclopropanes has also been observed (1, 4-7). In the present paper we examine in more detail the stereochemistry and kinetics of the thermal and

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				Product (%)						
Run Compound	Conditions	Time	1	2	3	5 + 6	7 + 8	Olefins*	Ratio (5:6)	
1	1	285°	75 min	14	6	Trace	37	43		97:3
2	1	hv	1 day	79	1		20	_	Trace	97:3
3	1	hv	7 days	11	3		84	_	Trace	97:3
4	2	283.5°	15 min	1.1	90.4	6.0	2.5	_		95:5
5	2	283.5°	1 h	3.0	79.4	12.0	4.7	0.9		95:5
6	2	283.5°	6 h	3.6	38.4	25.8	29.6	2.6	_	85:15
7	2	hv	6 h	1	94		2.3	_	Trace	97:3
8	2	hv	6 days	1	16	_	30	_	54	97:3
9	3	283.5°	3 min	0.1	1.2	98.5	0.2	_		15:85
10	3	283.5°	10 min	0.7	5.5	93.1	0.7		_	14:86
11	3	283.5°	1 h	2.5	20.0	71.5	5.8	_		44:56
12	3	283.5°	6 h	3.0	27.3	25.3	39.6	4.8	_	70;30
13	3	hv	3 h		3	95	0.6		1	15:85
14	3	$h\nu$	6 h	_	9	86	1.6		3	31:69
15	3	hv	6 days	2	14	8	26	_	51	74:26

TABLE 1. Product distribution of the thermal and photochemical reaction of 1-acetyl-1,2-dimethyl-3-phenylcyclopropanes 1-3

*The olefins referred to here are a mixture of α,β- and β,γ-unsaturated ketones resulting from a cyclopropane-to-propene type reaction. These olefins have been characterized previously (8).

photochemical conversion of a series of methyl cyclopropyl ketones to 4,5-dihydrofurans.

Stereochemistry

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 120.117.138.77 on 11/10/14 For personal use only. From an earlier study (8) we have on hand three stereoisomers of 1-acetyl-1,2-dimethyl-3phenylcyclopropane (1-3). The fourth possible isomer (4) has not been available. These ketones at 300 °C or on irradiation with 310 nm light (Rayonet Reactor) are converted to a variety of products illustrated in eqs. 1–3 by the reaction of 1.



Reaction 1 is the conversion of a cyclopropyl ketone to a dihydrofuran. This reaction is (at least, formally) a 1,3 signatropic shift from carbon to oxygen and in this case permits one to evaluate the stereochemistry of the migrating carbon. Reaction 2 is the cis:trans interconversion of cyclopropane stereoisomers and in this case is expected to occur exclusively through the breaking of the bond between the carbons bearing the phenyl and acetyl groups, since both of these groups would provide major stabilization of the intermediate diradical or transition state. Reaction 3 is a well-known ring opening of a cyclopropyl ketone carrying an alkyl group cis to the carbonyl group (9, 10). A further minor reaction encountered in our work results from a hydrogen migration yielding a cyclopropaneto-propene type ring opening.

Typical data that we have collected are presented in Table 1 for the reactions of 1, 2, and 3.

[1]

[2]

[3]

The structures of 1, 2, and 3 and the reaction of 1 to form 7 and 8 have been reported earlier (8). A series of dihydrofurans related to 5 and 6 and having a C-4 methyl and a C-5 phenyl have been reported by Scribe and Delepine (11). The stereochemical assignment to them was based on the argument that in the cis compounds the C-5 phenyl should shield the C-4 methyl and they reported values of 9.48 for the cis C-4 methyl against 8.85 τ for the *trans* C-4 methyl. The major dihydrofuran from 1 and 2 gave a C-4 methyl at 8.88 τ and the major dihydrofuran from 3 (run 9) gave a C-4 methyl at 9.50 τ and thus these compounds can be assigned the trans-5 and *cis*-6 structures respectively. As additional verification of this assignment we determined the nuclear Overhauser effect (n.O.e.) on the C-5 hydrogen (5.28 τ) in 5 that resulted from irradiation of the C-4 methyl. An enhancement of 23% was observed. The measured distances between these groups in models were 2.8 Å and >3.6 Å for 5 and 6 respectively. Thus the enhancement of 23% is only consistent with structure 5 (12).

The results of Table 1 suggest a reaction scheme such as Scheme 1 involving thermal or photochemical bond-breaking in the cyclopropanes, followed by ring closures to cyclopropane or dihydrofurans competitive with bond rotations at the diradical stage. The only significant amount of bond rotation, however, is in the thermal reaction of 2 or 3, whereby 2 and 3 are interconverted. This corresponds to the rotation of the terminal carbon of the trimethylene diradical species carrying one substituent (phenyl), in preference to that carrying two substituents. This effect of substituents on bond



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rotation rates has previously been noted by Berson *et al.* and has been described as a ponderal effect (13).

A secondary consequence of the interconversion of 2 and 3 is the variation, with degree of reaction, of the ratio of 5:6. The stereochemistry of the cyclopropane to dihydrofuran reaction needs to be determined at as early a stage as possible and when this is done it becomes clear that the cyclopropane to dihydrofuran reaction is not stereospecific. Bond rotation again competes with ring closure and it is significant that a greater degree of bond rotation occurs in the system which would lead to the dihydrofuran having the C-4 methyl and C-5 phenyl *cis.* It is particularly interesting that the photochemical and thermal reactions give the *same* stereoselectivity.

All of the above observations suggest that the cyclopropane to dihydrofuran reaction is not a concerted reaction, although there is some stereoselectivity. Similar conclusions have been made concerning the vinylcyclopropane to cyclopentene reaction where similar stereochemical evidence is available (14). Supporting stereo-

chemical evidence also comes from a study on the degenerate rearrangement of vinylcyclopropane which must pass through a diradical intermediate (15).

Of closer interest to our study is the photochemical conversion of cis- and trans-5-(1methylpropenyl)-3,4-dimethyl-4,5-dihydrofuran to 2-(1-methylpropenyl)-1,2-dimethylcyclopropane carboxaldehyde (7). Stereoselectivity was observed favoring retention at the migrating carbon and to almost the same degree as our results for the reverse reaction, with the cis isomer giving 80% retention and the trans 94%. Scribe and Wiemann (7), because of this selectivity, favored a concerted mechanism. The factor swinging our support to the diradical mechanism is the parallel results found for the thermal and photochemical modes of reaction. The possibility, however, of competitive concerted reactions cannot be overlooked (18).

To obtain a further correlation between our reaction and the vinylcyclopropane to cyclopentene reaction we have made a preliminary kinetic study. Unfortunately the reactions of 1, 2, and 3 are just too complicated for such a study and

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therefore we have looked at the reaction of *cis*and trans-1-acetyl-1-methyl-2-phenylcyclopropane (9 and 10).

Kinetics

Addition of phenyl diazomethane to methyl isopropenyl ketone at room temperature gives directly a 1:2 mixture of the isomeric 1-acetyl-1-methyl-2-phenyl cyclopropanes (eq. 4) Pre-

[4] $C_6H_5CHN_2 + CH_2 = C(CH_3)COCH_3$



sumably a pyrazoline is formed as an intermediate; however it is not stable at room temperature (16). The cyclopropanes were separated by v.p.c. and identified by their n.m.r. spectra. The major isomer has the acetyl and C-1 methyl at 7.87 and 8.98 τ respectively. The minor isomer has the acetyl methyl and the C-1 methyl at 8.33 and 8.54 τ . Thus based on the shielding effect by the phenyl the major isomer has the C-1 acetyl and the C-2 phenyl groups *trans* as in 10 and the minor isomer has the C-1 acetyl and the C-2 phenyl cis as in 9.

Samples of 9 or 10 when heated in realed ampoules, such that reaction would take place in the gas phase at 250-290°, led to an initial rapid equilibrium of 9 and 10, to the value of 15:85 respectively, followed by conversion to 2,3-dimethyl-5-phenyl-4,5-dihydrofuran (11). Kinetic runs made use of 9 and 10 close to equilibrium. The dihydrofuran proportion of the total samples rose to a maximum value of about 89%, at which time equilibrium between it and the cyclopropanes 9 and 10 was reached. Clearly there are a number of subtle substituent effects, which determine the position of such an equilibrium under thermal and photochemical conditions, and which as yet are still unclear (1-5, 7). The kinetic data are reported in Table 2 and yield by an Arrhenius plot E_a of 48.1 kcal/mol and log A of 14.9.

These kinetic parameters correlate well with those found for vinylcyclopropanes (17) with some selected values given in Table 3. One might however have anticipated a lower activation energy with both phenyl and acetyl groups capable of stabilizing the transition state. These

	$9 + 10 (15:85) \stackrel{\times}{\approx} 11 k_2$			
Temperature (°C)	$(k_1 + k_2) \times 10^5$ (s ⁻¹)	k ₁ :k ₂		
287.5	15.2	88.4:11.6		
279.6	8.10	88.8:11.2		
270.0	3.84	89.1:10.9		
262.5	2.00	89.4:10.6		

TABLE 2. Kinetic data for the reaction

 k_1

TABLE 3. Selected activation parameters for the conversion of some vinylcyclopropanes to cyclopentenes (17)

1.04

Compound	log A	Ea	
Vinylcyclopropane	13.5	49.6	
2-Cyclopropylpropene	13.99	50.9	
2-(1-Methylcyclopropyl)propene	14.14	50.5	

factors show up in the faster rate of reaction, however, since the rate for 9 and 10 is comparable to vinylcyclopropane at a temperature 60° below that for vinylcyclopropane. Thus the kinetics support the view that the cyclopropyl methyl ketone-to-dihydrofuran rearrangement is of the same mechanistic form as the vinylcyclopropane-to-cyclopentene rearrangement.

Experimental

The preparation and characterization of cyclopropanes 1-3 and products 7 and 8 have been reported earlier along with some general procedures used (8).

cis- and trans-2,3,4-Trimethyl-5-phenyl-4,5-dihydrofuran (6 and 5)

Several ampoules of about 920 µl volume containing 12 mg of 1 were degassed and sealed under vacuum and heated at 338° for 10 min. The separate samples were combined and v.p.c. analysis (20% FFAP at 205°) showed a major peak well separated and to lower retention time than 1, 2 or 3, or any possible unsaturated ketone product. The peak was collected and high resolution v.p.c. on a Perkin-Elmer 226 instrument using a Carbowax 20 M 0.01 in. i.d. \times 150 ft column at 175° showed it to be a 96:4 mixture of two components. For the major component: i.r. 1700 cm⁻¹, n.m.r. τ (60 MHz, CCl₄) 8.47 and 8.22 (singlets showing long-range coupling) for the C-2 and -3 methyls, 8.88 (doublet, J = 7.0 Hz) for the C-4 methyl, 7.33 (multiplet) for the C-4 hydrogen, 5.28 (doublet, J = 8.0 Hz) for the C-5 hydrogen, and 2.78 for the aromatic hydrogens.

Anal. Calcd. for C13H16O: C, 82.93; H, 8.57. Found: C, 82.74; H, 8.34.

To a solution of 36 mg of the above sample in 1.0 ml

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89.7:10.3

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 120.117.138.77 on 11/10/14 For personal use only. of CCl₄ was added 2.2 mg of *p*-dioxane (internal standard) and 50 µl of *sym*-tetrachloroethane (internal lock). Using an HA100 spectrometer the C-4 methyl peak was irradiated while the peaks for the C-4 and -5 hydrogens were being observed for nuclear Overhauser enhancements. The average enhancement to the C-4 hydrogen was 30% and that to the C-5 hydrogen 23%. Models of 5 and 6 gave the internuclear distances for the hydrogens of the C-4 methyl and the C-5 hydrogen of 2.8 and 3.6– 4.0 Å respectively, corresponding to expected enhancements of 21 and < 6% respectively (12). Coupled with the fact that the C-4 methyl appears at 8.88 τ compared to 9.50 in the minor isomer, we have assigned the *trans*stereochemistry 5 to the major dihydrofuran isomer

from 1. Photolysis of a sample of 100 mg of 1 in 100 ml of ether for 24 h using 310 nm radiation (Rayonet Reactor) gave a product which contained a peak (65%) at the same v.p.c. retention time as 5 and when isolated was found to have the same n.m.r. spectrum as 5, with peaks at τ 8.50 and 8.26, 8.90 (doublet), 7.35 (multiplet), 5.32 (doublet) and 2.80.

Several sealed ampoules of 3 were heated at 338° for 10 min. The products were combined and the dihydrofuran peak isolated by v.p.c. Analytical v.p.c. showed this sample to be a 83:17 mixture of 5 and 6 respectively. The n.m.r. spectrum of this mixture showed peaks for *cis*-2,3,4-trimethyl-5-phenyl-4,5-dihydrofuran (6) at τ 4.62 (doublet, J = 9.2 Hz) for the C-5 hydrogen and 9.50 (doublet, J = 7.2 Hz) for the C-4 methyl. The other peaks for 6 were not clearly separated from the peaks of 5.

Experimental Conditions for the Rearrangement Reactions

Samples of about 2.2 mg were degassed and sealed under vacuum in Pyrex tubes $(4.2 \times 100 \text{ mm} \text{ for the}$ thermal runs and $4.2 \times 50 \text{ mm}$ for the photochemical runs). For the thermal runs the tubes were placed in a constant-temperature salt $(\text{NaNO}_3-\text{KNO}_3)$ bath and samples removed at appropriate times for analysis. For the photochemical runs the tubes were placed in a Rayonet Reactor fitted with 310 nm lamps. Product distributions were monitored using a P.E. 226 analytical v.p.c. using a column (0.01 in. i.d. \times 150 ft) charged with Carbowax 20 M. Typical results are recorded in Table 1.

Samples of the dihydrofurans 5 and 6 as prepared above in the ratio of 96:4 and 83:17 respectively, were heated over 10 half-lives at 285° with no change in the ratio of 5 to 6. Similar samples were irradiated with 310 nm light for 15.5 h with again no change in the ratio of 5:6 being observed, although trace peaks corresponding to 1 and 2 were observable. Although dihydrofurans often readily polymerize (5, 7), control runs indicated that 5 and 6 did not show this tendency under the reaction conditions. They did, however, rapidly deteriorate on exposure to air either due to polymerization or hydration or both.

cis-² and trans-1-Acetyl-1-methyl-2-phenylcyclopropane (9 and 10)

Addition of 8.4 g (0.1 mol) of methyl isopropenyl ketone to a petroleum ether solution of phenyldiazo-

methane (prepared from 0.1 mol of benzaldehyde hydrazone and 0.1 mol of yellow mercuric oxide (8)) caused immediate evolution of nitrogen. After 2 h, the red color of the diazo compound had completely disappeared. Rotatory evaporation of the solvent followed by vacuum distillation (90-95° at 0.3 mm Hz) yielded 12.6 g of a slightly yellowed solution. The v.p.c. (20% FFAP, 205°, 60 ml/min) indicated two peaks in a 1:2 ratio with respective retention times of 7.7 and 9.3 min. The two peaks were separated and collected by v.p.c. The first peak was identified by n.m.r. as the cis-isomer 9 and the second peak as the *trans*-isomer **10**. For the *cis*-cyclopropyl ketone (9): i.r. 1695, 1605, 725, and 697 cm⁻¹; n.m.r. τ (60 MHz, CCl₄) 8.33 and 8.54 (singlets) acetyl and C-1 methyls respectively, 7.75 (triplet, J = 7.7 Hz) C-2 hydrogen, 8.09 (doublet of doublets, J = 4.6 and 7.5 Hz) one C-3 hydrogen, 9.04 (doublet of doublets, J = 8.4 and 4.6 Hz) other C-3 hydrogen, and 2.80 (aromatic).

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.76; H, 8.05. Found: C, 83.03; H, 8.25.

For the *trans*-cyclopropyl ketone (10): i.r. 1690, 1605, 778 and 698 cm⁻¹; n.m.r. τ (60 MHz, CCl₄) 7.87 and 8.98 (singlets) acetyl and C-1 methyls respectively, 7.34 (doublet of doublets J = 7.0 and 9.0 Hz) C-2 hydrogen, 8.37 (doublet of doublets, J = 4.2 and 9.0 Hz) one C-3 hydrogen, 8.94 (doublet of doublets, J = 4.2 and 7.0 Hz) other C-3 hydrogen, and 2.84 (aromatic).

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.76; H, 8.05. Found: C, 82.54; H, 8.02.

2,3-Dimethyl-5-phenyl-4,5-dihydrofuran (11)

Six 50 µl samples of a mixture of ketones 9 and 10 were sealed in ampoules $(4.2 \times 100 \text{ mm})$ and were heated at 335° for 10 min. The slightly charred samples were bulb-to-bulb vacuum distilled (bath temperature of 85–100° at 0.5 mm Hg). V.p.c. of this combined product (20% FFAP column at 205°) showed five peaks: The first of these peaks was the dihydrofuran 11; i.r. 1701 cm⁻¹, n.m.r. τ (60 MHz, CCl₄) 2.80 (singlet) phenyl hydrogens, 4.70 (doublet of doublets with J = 8.0 and 10.0 Hz) for the C-5 hydrogen, 6.7–7.8 (multiplet) for the C-4 hydrogens, 8.26 and 8.40 (singlets showing long range coupling) for the C-2 and -3 methyls.

Anal. Calcd. for C₁₂H₁₄O: C, 82.78; H, 8.05. Found: C, 82.43; H, 8.25.

The remaining peaks in the vapor chromatogram were identified as 9, 10, and two unsaturated ketones 3-methyl-5-phenyl-3- and -4-pentene-2-one which were identified by their n.m.r. These olefins were completely absent in the kinetic runs and became particularly noticeable as byproducts when the reaction vials were too small to allow all of the sample to enter the gas phase.

Kinetics

Samples (3.0-3.5 mg) of 9 and 10 near an equilibrium composition were sealed under vacuum after degassing in Pyrex ampoules ($4.2 \times 100 \text{ mm}$) and were heated in a constant temperature bath (a 50:50 mixture of sodium nitrate and potassium nitrate) equipped with a stirrer and a thermometer calibrated against an N.B.S. calibrated thermometer. The progress of the reaction was monitored by analyzing samples with an Aerograph Model A-90-P3 v.p.c. (20% FFAP, 205° , 120 ml/min helium) equipped with a thermal conductivity detector. A Honeywell Model Electronic 15 recorder having a disc

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²cis refers to the C-1 acetyl and C-2 phenyl,

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chart integrator was used to estimate the ratio of products.

Straight line fits were calculated by the method of least squares using a Hewlett Parkard 9100 Calculator equipped with a 9125A Calculator plotter. The results are presented in Table 2. The percent of dihydrofuran 11 at equilibrium varied from 88.4% at 287.5° to 89.7% at 254.9°.

It is estimated that the main source of error is in controlling the bath temperature to ± 0.4 °C leading to estimated error limits in E_a of $\pm 5\%$.

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- 1. C. L. WILSON. J. Am. Chem. Soc. 69, 3002 (1947).
- D. M. A. ARMITAGE and C. L. WILSON, J. Am. Chem. Soc. 81, 2437 (1959).
- 3. W. G. DAUBEN and G. W. SHAFFER. J. Org. Chem. 34, 2301 (1969).
- D. W. BOYKIN, JR. and R. E. LUTZ. J. Am. Chem. Soc. 86, 5046 (1964).
- 5. D. E. McGreer, M. G. VINJE, and R. S. McDANIEL. Can. J. Chem. 43, 1417 (1965).

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- P. SCRIBE, M. R. MONOT, and J. WIEMANN. Tetrahedron Lett. 5157 (1967).
 P. SCRIBE and J. WIEMANN. Bull. Soc. Chim. Fr. 2268
- 7. P. SCRIBE and J. WIEMANN. Bull. Soc. Chim. Fr. 2268 (1971).
- 8. D. E. MCGREER and J. W. MCKINLEY. Can. J. Chem. 49, 105 (1971).
- R. M. ROBERTS, R. G. LANDOLT, R. N. GREENE, and E. W. HEYER. J. Am. Chem. Soc. 89, 1404 (1967).
 D. E. MCGREER and N. W. K. CHIU. Can. J. Chem.
- D. E. MCGREER and N. W. K. CHIU. Can. J. Chem. 46, 2217 (1968).
- 11. P. SCRIBE and M. DELEPINE. C.R. 261, 160 (1965).
- 12. R. A. BELL and J. K. SAUNDERS. Can. J. Chem. 48, 1114 (1970).
- J. A. BERSON, D. C. THOMPKINS, and S. JONES. J. Am. Chem. Soc. 92, 5799 (1970).
- 14. P. H. MAZZOCCHI and H. J. TAMBURIN. J. Am. Chem. Soc. 92, 7220 (1970).
- M. R. WILLCOTT and V. H. CARGLE. J. Am. Chem. Soc. 91, 4311 (1969).
- D. E. McGreer and Y. Y. WIGFIELD. Can. J. Chem. 47, 3965 (1969).
- M. R. WILLCOTT, R. L. CARGILL, and A. B. SEARS. In Progress in physical organic chemistry. Vol. 9. Edited by A. Streitweiser, Jr. and R. W. Taft. John Wiley and Sons, Inc. New York. 1972.
- 18. J. A. BERSON. Acc. Chem. Res. 5, 406 (1972).