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SHIELDING EFFECTS IN TRICYCLOPROPYLMETHANE

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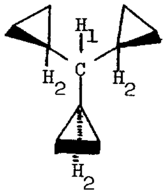
Proton nuclear magnetic resonance demonstrates the existence of a large temperature dependent shielding effect for the central tertiary methane hydrogen (H_1,I) in tricyclopropylmethane.

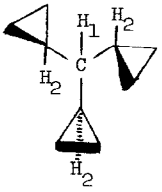
At room temperature the proton H_1 appears as a quartet, $J_{1,2} = 7.4$ Hz, 0.15 ppm upfield from internal tetramethylsilane and can be decoupled by irradiation at the methine cyclopropyl hydrogen frequency at 0.70 ppm. The chemical shift for proton H_1 is only slightly affected by an increase in temperature (Table I). It moves downfield 2.5 Hz for a temperature change from +31°C to +51°C. However, upon cooling the quartet resonance continues to move upfield reaching a value, apparently not a maximum, of 30 Hz upfield from TMS at -83°C.

Maercker and Roberts[1] have reported the chemical shift of the benzylic hydrogen in dicyclopropylphenylmethane (III) to be located at an unusually high field, 82 Hz upfield from the corresponding proton resonance in cumene. From models, and a calculation which predicts a diamagnetic effect of 92 Hz, Roberts and Maercker[1] believe that the most favorable conformation for the molecule is one in which the benzylic hydrogen is located just above the face of cyclopropane rings in a maximum shielding zone.

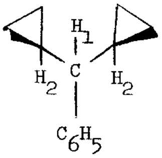
An overall average diamagnetic shielding or ring current effect is probably responsible for the high field position of proton H_1 in tricyclopropylmethane. This is substantiated by a comparison of the results on tricyclopropylmethane with isobutane (IV). At room temperature the chemical shift of the proton in question for IV is 1.71 ppm downfield from the corresponding proton in tricyclopropylmethane. However, conformer I, which shows all three cyclopropyl rings supplying maximum shielding, cannot be an accurate description of tricyclopropylmethane at room temperature. This is evident from the effect that lowering the temperature has on the chemical shift. Stuart-Briegleb models suggest that I (three rings up) and II (two rings up one ring down) are energy minima and presumably lower temperatures increase the populations of I and II at the expense of others (two rings diagonal one ring up, two rings diagonal one ring down, two rings down one up, etc.). The change in the coupling constant, $J_{1,2}$, from 7.4 Hz at 30°C to 8.4 Hz at -83°C supports this conclusion. In I and II the dihedral angles between protons H_1 and H_2 approach 180° or 0° and a larger coupling constant would be expected.



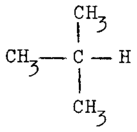
I



II



III



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-H$$

IV

Preliminary results show that similar temperature dependent chemical shifts are observed for the same tertiary protons in isopropyldicyclopropylmethane and p-fluorophenyldicyclopropylmethane, Table I. The temperature effect on the fluoro derivative, while slightly less pronounced, (15 Hz for a 88° temperature change) is still significant and indicates that at low temperature this methane hydrogen also experiences a more deshielded environment. At -80° a single sharp signal was observed for the heteronuclear decoupled fluorine resonance indicating either that one conformer population predominates, or that if two conformations exist they can not be distinguished under these conditions, either because a time average signal is observed or because the two fluorine chemical shifts are identical.

Tricyclopropylmethane[2,3], bp 47-48° (6mm), isopropyldicyclopropylmethane, bp 49-50° (7 mm), and p-fluorophenyldicyclopropylmethane, bp 85° (0.5 mm) were prepared in approximately 80% Yield by aluminum chloride-lithium aluminum hydride reduction[4] of the corresponding alcohols. Spectral and analytical analyses were consistent with the proposed structures and no ring-opened products were observed in the reduction.

TABLE I

NUCLEAR MAGNETIC RESONANCE DATA FOR CYCLOPROPYLMETHANES

IN CHLOROTRIFLUOROMETHANE

Compound	Temperature C°	Chemical Shift for Proton H_1	Coupling Constant $J_{1,2}$
Tricyclopropylmethane	51	6.5[a]	7.3
	41	7.6	7.4
	31	9.0	7.4
	8	13.6	7.4
	-13	16.3	7.6
	-24	18.6	7.6
	-35	19.8	7.8
	-53	22.8	8.0
	-70	26.8	8.2
	-83	29.1	8.2
Isopropyldicyclopropylmethane	31	733.5[c]	9.0,4.0[d]
	-60	757.0	9.0,3.8
p-Fluorophenyldicyclopropylmethane	31	372.0[e]	8.0
	-57	387.0	8.0

a) Chemical shift in Hz upfield from TMS. b) Coupling between methine cyclopropyl hydrogens and tertiary methane hydrogen H_1 in Hz. c) Chemical shift in Hz upfield from $CHCl_3$. d) The methane hydrogen is a triplet of doublets with the larger coupling assigned to the isopropyl hydrogen, established by decoupling the isopropyl proton resonance by irradiation at +538 Hz. e) Chemical shift in Hz upfield from CH_2Cl_2.

3. F. A. Carey and H. S. Tremper, *ibid*. *91*, 2967 (1969).

4. R. F. Nystrom and C. R. A. Berger, *ibid*. *80*, 2896 (1958).