sample by ^{1}H NMR, IR, and mass spectra, TLC, mp and mmp 42–43 °C). In addition, oxidation of **4** by sodium periodate–potassium permanganate in basic medium followed by methylation (CH_2N_2) and chromatography gave methyl 3,4-epoxynonenoate (**6**) in good yield.

This remarkably selective and unprecedented[8] internal epoxidation of peroxyarachidonic acid **3** to form 14,15-epoxyarachidonic acid, which clearly occurs by intramolecular oxygen transfer, indicates that the 15-membered cyclic structure **7** is energetically quite favorable compared with alternative geometries involving more proximate double bonds and smaller rings. It is clear from examination of space-filling models that structure **7** is free of serious internal nonbonded repulsion or angle strain, as would, for example, be associated with internal epoxidation of the $\Delta^{5,6}$ double bond of **3**. The sizable preference for **7** over the alternative structures suggests that there may be a tendency of arachidonic acid itself to adopt a strongly bent, "J"-like shape and that the favored transition state for oxygen transfer may be an (S_N2 like) arrangement with the center of the C=C π cloud attacking oxygen back side to and colinear with the O—O bond being broken.

Using a different reaction scheme the 5,6-oxide of arachidonic acid could also be obtained selectively. Treatment of pure arachidonic acid in THF–water (1.7:1) with 5 equiv of potassium bicarbonate and 8 equiv of potassium triiodide at 0–5 °C for 3 days, followed by rapid extractive isolation, afforded an unstable iodo δ-lactone as the only neutral product (R_f values of the lactone and **1,** 0.82 and 0.20, respectively, on silica gel plates using CH_2Cl_2–CH_3OH, 95:5). The oily iodo lactone was immediately treated with excess 0.2 N lithium hydroxide in THF–water (3:2) at 25 °C for 3 h. Extractive isolation and methylation of the product by diazomethane in ether afforded after chromatography 68% methyl 5,6-epoxyarachidonate,[9] the structure of which was established by hydrogenation (over Pd/C in ethyl acetate) to a saturated epoxide which was identical with methyl *cis*-5,6-epoxyeicosenoate.[10] The R_f values for the methyl esters of 5,6-epoxy- and 14,15-epoxyarachidonate (**4**) were 0.37 and 0.46, respectively, by TLC (silica gel) using hexane–ether (4:1).

In a similar way eicosa-*cis*-8,11,14-trienoic acid (**2**) could be converted in high yield into the corresponding peroxy acid derivative which at 0 °C for 70 h in ether–methylene chloride solution transferred oxygen preferentially to the $\Delta^{14,15}$ double bond to form the $\Delta^{14,15}$-epoxide of **2** in 94% isolated yield and >95% purity (TLC (silica gel) analysis).[11] The structure of the product (**8**) was demonstrated by comparison with an authentic sample[2] and by methylation (CH_2N_2) and hydrogenation (Pd/C in ethyl acetate) to methyl 14,15-epoxy-*cis*-eicosenoate, identical with a sample obtained as described above starting from **1**. The TLC (silica gel) R_f values found for the 14,15-, 11,12-, and 8.9-epoxides of **2** (cf. ref 2) were 0.36, 0.31, and 0.27, respectively (two developements using 95:5 methylene chloride–methanol).

The scope of these and related internal epoxidation reactions as a technique for selective oxidation of polyunsaturated fatty acids remains to be determined. Internal epoxidation does not seem to be a very favorable pathway in the case of peroxyoleic acid, since it was found with this substrate that internal epoxidation (i.e., reaction in very dilute solution) was relatively slow and further that an equimolar mixture of peroxyoleic acid and methyl oleate (each 0.15 M in methylene chloride–ether) was converted into a mixture of epoxyoleic acid and methyl epoxyoleate in a ratio of ~1:1.

As a result of the experiments described above, a multitude of new research opportunities present themselves. We are currently investigating logical extensions and a variety of approaches to internal selective epoxidation of polyunsaturated fatty acids, as well as biologically and chemically significant transformations of the products derived therefrom.[12]

References and Notes

(1) See T. K. Schaaf, *Annu. Rep. Med. Chem.*, **12,** 182 (1977).

(2) See S.-K. Chung and A. I. Scott, *Tetrahedron Lett.*, 3023 (1974). Studies in this laboratory have shown that intermolecular epoxidation of **1** yields each of the four possible monooxides which are readily separable as the methyl esters by chromatography on silica gel.

(3) To accelerate the reaction of the acylimidazole with hydrogen peroxide, presumably by generating a small concentration of the nucleophile HOO^-. In the absence of this catalyst the reaction was much slower. Anhydrous ethereal solutions of H_2O_2 were prepared by dissolving 90% H_2O_2 in ether and drying first over Na_2SO_4 and then two times over anhydrous $CaSO_4$.

(4) The function of the potassium bisulfate is to remove imidazole from the solution. Unless this is done, the peroxy acid **3** is rapidly reduced to the carboxylic acid **1**.

(5) Effectively complete conversion to peroxy acid occurs under these conditions. The formation or disappearance of peroxy acid **3** may be monitored by thin layer chromatographic analysis on silica gel using KI–starch spray for visualization and CH_2Cl_2–CH_3OH (95:5) for development (R_f values for **1** and **3,** ~0.2 and 0.6, respectively). The rate of the reaction **3** → epoxy acid is concentration independent. The peracid **3** showed infrared absorption due to carbonyl at 1748 cm^{-1} (in CCl_4) compared with 1700 cm^{-1} for **1**.

(6) By TLC (silica gel) and ^{1}H NMR analysis.

(7) Assigned structure fully consistent with ^{1}H NMR, IR, and mass spectral data.

(8) For fascinating examples of internally directed epoxidation reactions of a different character, see (a) K. B. Sharpless and R. C. Michaelson, *J. Am. Chem. Soc.*, **95,** 6136 (1973); (b) R. Breslow and J. M. Maresca, *Tetrahedron Lett.*, 623 (1977); and (c) B. M. Trost and T. N. Salzmann, *J. Chem. Soc., Chem. Commun.*, 571 (1975).

(9) For some other examples of the use of this technique for internal epoxidation, see (a) E. J. Corey and R. Noyori, *Tetrahedron Lett.*, 311 (1970); (b) H. O. House, R. G. Carlson, H. Müller, A. W. Noltes, and C. D. Slater, *J. Am. Chem. Soc.*, **84,** 2614 (1962); (c) P. A. Bartlett and J. Myerson, *ibid.*, **100,** 3950 (1978); (d) E. J. Corey, E. J. Trybulski, L. S. Melvin, Jr., K. C. Nicolaou, J. A. Secrist, R. Lett, P. W. Sheldrake, J. R. Falck, D. J. Brunelle, M. F. Haslanger, S. Kim, and S. Yoo, *ibid.*, **100,** 4618 (1978); and (e) E. J. Corey and T. Hase, *Tetrahedron Lett.*, in press.

(10) Prepared by successive reaction of *cis*-5-eicosenoic acid (Applied Science Laboratories) with diazomethane and *m*-chloroperoxybenzoic acid.

(11) Peroxy acid **3** shows higher selectivity in internal oxygen transfer to the $\Delta^{14,15}$ bond than does peroxy-**2,** as evidenced by the fact that the internal epoxidation with peroxy-**2** produces detectable amounts (~10%) of other epoxides at 25 °C in contrast to **3**.

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Proof of Existence of Cyclic $C_4H_7^+$ Ions in the Dilute Gas State

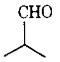
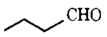
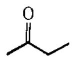
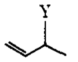
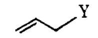
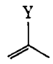
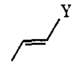
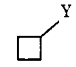
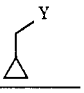
Sir:

In contrast to the impressive body of structural, spectroscopic, and kinetic data concerning cyclopropylcarbinyl and cyclobutyl cations in condensed media,[1,2] very little is known about the corresponding gaseous species, whose very existence has not been substantiated.

Gaseous $C_4H_7^+$ ions, to be sure, have long been detected by mass spectrometry, and appearance potentials of species labeled as "cyclobutyl" or "methylcyclopropyl" ions are listed in many compilations.[3] However, most authorities carefully point out the lack of experimental evidence for the cyclic structure of the species observed, and it is generally agreed[4] that the ionization and fragmentation of a cyclic neutral parent may well entail rearrangement to a linear structure. Such cautious positions are dictated, inter alia, by the very close values of the appearance potentials of the $C_4H_7^+$ ions obtained from cyclobutane and from the butenes.

Theoretical approaches have led to somewhat conflicting conclusions[5] concerning the relative stability of the $C_4H_7^+$ ions. The results of the most recent STO-3G calculations identify the cyclopropylcarbinyl cation in the bisected configuration as the most stable cyclic $C_4H_7^+$ structure, to which others, such as planar and puckered cyclobutyl cations, are predicted to

Table I. Relative Yields of the Products from the Gas-Phase Reactions of $C_4H_{7-n}T_n^+$ Decay Ions with Water and Ammonia

system composition,[a]		relative yields[b] of products, %								
NH_3	H_2O									
400		n.d.	n.d.	n.d.			28.8[d]		35.5[d]	35.7[d]
2	19	33.3	36.6	0.9	7.5[e]	4.1[e]	3.6[e]	4.3[e]	5.8[e]	4.0[e]
	25	6.8	26.5	19.3	9.7[e]	11.0[e]	7.1[e]	4.9[e]	5.3[e]	9.3[e]
	6	44.4	23.6	15.4	2.0[e]	1.8[e]	1.8[e]	2.4[e]	4.3[e]	3.4[e]

[a] Each 250-mL Pyrex bulb contained ~10 μCi of $c\text{-}C_4H_{8-n}T_n$ and O_2 (4.0 Torr). [b] Ratio of the activity found in each product to the total activity of the products identified. The amines were purified to constant specific activity over a 4-m tricresyl phosphate column at 70 °C and a 4-m diisodecyl phthalate column at 80 °C. The alcohols and the other oxygenated products were purified over a 10-m β,β′-oxydipropionitrile column at 80 °C and a 8-m diethylene glycol adipate column at 100 °C. Owing to the composition of the systems and to the purification techniques used, the yields refer only to the T atoms contained in stable positions, without any contribution from the T content of -OH and $-NH_2$ groups. [c] Below detection limits, corresponding to a relative yield of under 0.5%. [d] Y = NH_2. [e] Y = OH.

collapse without activation energy.[6,7] In view of the mechanistic and theoretical significance of the problem, a coordinated research effort was directed to the demonstration of the existence of cyclic $C_4H_7^+$ ions as free, unsolvated species in the dilute gaseous state, using a nuclear technique, based on the spontaneous β decay of suitably multitritiated precursors. The principles and applications of the technique have been reviewed.[8] The preliminary mass spectrometric part of the study was carried out at Argonne National Laboratory.[9] Tritiated cyclobutane was allowed to decay within a modified Model V-5900 ICR spectrometer from Varian Associates in order to determine its unimolecular decay-induced fragmentation pattern. The results demonstrated that $C_4H_7^+$ ions, of unknown structure(s), are by far the most abundant daughter ions, being formed from over 85% of the nuclear transitions, i.e.

$$c\text{-}C_4H_7T \xrightarrow{\beta\ \text{decay}} C_4H_7^+ + {}^3He + \beta^- \qquad (1)$$

and survive undissociated for a relatively long time (>10^{-5}s) within the resonance cell.

We now report the results of the conclusive radiochemical experiments, where labeled $C_4H_{7-n}T_n^+$ ions from the decay of multitritiated cyclobutane were allowed to react with nucleophiles such as water or ammonia in the dilute gaseous state. The neutral reaction products were analyzed by radio GLC.

Several curies of $c\text{-}C_4H_{8-n}T_n$, containing up to five T atoms per molecule, were obtained from the reaction of pure T_2 with $c\text{-}C_4H_6$ over a Pt black catalyst.[10] Separation from tritiated butanes, the major reaction products, and purification of $c\text{-}C_4H_{8-n}T_n$ were achieved by preparative GLC using an 8-m-long β,β′-oxydipropionitrile column at −20 °C.

The isotopic analysis of the purified sample by high-resolution mass spectrometry gave the following composition: $c\text{-}C_4H_7T$, 10.5 ± 1.0 mol %; $c\text{-}C_4H_6T_2$, 12.8 mol %; $c\text{-}C_4H_5T_3$, 26.6 mol %; $c\text{-}C_4H_4T_4$, 28.9 mol %; $c\text{-}C_4H_3T_5$, 16.2 mol %; cyclobutanes containing more than 5 T atoms per molecule, <5%.

Small fractions (~10 μCi) of the sample, diluted with $c\text{-}C_4H_8$ and again purified by preparative GLC were then introduced, together with the gaseous nucleophile(s) and O_2, used as a radical scavenger,[8] into Pyrex bulbs, subsequently sealed, and allowed to decay in the dark, at room temperature, for periods up to 1 year.

The tritiated neutral products from the reactions of the decay ions were separated and purified by preparative GLC after the addition of suitable carriers, repeating the chromatographic purification over two different columns until the specific activity of the recovered fractions, as measured by liquid scintillation spectrometry, reached a constant value.

The composition of the gaseous systems and the *relative* yields of the products identified are given in Table I. Owing to the specific purpose of the investigation, attention was focused on the oxygenated species and the amines formed from the reactions of the $C_4H_{7-n}T_n^+$ decay ions with water and ammonia, respectively, disregarding other major products, e.g., tritiated hydrocarbons and species such as HTO and NH_2T containing labile tritium atoms.

The *absolute* yields, defined as the ratio of the activity found in each product to the total activity of the $C_4H_{7-n}T_n^+$ daughter ions formed by the decay within the system, can be evaluated from the absolute activity and isotopic composition of the parent $c\text{-}C_4H_{8-n}T_n$, the storage time, the known abundance of the $C_4H_{7-n}T_n^+$ daughter ions from the decay, and the efficiency of the scintillation detector. Such calculations show that the overall absolute yields of the products identified is roughly 15–20% from the systems containing ammonia and 30–40% from those containing water.

The data of Table I show that the decay of multitritiated cyclobutane in gaseous nucleophiles such as H_2O and NH_3 yields a complex mixture of labeled products, mostly characterized by extensive skeletal rearrangement and whose nature and proportions are considerably affected by the composition and the pressure of the gaseous environment.

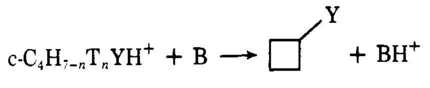
The isolation of tritiated cyclobutyl and cyclopropylcarbinyl derivatives in relatively low, but readily measured yields from all systems investigated, is the result most relevant to the specific purpose of the investigation. In fact, the formation of these *cyclic* neutral products can only be reasonably traced[11] to the reactions of the cyclic cations formed from the decay, e.g.

$$c\text{-}C_4H_{8-n}T_n \xrightarrow{\beta\ \text{decay}} c\text{-}C_4H_{7-n}T_n^+ + {}^3He + \beta^- \qquad (2)$$

with the gaseous nucleophiles, e.g.

$$c\text{-}C_4H_{7-n}T_n^+ + HY \rightarrow c\text{-}C_4H_{7-n}T_nYH^+ \qquad (3)$$

(where Y = NH_2 or OH) followed by proton transfer from the cyclic onium ion to a gaseous base, B, contained in the system,[12] e.g.



$$c\text{-}C_4H_{7-n}T_nYH^+ + B \longrightarrow \qquad + BH^+ \qquad (4)$$

From the above considerations, it follows that the observed formation of cyclobutanol (cyclobutylamine) and cyclopropylcarbinol (cyclopropylcarbinylamine) requires that cyclobutyl and, respectively, cyclopropylcarbinyl cations must exist in the dilute gaseous state at least for the time necessary to encounter a nucleophile. Using typical ion-neutral collision frequencies, lifetimes in excess of 10^{-9} s can be estimated in the systems at the lowest pressures.

Accordingly, both cyclobutyl and cyclopropylcarbinyl cations must be regarded as fully legitimate ionic intermediates, characterized by a significant local minimum on the $C_4H_7^+$ potential surface.

While these conclusions agree with theoretical results pointing to the appreciable stability of the cyclopropylcarbinyl ion in the bisected conformation, and the product distributions are also consistent with the view that acyclic species, such as 1-methylallyl cation, are most stable among $C_4H_7^+$ isomers, the alleged[7] lack of stability of the cyclobutyl cation is not supported by the experimental results.

Finally, the relatively low yields of cyclic neutral products are far from unexpected, and indeed the radiochemical experiments were designed to detect even smaller amounts of cyclobutyl and cyclopropylcarbinyl derivatives among the products.

In fact, even though most decay ions are formed in their electronic ground state,[8] some vibrational excitation necessarily arises from the different equilibrium positions of the constituent atoms in the parent cyclobutane molecule and the daughter cyclobutyl cation, which causes relaxation to the most stable structure of the latter. Following decay leading to such a strained structure as the cyclobutyl cation, even limited vibrational excitation in eq 2 is expected to cause extensive ring cleavage. Furthermore, owing to the exothermicity of eq 3, a certain fraction of the excited onium ions formed is likely to isomerize into more stable acyclic structures.

In conclusion, it appears that the overall results of the joint mass spectrometric[9] and radiochemical investigations begun in 1972 provide direct experimental evidence for the existence of cyclobutyl and cyclopropylcarbinyl cations as free, unsolvated species in the dilute gaseous state. A detailed analysis of their reactivity, equilibration, and competitive isomerization pathways will be reported in a forthcoming paper.

Acknowledgment. F.C. acknowledges financial support from CNR and thanks Professor G. Stöcklin for his interest in the work and hospitality at Institute 1, KFA, Jülich, West Germany, where M. Schüller helped in the c-$C_4H_{8-n}T_n$ preparation and Dr. A. Neubert performed the mass spectrometric analysis of the sample. The authors are also indebted to E. Possagno for providing some c-C_4H_6 and for prolonged care of the c-$C_4H_{8-n}T_n$ samples.

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(9) L. G. Pobo, S. Wexler, and S. Caronna, *Radiochim. Acta*, **19**, 5 (1973).

(10) The synthetic procedure represents a scaled-up version of the method described in ref 9.

(11) Strickly speaking, the results show only that *initially* cyclic cations give cyclic products. For the sake of argument, it is conceivable that these products are formed via a hypothetical reaction sequence involving *quantitative* cleavage of the initial cyclic ions to linear isomers, whose reactions with the nucleophile cause partial recyclization. However, apart from the conceptually awkward and uneconomical position of unnecessarily postulating two additional and opposite steps, the hypothetical recyclization of gaseous, linear $C_4H_{7-n}T_n^+$ ion appears singularly unlikely on energetic and entropic grounds.

(12) Deprotonation (eq 4) can readily occur in the presence of a large excess of the nucleophile, following stepwise clustering of several molecules of HY around the charged intermediate, according to the equation c-$C_4H_{7-n}T_nYH^+ + m\mathrm{HY} \rightarrow$ c-$C_4H_{7-n}T_nY + H(HY)^+$. The overall process is exothermic, even though proton transfer to a single HY molecule would be endothermic. For extensive mass spectrometric evidence on such cooperative deprotonation reactions, see K. Hiraoka and P. Kebarle, *J. Am. Chem. Soc.*, **99**, 360 (1977), and references therein.

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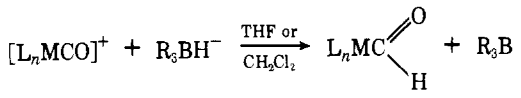
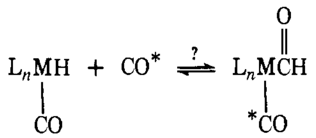
Neutral Metal Formyl Complexes: Generation, Reactivity, and Models for Fischer–Tropsch Catalyst Intermediates

Sir:

The availability of anionic metal formyl complexes from the reaction of hydride donors with neutral metal carbonyl complexes is now well established.[1-3] However, this potentially general methodology has not yet been extended to the preparation of *neutral* metal formyl complexes from *cationic* metal carbonyl precursors. Catalyst-bound formyls are believed to be initially formed intermediates in Fischer–Tropsch type processes,[4] and neutral formyl complexes might be expected to provide more precise models for their reactivity than anionic homologues. We report herein that the reaction of Li$(C_2H_5)_3BH$[5] with metal carbonyl cations provides a convenient entry into a number of neutral formyl systems (eq 1), one of which can be isolated in crystalline, analytically pure form. Further reactions of these complexes with BH_3, Li$(C_2H_5)_3BH$, and transition metal hydrides define additional modes of –CO or –CHO reduction which are relevant to (a) possible operative mechanisms of Fischer–Tropsch catalysts, (b) metal hydride carbonylation reactions (eq 2),[6] and (c) important but heretofore unexplained observations of other researchers.[7,8]



$$[L_nMCO]^+ + R_3BH^- \xrightarrow[CH_2Cl_2]{\text{THF or}} L_nMC{\overset{\displaystyle O}{\diagup\!\!\diagup}}\!\!\underset{\displaystyle H}{\diagdown} + R_3B \qquad (1)$$



$$\underset{\displaystyle CO}{\underset{|}{L_nMH}} + CO^* \overset{?}{\rightleftharpoons} \underset{\displaystyle {}^*CO}{\underset{|}{L_nM\overset{\displaystyle O}{\overset{\|}{C}}H}} \qquad (2)$$

Synthesis. The reaction of $[(C_5H_5)Re(CO)_2NO]^+BF_4^-$ (**1**)[7b,8] with 1.0 equiv of Li$(C_2H_5)_3BH$ at −23 °C in THF affords a product in quantitative yield (^1H NMR) whose spectral characteristics[9] establish its structure as the neutral formyl $(C_5H_5)Re(CO)(NO)(CHO)$ (**2**) (Scheme I). Although **2** thus prepared has a half-life of ~3 h at room temperature, extensive attempts at its isolation (via solvent removal, benzene or CH_2Cl_2 extraction, and subsequent concentration and/or addition of hexanes) have to date resulted only in impure powders.

The reaction of $[(C_5H_5)Re(CO)(PPh_3)NO]^+BF_4^-$(**3**)[10] with 1.0 equiv of Li$(C_2H_5)_3BH$ (or K(*sec*-$C_4H_9)_3BH$) at 22 °C in THF yields the much more stable formyl (C_5H_5)-$Re(PPh_3)(NO)(CHO)$ (**4**) (Scheme I).[11] Solvent removal, silica gel chromatography (under N_2 using hexanes–THF), and THF-hexane recrystallization afford honey-colored, analytically pure crystals[11] in 59% yield (dec pt (gradual) ~91 °C).

0002-7863/79/1501-1589$01.00/0