

base strength need not be observed in solutions since there the process is complicated by solvation effects.

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### Indirect Spin Saturation. IV.<sup>1</sup> The Effect of Saturating a Double Quantum Transition

Sir:

In nuclear magnetic resonance (nmr), transitions which are forbidden in the first order may be detected in the form of multiple quantum transitions at increased amplitude of the radiofrequency field.<sup>2</sup> The theory of

signals directly. For proton resonance in liquid this is difficult to realize. In strongly coupled systems, the lines are close together; in weakly coupled systems where there may be well-separated groups, multiple quantum transitions are less favorable.<sup>3</sup> However, the effect of saturating double quantum transitions can be studied for proton resonance in liquid crystal, where the dipole-dipole interaction is large, or for fluorine resonance (in both liquid and liquid crystal), where there are large indirect spin-spin couplings.

The  $F^{19}$  nmr of 1,2-dibromo-1,1-dichloro-2,2-difluoroethane contains five peaks at low temperature<sup>4,5</sup> (Figure 1A). The two equivalent fluorine atoms of the *trans* conformer gave rise to a singlet at  $-7.70$  ppm (*vs.*  $C_6H_5CF_3$ ). The AB quartet centered at  $-4.09$  ppm is due to the two fluorine atoms of the *gauche*

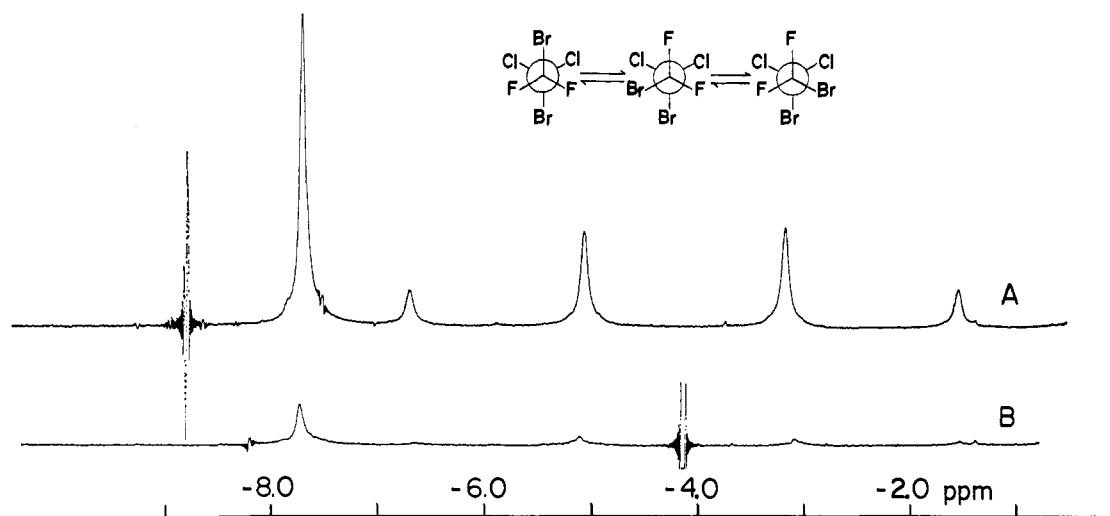


Figure 1. Fluorine-19 nmr spectra of 1,2-dibromo-1,1-dichloro-2,2-difluoroethane (mole fraction 0.15) in  $CS_2$  at  $-80^\circ$  and 94,077 MHz.  $\alpha,\alpha,\alpha$ -Trifluorotoluene (mole fraction 0.05) was used as internal lock at 0.0 ppm. (A) The beat at  $-8.77$  ppm, an irrelevant position, shows that a second stationary radiofrequency field was always on while sweeping the observing radiofrequency. (B) The beat at  $-4.09$  ppm shows an irradiation at the double quantum transition of the AB quartet.

multiple quantum transitions has been discussed by Yatsiv.<sup>3</sup> We wish to report here the effect of saturating a double quantum transition on the "normal" (single quantum) transitions. This effect can be applied to study relaxation and chemical exchange processes.

The direct saturation of an nmr transition by a strong radiofrequency field would equalize the populations of the spin levels connected by this transition. For an  $I = 1/2$ , two-spin AB system, there is only one double quantum transition, namely  $\alpha\alpha \rightarrow \beta\beta$ . If the relaxation processes are not too fast, this transition can be completely saturated by a strong radiofrequency field. The saturation would make the populations of all four spin levels equal. The single quantum transitions are then saturated indirectly. Similar arguments can be extended to more complex spin systems. Experimentally, the system to be studied should have well-separated nmr peaks, so that the strong irradiation at the double quantum transition would not influence the

conformers ( $\delta_{AB} = 3.13 \pm 0.01$  ppm,  $|J_{AB}| = 154.1 \pm 0.5$  Hz). The three conformers are in slow exchange because of the restricted rotation of the C-C bond. In order to avoid the change in the total intensity of the spectrum due to the turning on and off of a strong radiofrequency field ( $\gamma H_2/2\pi \approx 27$  Hz in this case), the latter was set at an irrelevant frequency when the normal spectrum was recorded (Figure 1A). When the radiofrequency field was set at the frequency of the double quantum transition, the AB quartet was almost completely saturated (Figure 1B). In this system, there is another interesting feature in the spectrum. When the center of the AB quartet was irradiated, the singlet due to the fluorines in the *trans* conformer was also partly saturated: its peak area was reduced to  $18 \pm 2\%$ . The saturation is caused by the transfer of demagnetization through chemical exchange.<sup>6</sup>

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## Bredt's Rule. II.<sup>1</sup> Synthesis of Bicyclo[4.2.1]non-1(2)-ene and Bicyclo[4.2.1]non-1(8)-ene

Sir:

We have postulated that a close relationship exists between the strain energy of bridged bicyclic bridgehead alkenes and the strain energy of *trans*-cycloalkenes.<sup>1</sup> This hypothesis leads to the prediction that bridged bicyclic alkenes in which the bridgehead double bonds are endocyclic in rings of at least eight members should be sufficiently stable to allow their synthesis and isolation. The pertinence of this simple relationship has been demonstrated in the synthesis of bicyclo[3.3.1]non-1-ene (3).<sup>1,2</sup> Lesko and Turner<sup>3</sup> have determined the strain energy of bicyclo[3.3.1]non-1-ene (3) to be of the same order of magnitude (*ca.* 12 kcal/mol) as the strain energies of *trans*-cyclooctene (9.2 kcal/mol) and *cis*-di-*t*-butylethylene (9.3 kcal/mol). An additional example of a bicyclic ring system having a bridgehead double bond endocyclic in an eight-membered ring has been provided in the synthesis of 9,9'-dehydrodianthracene.<sup>4</sup>

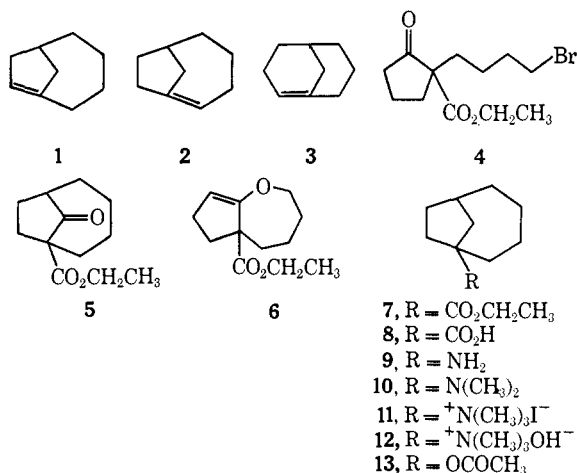
The bicyclo[4.2.1]nonanyl ring system offers an opportunity for further examination of the relationship between bridgehead alkenes and *trans*-cycloalkenes. Two bridgehead alkenes which have their double bonds endocyclic in eight-membered rings, bicyclo[4.2.1]non-1(8)-ene (1) and bicyclo[4.2.1]non-1(2)-ene (2), may be derived from this skeleton. We now report the synthesis and characterization of these highly strained alkenes using a synthetic sequence similar to that used to prepare bicyclo[3.3.1]non-1-ene (3).

Alkylation of the sodium enolate of 2-ethoxycarbonylcyclopentanone with 1,4-dibromobutane in di-

methylformamide produced the bromo keto ester 4 in 65% yield. Addition of the bromo keto ester 4 to a suspension of sodium hydride in benzene and dimethylformamide produced ethyl 9-oxobicyclo[4.2.1]nonane-1-carboxylate (5) in 21% yield along with the enol ether 6 in 31% yield. The keto function of 5 was reduced by conversion to the ethylene dithioketal followed by desulfurization with Raney nickel. The ester 7, produced in 65% yield, was hydrolyzed to the corresponding acid 8, mp 48°, which was transformed by the Curtius procedure into the bridgehead amine 9, mp 56°, in 80% yield. The primary amine 9 was methylated by the Clark-Eschweiler technique to give the tertiary amine 10, and treatment of 10 with methyl iodide afforded the quaternary salt 11, mp 284–287°, in 86% yield. The quaternary iodide 11 was transformed into the corresponding hydroxide 12 by treatment with silver oxide.

Pyrolysis of the quaternary ammonium hydroxide 12 at 140° produced two isomeric hydrocarbons in a 5:1 ratio, a solid, mp 44–46°, and a liquid, with retention times<sup>5</sup> 3.7 and 5.0 min, respectively. Also formed in the pyrolysis was the tertiary amine 10. The hydrocarbons were separated and purified by preparative vpc. The major isomer was shown to possess structure 1, and the minor isomer was shown to have structure 2 by the following spectral analysis and chemical degradation.

The mass spectra<sup>6</sup> of both isomers are nearly identical and show molecular ions at *m/e* 122 with isotope peaks at *m/e* 123 and 124 of the appropriate intensities for the formula C<sub>9</sub>H<sub>14</sub>. Both isomers reacted with acetic acid at room temperature to give bicyclo[4.2.1]nonan-1-yl acetate (13) which was identified by comparison of its infrared spectrum with that of an authentic sample.<sup>7</sup> The nmr of the major isomer (1) shows a broad "singlet" at  $\tau$  4.6 (1 H), a septet ( $J = 2.1$  Hz) centered at  $\tau$  7.2 (1 H), and a complex absorption from  $\tau$  7.55 to 9.05 (12 H). The infrared spectrum (CCl<sub>4</sub>) of 1 shows peaks at 3060 (=CH stretching) and 1607 cm<sup>-1</sup> (C=C stretching). The nmr spectrum of the minor isomer (2) shows a triplet ( $J = 7$  Hz) at  $\tau$  4.7 (1 H) and a complex absorption at  $\tau$  7.15–9.40 (13 H). The infrared spectrum of 2 shows bands at 3055 and 1655 cm<sup>-1</sup>. Since vinyl protons in cyclopentene rings generally show small coupling constants with adjacent aliphatic protons and the frequency observed for the carbon-carbon double bond stretching in the infrared ordinarily decreases with decreasing ring size, the spectral data indicate the major isomer has structure 1 and the minor isomer structure 2. Chemical degradation allowed definitive assignment of the position of the double bond in each compound. Oxidation of the major isomer (1) with potassium permanganate and sodium periodate<sup>8</sup> followed by methylation with diazomethane produced a keto ester which absorbed in the infrared at 1710 (seven-membered ketone) and 1745 cm<sup>-1</sup> (ester carbonyl). Oxidation of the minor isomer (2) and esterification with diazomethane produced a keto ester



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(6) We are indebted to Dr. M. Green for the mass spectra.

(7) It is a pleasure to acknowledge the assistance of Professor W. G. Dauben in furnishing reference spectra.

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