the frequencies corresponding to methyl rotation were treated separately, using Pitzer's tables.[49]

Acknowledgment. This investigation was supported by the Office of Basic Energy Sciences, Department of Energy, and National Science Foundation. M.A.M. acknowledges a Connecticut High Technology Scholarship. We thank Fairfield University for a grant of computer time.

Registry No. Butane, 106-97-8; pentane, 109-66-0; hexane, 110-54-3; 2-methylbutane, 78-78-4; 2,3-dimethylbutane, 79-29-8; methylcyclohexane, 108-87-2; octane, 111-65-9; 2,2-dimethylbutane, 75-83-2; cyclohexane, 110-82-7; heptane, 142-82-5.

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Application of Modern ^{3}H NMR Techniques to Analysis of Complex Isotopic Products from a Hydrogenation Reaction

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Received February 22, 1988

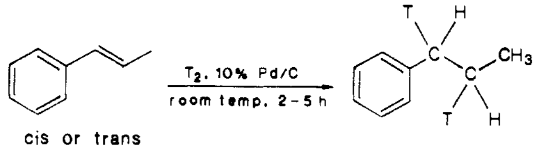
Abstract: A number of modern multiple pulse NMR techniques have been applied to tritium for the first time, demonstrating the power of this approach for analysis of complex isotopic mixtures. In particular, double quantum filtering, DEPT, and tritium homodecoupled BB-proton-decoupled one-dimensional spectra have been obtained. In addition, phase sensitive tritium COSY, tritium–proton correlation, and tritium *J*-resolved two-dimensional experiments are reported. These experiments yield a great deal of information about the isotopic distribution in the subject molecule—*n*-propylbenzene—produced by the catalytic tritiation of β-methylstyrene. Analysis of these NMR data has allowed us to reach some mechanistic conclusions about hydrogenation reactions.

High-resolution tritium NMR spectroscopy has been used routinely for almost 25 years in several laboratories around the world. Since the first observation of a high-resolution spectrum,[1] almost half the published work has originated from the Amersham/University of Surrey collaboration between Evans, Warrell, Elvidge, Jones, and their many co-workers.[2]

Although ^{3}H NMR analysis has been applied to analysis of heterogeneous and homogeneous catalysis,[3,4] determination of product purity,[5] and protein–ligand binding studies,[6] almost all experiments have involved only "onepulse" NMR spectroscopy. In the very recent past a few more adventurous experiments were conducted, including ^{3}H *J*-resolved,[7] ^{3}H–^{3}H COSY,[7,8] and several types of ^{3}H–^{1}H correlation experiments.[8]

As a further illustration and development of the usefulness of multipulse ^{3}H NMR we have conducted a series of NMR experiments on a sample of *n*-propylbenzene prepared by the catalytic tritiation of β-methylstyrene. A double quantum filter has been applied to one-dimensional spectra in order to directly observe the labeled molecules containing spin systems with greater than one tritium atom. *J*-resolved, ^{3}H–^{1}H correlation and phase-sensitive ^{3}H–^{3}H COSY spectra have also been obtained. Selective ^{3}H homodecoupling and ^{3}H–^{1}H DEPT spectra are reported for the first time. All these methods yield extensive information about the species in the reaction product mix and give guidance to the formulation of reaction mechanisms.

Scheme I



Experimental Section

Materials. β-Methylstyrene was obtained from the Aldrich Chemical Co. and used without further purification. The sample was a mixture of cis and trans isomers, and ^{1}H NMR spectroscopy showed the ratio to be approximately 6:94. Tritium gas was purchased from Oak Ridge National Laboratory and contained 97.9% T$_2$, with the largest contaminant being DT (1.76%). The catalyst was 10% Pd/C, supplied by Aldrich.

Catalytic Tritiation. β-Methylstyrene (1 mL) and catalyst (100 mg) were exhaustively degassed in a microhydrogenation apparatus by the application of several freeze–pump–thaw cycles. Tritium gas was admitted to a pressure of 86.7 kPa, and the substrate was thawed. Excess pressure (>101.3 kPa) was vented to the vacuum system, and the catalyst was added to the substrate. The reaction mixture was then stirred and kept at room temperature, and the uptake of gas was monitored. After 1 h the substrate was frozen (liquid N$_2$) and the residual T$_2$ pumped away. The flask was extensively flushed with N$_2$, and methanol (2 mL, ×2) was added to the mixture to remove any labile or dissolved tritium. After the volume was reduced (i.e., pumping the methanol away) the flask was removed from the vacuum line and the solution filtered. An aliquot of the filtrate was dissolved in C$_6$D$_6$ for NMR study.

A second preparation (500-μL substrate) varied in the following ways. When the reaction pressure had dropped to 12–20 kPa the flask was refilled with H$_2$ and the reaction allowed to proceed. This routine was repeated until uptake of H$_2$ ceased. No methanol was added during the subsequent workup procedure since there are no labile hydrogens on the expected product, but dissolved T$_2$ was removed by repeated N$_2$ flushing and several freeze–pump–thaw cycles. This also alleviated the large methanol peaks from the proton NMR spectra of this product. Deuteriochloroform was added to the reaction product to flush it through the filtration apparatus, and storage in this medium had dire consequences for the radiochemical purity of this sample. The solution became deeply

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Table I. Parameters for NMR Experiments and Pulse Sequences

parameter	^{1}H coupled	^{1}H dec	DQF	*J*-Res.	COSY	CORRTH	DEPT
pulse widths							
P1	5.0	5.0	5.3	4.9	5.3	15.8	15.0
P2			10.6				30.0
P3						4.9	5.3
P4							10.6
P0							various
TD: time domain size	8K	8K	8K	2K	2K	2K	8K
NS: no. of scans	20	16	100	192	256	240	100
SW: sweep width (Hz)	3000	3000	3000	1000	3000	3000	3000
D1: relaxation delay	3.63	3.63	3.63	1.0	0.6	0.6	3.63
other delays							
D0				3 μs	3 μs	3 μs	
D2			40 ms				68 ms
D3			3 μs				
D4						20 ms	
WDW/MC2: processing[a]	G	G	G/M	S/M	S/W	S/M	G
DP: decoupling power[b]		16H	16H	16H	16H		16H
NE: no. of expts				128	400	256	

	Pulse Sequences
^{1}H coupled	D1-P1-ACQ
^{1}H decoupled	D1-P1-ACQ (with composite pulse decoupling (WALTZ))
double quantum filtered	D1-P1($\pi/2$)-D2($1/4J_{TT}$)-P2(π)-D2-P1-D3-P1-ACQ(CPD)
J-Res.	D1-P1-D0-P2-D0-ACQ (CPD)
COSY	D1-P1-D0-P1-ACQ(CPD)
CORRTH	D1-P1($\pi/2_H$)-D0-P1 (CPD) P3($\pi/2_T$)-ACQ
DEPT	D1-P1($\pi/2_H$)-D2($1/2J_{TH}$)-P2(π_H)-D2-P0 (CPD) P3($\pi/2_T$) P4(π_T)-D2-ACQ

[a] Apodization functions were: G, Gaussian multiplication; or S, sine–bell window. Intensity calculation algorithms were: M, magnitude calculation; W, phase sensitive calculation. [b] A decoupling power of 16H corresponds to ~460 mW of root-mean-square power when composite pulse decoupling is used.

colored and viscous, and the ^{3}H NMR spectrum started to show additional peaks within a matter of several weeks. This phenomenon has been observed in this laboratory for a number of tritiated substrates stored in chloroform solution.

The NMR samples contained 23.4 GBq (632 mCi) and 80.7 GBq (2.18 Ci) of tritium in 200 μL, respectively. The two samples gave identical tritium NMR spectra, and all the tritium spectra reported in this work were conducted on the lower activity sample.

NMR Spectroscopy. Samples were made to a volume of 200 μL in Teflon tubes (Wilmad, No. 6005), which were then placed inside 5-mm glass NMR tubes having a screw cap (Wilmad, 507-TR-8″). NMR spectroscopy was carried out on an IBM Instruments Inc. AF-300 spectrometer (^{3}H at 320 MHz, ^{1}H at 300 MHz), using a ^{3}H/^{1}H 5-mm dual probe. A high-quality ^{3}H band stop, ^{1}H band pass filter (Cir-Q-Tel Inc., FBT/20-300/3-6/50-3A/3A) was placed in the proton decoupling line of the instrument. The spectrometer was also equipped with an X-nucleus decoupling unit (Bruker BSV-3), with a selective tritium insert to yield up to 80W of power at a programmable frequency. The signals from this external unit were routed to the probehead by way of a directional coupler placed in-line between the ^{3}H pre-amplifier and the observe channel of the probe. Conditions and spectral parameters for the NMR experiments are given in Table I, and all spectra were acquired at 297K with the sample spinning. Referencing of chemical shifts was achieved by generation of a ghost ^{3}H TMS signal from internal TMS in the ^{1}H NMR spectrum.[9]

Results and Discussion

A simple representation of the tritiation reaction is shown in Scheme I. "Normal" ^{3}H NMR analyses of this sample were carried out, including a ^{1}H-coupled spectrum (Figure 1a) and a ^{1}H-decoupled spectrum (Figure 1b), and a ^{1}H NMR spectrum is provided for comparison (Figure 1c). It is clear from these spectra that some tritium has been incorporated into the methyl position, possibly prior to hydrogenation. Integration of the spectra shows that the α-CH$_2$:β-CH$_2$:CH$_3$ tritium ratio is 40:50:10. Certainly the reaction product mixture is complex and does not yield the simple doublet at each methylene chemical shift expected from the simple hydrogenation shown in Scheme I.

A noticeable feature of the ^{1}H spectrum in Figure 1c is the appearance of a triplet, slightly offset from the major CH$_3$ triplet (see inset). This pattern arises because the methyl protons of the molecules having ^{3}H at the β-carbon (mostly Ph–CHT–CHT–CH$_3$ species) have a slightly different shielding (i.e. chemical shift) than those in Ph–CH$_2$–CH$_2$–CH$_3$ molecules. This is the 2° tritium isotope effect on the ^{1}H chemical shift of the methyl protons.

A common method for clarifying coupling relations in simple systems is application of selective decoupling. In this instance it is necessary to enable selective tritium irradiation, broadband proton decoupling, and tritium observation with adequate filtering of the respective inputs—this is a demanding instrumental task. Figure 1d shows the effect of homodecoupling ^{3}H at the α-CH$_2$ position. The β-CH$_2$ pattern is altered, but it is still complex, while the methyl signals are naturally unaffected. Irradiation of the β-CH$_2$ position (Figure 1e) affects the patterns at both the α-CH$_2$ and CH$_3$ positions. At first it seems surprising that the methyl pattern becomes *more* complex with irradiation of its coupling partner, but this arises because the coupling constants and isotope shifts among various methyl tritiated species lead to superposition of signals when the β-CH$_2$ is not irradiated. The reasons for the complexity of the selectively decoupled spectra will become clearer in later discussions of the 2D NMR experiments, particularly the *J*-resolved.

By spectroscopic means it is possible to select ensembles containing more than a certain number of spins from a spread of multiply labeled molecules in a population.[10] In particular it is possible to observe the spin systems with >1, >2, ..., nuclei, and this technique has recently been applied to the resolution of hydrogen-containing species in a sample of highly deuteriated hexane.[11] By use of such filtered spectra, we wish to determine what proportion of 1-, 2-, or 3-tritium containing molecules exist in the reaction mixture. A double-quantum-filtered one-dimensional tritium spectrum (selecting molecules with ≥2 tritons) is shown in Figure 1f, and it can be seen that the uneven major

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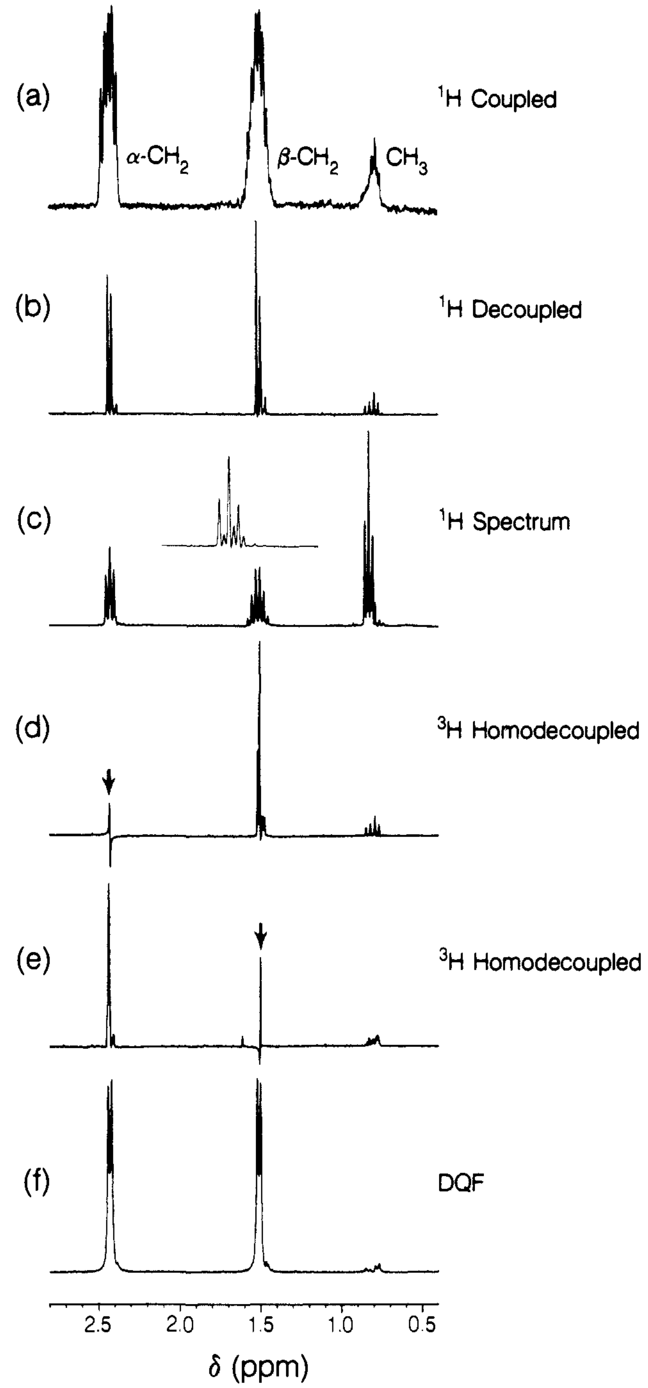

Figure 1. One-dimensional NMR spectra of tritiated *n*-propylbenzene. A Lorentz–Gaussian window function (LB -2, GB 0.2) was applied to all FIDs, and the data were zero-filled from 8 to 16 K before Fourier transformation. (a) Proton-coupled 320-MHz ^{3}H spectrum. (b) Proton-decoupled tritium spectrum. (c) 300-MHz proton spectrum of the product of the second tritiation reaction. The inset shows an expansion of the methyl region, 0.6–1.0 ppm. (d and e) Proton-decoupled tritium spectra with selective decoupling at the arrowed frequencies. (f) Proton-decoupled double quantum filtered tritium spectrum. Magnitude calculation of signal intensity.

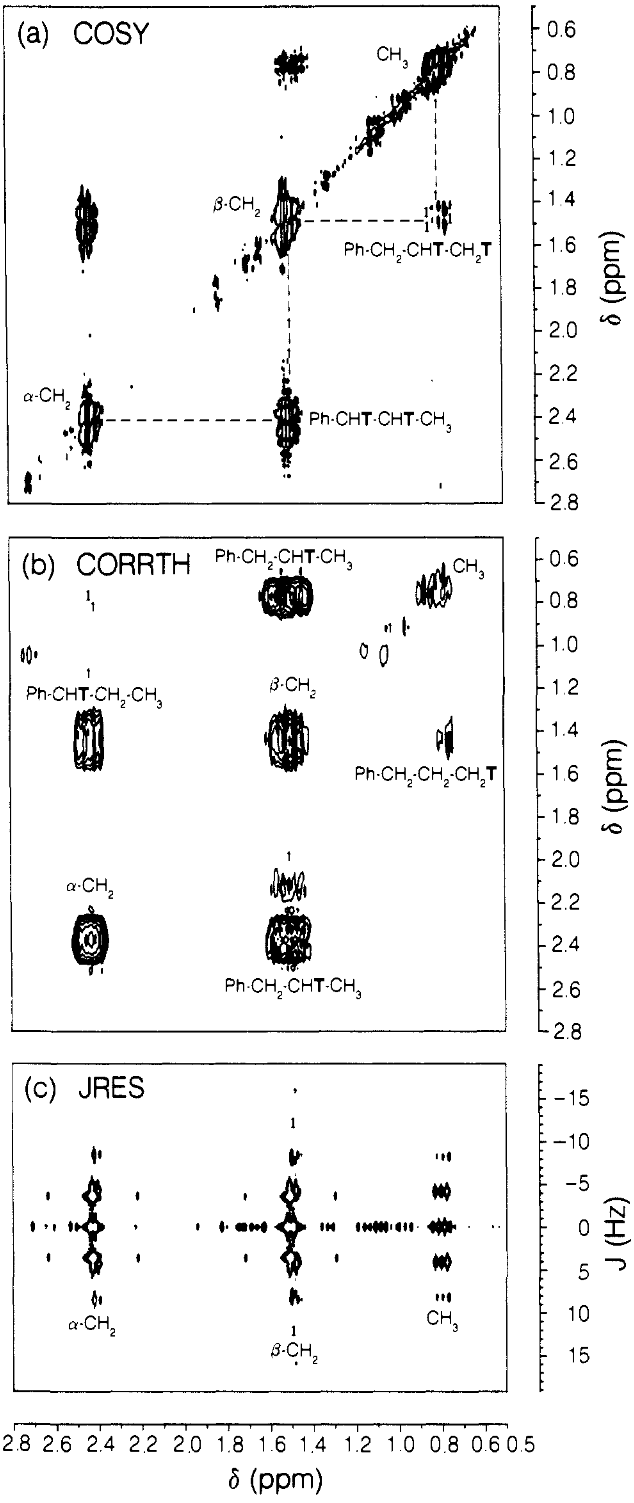

Figure 2. Two-dimensional ^{3}H NMR spectra of *n*-propylbenzene. (a) Contour plot of proton-decoupled phase-sensitive ^{3}H–^{3}H COSY data. A sine-bell window function was applied in both dimensions, 2K × 2K transform, with phase sensitive intensity calculation. (b) Contour plot of ^{3}H–^{1}H CORRTH data. Sine–bell window functions were applied in both dimensions, 2K × 1K transform, with magnitude calculation of peak intensities. (c) Contour map of a ^{1}H-decoupled ^{3}H *J*-resolved experiment. Sine–bell window functions were applied in both dimensions, 2K × 512W transform, with magnitude calculation of peak intensities. The data were "tilted" and "symmetrized".

doublets for each of the methylenes are now equal in intensity, i.e., a singlet that overlaid the low-field line of each doublet has been removed (cf. Figure 1b). Similar analyses can be applied with higher quantum filters but may give non-uniform intensities in this particular application since molecules containing 3 or more tritium atoms may have many different coupling relations among them. A second complication is that equivalent tritons on the same carbon do not split one another and hence are also "filtered" out.

A homonuclear 2D correlated spectrum (COSY) is shown in the contour plot in Figure 2a. The coordinates of correlation (off-diagonal) peaks give the chemical shifts of scalar-coupled ^{3}H nuclei in the sample. In this instance the ^{3}H–^{3}H COSY experiment confirms that the quantity of X–CHT–CH$_x$T$_y$ species is non-trivial, since the cross peaks for the β-CH$_2$ to CH$_3$ coupling are readily observable (at coordinates (1.45, 0.8) and (0.8, 1.45)). For many small organic compounds the use of phase-sensitive[12]

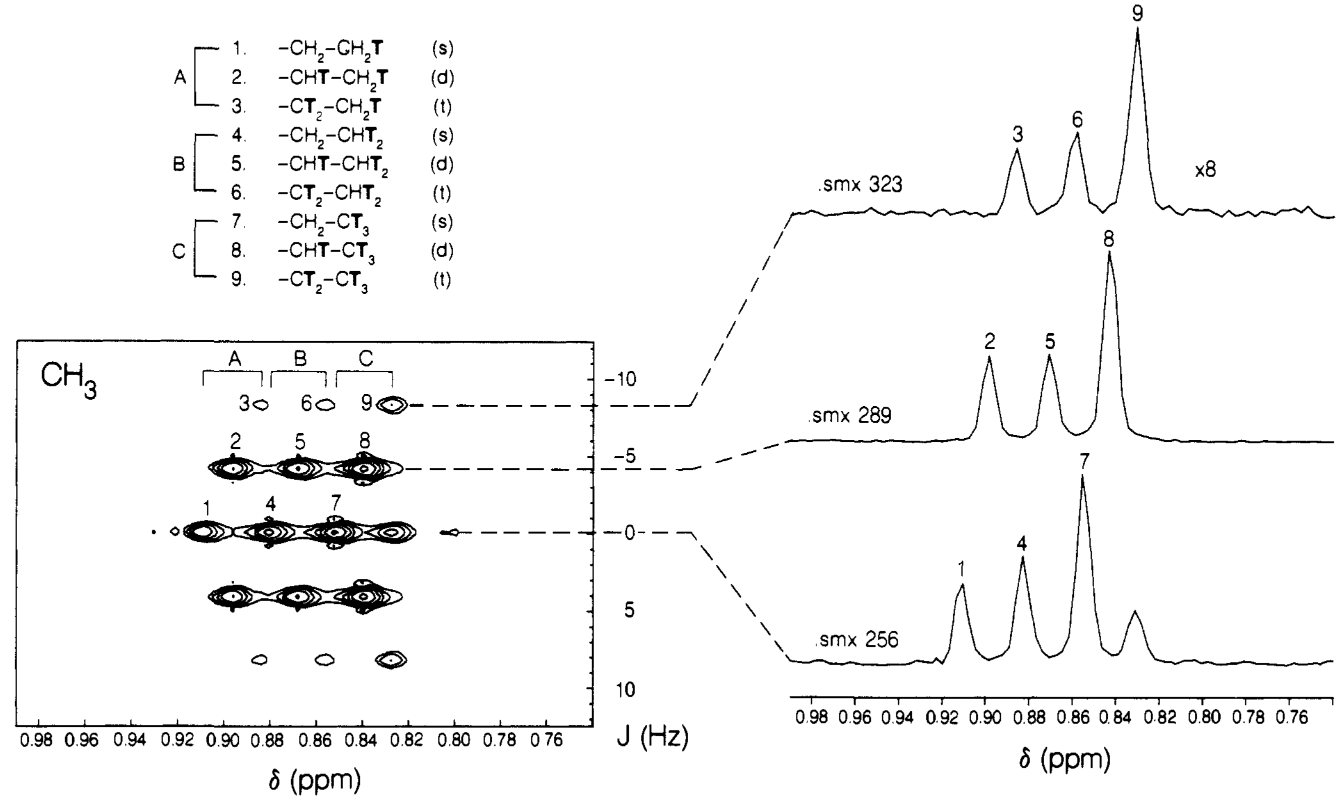

Figure 3. Methyl section (0.68–0.93 ppm) of the proton-decoupled tritium J-resolved spectrum of n-propylbenzene, with data processing as in Figure 2c.

or double-quantum-filtered correlation experiments allows the resolution of many of the coupling constants from the cross peak fine structure. However, in this case there are actually several differently labeled isotopic species present (as discussed further below), which give rise to overlapping cross peaks, obscuring the fine structure. Extended coherence transfer experiments[13] (RELAY) were also performed, and while cross peaks (e.g., α-CHT $\leftrightarrow$ CH_2T) could be observed, the intensities are not informative due to their dependence on coupling constants. The cross peaks are also weak due to the low abundance of the Ph–CHT–CHT–CH_2T species necessary for coherence propagation. These experiments require long blocks of spectrometer time (2 days were used for the RELAY experiment) and will probably be useful only to verify the presence of specific multiply labeled species.

Heteronuclear correlation experiments are generally used to correlate the chemical shifts of protons with an X-nucleus, such as carbon. In this case tritons are the X-nuclei, and since ^3H and ^1H shifts are equivalent the ^3H–^1H (T–H) correlation map (Figure 2b) appears very similar to the COSY. Whereas a COSY spectrum is usually symmetric about the diagonal, an interesting feature of the T–H correlation experiment in Figure 2b is the vast difference in size for the cross peaks for CH_2–CH_3 coupling. This arises from the difference in populations of X–CHT–CH_3 (large crosspeak) and X–$CH_2CH_xT_y$ (small crosspeak) species.

An additional feature of T–H correlation experiments, previously noted,[8] is the difficulty in acquiring ^1H decoupled spectra, as is routinely done for ^{13}C–^1H cases. This difficulty arises because of the delay used to refocus antiphase multiplets before proton decoupling in the tritium dimension. The majority of C–H couplings lie in the range 120–170 Hz (i.e., $1/2J = 4.2 - 2.9$ ms), and a compromise may be chosen where the efficiency of magnetization transfer is acceptable for all carbons. However, T–H couplings may vary over the range 2–16 Hz ($1/2J = 250 - 31$ ms), and any specific tritium atom may have a large number of different couplings, in addition to further T–T interactions. Hence, an "average" coupling constant is very difficult to choose, and proton-decoupled correlation spectra tend to show poor signal to noise.

J-resolved spectroscopy[14] allows the display of chemical shift and coupling constant data on different axes in a 2D map (i.e., resolves them) and thereby simplifies the interpretation of both. Several ^3H J-resolved experiments were conducted, both with and without proton decoupling. The experiment without ^1H decoupling is so complex as to almost defy interpretation. However, a great deal of information may be extracted by close inspection of the proton-decoupled J-resolved experiment (Figure 2c).

In consideration of the methyl pattern of the "tilted, symmetrized" J-resolved spectrum in Figure 2c (expanded in Figure 3) we observe several facts—first, there appears to be a repeating and slightly overlapped singlet–doublet–triplet pattern, each repetition moved successively to lower chemical shift (higher field). This must be due to the following species: X–CH_2–CH_2T, singlet; X–CHT–CH_2T, doublet; and X–CT_2–CH_2T, triplet.

The small increment to higher field within each pattern is the 2° tritium isotope shift induced by addition of a T at the β-CH_2. The whole pattern is repeated to higher field for CHT_2 and CT_3 methyl species, which provides a good measure of the 1° tritium isotope shift, and this has previously been measured as approximately 0.025 ppm (2.4 Hz) at a resonant frequency of 96 MHz.[15] The other information available from these data is the various T–T coupling constants. In addition, inspection of slices parallel to the ω_2 dimension of the experiment shows that the CT_3 species are the most populous, which is a piece of mechanistic information that may be important. In particular, the –CH_2–CT_3 species is present in about one-half the amount of the –CHT–CT_3, while the –CT_2–CT_3 species is present at about a quarter that amount. Projection of the methyl region of the untilted and tilted J-resolved data gives methyl patterns very similar to those obtained through the selective decoupling experiments shown in spectra d and e of Figure 1. Note that the number of tritium atoms in the α-CH_2

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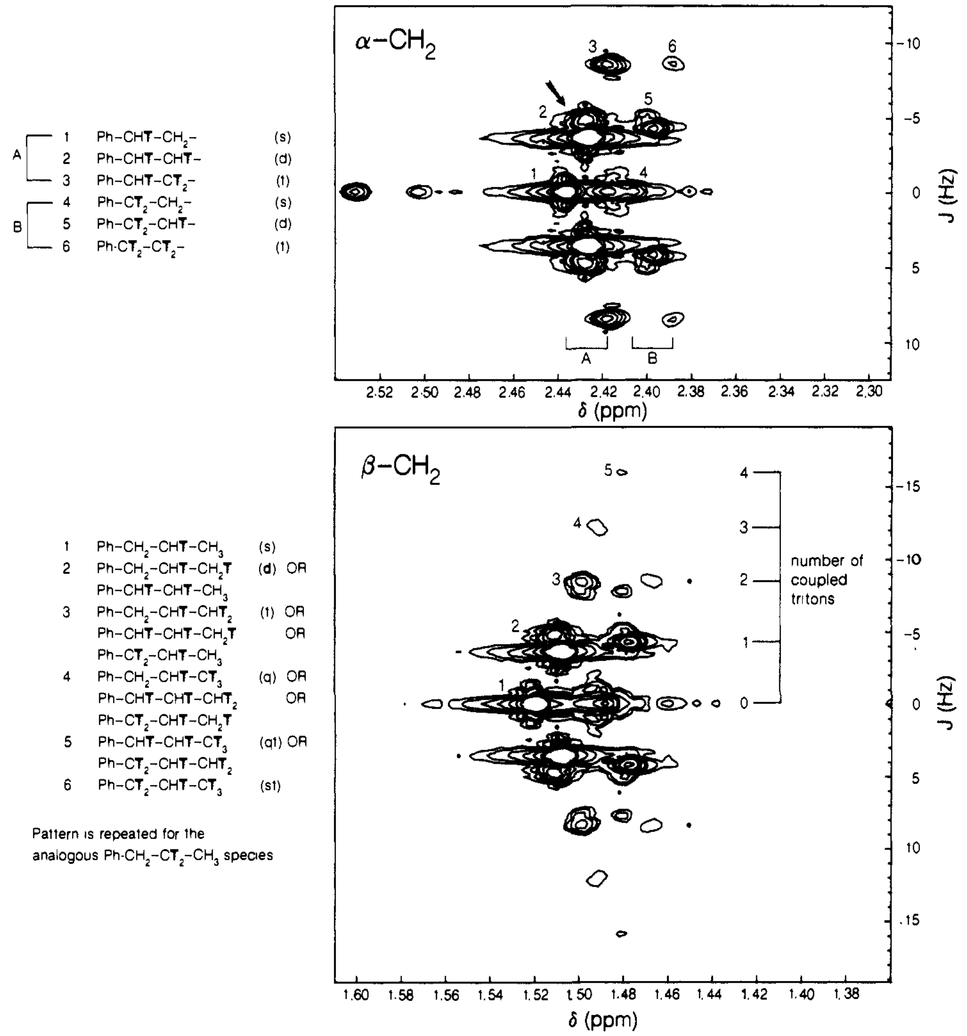

Figure 4. Proton-decoupled tritium *J*-resolved spectra of *n*-propylbenzene, with data processing as in Figure 2c. (a, top) α-CH_2 section, 2.29–2.54 ppm. (b, bottom) β-CH_2 section, 1.36–1.61 ppm.

position does not affect any of the above analyses of the CH_3 portion of the spectrum.

A similar inspection may be made of the α-CH_2 spectrum (Figure 4a), and qualitatively the same information is available. In this case, the most abundant species have one T at the α position, as may be predicted from the one-dimensional spectrum. An unusual feature of the Ph–CHT–CHT–X pattern is the doubling of peaks (arrowed). Our interpretation of this pattern (especially since it disappears for the Ph–CT_2–CHT–X pattern) is that the coupling constants for tritons in anti (or trans) and gauche conformations are different, and these species arise from cis addition of tritium to the cis and trans olefins, respectively. Note that cis hydrogenation of the cis olefin gives rise to the erythro (*S*,*S* and *R*,*R*) enantiomers. When the bulky methyl and phenyl groups are in the favorable anti conformation, the tritons are also anti to one another. In the NMR spectrum, this leads to the small doublet (10%), with the larger J_{TT} (9.52 Hz). Similarly, cis tritiation of the trans olefin gives the tritons in the gauche conformation in the threo (*S*,*R* and *R*,*S*) enantiomers, leading to the larger doublet (90%) with smaller J_{TT} (7.32 Hz). The minor difference in ratio of the products (10:90) from the starting olefins (6:94) may be explained by the known facility of cis/trans isomerization over heterogeneous metal catalysts.[16]

The β-CH_2 has a more complicated pattern (Figure 4b), as it must, since it can couple either to the α-CH_2 or the CH_3 tritons. The spectrum is slightly simplified by the similarity of the *J*'s for these interactions, so that the pattern for Ph–CHT–CHT–CT_3 is identical with that for Ph–CT_2–CHT–CT_2H, within the resolution of the experiment. The isotope shift and coupling constant data from analysis of the *J*-resolved experiment are listed in Table II.

Table II. Isotope Effects and Coupling Constants

			Hz	ppm
methyl	1° isotope effect[a]		8.8	0.028
	2° isotope effect[a]		3.9	0.012
	coupling constant[b]	from doublet	8.06	
		from triplet	8.18	
β-methylene	1° isotope effect		9.8	0.031
	2° isotope effect		2.9	0.009
			3.9	0.012
	coupling constant	from CTH d (small)	9.52	
		from CTH d (large)	7.32	
		from triplet	8.42	
		from CT_2 doublet	8.54	
α-methylene	1° isotope effect		9.8	0.031
	2° isotope effect		2.9	0.009
	coupling constant	from CTH d (small)	9.52	
		from CTH d (large)	7.08	
		from triplet	8.42	
		from CT_2 doublet	8.30	

[a] Error is ±0.003 ppm (0.97 Hz). [b] Error is ±0.12 Hz.

In summary of the *J*-resolved data, there seems to be evidence for most of the 35 possible alkyl-*tritiated* species in the mixture, of course at widely varying concentrations. Nevertheless, this is a disturbing result for such a simple and well-understood reaction as that initially undertaken.

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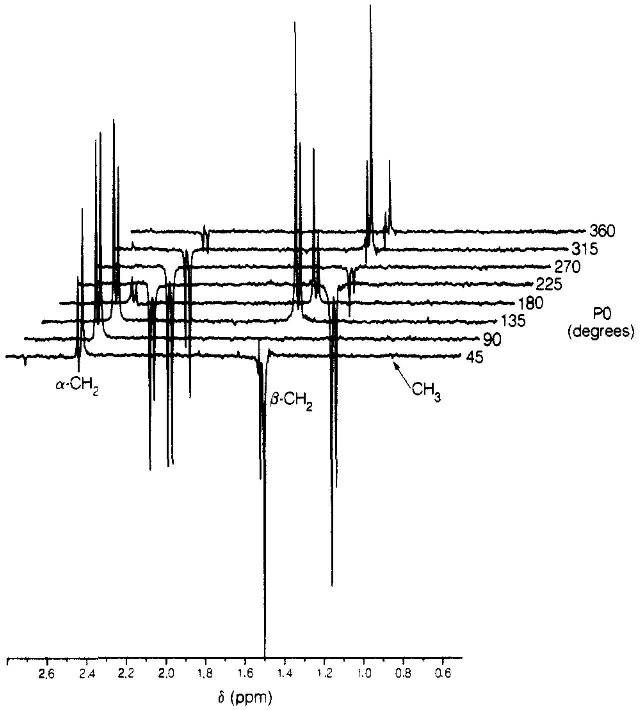

Figure 5. Proton-decoupled tritium DEPT spectra of *n*-propylbenzene. Spectra were acquired with an increasing selection pulse width (P0), starting with 45° (7.5 μs) in the foreground and increasing in 45° steps to 360°. Spectra are scaled and phased relative to spectrum number three (135°, 22.5 μs).

Polarization transfer experiments are the basis of many of the modern NMR techniques. In this connection, tritium is a unique nucleus because it is of higher gyromagnetic ratio than protons, implying that polarization transfer experiments from H to T will give lower sensitivity than ^{3}H alone (cf. ^{13}C, where the enhancement through this mechanism is a factor of 4).[17] In particular, the DEPT experiment[18] is widely used to give greatly enhanced detection of low γ nuclei such as ^{13}C by use of couplings to high γ nuclei (i.e., protons), and as a spectral editing technique to aid in the assignment of ^{13}C spectra.

DEPT experiments were conducted for a range of polarization transfer delays ($1/2J_{TH}$) and selection pulse widths. The optimum transfer was obtained for D2 = 68 ms, which corresponds to a J_{TH} of 7.31 Hz (and matches well with the splittings calculated from the data in Table II). The intensity and phase of the major signals in the spectrum varies greatly with the selection pulse width (P0), as shown in Figure 5. This is because a triton may have many more neighboring protons with significant coupling (commonly 5, maximum 9) than can couple to any carbon nucleus ($\leq$3), and it is common for another triton to also couple to the triton of interest, with a coupling constant of similar magnitude to the T–H constant. These factors complicate the observation of DEPT or INEPT spectra, but they make ^{3}H an interesting NMR phenomenon in addition to its utility as a tracer.

Mechanistic Discussions

In the initial high-resolution ^{3}H NMR publication[1] the pattern of hydrogenation of phenylacetylene to yield ethylbenzene gave two-thirds of the tritium in the methyl position. This anomaly, and others involving uneven addition of tritium across double bonds and vinylic or allylic exchange, has not been solved in the intervening 20 years, even though ^{3}H NMR spectroscopy has provided many illustrations of these phenomena.[19-22] In fact, few instances exist in the literature where heterogeneous tritiation reactions have been analyzed carefully by ^{3}H NMR techniques and *not* shown some deviation from the theoretical, even addition of atoms.

These mechanistic indicators are not observed when hydrogen is used in place of deuterium or tritium. To the synthetic organic chemist conducting general hydrogenation reactions, these interfering reactions (leading most importantly to isomerization products) are essentially invisible, appearing only through poor yield of the desired material. Until recently, the use of deuterium gave only the number of deuterium atoms incorporated, since analytical techniques could not give reliable positional information. Although ^{2}H NMR spectroscopy has corrected this deficiency and proved an extremely valuable technique,[23] it should be recalled that it has 1% the sensitivity and $<^1/_6$ the resolution of ^{3}H NMR spectroscopy, as well as broader natural line widths resulting from quadrapolar relaxation mechanisms.

In some cases asymmetric addition across double bonds can be exaggerated[22]—in the tritiation of 2-acetamidoacrylic acid 95% of the activity was found in the terminal methyl group, and multiply tritiated species were observed by ^{3}H NMR spectroscopy. In the present work at least two points are clear from the NMR analyses. First, 10% of the incorporated label is in the allylic methyl position. Second, the *J*-resolved data in Figure 3 show that the most abundant tritiated methyl species have three tritium atoms on the methyl carbon, and there are clearly species present with at least five tritons in the alkyl chain.

There are two main lines of thought on the mechanism of hydrogenation reactions. The traditional mechanism[24] involves the formation of metal–carbon bonds and desorption of the hydrocarbon with addition of locally adsorbed hydrogen atoms. A more recent proposal[25] suggests that a monolayer of carbonaceous (i.e., hydrogen deficient) material is formed on the metal surface, and hydrogenation occurs by hydrogen transfer from these species to the other adsorbed olefins (i.e., those above the monolayer).

We feel that there are several points to be made from the results in this present work, even though it was not intended as a rigorous study of hydrogenation mechanisms. First, isolated tritium atoms in the addition product probably arise due to dilution of the T_2 with extraneous hydrogen. This problem has been widely observed in tritiation experiments, and it leads to less than theoretical specific activities in tritiated products. One source of hydrogen is almost certainly from the catalyst surface,[22] and it is not eliminated by extensive high-vacuum degassing of the catalyst before reaction. Other ways of removing this dilution factor have not been rigorously explored to date.

A large proportion of the CT_3 species in the reaction product mix is in the form $-CH_2-CT_3$ (ca. 30%, Figure 3, peak 7), and it is very unlikely that this proportion could arise through simple double bond migration reactions. We propose that this class of isotopomer is formed by direct hydrogen exchange of the CH_3 position in the olefin, and it seems likely that the exchange step would involve an intermediate where the terminal carbon is multiply bonded to the metal surface. In any event, exchange is rapid compared to desorption, as supported by the *small quantity* of *highly tritiated* exchange products.

The data presented here do not distinguish between the possible hydrogenation mechanisms. However, the presence of exchange products suggests that adsorption to the metal is reversible, and

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this observation sits more comfortably with the earlier mechanism than with recent proposals.

Conclusions

The present work confirms that large amounts of useful information may be obtained through application of modern NMR techniques to ^3H. Different methods have applicability under different circumstances.

Double quantum filtering (or more general multiple quantum filtering) is quite useful for isolating ^3H coupled ^3H multiplets. Since isotope shifts and coupling constants are very similar in magnitude (at this field strength) complex "multiplets" may arise from either. Filtering allows for identification of true coupled multiplets with the possibility for selection based on the number of spins involved. The drawback is that excitation of different multiplets may not be uniform (due to differences in coupling constant), and hence intensities in filtered spectra may not accurately reflect the concentration of any particular species in solution.

Polarization transfer methods (DEPT or INEPT) also offer some opportunities for introducing selectivity into experiments. In this case the selection method depends upon T–H couplings rather than T–T. As such it will be useful for distinguishing among molecules with different numbers of protons equivalently coupled to tritons. As with multiple quantum filtering methods, the limitation arises from the frequent lack of equivalence in coupling constants and the resulting non-uniformity of excitation.

J-resolved experiments are quite powerful in analysis of mixtures of isotopic species. Since *both* 1° and 2° isotope shifts are larger than line widths, and all T–T couplings appear only in the ω_1 dimension, many different closely related isotopomers can be distinguished. The experiment does not require selection based on coupling constant, hence it can be quite quantitative, and problems are likely to occur only in the case of strong couplings among the tritons. The small number of experiments required in ω_1 makes this a faster experiment than 2D correlated spectroscopy. Ambiguities which arise from combined isotope shifts from several neighbors may be resolved through multiple quantum filtering or RELAY types of experiments when concentrations of such species are high enough.

Correlated experiments, including both T–T COSY and T–H correlation, perform as expected, but they require relatively long acquisition times and high sample activities. Often spectra are simple enough that chemical shifts and multiplicities can establish the labeling pattern. However, when the presence of neighboring tritons must be established the T–T COSY will be useful, and similarly the T–H correlated experiment can help establish the presence of specific T–H pairs. Other correlated experiments (RELAY, multiple quantum 2D, etc.) will probably not be regularly used due to low sensitivity and to the fact that extended coupled T networks do not usually result from common labeling schemes.

It is important to note that the distribution of labeled products from even a simple "hydrogenation" reaction is complex. When a complete understanding of the isotope distribution in products is required the multiple pulse NMR methods will be very important. It is clear that simple notions about reaction mechanisms may be approximately followed, but there are likely to be many side products (at small to moderate concentrations) that will also have to be considered. "Hidden" reactions at allylic positions could prejudice stereochemical yields in many routine hydrogenation reactions.

Acknowledgment. P.G.W. and H.M. are supported by the Biotechnology Resources Program, Division of Research Resources, U.S. National Institutes of Health under Grant P41 RR01237-06, and by the U.S. Department of Energy under Contract DE-AC03-76SF00098. D.E.W. also thanks the Health Effects Research Division, OHER, of the U.S. Department of Energy for continuing support.

Registry No. $PhCHTCHTCH_3$, 117067-85-3; $PhCH_2CHTCH_3$, 117067-86-4; $PhCT_2CHTCT_3$, 117067-87-5; *cis*-β-methylstyrene, 766-90-5; *trans*-β-methylstyrene, 873-66-5; tritium, 10028-17-8; *n*-propylbenzene, 117067-88-6.

Electron Spin Resonance and Electron Spin Echo Spectroscopic Studies of Catalytic Dimerization of Ethylene on Palladium-Exchanged Na–X and Ca–X Zeolites. Proposed Reaction Mechanism for Ethylene Dimerization

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Received February 22, 1988

Abstract: Both NaPd–X and CaPd–X zeolites are shown to dimerize ethylene selectively to *n*-butenes after an induction period, which is decreased with an increase of palladium content and is less for CaPd–X than for NaPd–X due to location of more Pd species at sites accessible to ethylene. A shorter induction period is also seen at higher reaction temperature due to migration of Pd species toward sites accessible to ethylene. Paramagnetic Pd^+ species C ($g_\parallel = 2.53$) and D ($g_\parallel = 2.33$–2.34), both with $g_\perp$ values of 2.10, are observed to form prior to ethylene dimerization and have been assigned to Pd^+–C_2H_4 and Pd^+–$(C_2H_4)_2$, respectively. These species are considered to be active intermediates for the reaction. When ethylene is dimerized to butene, paramagnetic species, assigned to Pd^+ coordinated to butenes, are observed. Ethylene dimerization on the Pd-exchanged zeolites is suggested to occur via coordination of two ethylene molecules to a Pd^+ paramagnetic species. The initial 1-butene product is isomerized to an equilibrium composition of *n*-butenes with *trans*-2-butene predominant. All catalysts are found to deactivate during ethylene dimerization probably due to reduction of Pd species to atomic Pd.

Palladium-exchanged zeolites are used as catalysts for hydrocracking,[1] hydrogenation,[2,3] and dimerization of small olefins.[4–9] However, little work has been done on the nature of the active palladium species or on its site and immediate environment in the

0002-7863/88/1510-8044$01.50/0