boration first with thexylborane (5 equiv, −78 °C with slow warming to −23 °C) and then with borane itself (4 equiv, −23 °C, 12 h) gave the triols **5** and **6** in 90% yield.[9] NMR analysis of the crude product showed the ratio of the desired *meso* (**5**) to the undesired *dl* (**6**) triols to be 5:1, and pure *meso*-**5** (^{13}C ($CDCl_3$) δ 143.9, 128.6, 127.8, 127.0, 86.8, 79.0, 71.2, 65.3, 36.3, 11.3) was easily isolated by crystallization from ether (mp 186–187 °C).

Conversion to the second diene for the last double hydroboration required nine straightforward steps (average yield per step = 90%). These steps were triol protection ($Me_3SiCH_2CH_2OCH_2Cl$, *i*-Pr_2NEt),[10] catalytic detritylation (H_2, $Pd(OH)_2/C$, EtOH), oxidation ($(COCl)_2$, Me_2SO, Et_3N),[11] 1,1-dibromoalkene formation (CBr_4, Ph_3P), and conversion to the acetylide (BuLi, THF)[12] with trapping by ethyl chloroformate to yield **7** (Scheme III). Addition of methylcuprate (Me_2CuLi, THF, −78 °C),[13] reduction ($LiAlH_4$, Et_2O), tritylation (Ph_3CCl, Et_3N, DMAP), and finally deprotection of the three secondary alcohols (Bu_4NF, HMPA, 85 °C) gave **8**. Hydroboration as described for **4** gave a 76% yield of pentaols which were shown by HPLC and NMR to consist of a 4:1 mixture of *meso*-**9** (^{13}C ($CDCl_3$) δ 143.9, 128.6, 127.8, 127.0, 86.9, 78.8, 72.6, 72.4, 65.3, 37.7, 35.9, 11.4, 10.3) and *dl* products. Although **9** could be isolated by MPLC at this point, it was more convenient to monomethylate one of the less hindered hydroxyls (CH_3I, Ag_2O, 25 °C; 63%) catalytically detritylate (84%), and then isolate pure **10** (mp 192 °C) by simple flash chromatography. The structure of **10** was shown to be correct at this point by conversion to a degradation product of rifamycin SV.[14]

Final transformation of **10** to the rifamycin ansa chain intermediate **11** was effected in ten steps (20% overall yield) by using standard methodology (see supplementary data).[15]

Registry No. 1, 13019-19-7; **2**, 71581-36-7; **3**, 85067-65-8; **4**, 85067-66-9; **5**, 85067-67-0; **6**, 85114-72-3; **7**, 85067-68-1; **8**, 85067-69-2; **9**, 85067-70-5; **10**, 85067-71-6; **11**, 85067-72-7; **1** (trimethylsilyl derivative), 76966-15-9; **1** (*tert*-butyldimethylsilyl derivative), 85067-73-8; **1** (*tert*-butyldiphenylsilyl derivative), 85067-74-9; **1** (trityl derivative), 85067-75-0; **1** (benzyloxymethyl derivative), 85067-76-1; **1** (acetyl derivative), 26077-07-6; **1** (trifluoroacetyl derivative), 85067-77-2; **1** (9-borabicyclo[3.3.1]nonane derivative), 85082-22-0; **2** (benzyloxymethyl derivative), 85067-78-3; **2** (trifluoroacetyl derivative), 85067-79-4; **3** (benzyloxymethyl derivative), 85067-80-7; *threo*-2-methyl-1,3-heptanediol, 85067-81-8; *erythro*-2-methyl-1,3-heptanediol, 85067-82-9; *meso*-6-methyl-5,7-undecanediol, 85067-83-0; *dl*-6-methyl-5,7-undecanediol, 85114-73-4; *threo*-2-methyl-3-(trimethylsilyloxy)-1-heptanol, 85067-84-1; *threo*-2-methyl-3-(*tert*-butyldimethylsilyloxy)-1-heptanol, 85067-85-2; *threo*-2-methyl-3-(*tert*-butyldiphenylsilyloxy)-1-heptanol, 85067-86-3; *threo*-2-methyl-3-(trityloxy)-1-heptanol, 85067-87-4; *threo*-2-methyl-3-(benzyloxymethoxy)-1-heptanol, 85067-88-5; *threo*-2-methyl-3-(acetyloxy)-1-heptanol, 85067-89-6; *threo*-2-methyl-3-(trifluoroacetyloxy)-1-heptanol, 85067-90-9; *threo*-2-methyl-3-(bicyclo[3.3.1]nonane-9-borato)-1-heptanol lithium salt, 85067-91-0; (5*R**,6*R**,7*S**)-6-methyl-7-(benzyloxymethoxy)-5-undecanol, 85067-92-1; (5*R**,6*R**,7*S**)-6-methyl-7-(trifluoroacetoxy)-5-undecanol, 85067-93-2; (5*S**,6*R**,7*S**)-6-methyl-7-(benzyloxymethoxy)-5-undecanol, 85115-13-5.

Supplementary Material Available: ^1H NMR data for compounds **1–10** and preparations are described for authentic 1,3-diols and for the conversion of **10** to **11** (11 pages). Ordering information is given on any current masthead page.

---

[9] Reaction of the diene **4** did not go to completion with $ThBH_2$ alone. The *meso*:*dl* ratio was essentially the same as when the product was formed (in reduced yield) with only $ThBH_2$.

[10] B. H. Lipshutz and J. J. Pegram, *Tetrahedron Lett.*, **21**, 3343 (1980).

[11] A. J. Mancuso, S.-L. Huang, and D. Swern, *J. Org. Chem.*, **43**, 2480 (1978).

[12] E. J. Corey and P. L. Fuchs, *Tetrahedron Lett.*, 3769 (1972).

[13] E. J. Corey and J. A. Katzenellenbogen, *J. Am. Chem. Soc.*, **91**, 1851 (1969).

[14] **10** was cleaved ($NaIO_4$, MeOH) and reduced ($LiAlH_4$) to a racemic pentaol (mp 115–117 °C). Rifamycin SV was ozonized (MeOH, −25 °C) and worked up reductively ($NaBH_4$) to give after deacetylation an optically active pentaol (mp 142–145 °C) that was indistinguishable from the synthetic material by IR, ^1H NMR, MS, and ^{13}C NMR ((CD_3COCD_3) δ 83.2, 78.6, 75.8, 71.8, 68.1, 63.2, 59.1, 38.8, 38.4, 36.8, 36.7, 13.6, 10.9, 10.8, 10.2).

[15] This work was supported by grants from the National Institutes of Health and the National Science Foundation.

Chemistry of Carbynes: Reaction of CF, CCl, and CBr with Alkenes

B. P. Ruzsicska, A. Jodhan, H. K. J. Choi, and
O. P. Strausz*

Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada T6G 2G2

T. N. Bell

Department of Chemistry, Simon Fraser University
Burnaby, British Columbia, Canada V5A 1S6

Received December 30, 1982

Carbynes, the monovalent carbon radical family comprising CH and its derivatives, represent the least explored and understood variety of carbon radicals especially when contrasted to their nearest analogues, the carbenes.[1] The primary reason for this lies in the unavailability of a suitable, clean, general source for producing carbynes under conditions applicable to kinetic and mechanistic studies. Consequently, each of the carbyne species—CH, CCl, CBr, CCO_2Et—for which the chemistry has been investigated to date has been generated in an individual way. Each method is complicated by the formation of a number of other reactive radicals, and in fact the carbynes invariably represent only a minor product of the decomposition of the source compound.

CH, CCl, and CBr have been studied in the gas phase by flash and laser photolysis or pulsed radiolysis using C_1 and C_2 hydrocarbons and their halo derivatives as the source material. It was possible by these techniques to measure absolute rate constants for a series of reactions of CH, CCl, and CBr; however, this kinetic approach did not permit the establishment of the mechanistic details of the reactions, which were inferred on the basis of assumed analogies.

On the other hand, the chemistry of CCO_2Et has been investigated in the solution phase.[2] The results of kinetic studies and product analyses suggest that the ground-state doublet carbethoxymethylidyne generated via the in situ photolysis of mercury bis(diazoacetate) ($EtO_2CCN_2HgCN_2CO_2Et$) undergoes concerted, stereospecific cycloaddition to alkenes, regioselective insertion into the C–H bonds of alkanes, alkenes, and alcohols, polar addition to the O–H bonds of alcohols, and cycloaddition to aromatics resulting in ring-expanded products. Hydrogen abstraction did not appear to occur, and absolute rate constants could not be measured.

CH is isoelectronic with the nitrogen atom but in contrast has an electron configuration $1\sigma^2 2\sigma^2 3\sigma^2 1\pi$, giving rise to a $^2\Pi$ ground electronic state. The result is an orbital occupancy that is unique in carbon radical chemistry, in which there is a doubly occupied (lone pair) σ orbital and a singly occupied and an empty π orbital localized on the carbon atom. This electron deficiency endows carbynes with a high reactivity and a distinct electrophilic character. In the case of halocarbynes, overlap between the p_π orbitals of carbon and those of the halogen results in partial multiple-bond formation characterized by the electron configuration$...w\pi^4 x\sigma^2 v\pi^1$ and an accompanying decrease in chemical reactivity.

The purpose of the present communication is to report the first chemical studies of fluoromethylidyne (CF) and the results of a comparative study of CF, CCl, and CBr with a series of alkenes under similar experimental conditions. These halomethylidynes were produced by the flash photolysis of $CHFBr_2$, $CHClBr_2$, and $CHBr_3$, respectively, using the same apparatus and experimental techniques as in previous studies on CCl and CBr.[1] Monitoring of the carbyne concentrations was done by kinetic absorption spectroscopy using the Q_1, P_1 and P_2 bands of the ($\tilde{A}^2\Sigma^+–\tilde{X}^2\Pi(a)$,

---

[1] James, F. C.; Choi, H. K. J.; Ruzsicska, B. P.; Strausz, O. P.; Bell, T. N. "Frontiers of Free Radical Chemistry"; Pryor, W. A., Ed.; Academic Press: New York, 1980; pp 139–170.

[2] Strausz, O. P.; Kennepohl, G. J. A.; Garneau, F. X.; DoMinh, T.; Kim, B.; Valenty, S.; Skell, P. S. *J. Am. Chem. Soc.* **1974**, *96*, 5723.

0002-7863/83/1505-2489$01.50/0

Table I. Absolute Rate Constants for the Reactions of Methylidynes with Alkenes

alkene	$10^{-9}k$, $M^{-1}\,s^{-1}$			
	CH	CF	CCl	CBr
C_2H_4	69 ± 6[a] 130 ± 50[b]	0.04 ± 0.01	0.16 ± 0.01 0.13 ± 0.01[c]	0.52 ± 0.02
C_3H_6		0.3 ± 0.1	1.0 ± 0.1	3.0 ± 0.3
1-C_4H_8		0.4 ± 0.1	1.7 ± 0.2	3.5 ± 0.3
trans-2-butene		1.1 ± 0.2	2.6 ± 0.2	7.4 ± 0.8
2-methyl-2-propene		1.1 ± 0.3	3.5 ± 0.3	8.0 ± 1.0
2-methyl-2-butene			8.0 ± 1.0	17 ± 2
2,3-dimethyl-2-butene			14 ± 3	23 ± 6
cyclohexene			3.1 ± 0.2	
1,3-cyclohexadiene			1.4 ± 0.2	
1,4-cyclohexadiene			3.7 ± 0.2	

[a] Reference 3. [b] Reference 4. [c] Reference 5; 25 ± 3 °C; errors are standard deviation; *cyclo*alkenes ~100–120 measurements; others, ~220–480 measurements.

1–0) transition at 223.79, 223.88, and 224.18 nm for CF; the Q_1 band of the $(\tilde{A}^2\Delta(b)\text{–}\tilde{X}^2\Pi(a), 0\text{–}0)$ transition at 277.87 nm for CCl; and the Q_1 band of the $(\tilde{A}^2\Delta(a)\text{–}\tilde{X}^2\Pi(a))$ transition at 301.34 nm for CBr.

The absolute rate constants obtained for the reaction of CF with five alkenes, of CCl with ten alkenes, and of CBr with seven alkenes along with the only rate constant reported in the literature for the reaction of methylidyne with an alkene, namely ethylene, are presented in Table I.

As seen from the data, CF reacts with alkenes, as do the other two halomethylidynes studied before. By far the most reactive species of the four methylidynes studied quantitatively to date is CH; it reacts about 3 orders of magnitude faster than the halomethylidynes. For the halomethylidynes the order of reactivity is CF < CCl < CBr and the ratio of rate constants is ≈1:3–4:9–13 throughout the series. All three halomethylidynes exhibit a distinct electrophilic character as manifested by the increase in reactivity with increasing alkyl substitution on the alkenic carbon. In the case of CCl this increase is nearly 2 orders of magnitude in going from ethylene to tetramethylethylene. The reactivity of CCl with *trans*-2-butene, cyclohexene, and 1,4-cyclohexadiene is nearly identical and is in the order expected. The low value of the rate constant for 1,3-cyclohexadiene is in agreement with the electrophilicity of carbynes and rules out a radical-like reactivity for them.

The observed trend in the relative reactivities of the three halomethylidynes can be interpreted in terms of the relative amount of p_π–p_π overlap between the halogen and carbon. The values of the C–X bond dissociation energies, 131, 81, and 75 kcal/mol, and bond lengths, 1.27, 1.65, and 1.82 Å for CF, CCl, and CBr, respectively, reflect this p_π–p_π overlap, which increases when the size of the halogen p_π orbital approaches the size of the carbon p_π orbital. Hence, the strongest partial triple bond, and consequently the lowest reactivity, will be encountered with CF and the weakest triple-bond character and highest reactivity with CBr. This interpretation of π-bond strength and its effect on chemical reactivity is also in agreement with spectroscopic observations. The spectroscopic transition $^2\Delta \leftarrow {}^2\Pi$ in halomethylidynes is due to promotion of an electron from the $x\sigma$ orbital to the $v\pi$ orbital. The energy of this transition increases in the order CBr < CCl < CF and reflects increasing orbital energy separation. If the $v\pi$ orbital, which is antibonding in halomethylidynes, increases in energy, then the orthogonal bonding $w\pi$ orbital must decrease in energy. Therefore the increasing transition energy reflects stronger π bonding.

By analogy with CCO_2Et the primary product of the reaction $CX(\tilde{X}^2\Pi)$ + alkene is postulated to be a vibrationally excited cyclopropyl radical, C–C–C–X, which may undergo further unimolecular reactions. Ab initio molecular orbital calculations on the CH + C_2H_4 system predict that the reaction proceeds along a non-least-motion symmetry-allowed path and features a zero activation energy.[6] This is in agreement with the high experimental rate constant, ~10^{11} $M^{-1}\,s^{-1}$. The cycloaddition reactions of halomethylidynes probably follow a similar non-least-motion reaction path and are predicted to feature progressively increasing but small activation energies in the order CBr < CCl < CF.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for continuing financial support.

Registry No. CF, 3889-75-6; CCl, 3889-76-7; CBr, 3889-77-8; C_2H_4, 74-85-1; C_3H_6, 115-07-1; 1-C_4H_8, 106-98-9; *trans*-2-butene, 624-64-6; 2-methyl-2-propene, 115-11-7; 2-methyl-2-butene, 513-35-9; 2,3-dimethyl-2-butene, 563-79-1; cyclohexene, 110-83-8; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1.

---

(3) Bosnali, M. W.; Perner, D. *Z. Naturforsch., A* **1971**, *26A*, 625.

(4) Butler, J. E.; Goss, L. P.; Lin, M. C.; Hudgens, J. W. *Chem. Phys.* **1981**, *56*, 355.

(5) Tiee, J. J.; Wampler, F. B.; Rice, W. W. *Chem. Phys. Lett.* **1980**, *73*, 519.

(6) Gosavi, R. K.; Strausz, O. P.; Gunning, H. E. *Chem. Phys. Lett.* **1980**, *76*, 159.

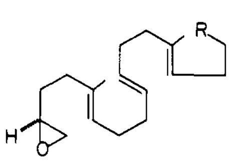
Direct Total Synthesis of Traditional Sterols by Tricyclization of Polyunsaturated Cyclohexene Oxides

Eugene E. van Tamelen* and Jih Ru Hwu

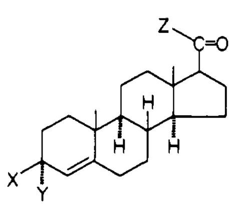
Department of Chemistry, Stanford University
Stanford, California 94305

Received July 12, 1982

This laboratory recently recorded[1] the detection of (±)-allopregnanolone (4,5α-dihydro-**2a**) as a product resulting from the nonenzymic cyclization of an acarbocyclic monosubstituted 1,2-oxide (**1**), a reaction of distinct theoretical interest. Now, by appropriate structural modification of the starting material, we have developed an approach of more practical import, in which polycyclization of the 1,2-oxide type **3**[2] yields, directly and efficiently, substances such as (±)-3β,5β-dihydroxypregnan-20-one



1



2

a X = OH; Y = H; Z = CH_3
b X, Y = O; Z = CH_3
c X, Y = O; Z = OH

---

(1) van Tamelen, E. E.; Leiden, T. M. *J. Am. Chem. Soc.* **1982**, *104*, 2061.

(2) For the monocyclization of similar but simpler cyclohexene oxides, see: Marsham, P.; Widdowson, D. A.; Sutherland, J. K. *J. Chem. Soc., Perkin Trans. 1* **1974**, 238.