Nuclear Magnetic Resonance Studies on the Acetolysis and Trifluoroacetolysis of Trianisylvinyl-2-^{13}C Bromide

Mitsuo Oka and Choi Chuck Lee
Department of Chemistry and Chemical Engineering, University of Saskatchewan, Saskatoon, Saskatchewan S7N 0W0

Received June 24, 1974

Mitsuo Oka and Choi Chuck Lee. Can. J. Chem. **53**, 320 (1975).

The product from the reaction of trianisylvinyl-2-^{13}C bromide (**3**—Br-2-^{13}C) with HOAc–AgOAc or with CF_3COOH–CF_3COOAg was converted to 1,2,2-trianisylethanol-x-^{13}C (**4**—x-^{13}C) and examined for isotopic scrambling by the use of relative intensity ratios in the c.m.r. spectra with the CH_3O absorption as the internal standard, or by the intensities of the ^{13}C satellites in the p.m.r. spectra. About 20 and 50% rearrangements of the ^{13}C-label from C-2 to C-1 were found, respectively, for the acetolysis and trifluoroacetolysis. The results are in accord with the suggestion that there may be a competition between 1,2-aryl shifts in the triarylvinyl cation or ion-pair and the reaction of the ion with solvent to give product.

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Le produit de la réaction du bromure de trianisylvinyl-2-^{13}C (**3**—Br-2-^{13}C) avec AcOH–AcOAg ou avec CF_3COOH–CF_3COOAg a été transformé en trianisyl-1,2,2 éthanol-x^{-13}C (**4**—x-^{13}C). Faisant appel à la résonance magnétique nucléaire du carbone et utilisant l'absorption du OCH_3 comme référence interne, on a pu déterminer la compétition isotopique dans ces produits; une autre méthode d'arriver au même résultat est d'examiner l'intensité des bandes satellites ^{13}C dans le spectre r.m.n. du proton. On a trouvé environ respectivement 20 et 50% de réarrangement du ^{13}C de la position C-2 vers la position C-1 dans les réactions d'acétolyse et de trifluoroacétolyse. Ces résultats concordent avec l'hypothèse qu'il peut y avoir une compétition entre les déplacements 1,2 des groupes aryles dans le cation triarylvinyle ou une paire d'ion et la réaction de l'ion avec le solvant pour donner le produit. [Traduit par le journal]

In the preceding paper (1), the extent of isotopic scrambling in the reaction of triphenylvinyl-2-^{13}C bromide (**1**—Br-2-^{13}C) with HOAc–AgOAc was measured using ^{13}C n.m.r. and the ^{13}C satellites of ^{1}H n.m.r. The results, indicating 6.8 ± 0.9% rearrangement arising from 1,2-phenyl shifts across the double bond in the triphenylvinyl cation, were found to be in agreement with analogous scrambling data obtained from the same reaction with **1**—Br-2-^{14}C (1). In this work, the reaction product, **1**—OAc-x-^{13}C, was converted to 1,2,2-triphenylethanol-x-^{13}C (**2**—x-^{13}C) and the ^{13}C enrichments in the C-1 and C-2 positions of this product molecule were measured from c.m.r. intensity ratios utilizing the total intensities of the *o*, *m*, and *p*-carbons of the aromatic rings as a reference standard. The present work extends the study on the use of n.m.r. to measure isotopic scrambling in ^{13}C labeled systems. The reactions investigated are those of tri-*p*-methoxyphenylvinyl-2-^{13}C bromide (trianisylvinyl-2-^{13}C bromide, **3**—Br-2-^{13}C) with HOAc–AgOAc and with CF_3COOH–CF_3COOAg. The method (2) is based on measurements of relative intensities in the c.m.r. spectrum with respect to a suitable internal standard, and in the present work, the CH_3O absorption containing ^{13}C in its natural abundance is utilized as such an internal standard.

3—Br-2-^{13}C was prepared in a manner similar to the preparation of **1**—Br-2-^{13}C (1). Reaction of *p*-$CH_3OPhCH_2{}^{13}COOEt$ with *p*-$CH_3OPhMgBr$ gave 1,1,2-trianisylethanol-1-^{13}C which on treatment with Br_2 in HOAc yielded the desired trianisylvinyl-2-^{13}C bromide (**3**—Br-2-^{13}C). The acetolysis of **3**—Br-2-^{13}C in the presence of AgOAc was carried out at reflux temperature for 2 h as described by Rappoport and Gal (3), while the trifluoroacetolysis in the presence of CF_3COOAg was effected at room temperature for 10 min. The reaction product, **3**—OAc-x-^{13}C or **3**—$OOCCF_3$-x-^{13}C, was reduced twice successively with $LiAlH_4$ (4) to give 1,2,2-trianisylethanol-x-^{13}C (**4**—x-^{13}C) for n.m.r. examination.

The ^{1}H-decoupled ^{13}C n.m.r. spectrum of ordinary **4** with ^{13}C in its natural abundance, in $CDCl_3$ as solvent and as the locking compound, is shown in Fig. 1*A*. The chemical shifts from the c.m.r. spectra as well as data from the p.m.r. spectra of **4** are given in Table 1. From Fig. 1*A*, the intensity ratios for the unenriched **4**, I_1/I_s, I_2/I_s, and I_2/I_1, where I_1, I_2, and I_s are the

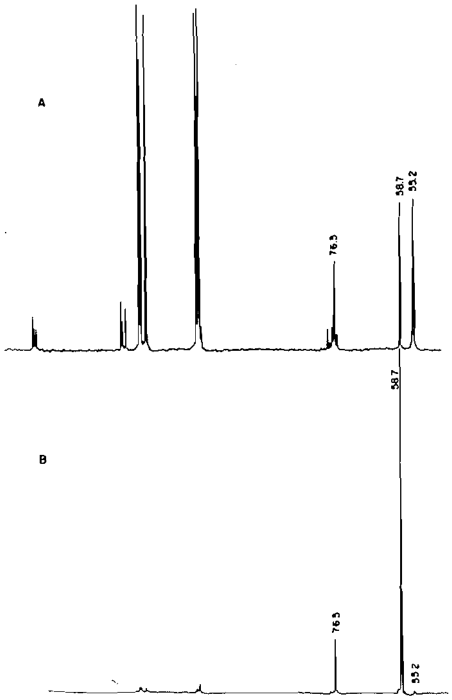

FIG. 1. ^{1}H-decoupled ^{13}C n.m.r. spectra of unenriched 1,2,2-trianisylethanol (4) (*A*) and of 1,2,2-trianisylethanol—x-^{13}C (4—x-^{13}C) (*B*) derived from acetolysis of 90% enriched trianisylvinyl-2-^{13}C bromide (3—Br-2-^{13}C).

integrated intensities of C-1, C-2, and the $\bar{C}H_3O$ standard, respectively, were measured, and the results are given in Table 2.

Figure 1*B* shows the ^{1}H-decoupled ^{13}C n.m.r. spectrum of 4—x-^{13}C derived from the acetolysis, in the presence of AgOAc, of 3—Br-2-^{13}C prepared from BaCO$_3$-^{13}C that was commercially designated as 90% enriched. While I_2/I_1 could be measured from Fig. 1*B*, the CH$_3$O absorption, I_s, was too weak; but with an amplified spectrum, I_1/I_s was obtained (Table 2). A duplicate experiment was carried out using 45% enriched 3—Br-2-^{13}C, while a third measurement was made by diluting the 90% enriched 4—x-^{13}C with carrier to give 9% enrichment. Using the appropriate intensity ratios and calculations as illustrated in the Experimental section, the scrambling of the label from C-2 to C-1 for the various experiments were obtained. The results, showing about 20 ± 1% rearrangement, are summarized in Table 2. Also included in Table 2 is the result, indicating about 50% rearrangement, calculated from the c.m.r. intensity ratios for the 4—x-^{13}C derived from trifluoroacetolysis, in the presence of CF$_3$COOAg, of 45% enriched 3—Br-2-^{13}C.

The ^{13}C scrambling from C-2 to C-1 was also measured by the ^{13}C satellite intensities in the ^{1}H n.m.r. spectra of 4—x-^{13}C obtained from acetolysis or trifluoroacetolysis of 90% enriched 3—Br-2-^{13}C. Figure 2 shows a p.m.r. spectrum of 4—x-^{13}C derived from the trifluoroacetolysis. Data on chemical shifts and coupling constants are summarized in Table 1. From the amplified portion of the spectrum, it is seen that the upfield portions of the satellites for the C-1 and C-2 protons, H$_a$ and H$_b$, are complicated by overlaps. The total satellite intensity is, therefore, taken as twice the integrated area of the downfield half of the H$_a$ and H$_b$ satellites. It may be also noted that the H$_b$ absorption is clearly split by long range coupling with the ^{13}C at C-1 as indicated in Fig. 2. From the intensity values for the C-1 proton, C-1 satellites, C-2 proton, and C-2 satellites, calculations as shown in the Experimental section gave the extents of ^{13}C scrambling from C-2 to C-1 as 21 and 50%, respectively, for the acetolysis and trifluoroacetolysis (Table 2).

1,2-Anisyl shifts across the double bond in the triarylvinyl cation have been observed in the solvolysis of 2,2-dianisyl-1-phenylvinyl bromide (5) in HOAc–AgOAc (5) and in CF$_3$CH$_2$OH or 60% EtOH (6).[1] Considerations of the kinetics, stereochemistry, and nature of products in reactions of 5 and related triarylvinyl systems (5, 6) have led to the conclusion that such solvolyses proceed via the S$_N$1 mechanism without β-aryl participation. The rearrangement of the 2,2-dianisyl-1-phenylvinyl cation to the 1,2-dianisyl-2-phenylvinyl cation took place readily since the latter ion, with the anisyl substituent at C-1, is more stable. The present results demonstrate the occurrence of degenerate 1,2-anisyl shifts in the trianisylvinyl cation. As suggested earlier in accounting for the different extents of degenerate 1,2-phenyl shifts in the triphenylvinyl system (4), there may be a competition between 1,2-aryl shift in the triarylvinyl cation or ion-pair and the reaction of the ion with solvent to give product. Thus, a greater extent of rearrangement may be related to a longer lifetime of the cation or ion-pair. In the present work, about 20% 1,2-anisyl shift is

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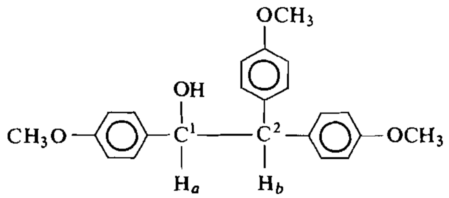
[1] For references to other 1,2-aryl shifts and general reviews on reactions of vinyl cations, see literature cited in ref. 4.

TABLE 1. Carbon-13 and proton n.m.r. of 1,2,2-trianisylethanol (**4**)



(*a*) Carbon-13 magnetic resonance

C	δ, p.p.m. from TMS in	
	CDCl$_3$	Acetone-d_6
C-1	76.5	76.6
C-2	58.7 $J_{^{13}C_1{}^{13}C_2}$ = 38 Hz	59.0
CH$_3$O	55.2	55.2(55.12, 55.16, 55.24)*
Aromatic carbons	113.4, 113.6, 114.1 128.0, 129.4, 129.8	113.6, 113.9 128.7, 130.2, 130.6
Aromatic quaternary carbons	133.5, 134.3, 134.7 157.7, 158.3, 158.7	135.6, 136.1, 137.1 158.3, 158.7, 159.1

(*b*) Proton magnetic resonance

Proton		δ (CDCl$_3$), p.p.m. from TMS
OH	1H broad singlet	2.21
OCH$_3$	9H 3 singlets	3.60, 3.65, 3.68
H$_b$	1H doublet $J_{H_aH_b}$ = 9 Hz $J_{^{13}CH_b}$ = 128 Hz $J_{^{13}CCH_b}$ = 5 Hz	4.07
H$_a$	1H doublet $J_{^{13}CH_a}$ = 142 Hz	5.17
Aromatic	12H multiplets	6.50–7.30

*Numbers in parentheses show the three methoxyl absorptions when the spectral width was expanded from 5000 Hz to 1000 Hz.

TABLE 2. ^{13}C scrambling data from the ^{13}C and ^{1}H n.m.r. spectra of 1,2,2-trianisylethanol-*x*-^{13}C (**4**—*x*-^{13}C) derived from acetolysis or trifluoroacetolysis of trianisylvinyl-2-^{13}C bromide (**3**—Br-2-^{13}C)

Designated ^{13}C enrichment (%)*		Intensity ratios†			Calculated ^{13}C enrichment (%)	^{13}C rearrangement from C-2 to C-1 (%)
		I_1/I_s	I_2/I_s	I_2/I_1		
Unenriched **4**		0.586	0.982	1.68		
Acetolysis						
c.m.r.	90	10.4		6.54	91	20
	45	5.43	33.7		46	20
	9	1.49	7.73		9.3	18
p.m.r.	90				87	21
Trifluoroacetolysis						
c.m.r.	45	14.0	23.2		50	50
p.m.r.	90				92	50

*Based on the commercial designation of 90% enrichment without dilution or diluted with carrier by factors of 2 and 10.
†I_1, I_2, and I_s are, respectively, the integrated c.m.r. intensities for C-1, C-2, and the CH$_3$O internal standard.

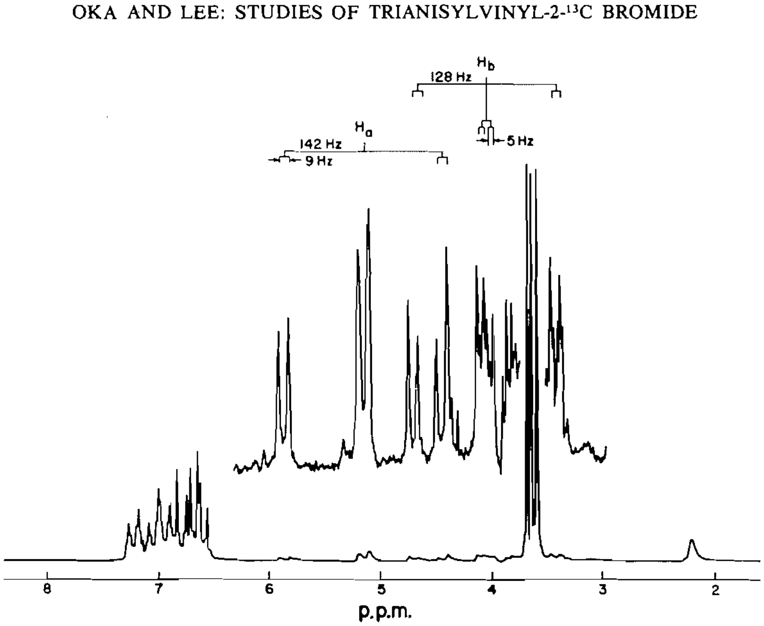


FIG. 2. ^{1}H n.m.r. spectrum of 1,2,2-trianisylethanol—x-^{13}C (4—x-^{13}C) derived from trifluoroacetolysis of 90% enriched trianisylvinyl-2-^{13}C bromide (3—Br-2-^{13}C).

found in the reaction of 3—Br-2-^{13}C with HOAc–AgOAc, and this compares with about 7% rearrangement arising from 1,2-phenyl shifts in the analogous reaction with 1—Br-2-^{13}C (1). The difference reflects the greater migratory aptitude of the anisyl group and probably also suggests a longer lifetime for the more stable trianisylvinyl cation as compared to the triphenylvinyl cation. For the trifluoroacetolysis, the extremely low nucleophilicity of the solvent (7, 8) allows the 1,2-anisyl shift to compete favorably to give the completely scrambled trianisylvinyl cation with 50% rearrangement, and this is in accord with the previous finding (4) that in solvolytic studies with triphenylvinyl-2-^{14}C triflate, the highest rearrangement was observed in the solvent of lowest nucleophilicity.

Experimental

1,1,2-Trianisylethanol-1-^{13}C

p-Methoxyphenylacetic acid-1-^{13}C was prepared from reaction of p-CH_3OPhCH_2MgCl with $^{13}CO_2$ from 90% enriched $Ba^{13}CO_3$ (Merck, Sharp and Dohme of Canada Ltd.) as previously described for the analogous preparation of p-$CH_3OPhCH_2{}^{14}COOH$ (9). Esterification of the labeled acid in absolute EtOH in the presence of a catalytic amount of H_2SO_4 gave a 97% yield of the ester, p-$CH_3OPhCH_2{}^{13}COOCH_2CH_3$, p.m.r. ($CCl_4$) δ 1.20 (CH_3 of Et, t, $J = 7$ Hz), 3.42 (CH_2, $J_{^{13}CCH} = 8$ Hz), 3.70 (CH_3O, s), 4.07 (CH_2 of Et, q of d, $J_{^{13}CCH} = 4$ Hz), 6.67–7.20 (aromatic, m).

To the Grignard reagent prepared from 11.2 g (0.060 mol) of p-CH_3OPhBr and 2.0 g (0.082 mol) of Mg in 80 ml of tetrahydrofuran (THF) was added over a period of 1 h a solution of 3.7 g (0.019 mol) of p-CH_3OPhCH_2-$^{13}COOC_2H_5$ in 35 ml of THF. The reaction mixture was refluxed for 2 h and then poured into a solution of 20 g NH_4Cl and 4 ml NH_4OH in 200 ml H_2O. The THF layer was separated and the aqueous layer was extracted twice with ether. The combined THF solution and ether extract was washed with H_2O and dried over $MgSO_4$. After removal of the solvent, the residual product was washed with CCl_4 and then recrystallized from EtOH to give 4.4 g (63%) of 1,1,2-trianisylethanol-1-^{13}C, m.p. 129° (lit. (10) m.p. 130–131°), p.m.r. ($CDCl_3$) δ 2.23 (OH, broad s), 3.52 (CH_2, $J_{^{13}CCH} = 4$ Hz), 3.73, 3.77 (three CH_3O two singlets), 6.60–7.43 (aromatic, m).

Trianisylvinyl-2-^{13}C Bromide (3—Br-2-^{13}C) (4)

A solution of 2.1 g (0.013 mol) of Br_2 in 10 ml of HOAc was added dropwise with stirring to a solution of 4.2 g (0.012 mol) of 1,1,2-trianisylethanol-1-^{13}C in 200 ml of HOAc. The reaction mixture was stirred at room temperature for 7 h and then poured into 250 ml of H_2O containing 1.0 g of $Na_2S_2O_3$. The product was collected by filtration, washed with H_2O, and recrystallized from CH_3OH to give 3.2 g (65%) of 3—Br-2-^{13}C, m.p. 120–122° (lit. (10) m.p. 119–121°), p.m.r. ($CDCl_3$) δ 3.70, 3.77, 3.80 (three CH_3O, three singlets), 6.53–7.07 (aromatic, m). Comparison of the c.m.r. spectra of the labeled 3—Br-2-^{13}C and the unlabeled 3—Br indicated that the ^{13}C enrichment was located only at one quaternary carbon at 141.7 p.p.m. and this absorption was assigned to C-2 of the 3—Br-2-^{13}C.

Acetolysis of Trianisylvinyl-2-^{13}C Bromide (3—Br-2-^{13}C) (3)

In a typical run, a mixture of 0.90 g (2.1 mmol) of 90% enriched 3—Br-2-^{13}C, 0.38 g (2.3 mmol) of AgOAc, 13 ml of HOAc, and 1.0 ml of acetic anhydride was heated under reflux for 2 h. The hot solution was filtered, most of the solvent evaporated off, the residue redissolved in cyclohexane, and the solution was again filtered. After removal of the solvent from the cyclohexane solution, the residual trianisylvinyl-*x*-^{13}C acetate (**3**—OAc-*x*-^{13}C), recovered as an oil, p.m.r. ($CDCl_3$) δ 2.00 (AcO, s), 3.77, 3.82 (three CH_3O, two singlets), 6.67–7.33 (aromatic, m), and was utilized directly for reduction to 1,2,2-trianisylethanol-*x*-^{13}C (**4**—*x*-^{13}C). In preliminary larger scale runs with unlabeled material, **3**—OAc, recrystallized from EtOH, m.p. 97–98° (lit. (3) m.p. 97–98°), was obtained in yields of more than 90% as reported by Rappoport and Gal (3).

Trifluoroacetolysis of Trianisylvinyl-2-^{13}C Bromide (3—Br-2-^{13}C)

When 0.90 g (2.1 mmol) of **3**—Br-2-^{13}C and 0.50 g (2.3 mmol) of CF_3COOAg were added to 13 ml of CF_3COOH, a purple color developed and the mixture was stirred at room temperature for 10 min. The solution was filtered, the solvent removed at room temperature under reduced pressure, the residue redissolved in cyclohexane, and the solution was again filtered. After removal of the solvent from the cyclohexane solution, the residual **3**—$OOCCF_3$-*x*-^{13}C was recovered as an oil, p.m.r. ($CDCl_3$) δ 3.75, 3.78 (three CH_3O, two singlets), 6.67–7.30 (aromatic, m), and was utilized directly for reduction to **4**—*x*-^{13}C. In preliminary runs with unlabeled material, the oily **3**—$OOCCF_3$ was obtained in about 50% yield, the mass spectrum of which show *m/e* 458 as the molecular ion and the base peak.

1,2,2-Trianisylethanol-x-^{13}C (4—x-^{13}C)

The **3**—OAc-*x*-^{13}C and **3**—$OOCCF_3$-*x*-^{13}C, obtained from acetolysis and trifluoroacetolysis, respectively, were reduced successively twice with $LiAlH_4$ to give **4**—*x*-^{13}C (4). The following is a typical experiment.

The **3**—OAc-*x*-^{13}C obtained from the acetolysis of 0.90 g of 90% enriched **3**—Br-2-^{13}C was dissolved in 35 ml of THF and 1.0 g of $LiAlH_4$ was added portionwise. After the reaction mixture was refluxed for 5 h, H_2O was added and the resulting material was extracted 4 times with ether. The combined extract was washed with H_2O, dried over Na_2SO_4, and the ether was removed to give a product, the p.m.r. analysis of which indicated that it was a 30:70 mixture of the ketone, $AnCOCHAn_2$-*x*-^{13}C, and the alcohol, **4**—*x*-^{13}C. The product mixture was redissolved in 40 ml of THF and treated once more with 1.0 g of $LiAlH_4$ as described above. The recovered colorless product was recrystallized from EtOH, giving 0.50 g of pure **4**—*x*-^{13}C, m.p. 113–114°.

Anal. Calcd. for $C_{23}H_{24}O_4$ (90% ^{13}C enriched for one C atom): C, 75.86; H, 6.62. Found: C, 76.09; H, 6.70.

Nuclear Magnetic Resonance Studies

The ^{1}H-decoupled ^{13}C n.m.r. spectra were obtained at 25.2 MHz on a Varian XL-100-15 spectrometer operating in the FT mode. The spectra were collected with 0.4 s acquisition time, a pulse width of 50 μs, for a 5000 Hz spectral width or with 2.0 s acqusition time, a pulse width of 90 μs, for a 1000 Hz spectral width, by a 6201/i computer with 8K memory. The data length for all spectra were 4960 points. The accumulation time was 0.5–2.0 h depending on amounts of sample (0.1–0.5 g) which were examined in 12 mm sample tubes in either $CDCl_3$ or acetone-d_6. The assignments for C-1 and C-2 of 1,2,2-trianisylethanol-*x*-^{13}C (**4**—*x*-^{13}C) (Table 1 and Fig. 1) were confirmed by mass spectrometry in that the fragmentation of **4**—*x*-^{13}C showed that the An_2CH^+ fragment was much more enriched in ^{13}C than the $AnCHOH^+$ fragment. These assignments are also consistent with the corresponding chemical shifts for C-1 and C-2 of 1,2,2-triphenylethanol-*x*-^{13}C (**2**—*x*-^{13}C) which were assigned unambiguously by ^{14}C data (1).

As an illustration of the calculation of the ^{13}C scrambling from C-2 to C-1 in the **4**—*x*-^{13}C using the intensity ratios I_1/I_s, I_2/I_s, and I_2/I_1 (Table 2), take as an example the data from the acetolysis of 90% enriched **3**—Br-2-^{13}C. If we designate $I_1{}^0$ and $I_1{}^*$ as the ^{13}C absorption due to the naturally abundant ^{13}C at C-1 and to the ^{13}C enrichment at C-1, from Table 2, it is seen that

$$I_1{}^0/I_s = 0.586,$$

and

$$I_1/I_s = (I_1{}^0 + I_1{}^*)/I_s = 10.4$$

Hence

$$(I_1{}^0 + I_1{}^*)/I_1{}^0 = 10.4/0.586 = 17.7$$

Converting the intensities to % ^{13}C

$$(1.1 + I_1{}^*)/1.1 = 17.7$$

Therefore, the ^{13}C enrichment at C-1 = $I_1{}^*$ = 18%.

Where I_2/I_s is also measured from the c.m.r. spectrum, $I_2{}^*$ can be calculated in the same way.

In the **4**—*x*-^{13}C from the experiment with 90% enrichment, I_s was too weak in comparison to I_2 for an accurate measurement of I_2/I_s, hence I_2/I_1 was utilized. Since

$$I_2/I_1 = (I_2{}^0 + I_2{}^*)/(I_1{}^0 + I_1{}^*) = 6.54,$$

and

$$I_2{}^0/I_1{}^0 = 1.68$$

$$\frac{(I_2{}^0 + I_2{}^*)I_1{}^0}{(I_1{}^0 + I_1{}^*)I_2{}^0} = 6.54/1.68 = 3.89$$

Converting the intensities to % ^{13}C

$$\frac{(1.1 + I_2{}^*)1.1}{(1.1 + 18)1.1} = 3.89$$

Therefore,

$$\text{The } ^{13}\text{C enrichment at C-2} = I_2{}^* = 73\%$$

Hence, the calculated ^{13}C enrichment = 18 + 73 = 91% and the ^{13}C rearrangment from C-2 to C-1 = (18/91) × 100 = 20%.

The p.m.r. spectra were obtained using a Varian HA-100 spectrometer. Determinations of ^{13}C scrambling by satellite intensities were carried out using products derived from acetolysis or trifluoroacetolysis of 90% enriched **3**—Br-2-^{13}C. For the trifluoroacetolysis, from a set of three spectra (an example is given in Fig. 2), the average intensity values for the C-1 proton, C-1 satellites, C-2 proton, and C-2 satellites, respectively, were found to be 49, (2 × 22), 47, and (2 × 21). Hence, the ^{13}C contents at C-1 and C-2, respectively, were [44/(49 + 44)] × 100 = 47% and [42/(47 + 42)] × 100 = 47%. Thus ^{13}C enrichments at each of C-1 and C-2, would be 47 − 1.1 = 46%, giving a total enrichment of 92% and a scrambling of the label from C-2 to C-1 of (46/92) × 100 = 50%. In a similar way, the p.m.r. spectra of the **4**—*x*-^{13}C derived from the acetolysis of 90% enriched **3**—Br-2-^{13}C gave average intensity values for the C-1 proton, C-1 satellites, C-2 proton, and C-2 satellites of 50, 12, 21, and 48, respectively, and these intensities corresponded to a 21% ^{13}C scrambling from C-2 to C-1.

The financial support given by the National Research Council of Canada and the technical assistance in obtaining the c.m.r. and p.m.r. spectra given by Mr. Mytosk Mazurek of the Prairie Regional Laboratory of the National Research Council are sincerely acknowledged.

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