A reasonable reaction path for the herein described synthesis of $Ir(C_6N_4H)CO(TCNE)(PPh_3)_2$ would involve initial formation of a hydrido-π-olefinic complex, followed by a 1,4-addition[8c] to the TCNE to give a coordinatively unsaturated planar iridium(I) complex. That 1,4 addition occurs with tetracyanoethylene instead of the usual 1,2 addition as with unsaturated hydrocarbons is understandable in view of the electronic structure of TCNE, for which calculations[10] have shown a buildup of negative charge on the nitrile nitrogens relative to the olefinic carbon atoms. Thus, transfer of H as hydride is implied and the electrophilic iridium attacks a nitrogen atom to give $Ir(C_6N_4H)(CO)(PPh_3)_2$. Subsequent reaction of this coordinatively unsaturated compound with a second molecule of TCNE would give the product. Allowing for Ir–H addition being 1,4 instead of 1,2, these reaction steps are analogous to those often proposed in the polymerization of olefins as catalyzed by transition metal catalysts, and the structure reported herein is the first to be described of such a model intermediate compound in olefin polymerization.

Acknowledgment. This work was supported by grants from the National Science Foundation.

(10) J. Halper, W. D. Closson, and H. B. Gray, *Theor. Chim. Acta*, 4, 174 (1966).

J. S. Ricci, James A. Ibers
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

M. Shirley Fraser, W. H. Baddley
Coates Chemical Laboratory, The Louisiana State University
Baton Rouge, Louisiana 70803

Received March 11, 1970

Dynamic Stereochemistry—a Comparator for Electron Impact and Pyrolytic Elimination of Acetic Acid from Acetates[1]

Sir:

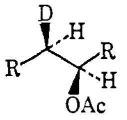
Electron impact induced elimination reactions are demonstrably sensitive to the differences between diastereotopic hydrogens.[2] We now report the utilization of such stereochemically nonequivalent groupings[3] in a study of the 1,2 elimination of acetic acid from 2-butyl acetate and 1,2-diphenyl ethyl acetate which not only uncovers the conformational prerequisites for reaction but also demonstrates that these fragmentations follow a course which parallels their pyrolytic counterparts.[4] The diastereomeric 3-deuterio *sec*-butyl acetates (**1** and **2**)[5] and 2-deuterio-1,2-diphenyl ethyl acetates (**3** and **4**) were prepared as described.[6,7] Table I presents the compounds studied as well as the mass spectral data for loss of acetic acid from these materials.

Table I[a,b]

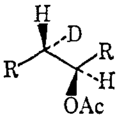
Compd	M − DOAc/M − HOAc 70 eV	 15 eV
1	25/75	27/73
2	16/84	18/82
3	49/51	50/50
4	24/76	24/76

[a] The spectra were obtained on an MS-902 spectrometer at *ca.* 50° source temperature *via* direct inlet for **3** and **4** and ambient temperature glass inlet for **1** and **2**. [b] The deviations in Table I are *ca.* ±2% (absolute) for the 70-eV runs and ±1% (absolute) for the low-voltage data. The low temperature was attained with a water-cooled source with air and/or water as the coolant. The electron voltages are nominal.

The data in Table I reveal both a stereochemical dependence as well as a greater average loss of deuterated acetic acid from **3** and **4** over **1** and **2**. The latter result most likely derives from the intervention of abstraction from the undeuterated methyl groups in **1** and **2**,[8] in contrast with the C-2 site specificity in **3** and **4**. The mass spectra of 1,2,2-trideuterio- and 2,2-dideuterio-1,2-diphenyl ethyl acetates[9] exhibit no loss of HOAc demonstrating the sole C-2 elimination in **3** and **4**.



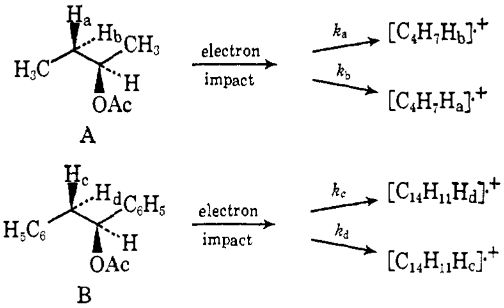
1, R = CH_3
3, R = C_6H_5



2, R = CH_3
4, R = C_6H_5

Chart I exhibits the kinetic relationships for the elimination of the diastereotopic hydrogens from both *sec*-butyl acetate and 1,2-diphenyl ethyl acetate. Our present task is to transpose the data in Table I into quantitative assignments for k_a/k_b and k_c/k_d and thereby into the conformational insights we seek.

Chart I[a]



[a] The rate constants shown represent values averaged over the range of energy states accessible to the reacting molecular ions.

Curtin[6] has previously shown in the case of the pyrolysis of **3** and **4** that k_c/k_d is equal to the square root of the product of the deuterated to undeuterated stilbene in **3** and undeuterated to deuterated stilbene in **4**. Since in the mass spectrometer we may equate the ratio of two ion intensities to the rate constants for the formation of the ions,[10] it will follow that Curtin's analysis[6] may be

---

[1] This research has been carried out with the support of a grant from the National Institute of General Medical Sciences.

[2] M. M. Green, *J. Amer. Chem. Soc.*, 90, 3872 (1968).

[3] K. Mislow and M. Raban, *Top. Stereochem.*, 1, 1 (1967).

[4] C. H. DePuy and R. W. King, *Chem. Rev.*, 60, 431 (1960).

[5] P. S. Skell and W. L. Hall, *J. Amer. Chem. Soc.*, 86, 1557 (1964).

[6] D. Y. Curtin and D. B. Kellom, *ibid.*, 75, 6011 (1953).

[7] All deuterated compounds including intermediates were shown to be identical with authentic proteum materials by either melting point and/or vapor phase chromatography.

[8] Earlier work on acetates has demonstrated abstraction from various β positions as well as some 1,3 loss of acetic acid. See: W. Benz and K. Biemann, *J. Amer. Chem. Soc.*, 86, 2375 (1964); W. S. Briggs and C. Djerassi, *J. Org. Chem.*, 33, 1612 (1968).

[9] Determined under conditions identical with those for the data in Table I. The compounds were prepared by Grignard reaction of the appropriately deuterated benzyl chloride and benzaldehyde. Monodeuteriobenzaldehyde was prepared as reported previously: D. Seebach, B. W. Erickson, and G. Singh, *ibid.*, 31, 4303 (1966).

[10] The ion intensities (*e.g.*, M − HOAc/M − DOAc) are related to each other exactly as would be the weight of two products obtained from a single starting material in a unimolecular competition, namely as the

Table II[a]

		k_a/k_b[b]	I[b]	k_a/k_b[c]	I[c]	k_c/k_d[d]	I[d]
Electron impact	70 eV	1.56 ± 0.1	1.0	1.58 ± 0.15	1.2 ± 0.2	1.74 ± 0.1	1.82 ± 0.1
	15 eV	1.50 ± 0.1	1.0	1.44 ± 0.05	0.8 ± 0.3	1.78 ± 0.1	1.78 ± 0.1
Pyrolysis[e]				1.86	1.6	12	2.7

[a] Refer to Chart I. [b] Derived from Table I with I assumed to be 1.0 (see text). [c] Calculated by directly comparing the peak intensities between **1** and **2** on the same scale as discussed in the text. [d] Derived from Table I using Curtin's analysis.[6] [e] Data from ref 5 and 6.

applied to obtain the desired ratio of k_c/k_d by utilizing the ion intensities at M − HOAc and M − DOAc (Table I).[11] Further, the isotope effect (I) may be calculated[6] by simply inverting one of the ion ratios. The results of these calculations are given in Table II.

The presence of other rate constants k_i for loss from the methyl groups from **1** and **2** disallows Curtin's kinetic analysis for the *sec*-butyl system. Nevertheless the necessary rate ratios may be obtained in another manner. The ratio of M − DOAc/(M − DOAc + M − HOAc) is equal to $Ik_a/(Ik_a + k_b + k_i)$ in **1** and $Ik_b/(Ik_b + k_a + k_i)$ in **2**. If I were 1, the quotient of these ratios from **1** and **2** would yield k_a/k_b. This assumption has been made to obtain the values of k_a/k_b in Table II (first column). As demonstrated below this ratio of k_a/k_b is correct.

If one could measure the ion intensities for M − DOAc in **1** and **2** on the same scale (*i.e.*, from the same number of molecular ions) the value obtained would be simply Ik_a/Ik_b or k_a/k_b.[10] Further, the difference between the M − DOAc ion intensities is equal to $I(k_a - k_b)$ while the difference between the M − HOAc intensities (all on the same scale) yields $k_a - k_b$. In this manner both I and k_a/k_b could be obtained. This procedure can be executed in the case of **1** and **2** since all the ions of higher *m/e* than M − H(D)OAc exhibit a nearly constant relationship between the spectra of **1** and **2**. This constant relationship is indeed a factor which allows the two spectra to be placed on an equivalent sensitivity scale. This procedure (various runs and scale factors) yielded the results shown in Table II, which also includes the pyrolytic data. A similar attempt for **3** and **4** was less satisfactory since the various ions other than M − H(D)OAc were not related by a constant factor.[12]

The observation of metastable peaks for loss of acetic acid in both series,[13] the low temperature of the ion source (*ca.* 50°),[14] and previous comparative observations of acetic acid loss by electron impact and cold photoionization[15] strongly support the electron impact induced nature of these fragmentations.

The only reasonable interpretation of the electron impact induced k_a/k_b and k_c/k_d ratios (Table II) is that loss of acetic acid occurs by a *cis* process[16] with preference for an *anti* relationship between the methyl groups in **1** and **2** and the aromatic rings in **3** and **4**. Further, the data in Table II allow a detailed comparison between the electron impact and pyrolytic eliminations. Although the results show a clear qualitative parallel in that $k_a > k_b$ and $k_c > k_d$ and further that I is greater for C_6H_5 in both series, a quantitative correspondence is both lacking and expectable. A significant entropy term ($\Delta\Delta S^{\neq}$), absent in the case of the *sec*-butyl acetates but arising from the restricted rotation in the abstraction of H_d, likely contributes to the stereospecificity in the pyrolysis of 1,2-diphenyl ethyl acetate. Since the electron impact induced eliminations take place from molecular ions of low internal energy,[17] a state in which the mass spectral counterpart of the entropy term (frequency factor) is deemphasized,[18] it follows that under electron impact the difference in stereospecificities should be lessened over that observed pyrolytically as is the case.

These results suggest, at least for these molecules, that promotion to the ionized state does not involve a substantial perturbation of the structural parameters of the neutral precursor.

---

ratio of their rate constants (actually average rate constants in the case of the ions). The subsequent decomposition of the ions (M − H(D)-OAc) is effectively repressed at beam energies near threshold.

(11) Since Curtin[6] was measuring the deuterium content of *trans*-stilbene, he could seek the stereospecificity of the reaction (*i.e.*, *cis* or *trans* elimination). In our case, we have no reason to suppose that loss of H_c or H_d leads to *trans*- or *cis*-stilbene or even an ion with a stilbene structure at all. See P. F. Donaghue, P. Y. White, J. H. Bowie, B. D. Roney, and H. J. Rodda, *Org. Mass Spectrom.*, **2**, 1061 (1969).

(12) This calculation depends on the spectra showing only local dependence (*i.e.*, M − H(D)OAc) on the stereochemistry. Such local dependence is most likely to be found in compounds which differ by diastereotopic deuterium incorporation—a potentially small perturbation.

(13) Measured by varying the accelerating voltages. See: M. Barber and R. M. Elliott, Abstracts of Papers of 12th Annual Conference on Mass Spectrometry, ASTM E-14, Montreal, 1964, p 150.

(14) We have studied the loss of acetic acid at various temperatures on both the MS-902 and a CEC-103-C spectrometer and find a highly reproducible diminution of the stereospecificity at higher temperatures. For example for CH_3 at 125° $k_a/k_b = 1.3$.

(15) See Briggs and Djerassi in ref 8.

(16) The pyrolytic process is stereospecifically *cis* as shown by Skell.[5] The apparent *trans* elimination in the 1,2-diphenyl ethyl acetates almost surely arises from initially produced *cis*-stilbene isomerizing to *trans* as noted by Curtin (see references to Table I in Curtin's paper[6]).

(17) The invariance of the results on change of beam energy from 70 eV to near threshold (Tables I and II) does not alter this argument since the ions produced near threshold must have low internal energies. The lack of dependence of competitive eliminations on beam energy has precedence in chloride and acetates. See: A. M. Duffield, S. D. Sample, and C. Djerassi, *Chem. Commun.*, 193 (1966); Briggs and Djerassi, ref 8 herein.

(18) This follows from the quasi-equilibrium theory and the derived kinetic expression. See: R. G. Cooks, I. Howe, and D. H. Williams, *Org. Mass Spect.*, **2**, 137 (1969), and numerous references therein.

Mark M. Green, J. Michael Moldowan
David J. Hart, Jeffrey M. Krakower
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48104

Received January 16, 1970

The Biogenetically Modeled Total Synthesis of (±)-Minovine[1]

Sir:

The biogenetic speculations of Wenkert[2a] concerning the origin of *Aspidosperma* and *Iboga* alkaloids entail

---

(1) Presented at the Third Natural Products Symposium, Mona, Jamaica, Jan 5–9, 1970.

(2) (a) E. Wenkert, *J. Amer. Chem. Soc.*, **84**, 98 (1962); (b) A. A. Qureshi and A. I. Scott, *Chem. Commun.*, 945, 947, 948 (1968); A. I. Scott, P. C. Cherry, and A. A. Qureshi, *J. Amer. Chem. Soc.*, **91**, 4932 (1969).