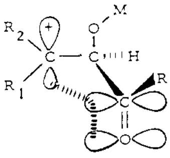
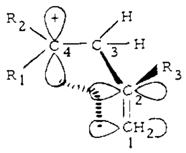
However, our stereochemical studies show that migration in both **3** and **4** occurs exclusively from the *least stable conformer* where departure of the leaving group can be assisted by the *carbonyl* carbon as depicted in **6.** The resulting NGP is quite



6



7

analogous to the 1,3 interaction in a homoallylic cation **7** which results in a cyclopropylcarbinyl cation. In the present reaction, however, we do not suggest that a cyclopropyloxenium ion[8c] is at an energy minimum, but, rather, a transition state. Entropic considerations favor the 1,3-carbon interaction over the more generally observed carbonyl participation at oxygen which would produce a strained four-membered oxetane that *does not lead to carbonyl migration.*[15] The overall stereochemistry of **1** → **3** → **5** also excludes an epoxide intermediate where one inversion (**3** →**2**) would be required.

Additional lines of evidence that support a concerted acyl migration are (a) thermal rearrangement of optically pure (+)-**1** on a gas chromatography column (20% SE-30 on Chromosorb P) afforded optically pure (−)-**5** (91%) with 100% stereospecificity at 200°; (b) quantitative rearrangement of **1** in nonpolar solvents is complete in <2 s;[8b] (c) carbonyl migration is impeded when excess (2.5 equiv) $MgClO_4$ is used as the Lewis acid catalyst and the carbonyl group is complexed (the major product from **2** is 1,3-diphenyl-1,2-butanedione as the result of a 1,2-hydride shift); and (d) in a polar solvent like CH_3OH, where the α-methylbenzyl cation at C-3 can be stabilized, and NGP is not necessary, no trace of carbonyl migration could be detected.[8b]

In conclusion, the surprising facility with which a carbonyl group migrates suggests that a unique type of stabilization is involved in the transition state. Our experimental and theoretical studies[8c,15] have provided the first evidence for NGP at carbonyl carbon.

Acknowledgment. The authors acknowledge support from the National Science Foundation (CHE 76 21992). R.D.B. also thanks Professor Roald Hoffmann for his generous hospitality during his sabbatical leave at Cornell University where this manuscript was written.

References and Notes

(1) Capon, B.; McManus, S. P. "Neighboring Group Participation", Plenum Press: New York, 1976; Vol. 1.

(2) Cram, D. J. *J. Am. Chem. Soc.*, **1949**, *71*, 3863. Lancelot, C. J., Cram, D. J.; Schleyer, P. V. R. "Carbonium Ions", Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, p 1347.

(3) (a) Collins, C. J. *Acc. Chem. Res.* **1971**, *4*, 315. (b) Collins, C. J. In "Carbonium Ions", Olah, G., Schleyer, P. v. R., Ed.; Wiley-Interscience: New York, 1968, p 307. (c) Collins, C. J. *Q. Rev., Chem. Soc.* **1960**, *14*, 357.

(4) Benjamin, B. M.; Schaeffer, H. J.; Collins, C. J. *J. Am. Chem. Soc.* **1957**, *79*, 6160.

(5) Collins, C. J., Staum, M. M.; Benjamin, B. M. *J. Org. Chem.*, **1962**, *27*, 3525. Benjamin, B. M.; Collins, C. J. *J. Am. Chem. Soc.* **1961**, *83*, 3662.

(6) (a) Bunton, C. A.; Hadwick, T.; Llewellyn, D. R.; Pocker, Y. *Chem. Ind. (London)* **1956**, 547. (b) Bunton, C. A.; Hadwick, T.; Llewellyn, D. R.; Pocker, Y. *J. Chem. Soc.* **1958**, 403. Pocker, Y. *Chem. Ind. (London)* **1959**, 332. (c) Collins, C. J.; Rainey, W. T.; Smith, W. B.; Kaye, I. A. *J. Am. Chem. Soc.* **1959**, *81*, 460.

(7) (a) Cram, D. J.; McCarty, J. E. *J. Am. Chem. Soc.* **1957**, *79*, 2866. (b) Synder, E. I. *ibid.* **1969**, *91*, 5118. (c) Jablonski, R. J.; Snyder, E. J. *ibid.* **1969**, *91*, 4445.

(8) (a) Domagala, J. M.; Bach, R. D.; Wemple, J. *J. Am. Chem. Soc.* **1976**, *98*, 1975. (b) Domagala, J. M.; Bach, R. D. *ibid.* **1978**, *100*, 1605. (c) Bach, R. D.; Domagala, J. M. *Tetrahedron Lett.* **1976**, 4025.

(9) Wasserman, H. H.; Aubrey, N. E. *J. Am. Chem. Soc.* **1956**, *78*, 1726.

(10) The absolute configuration of (−)-**3** and the stereospecificity attending its formation was independently established. (−)-Chlorohydrin **3** (53% optically pure) was oxidized under mild conditions with periodic acid to (−)-2-chloro-2-phenylpropanal, $[\alpha]^{25}{}_{D}$ −10.1° (*c* 3.6, C_6H_6). The aldehyde was further oxidized with CrO_3 to (−)-(*R*)-2-chloro-2-phenylpropionic acid, $[\alpha]^{25}{}_{D}$ −13.4° (*c* 4.1, C_6H_6), of known absolute configuration in 51% optical purity (based upon a reported rotation).[11] These data corroborate our earlier assignment of the absolute configuration of **1** and **2**.

(11) (a) McKenzie, A.; Clough, G. W. *J. Chem. Soc.* **1910**, 1016. (b) Cowdrey, W. A.; Hughes, E. D.; Ingold, C. K.; Masterman, S.; Scott, A. D. *ibid.* **1937**, 1252.

(12) Helder, R.; Hummelen, J. C.; Laane, R. W. P. M.; Wiering, J. S.; Wynberg, H. *Tetrahedron Lett.* **1976**, 1831.

(13) Hanack, M. "Conformational Theory", Academic Press: New York, 1965.

(14) For other examples of acyl migration in a halohydrin, see the following. House, H. O. *J. Am. Chem. Soc.* **1956**, *78*, 2298. Kagan, J.; Agdeppa, D. A.; Meyers, D. A.; Singh, S. P.; Walters, M. J.; Wintermute, R. D. *J. Org. Chem.* **1976**, *41*, 2355.

(15) Ab initio calculations on the comparable rearrangement of a protonated α,β-epoxyaldehyde clearly show that participation by carbon has a much lower E_a even though formation of the oxetane is thermodynamically favored, and an extensive search of the potential energy surface for this rearrangement is in complete accord with a concerted migration with the proposed cyclopropyloxenium ion[8c] on the reaction pathway (unpublished results).

(16) John M. Domagala was the recipient of a National Science Foundation Predoctoral Fellowship.

John M. Domagala,[16] Robert D. Bach*
Department of Chemistry, Wayne State University
Detroit, Michigan 48202

Received December 4, 1978

Applications of Homonuclear Two-Dimensional *J* Spectroscopy: an Alternative to Broad Band Heteronuclear and Homonuclear Decoupling

Sir:

The purpose of this communication is to show that high resolution homonuclear (proton) two-dimensional *J* (2-D *J*) spectroscopy[1-3] provides a convenient method for distinguishing between homonuclear and heteronuclear scalar spin couplings in complex molecules. This potential is illustrated for the $^1H-^{19}F/^1H-^1H$ couplings of 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-β-D-glucopyranosyl fluoride (**1**) and for the $^1H-^{31}P/^1H-^1H$ couplings of 4,4-dideuterio-2-oxo-2-phenoxy-5-phenyl-1,3,2-dioxaphosphorinane (**2**).

It is not appropriate to explain here the details of a proton 2-D *J* experiment.[1-3] Basically it involves the measurement of a series of time-domain free induction decay signals, as a function of two time variables, t_1 and t_2, which are then double Fourier transformed to give a 2-D *J* spectrum represented as a function of two frequency variables, f_1 and f_2, which are set orthogonal to each other. Distinction between homonuclear and heteronuclear couplings may be made by displaying projections[4] of the 2-D *J* spectrum onto different axes.

Homonuclear ($^1H-^1H$) couplings of a *weakly coupled* system are conveniently measured from the *partial J spectra*[5] which are obtained by projecting sections[6] of the 2-D *J* spectrum onto the f_1 axis. The lines in a *J* spectrum are symmetrically disposed about zero frequency and are separated by the $^1H-^1H$ couplings;[7] they are due to *J* modulation[5,8] of components of a resonance in the t_1 dimension, as a result of the inversion of proton spin states by the 180° refocussing pulse in the spin-echo pulse sequence.[9] Since the spin states of heteronuclei are not directly affected by this 180° pulse, the components due to heternuclear coupling are refocussed at the end of the evolution period (t_1) and hence the heteronuclear couplings are suppressed from the *J* spectrum. In this sense signals separated by heteronuclear scalar coupling behave similarly to *weakly coupled* proton chemical-shift components.

Heteronuclear scalar spin couplings, together with the proton chemical shifts, are conveniently obtained from a skew projection[2,10] of the 2-D *J* spectrum. Now, all of the $^1H-^1H$ couplings are suppressed and each proton resonance of a weakly coupled spin system gives a single line at its chemical shift, imparting to the skew projection the appearance of a proton-decoupled proton spectrum, with splittings from the

0002-7863/79/1501-3120$01.00/0

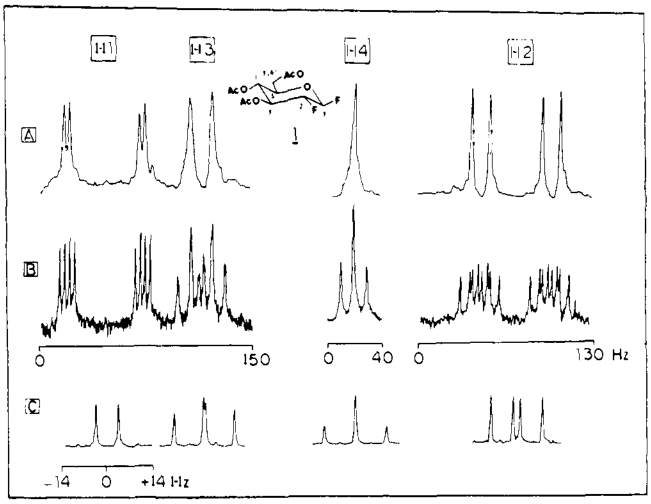


Figure 1. B shows regions of the normal ^{1}H FT spectrum (270 MHz) of **1** (0.1 M in benzene-d_6); A shows the corresponding skew projections of the 2-D J spectrum (plotted in the power mode with sine bell and exponential multiplication of the time-domain signals in the t_2 and t_1 dimensions, respectively) in which each proton appears to be completely proton decoupled and only the chemical shifts and ^{1}H-^{19}F couplings are observed. Each partial J spectrum shown in C is only a function of the appropriate ^{1}H-^{1}H coupling constants; since instrumental line broadening in the t_1 dimension is now minimized, the ^{1}H-^{1}H coupling constants can be accurately measured.

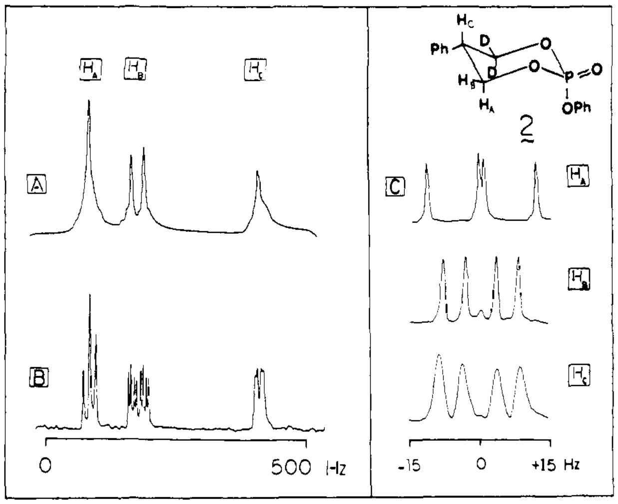


Figure 2. The high-field region of the conventional ^{1}H FT spectrum (270 MHz) of **2** (0.1 M in benzene-d_6) is shown in B. The corresponding skew projection, A, shows the ^{1}H$_B$-^{31}P coupling, while all ^{1}H-^{1}H couplings are suppressed; note that the lines show broad "tails" owing to use of the absolute-mode display. The partial J spectra of the protons shown in C give the ^{1}H-^{1}H couplings.

heteronuclear couplings still remaining.

The spectra of the difluoro sugar **1** shown in Figure 1 serve to illustrate the distinction between ^{1}H-^{19}F and ^{1}H-^{1}H couplings. Regions of the conventional ^{1}H FT spectrum are shown in Figure 1B; although the large geminal ^{1}H-^{19}F couplings (~50 Hz) are obvious, distinction between the other couplings is less clear. In the skew projections of the corresponding regions shown in Figure 1A, all of the homonculear (^{1}H-^{1}H) couplings have been suppressed, leaving only the ^{1}H-^{19}F splittings, which can easily be measured. Although the magnitudes of the ^{1}H-^{1}H couplings could now have been interpolated from the normal spectrum, more convenient and accurate measurements were obtained from the partial J spectra (Figure 1C). Owing to the refocussing of the magnetic field inhomogeneity effects at the end of the evolution period, the line widths in the partial J spectra are mainly determined by spin-spin relaxation times rather than instrumental effects;[11] as a typical example of the resultant resolution enhancement, the small difference between the two vicinal couplings for H-3 ($J_{3,2}$ = 9.02, $J_{3,4}$ = 9.45 Hz) is clearly resolved in Figure 1C.

Figure 2 illustrates similar studies of **2**, which exhibits ^{1}H-^{1}H and ^{1}H-^{31}P couplings. Although the coupling of phosphorus to the equatorial proton (J = 22,8 Hz) can be measured from the skew projection (Figure 2A), coupling to the axial proton (1.4 Hz) is not resolved; this loss of resolution is mainly due to both the instrumental line broadening and poor digital resolution in the f_2 dimension.[3,12]

It is clear that the methods summarized here have the merit that scalar couplings from any number of different heteronuclei may be simultaneously suppressed, regardless of their chemical shift separation, without the need for any modification of the spectrometer or probe; thus for example, simultaneous decoupling of both ^{19}F and ^{31}P could be effectively achieved. We believe that this will lead to a number of important chemical applications.

Acknowledgments. It is a pleasure to thank Dr. Gareth Morris for his continued advice. This work was supported by operating grants from the National Research Council of Canada (A 1905 to L.D.H.).

References and Notes

(1) W. P. Aue, E. Bartholdi, and R. R. Ernst, *J. Chem. Phys.*, **64**, 2229 (1976).
(2) W. P. Aue, J. Karhan, and R. R. Ernst, *J. Chem. Phys.*, **64**, 4226 (1976).
(3) G. Bodenhausen, R. Freeman, R. Niedermeyer, and D. L. Turner, *J. Magn. Reson.*, **26**, 133 (1977).
(4) Digital summation of selected traces of a 2-D J spectrum.
(5) R. Freeman and H. D. W. Hill, *J. Chem. Phys.*, **54**, 301 (1971).
(6) K. Nagayama, P. Bachmann, K. Wüthrich, and R. R. Ernst, *J. Magn. Reson.*, **31**, 133 (1978).
(7) G. Bodenhausen, R. Freeman, G. A. Morris, and D. L. Turner, *J. Magn. Reson.*, **31**, 75 (1978).
(8) R. Freeman and H. D. W. Hill, "Dynamic nuclear Magnetic Resonance", F. A. Cotton and L. M. Jackman, Eds., Academic Press, New York/London, 1975, Chapter 5.
(9) H. Y. Carr and E. M. Purcell, *Phys. Rev.*, **94**, 630 (1954).
(10) A projection onto an axis such that $\partial f_2/\partial f_1 = -1$; if f_1 and f_2 axes were plotted on the same scale this axis would be set at 45° to the f_2 axis.
(11) G. Bodenhausen, R. Freeman, R. Niedermeyer, and D. L. Turner, *J. Magn. Reson.*, **24**, 291 (1976).
(12) To make efficient use of the computer storage and operating capacity it is usually advantageous to limit the digital resolution in the f_2 dimension.

Laurance D. Hall,* Subramaniam Sukumar
Department of Chemistry, University of British Columbia
Vancouver, British Columbia, Canada, V6T 1W5

Received December 26, 1978

Reaction of Aromatic Diazonium Salts with Carrier-Free Radioiodine and Astatine. Evidence for Complex Formation

Sir:

The understanding of the dediazoniation process is complicated by the fact that its mechanism is not unique but quite dependent on the reaction conditions.[1,2] Dediazoniation can occur by both ionic and free-radical paths. In particular, in the case of iododediazoniation, which may be carried out in acidic aqueous solutions without major hydrolysis even in the absence of a catalyst, several mechanisms have been discussed.[3-6] All of them, however, draw an analogy to the Sandmeyer type by assuming a redox step with radical intermediates.

Tracer experiments with radiohalogens in the picomole region can provide new information on the question of complex formation, which should be particularly favorable in the case of the heaviest halogen astatine. Since this is a radioelement with rather short-lived isotopes (^{211}At, $T_{1/2}$ = 7.2 h), only

0002-7863/79/1501-3121$01.00/0