benzene, p-chloronitrobenzene, o-nitrophenol, potassium acetate (Wako), bis(1,2-diphenylphosphino)ethane (Stream), and 2-octanol (Fluka) were used as purchased. $RhCl(CO)(PPh_3)_2$,[14] $PhH(CO)(PPh_3)_3$,[15] and $Rh_2Cl_2(CO)_4$[16] were prepared according to the methods reported previously.

Catalytic Reduction of Aromatic Nitro Compounds by Secondary Alcohols. Example I. To a solution containing 0.196 g (2.0×10^{-3} mol) of KOAc, 0.5 mL (5.0×10^{-3} mol) of nitrobenzene, and 6.2 mL of cyclohexanol in a side-arm flask was added 0.0276 g (4.0×10^{-5} mol) of $RhCl(CO)(PPh_3)_2$. The system was then heated under a nitrogen atmosphere at 150 °C for 7 h. A ^1H NMR and an infrared spectrum of the solution were recorded. The solution after a bulb-to-bulb distillation was analyzed on the above gas chromatograph with toluene as the internal standard. The products, cyclohexanone, and aniline were identified by comparing the NMR, IR, and GC spectra with those of the authentic samples. The yield (Table I) and the product ratio (Table II) were calculated from the relative peak areas in the NMR spectra or in the gas chromatograms. The same method was used in the reduction of other nitro compounds by cyclohexanol.

Example II. To a solution containing 0.196 g (2.0×10^{-3} mol) of KOAc, 0.50 mL (5.0×10^{-3} mol) of nitrobenzene, and 6.2 mL of isopropyl alcohol in an ampule was added 0.0276 g (4.0×10^{-5} mol) of $RhCl(CO)(PPh_3)_2$, and the ampule was then evacuated, sealed, and heated at 150 °C for 7 h. The products were analyzed by the same method as in example I. The yield of aniline was 100%. When 2-butanol was used to reduce nitrobenzene, this technique was also employed.

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Registry No. $RhCl(CO)(PPh_3)_2$, 15318-33-9; $RhH(CO)(PPh_3)_3$, 17185-29-4; $RhCl_3$, 10049-07-7; PPh_3, 603-35-0; $P(OPh)_3$, 101-02-0; $Ph_2PCH_2CH_2PPh_2$, 1663-45-2; $Rh_2Cl_2(CO)_4$, 14404-25-2; nitrobenzene, 98-95-3; cyclohexanol, 108-93-0; 2-octanol, 123-96-6; 2-butanol, 78-92-2; 2-propanol, 67-63-0; aniline, 62-53-3; o-nitrotoluene, 88-72-2; m-nitrotoluene, 99-08-1; p-nitrotoluene, 99-99-0; o-chloronitrobenzene, 88-73-3; p-chloronitrobenzene, 100-00-5; p-nitrophenol, 100-02-7; 3-methylbenzenamine, 108-44-1; 4-methylbenzenamine, 106-49-0; 2-methylbenzenamine, 95-53-4; 2-chlorobenzenamine, 95-51-2; 4-chlorobenzenamine, 106-47-8; 4-aminophenol, 123-30-8; 2,4-dinitrotoluene, 121-14-2; 2,4-dinitroaniline, 97-02-9; 2,4-dinitrochlorobenzene, 97-00-7.

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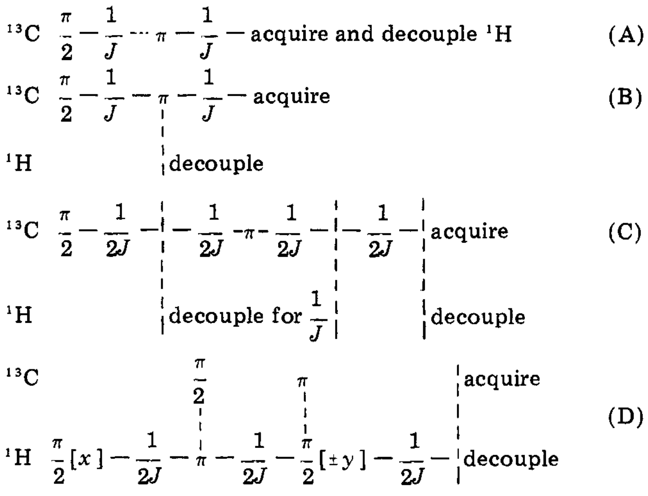
Communications

Strategy for the Generation of ^{13}C Subspectra. Application to the Analysis of the ^{13}C Spectrum of the Antibiotic Ristocetin

Summary: Three heteronuclear multipulse methods, combined to routinely generate accurate ^{13}C subspectra of differing ^1H multiplicity, are applied as a test of the strategy to the antibiotic ristocetin.

Sir: Elucidation of the structure of an organic compound is facilitated by determination of the number of protons directly attached to each carbon atom. A popular method, SFORD ^{13}C spectroscopy[1] is of limited use for large molecules because of overlapping multiplets and poor signal-to-noise. A more attractive alternative is to generate individual methine (CH), methylene (CH_2), methyl (CH_3), and quaternary (q) ^{13}C subspectra. A degree of such spectral editing has been achieved with the INEPT pulse sequence,[2,3] but this is too sensitive to variations in $^1J_{^{13}C-^1H}$ for confident application to unknown compounds,[4] especially large complex molecules like ristocetin.



We have generated CH/CH_3 and CH_2/q subspectra by spin-echo sequences utilizing the proton-flip method[4] (sequences A and B are the gated-decoupled equivalents[5]), CH_2/q subspectra at one-third and full intensity, respectively using sequence C,[6] and CH subspectra using the EPT sequence D,[7] and in each case we demonstrated a relative insensitivity to variations in $^1J_{^{13}C-^1H}$ values. Here we combine these three methods (sequences A to D) to provide accurate subspectra generation and as a stringent test we apply the strategy to ristocetin.

The alternative gated-decoupling method (sequences A and B) was used for two reasons. Proton refocusing pulses are not used and are not a source of error. Secondly, and

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[6] Pegg, D. T.; Bendall, M. R.; Doddrell, D. M. *J. Magn. Reson.* **1982**, *49*, 32. Note that the decoupling irradiation used for the burst in sequence C must provide randomization of the ^1H spins over three dimensions, unlike normal decoupling irradiation. This can be achieved by changing the 180° random phase changes of normal decoupling irradiation to 90° random phase changes.

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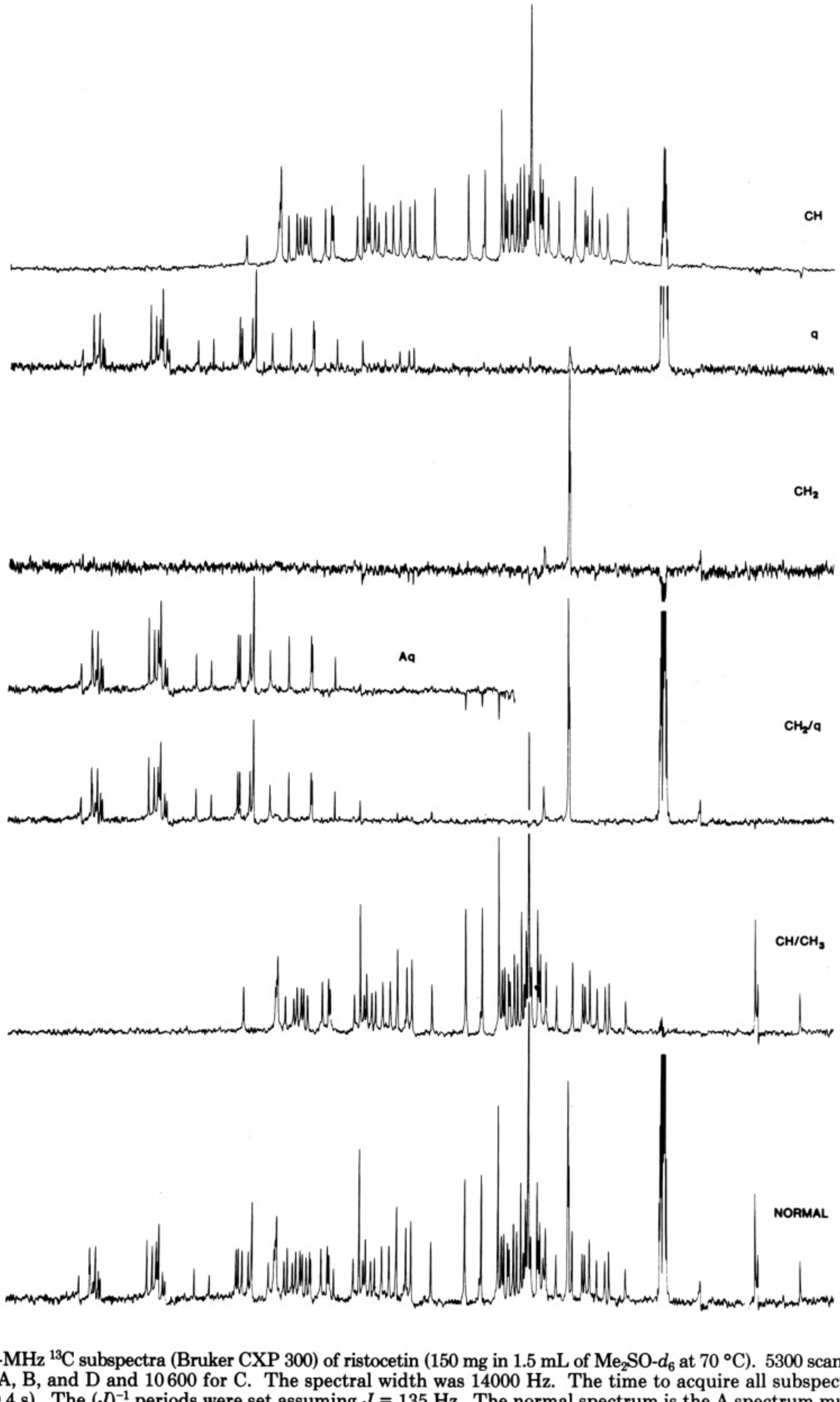

Figure 1. 75.5-MHz ^{13}C subspectra (Bruker CXP 300) of ristocetin (150 mg in 1.5 mL of Me_2SO-d_6 at 70 °C). 5300 scans were accumulated for sequences A, B, and D and 10 600 for C. The spectral width was 14000 Hz. The time to acquire all subspectra was about 14 h (recycle time 0.4 s). The $(J)^{-1}$ periods were set assuming $J = 135$ Hz. The normal spectrum is the A spectrum multiplied by 2. The combinations used (given in the text) lead to the same resonance intensities in different spectra except for the CH subspectrum where the comparison depends on the relative efficiency of polarization transfer and NOE. The different combinations lead to different noise levels. The CH_2/q and q subspectra are not accurate for the aromatic region. The aromatic q carbon subspectrum (Aq) was obtained from the combination [A + 1.3 B] to allow for the larger average aromatic J value. Aliphatic CH groups produce "down" errors in the Aq spectrum. The Me_2SO-d_6 signal is like a q signal and this near-saturated signal is cancelled in the CH/CH_3 and CH_2 spectra to an accuracy of 1.5% and 4%, respectively. The phase alternation within sequence D is less successful in cancelling the Me_2SO signal in the CH spectrum because of the long Me_2SO T_1, and the four scan cycles used. It can be reduced to negligible levels if sequence D is run separately and continuously. The only ambiguous assignment is the upfield signal in the q spectrum, which could be a q signal or a CH_2 residual. The latter is true and it probably occurs because of a larger than usual J value. The ambiguity could be resolved by further experiment as described in the text.

most importantly, by setting the length of the burst of decoupling irradiation at $(J)^{-1}$ s for sequence C, the total sequence time prior to acquisition is the same for sequences A to C. This is not possible with the proton-flip method. Unavoidable inhomogeneity in the π[C] pulse leads to phase errors,[4,8] which are different from one resonance to the next but are the same for each resonance in the three A to C spectra (same sequence time) and are cancelled when combination of the three spectra results in resonance subtraction. If different sequence times were used, the phase errors would differ in the three spectra and could not be cancelled. In subspectral generation the cancellation of unwanted signals is the prime requirement.

Four scans were averaged separately for sequences A, B, and D and eight scans for sequence C, repetitively. This permits the use of phase cycling and the repetition compensates for drifts in spectrometer parameters. The sequence A data was Fourier transformed and manually phase corrected. This phase correction can then be used for B and C but not for the D spectra. The spectra were then combined as previously described[4,6,7]: [A–B] yields a CH_3/CH subspectrum, [A + B] a CH_2/q subspectrum, $^3/_2$[A + B–C] a CH_2 subspectrum, $^3/_2(C-{}^1/_3[A + B])$ a q subspectrum; $^3/_2(D-x[A - B])$ a CH subspectrum. The experimental parameter, x (in our case, 0.04), depends on the spectrometer probe geometry.[7] The $^3/_2$ fractions are used to keep the resonance intensities the same for all spectra. Much of this procedure may be automated. An accurate CH_3 subspectrum cannot be generated because the A and B phase errors differ from the D phase errors.

The ristocetin subspectra are shown in Figure 1. The phase and intensity errors in the subspectra result from inhomogeneous pulses over the wide spectral width, but unambiguous assignments are given. When this data was combined with more accurate intensity data (reverse-gated ^{1}H decoupled spectrum, i.e., no NOE, recycle time 3 s) we concluded that ristocetin had the following carbon-type composition: $(q\text{-}C)_{30\pm1}(CH)_{56\pm2}(CH_2)_{6\pm1}(CH_3)_4$. The actual numbers of carbons of each type, as determined by extensive structural studies,[9-11] and a ^{13}C study[11] (using almost all existing applicable assignment techniques, excepting that given in the present work) are 29, 57, 5, and 4, respectively. The ambiguities associated with the numbers in the present work arise from difficulties in assessing the intensities of overlapping signals and could be resolved by a more careful reverse-gated experiment (e.g., longer recycle time).

The aromatic region can be studied as described in Figure 1, or for spectra with a substantial gap between the aromatic and aliphatic spectrum regions, it is preferable to study the two regions in separate experiments, enabling the use of smaller spectrum widths and thus more accurate pulses. In the latter case it is only necessary to use sequences A and B for the aromatic region and the $(J)^{-1}$ times are set by assuming $J = 170$ Hz.

Unlike previous subspectral studies on the ^{13}C aliphatic region, the three methods combined in sequences A to D are reasonably tolerant of divergence from the compromise J value assumed, and $J = 135$ Hz is a good compromise. This may need to be increased in some cases, for example to 140 Hz for compounds with monohalogenated groups. The method will not be accurate for groups with two electronegative substituents, but signals from such groups will usually be obvious as they will partly occur in two or more of the subspectra. Signals from groups with divergent J values can be further studied by repeating some or all of the sequences on a narrower spectrum width assuming a new J value.

The method requires about 5 times more accumulation time than a normal decoupled spectrum, which compares favorably with the less useful SFORD method. The spectra in Figure 1 represent a first attempt, on this complex molecule, of a method devised using simpler compounds. Its successful application here should ensure its use by organic chemists as an adjunct to traditional NMR techniques.

Acknowledgment. The Bruker CXP 300 is owned by the Brisbane NMR Centre and sited at Griffith University.

Registry No. Ristocetin, 11021-66-2.

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[8] An inhomogeneous π pulse leaves a component of a magnetization vector unrefocused. The phase of this component depends on the total free precession time and the chemical shift off-resonance.[3]

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Influence of an α-Cyano Function on Charge Delocalization in the Benzyl Cation. Relationship between Inductive Destabilization and Conjugative Stabilization by the Cyano Group

Summary: The solvolytic behavior of a series of substituted acetophenone cyanohydrin methanesulfonates has been studied in 2,2,2-trifluoroethanol. A ρ value of −6.70 was observed when the rate data was evaluated vs. Brown's σ^+ values.

Sir: As part of the extensive activity which currently exists in the investigation of the influence of strongly electron-withdrawing substituents on the formation of carbocation intermediates,[1-3] we have studied the effect of the α-cyano

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