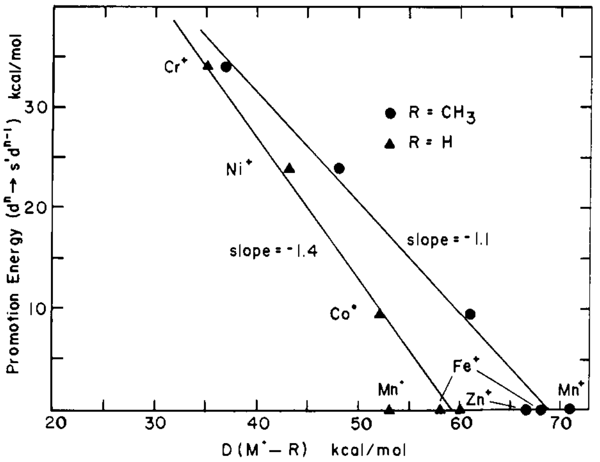

Figure 1. Promotion energy vs. metal ion hydride bond energies (triangles) and metal ion methyl bond energies (circles) for Cr^+, Mn^+, Fe^+, Co^+, Ni^+ and Zn^+. The promotion energy is between the lowest states derived from the $3d^n$ and the $3d^{n-1}4s^1$ configurations.

metal 4d orbitals are used in σ bonding for the second-row transition-metal series. This conclusion is in agreement with the considerations of Scott and Richards[11] relating to bonding in the second-row neutral metal hydrides.

No simple correlation such as Figure 1 could be found for the metal carbene or metal oxide bond energies.[16] Since these bonds probably include substantial π character, it is not surprising that no single metal electronic configuration is appropriate in all cases. It should also be noted that the metal carbene and oxide bond energies do not correlate with one another as do the hydride and methyl bond energies. This may indicate that metal carbene and metal oxide bonding are not as similar as might first be imagined.

The reactivity of the five transition-metal ions with alkanes may be understood in terms of the thermochemistry in Table I. Fe^+, Co^+, and Ni^+ have been observed to cleave and dehydrogenate alkanes containing three or more carbons in facile exothermic reactions.[6,17-19] If the second metal hydride and methyl bond energies for these three metals are comparable to the first, then insertion of the metal ions into C–H or C–C bonds, the first step in reaction with alkanes, is substantially exothermic. Fe^+ is indiscriminate in inserting into C–C and C–H bonds, Ni^+ is more selective in comparison, and the behavior of Co^+ is intermediate.[17] For example, Fe^+ inserts more readily into the stronger terminal C–C bonds of hydrocarbons than either Co^+ or Ni^+.[17,18] These observations are in accordance with the bond energies summarized in Table I. Mn^+ and Cr^+, however, are not observed to react at all with alkanes.[8,18,19] For Cr^+, this appears to be due to the weakness of the chromium hydride and methyl bonds. Manganese ions present an interesting dilemma. We believe the failure of Mn^+ to react with alkanes is due to a weak *second* metal–ligand bond which must form with participation of the half-filled d shell. In bonding to what is probably a high-spin configuration, the loss of considerable electron-exchange energy weakens the resultant bond. Indeed, this is precisely why $Cr^+(^6S, 3d^5)$ has such a weak *first* bond.

Acknowledgment. This work was supported in part by the United States Department of Energy.

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(15) Beauchamp, J. L., unpublished results.

(16) See also ref 3. Interestingly, a correlation between the bond energies of the lanthanide monoxides and the promotion energy between states derived from the configurations $4f^n6s^2$ and $4f^{n-1}5d6s^2$ has been noted (Murad, E.; Hildenbrand, D. L. *J. Chem. Phys.* **1980**, *73*, 4005).

(17) Houriet, R.; Halle, L. F.; Beauchamp, J. L., to be published.

(18) A detailed comparison of the reactions of the group 8 transition-metal ions and the relationship of thermochemical properties to reactivity will be presented elsewhere (Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L., to be published).

(19) Allison, J.; Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1332. Freas, R. B.; Ridge, D. P. *Ibid.* **1980**, *102*, 7129.

Synthesis of 11α,9α-Epoxymethanothromboxane A_2: A Stable, Optically Active TxA_2 Agonist

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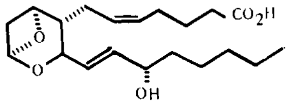
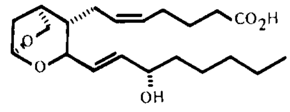
Received October 20, 1980

The structural elucidation of rabbit aorta contracting substance, subsequently renamed thromboxane A_2 (**1**, TxA_2), by Samuelsson and co-workers constitutes a noteworthy achievement in the chemistry of eicosanoids.[1,2] The ephemeral nature of **1** ($t_{1/2}$ of ca. 32 s at 37 °C in pH 7 aqueous solution), however, has prevented extensive evaluation of its potent pharmacological effects (e.g., platelet aggregation and vasoconstriction).[3] To circumvent the chemical instability of TxA_2, several carbon congeners have been synthesized.[4-9] None of these analogues, however, displays the biological profile of the natural material. We wish to report the synthesis of a stable, chiral analogue of TxA_2 (**2**), as well as a positional isomer (**28**), in which the labile oxetane ring of TxA_2 is replaced by a stable tetrahydrofuran moiety. Initial pharmacological evaluation indicates that **2** is the *first compound* to exhibit TxA_2 agonist activity in rabbit platelet rich plasma and on the isolated rabbit aorta, to be devoid of antagonist effects in these systems, and to be without appreciable thromboxane synthetase inhibiting activity.



1



2

The key synthetic transformation leading to the construction of the bridged tetrahydrofuran ring of **2** was envisioned as being the stereoselective insertion of a methylene unit into the lactone moiety of chiral **3**.[10] This construct began with the alkylation of lactone **3** (Scheme I) with benzyl bromide (5 equiv) and NaH (2 equiv) in hexamethylphosphoramide for 3 h to give, after silica gel chromatography, **4**[11,12] (65%). Reaction of lactone **4** with dimethylamine (10 equiv) in THF for 24 h (**5**:[11] mp 133–135 °C) followed by oxidation with Jones reagent (1.5 equiv) at −10 °C provided, after silica gel chromatography, **6**[11] (79% from **4**), mp 126–128 °C. Treatment of ketone **6** with the lithium salt of *N*,*S*-dimethyl-*S*-phenylsulfoximine[13] (3 equiv) in THF at −78 °C for 2 h (vide infra) followed by reductive elimination of the β-hydroxysulfoximine intermediate with aluminum amalgam (15

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(1) Hamberg, M.; Svensson, J.; Samuelsson, B. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 2994.

(2) For reviews, see: (a) Schaaf, T. K. *Annu. Rep. Med. Chem.* **1977**, *12*, 182. (b) Nicolaou, K. C.; Smith, J. B. *Ibid.* **1979**, *14*, 178.

(3) Needleman, P.; Kulkarni, P. S.; Raz, A. *Science* (*Washington*, DC) 1977, 195, 409.

(4) Nicolaou, K. C.; Magolda, R. L.; Smith, J. B.; Aharony, D.; Smith, E. F.; Lefer, A. M. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 2566.

(5) Ansell, M. F.; Caton, M. P. L.; Palfreyman, M. N.; Stuttle, K. A. J. *Tetrahedron Lett.* **1979**, 4497.

(6) Ohuchida, S.; Hamanaka, N.; Hayashi, M. *Tetrahedron Lett.* **1979**, 3661.

(7) Corey, E. J.; Ponder, J. W.; Ulrich, P. *Tetrahedron Lett.* **1980**, 137.

(8) Maxey, K. M.; Bundy, G. L. *Tetrahedron Lett.* **1980**, 445.

(9) Nicolaou, K. C.; Magolda, R. L.; Claremon, D. A. *J. Am. Chem. Soc.* **1980**, *102*, 1404.

(10) Corey, E. J.; Shibasaki, M.; Knolle, J. *Tetrahedron Lett.* **1977**, 1625.

(11) All structural assignments were supported by proton magnetic resonance, infrared, and mass spectral data.

(12) Unless indicated, products were obtained as viscous oils.

(13) Johnson, C. R.; Shanklin, J. R.; Kirchoff, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 6462.

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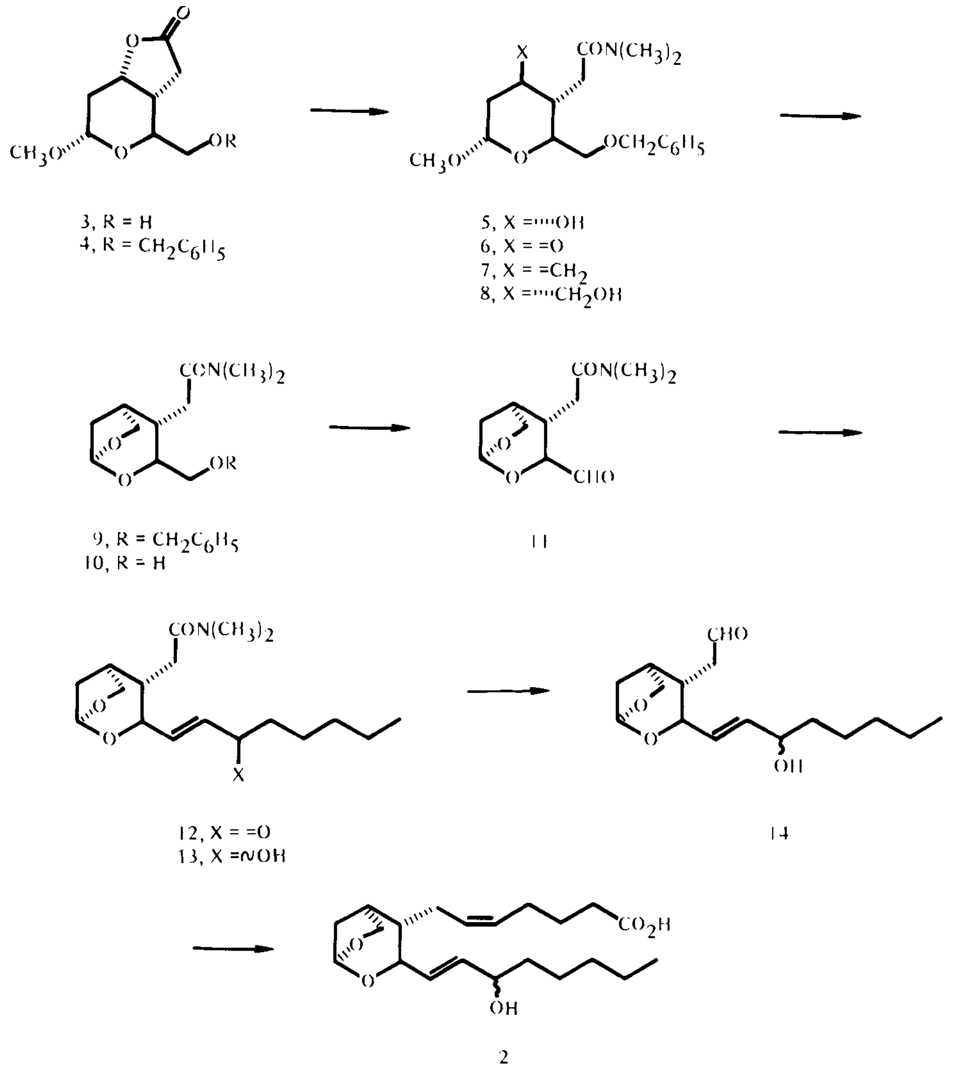

equiv) in aqueous HOAc at 25 °C for 2.5 h afforded, after silica gel chromatography, **7**[11] (50%), mp 40–42 °C. Hydroboration of olefin **7** with 9-borabicyclo[3.3.1]nonane[14] (12 equiv) in refluxing THF for 1.5 h and oxidation of the intermediate with 30% H_2O_2 (24 equiv) and 5 N NaOH (0.33 equiv) at 25 °C for 2 h gave, after silica gel chromatography, **8**[11,12] (68%). Treatment of alcohol **8** with *p*-toluenesulfonic acid monohydrate (1 equiv) in CH_2Cl_2 for 3 h provided **9**.[11,12] Hydrogenolysis of crude **9** under 50 psi of hydrogen for 1 h in 5% HOAc in EtOH using 5% Pd/C as catalyst[15] afforded **10**[11,12] (67% from **8**).

Oxidation of crude alcohol **10** with 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide[16] (3 equiv), Me_2SO (4 equiv), and pyridinium trifluoroacetate (0.5 equiv) in toluene for 2 h followed by filtration and concentration without aqueous workup afforded **11**,[11,12] which was immediately condensed with the sodium salt of dimethyl (2-oxoheptyl)phosphonate[17] in THF for 2 h to give, after silica gel chromatography, **12**[11,12] (31% from **10**). Reduction of ketone **12** with lithium triethylborohydride (1 equiv) at −78 °C for 15 min (**13**[11,12]) followed by treatment with a solution of lithium triethoxyaluminum hydride in ether[18] at −5 °C for 1 h (**14**[11,12]) and a Wittig reaction with the ylide from 5-(triphenylphosphono)pentanoic acid[19] in Me_2SO provided, after silica gel chromatography, **2**[20] as a mixture of C_{15} epimers.

The lactone **3**[10] (Scheme II) was also acylated with benzoyl chloride (1.1 equiv) in pyridine/CH_2Cl_2 at 0 °C for 2 h and 25 °C for 18 h (**15**,[11] 89%, mp 102–103 °C) followed by treatment with dimethylamine (**16**,[11] quantitative, mp 97–99 °C) and oxidation with Jones reagent as described above to give **17**[11] (96%, mp 64–66 °C). Treatment of ketone **17** with the ylide from methyltriphenylphosphonium bromide[21] failed to provide any identifiable product probably due to ester cleavage and/or β elimination caused by the strongly basic character of this reagent. Consistent with this hypothesis, ketone **17** was smoothly converted into the corresponding α,β-unsaturated ester[22] with the ylide from

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(14) Knights, E. F.; Brown, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 5280.

(15) Schaaf, T. K.; Corey, E. J. *J. Org. Chem.* **1972**, *37*, 2921.

(16) Use of this water-soluble diimide allows in contrast to standard practice (Sheehan, J. C.; Cruickshank, P. A.; Boshart, G. L. *J. Org. Chem.* **1961**, *26*, 2525), for facile removal of the aldehyde **11** from the less-soluble diimide and urea byproduct without aqueous workup.

(17) Corey, E. J.; Vlattas, I.; Andersen, N. H.; Harding, K. *J. Am. Chem. Soc.* **1968**, *90*, 3247.

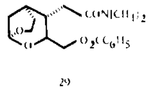
(18) Brown, H. C.; Tsukamoto, A. *J. Am. Chem. Soc.* **1964**, *86*, 1089.

(19) Corey, E. J.; Weinshenker, N. M.; Schaaf, T. K.; Huber, W. *J. Am. Chem. soc.* **1969**, *91*, 5675.

(20) (a) ^{1}H NMR (60 MHz, $CDCl_3$) δ 5.70 (m, 2 H, *trans*-CH=CH), 5.37 (m, 3 H, *cis*-CH=CH, OCHO); IR ($CHCl_3$) 1700 cm^{-1} (carbonyl); MS ($C_{21}H_{32}O_4$, *p*-H_2O), *m/e* calcd, 348.2300; found, 348.2267. (b) While the mixture of C_{15} epimers was used for initial biological evaluation, the dimethylamide, **13**, could be separated by analytical TLC (EtOAc, 3 passes, R_f = 1.80 and 1.25). (c) A sample of **2** has been kept at −10 °C for 1 year without degradation as judged by TLC and mass spectral analysis.

(21) Wittig, G.; Schöllkopf, U. *Org. Synth.* **1960**, *40*, 66.

(22) This α,β-unsaturated ester was converted by hydrogenation (10% Pd on C in EtOH), reduction (lithium borohydride in THF), and cyclization (*p*-toluenesulfonic acid in CH_2Cl_2) into the bicyclic ester **29**, which may be transformed into the bis-homocongener of TxA_2.



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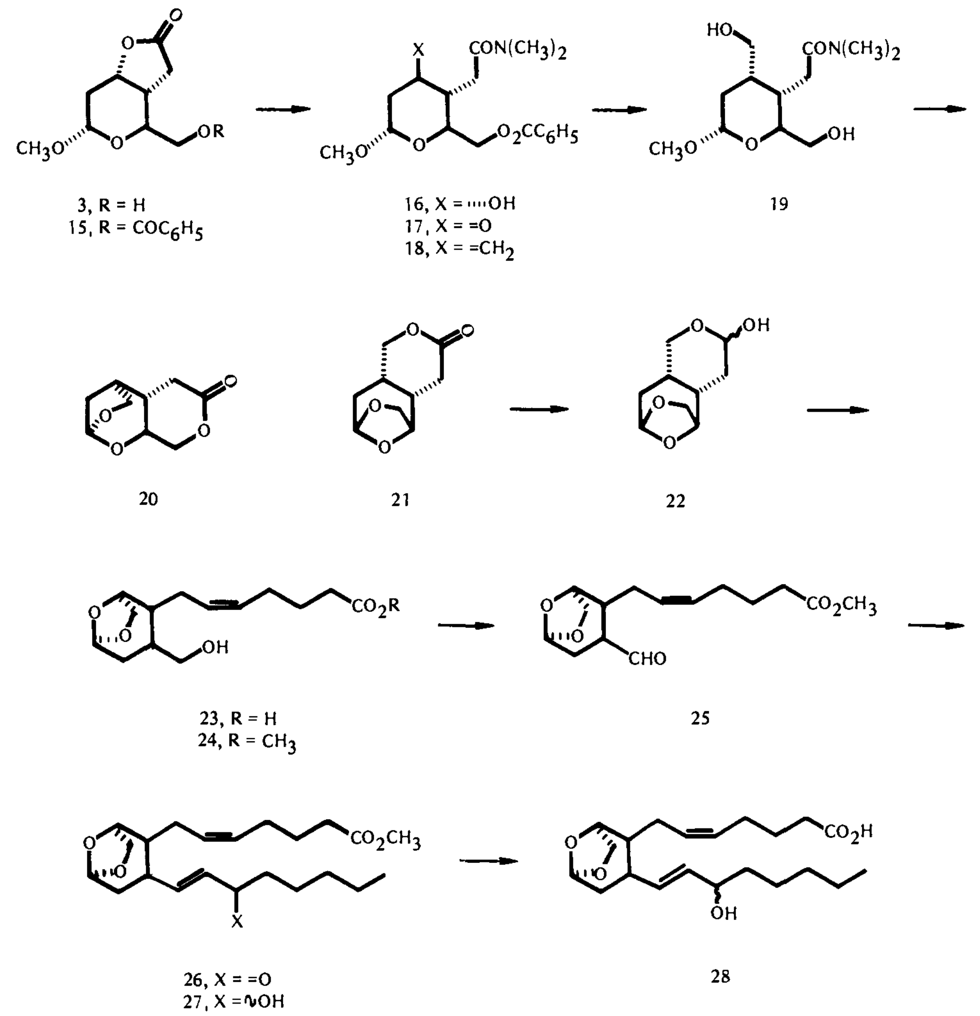
Scheme II



trimethyl phosphonoacetate.[23] Consequently, the olefin $\mathbf{18}^{11,12}$ (59%) was prepared by treating ketone **17** with the lithium salt of *N*,*S*-dimethyl-*S*-phenylsulfoximine followed by reductive elimination and benzoylation[24] as described above. Thus, use of Johnson's sulfoximine reagent provides a method of methylenating ketones in base-sensitive molecules.[25] Hydroboration/oxidation of olefin **18** as described above afforded $\mathbf{19}^{11,12}$ (45%). Cyclization of diol **19** with *p*-toluenesulfonic acid monohydrate (1 equiv) in CH_2Cl_2 for 18 h provided, after silica gel chromatography, $\mathbf{21}^{11}$ (50%, mp 122–123 °C) and not the alternative isomer **20**.[26,27]

Presumably, the formation of **21** was the result of thermodynamic control as evidenced by the isomerization of alcohol **10** with *p*-toluenesulfonic acid to give the same product, **21**. The availability of **21** allowed the synthesis of an analogue of **2**, which commenced with the reduction of lactone **21** with diisobutylaluminum hydride (1.1 equiv) in toluene at −78 °C for 1.5 h ($\mathbf{22}^{11,12}$), followed by a Wittig reaction with the ylide from 5-(triphenylphosphono)pentanoic acid in Me_2SO to provide, after silica gel chromatography, $\mathbf{23}^{11,12}$ (61% from **21**). Treatment of acid **23** with an excess of ethereal diazomethane ($\mathbf{24}^{11,12}$) followed by oxidation ($\mathbf{25}^{11,12}$) and condensation with the sodium salt of dimethyl (2-oxoheptyl)phosphonate as described above afforded, after silica gel chromatography, $\mathbf{26}^{11,12}$ (49% from **23**). Reduction of ketone **26** with lithium triethylborohydride ($\mathbf{27}^{11,12}$) followed by hydrolysis with methanolic NaOH gave, after silica gel chromatography, the isomeric homo-TxA_2 analogue $\mathbf{28}^{28}$ (88% from **26**).

Initial pharmacological evaluation has found homo-TxA_2 **2** to be 25–30 times less potent in contracting superfused rabbit aorta spiral strips[29] than TxA_2. Isomeric **28** is 60 times less potent than **2** in this system, and neither **2** nor **28** antagonized the contracting effects of TxA_2 at nonagonist doses. Homo-TxA_2 **2** is 700–1000 times less effective than TxA_2, and **28** is inactive, in inducing reversible platelet aggregation in rabbit platelet rich plasma.[30] The weaker platelet aggregating agonist activity of **2** relative to its effects on the isolated rabbit aorta may be due to plasma protein binding.[31] Neither **2** nor **28** antagonized the platelet aggregating effects of TxA_2, and neither compound exhibited appreciable

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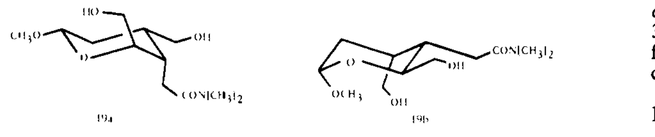
(23) Wadsworth, W. S., Jr.; Emmons, W. D. *Org. Synth.* **1965**, *45*, 44.

(24) Partial cleavage of the benzoyl ester occurs under the reaction conditions, thereby necessitating reprotection of the alcohol function.

(25) Bundy, G. L. *Tetrahedron Lett.* **1975**, 1957.

(26) Compound **21** may also be the product of kinetic control since S_N2 displacement is expected to be more facile from conformer **19a** than from **19b**.



(27) Treatment of lactone **20** with dimethylamine in THF provides a hydroxy amide, which exhibits a TLC mobility (R_f = 0.38, 10% MeOH in $CHCl_3$) different from that of **10** (R_f = 0.32).

(28) (a) ^1H NMR (60 MHz, $CDCl_3$) δ 6.03 (s, 2 H, OH), 5.43 (m, 5 H, *cis*- and *trans*-CH═CH, OCHO); MS ($C_{21}H_{32}O_4$, *p*-H_2O), *m*/*e* calcd, 348.2300; found, 348.2314. (b) While the mixture of C_{15} epimers was used for initial biological evaluation, the ester, **27**, could be separated by silica gel chromatography using mixtures of ether in toluene as eluants.

(29) Carty, T. J.; Stevens, J. S.; Lombardino, J. G.; Parry, M. J.; Randall, M. J. *Prostaglandins* **1980**, *19*, 671.

(30) Blackwell, G. J.; Duncombe, W. G.; Flower, R. J.; Parsons, M. F.; Vane, J. R. *Br. J. Pharmacol.* **1977**, *59*, 353.

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human platelet thromboxane synthetase inhibiting activity in vitro.[32] In summary, the biological profile displayed by **2** is consistent with that of a TxA_2 agonist. The agonist profile of **2**, in contrast to the mixed activities exhibited by the carbon analogues of TxA_2, indicates that the bicyclic acetal structure of TxA_2, the assignment of which was based on indirect evidence,[1] plays a key role in the activity of the natural material. Furthermore, the reduced activity exhibited by **28** suggests that position of the acetal oxygens is important for activity. A detailed description of these results will be the subject of a forthcoming publication.

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(32) Needleman, P.; Moncada, S.; Bunting, S.; Vane, J. R.; Hamberg, M.; Samuelsson, B. *Nature (London)* **1976**, *261*, 558.

Discrimination of $C_3H_3^+$ Structures on the Basis of Chemical Reactivity

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The ion $C_3H_3^+$ is one of the more ubiquitous ions observed in the mass spectral patterns of organic compounds. It is also the most abundant ion species observed in fuel-rich acetylene and benzene flames,[1] where it has been suggested to be an important precursor in the mechanism leading to soot formation.

There is ample evidence from studies of metastable ion fragmentation processes and measurements of kinetic energy release in such fragmentations in alkanes,[2] allyl halides,[3] the 1-halo-1-propynes,[4] and the propargyl halides[4,5] that $C_3H_3^+$ exists in two structures. According to theoretical calculations,[6] the cyclic $C_3H_3^+$ structure (with a heat of formation of 11.1 eV) is the most stable isomer. The propargyl ion, CH_2CCH^+, with a heat of formation approximately 1 eV higher, is the next most stable form.[4] These have been identified as the most probable structures for the $C_3H_3^+$ ions observed in the fragmentation processes.[2-5]

Although a few rate constants and reaction mechanisms for $C_3H_3^+$ have been reported,[7] only Munson[8] in a 1967 study of the ionic reactions in *n*-butane remarked on the "peculiar" pressure dependence of the abundance of $C_3H_3^+$, which he suggested might be caused by the presence of two different $C_3H_3^+$ species. All other kinetic measurements have tacitly assumed that the reactant $C_3H_3^+$ species had a unique structure.

Here we report results on the kinetics of the reactions of $C_3H_3^+$ species which show that both isomers retain distinct identities as long as $\sim 10^{-3}$ s (the collision interval in the ion cyclotron resonance spectrometer) and that their chemistry is quite different. The formation of $C_3H_3^+$ in a number of precursor compounds through dissociative charge-transfer processes is shown to result in strongly energy-dependent variations in the relative abundances of the two isomers. Reactions of both isomers with a number of organic compounds, including acetylene and benzene, were observed.

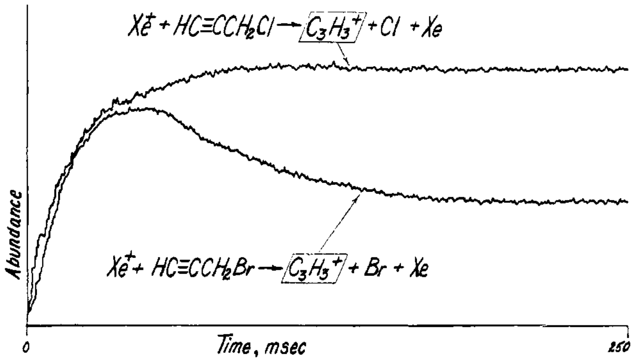

Figure 1. The abundance of $C_3H_3^+$ ions in $Xe–CH\equiv CCH_2Br$ (20:1) and $Xe–CH\equiv CCH_2Cl$ (20:1) mixtures as a function of time. Nominal electron energy, 60 eV; total pressure, 10^{-5} torr.

A pulsed ion cyclotron resonance spectrometer (ICR) was utilized in this work.[9] A description of the approach used to distinguish between isomeric ions through their kinetic differences has been given.[10,11]

Figure 1 shows the abundance of $C_3H_3^+$ as a function of time in two different systems ($Xe–CH\equiv CCH_2Br$ and $Xe–CH\equiv CCH_2Cl$ mixtures), chosen as an illustration of a system in which two distinct populations of $C_3H_3^+$ are evident, and a system in which all $C_3H_3^+$ ions apparently have the same (unreactive) structure. In the $CH\equiv CCH_2Br$ system, a fraction of the $C_3H_3^+$ ions react rapidly with the parent molecule

$$\mathit{C_3H_3}^+ + \mathrm{C_3H_3X} \rightarrow \mathrm{C_6H_6^+} + \mathrm{X} \qquad (1)$$

(where X is Br for the $CH\equiv CCH_2Br$ reactant, and $\mathit{C_3H_3}^+$ is the more reactive isomer, to be distinguished from ($C_3H_3^+$), the other isomer). An upper limit of 10^{-12} cm^3/molecule·s can be ascribed to the rate constant for reaction of ($C_3H_3^+$) with $CH\equiv CCH_2Br$, while $\mathit{C_3H_3}^+$ reacts at essentially every collison.

The relative abundances of the $\mathit{C_3H_3}^+$ and ($C_3H_3^+$) populations are given in Table I for various binary systems where $C_3H_3^+$ is predominantly produced by the dissociative charge-transfer process[12]

$$\mathrm{M^+ + C_3H_3X \rightarrow C_3H_3^+ + X + M} \qquad (2)$$

(where X is a halogen atom, and M represents a rare gas atom or a diatomic or triatomic molecule). The rate constants for the overall charge transfer from M^+ to C_3H_3X are also given in Table I. In every case measured here, the charge transfer occurs at every collison; the variations in the rate constants listed in Table I follow with remarkable fidelity the changes predicted from the changes in the reduced mass of the various reacting pairs. The photoelectron spectra of $CH\equiv CCH_2Cl$ and $CH\equiv CCH_2Br$[13] consist of well-defined bands with a gap between $\sim$11.5 and $\sim$14.5 eV; yet charge-transfer processes which fall within this energy gap

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(1) (a) Michaud, P.; Delfau, J. L.; Barassin, A. Proceedings of the Eighteenth Symposium (International) on Combustion, 1981; p 443. (b) Olson, D. B.; Calcote, H. F. "Particulate Carbon: Formation during Combustion"; Proceedings of the General Motors Symposium, Warren, MI, Oct 15–16, 1980. (c) Olson, D. B.; Calcote, H. F. Proceedings of the Eighteenth Symposium (International) on Combustion, 1981; p 453.

(2) Goldberg, P.; Hopkinson, J. A.; Mathias, A.; Williams, A. E. *Org. Mass Spectrom.* **1970**, *3*, 1009.

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(6) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 10.

(7) (a) Lin, M. S. C.; Harrison, A. G. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *17*, 97. (b) Abramson, F. P.; Futrell, J. H. *J. Phys. Chem.* **1968**, *72*, 1994. (c) Fuchs, R. *Z. Naturforsch. A* **1961**, *16A*, 1027. (d) Harrison, A. G. *Can. J. Chem.* **1963**, *41*, 236. (e) Pottie, R. F.; Lorquet, A. I.; Hamill, W. H. *J. Am. Chem. Soc.* **1962**, *84*, 529. (f) Derwich, G. A. W.; Galli, A.; Giardini-Guidoni, A.; Volpi, G. G. *J. Chem. Phys.* **1964**, *41*, 2998. (g) Bone, L. J.; Futrell, J. H. *Ibid.* **1967**, *46*, 4084. (h) Virik, L. I.; Safik, Y. A.; Dzagachpakyak, R. V. *Khim. Vys. Energ.* **1967**, *1*, 417. (i) Virik, L. I.; Safik, Y. A.; Dzagachpakyak, R. V.; Motsahrv, G. V. *Ibid.* **1969**, *3*, 23. (j) Wexler, S.; Marshall, R. *J. Am. Chem. Soc.* **1964**, *86*, 781.

(8) Munson, M. S. B. *J. Phys. Chem.* **1967**, *71*, 3966.

(9) Lias, S. G.; Eyler, J. R.; Auslos, P. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *19*, 219.

(10) Jackson, J.-A. A.; Lias, S. G.; Ausloos, P. *J. Am. Chem. Soc.* **1977**, *99*, 7515.

(11) Shold, D. M.; Ausloos, P. *J. Am. Chem. Soc.* **1978**, *100*, 7915.

(12) The relative abundances of $\mathit{C_3H_3}^+$ and ($C_3H_3^+$) listed in Table I were derived from experimental tracings of ion abundance as a function of time, like those pictured in Figure 1. The abundance of ($C_3H_3^+$) is taken as equal to the observed abundance of unreactive ions (i.e., the flat portion of the curve seen at long times), while the abundance of $\mathit{C_3H_3}^+$ is estimated by taking the difference between the observed maximum in the curve and the level portion. It is recognized that this procedure necessarily underestimates the relative importance of the $\mathit{C_3H_3}^+$ population because a fraction (estimated from the rate of increase of the corresponding product ions to be about 10–30%) will have reacted with the parent molecule by the time the maximum is reached.

(13) Botter, R.; Gounell, Y.; Henry, Y.; Jullien, J.; Menes, F.; Salgadi, D. *J. Electron Spectrosc. Relat. Phenom.* **1977**, *10*, 393.