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SYNTHESIS AND NMR SPECTRA OF SYN- AND ANTI-TRICYCLO[3.2.2.$0^{2,4}$]NON-6-ENE

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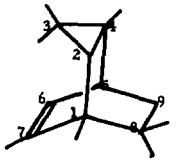
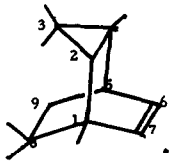
The diamagnetic anisotropy of the double bond and long range shielding effects in n.m.r. spectra have been the subject of a number of theoretical and experimental studies.[1] Efforts to test the predictions of the sign and magnitude of such effects have been hampered by the lack of detailed spectral data and sufficient model compounds to provide an empirical "map" of the anisotropy of the double bond. In the course of synthetic work on another problem, we have had occasion to prepare several compounds with the tricyclo[3.2.2.$0^{2,4}$]nonane skeleton which are well-suited to contribute to such a body of data.

syn-Tricyclo[3.2.2.$0^{2,4}$]non-6-ene (I) was prepared directly by the Diels-Alder addition of cyclopropene (generated by the reaction of allyl chloride with sodium amide according to the procedure of Closs[2]) to 1,3-cyclohexadiene. The average yield of I based on sodamide and allyl chloride was two to five percent; this corresponds to 20 - 50% yield from cyclopropene using Closs' estimate of the yield of cyclopropene from sodamide as 10%. anti-Tricyclo-[3.2.2.$0^{2,4}$]non-6-ene (II) was prepared from the cycloheptatriene-maleic anhydride adduct which was hydrogenated and hydrolyzed to the corresponding diacid. Decarboxylation of the diacid by electrolysis or lead tetraacetate decarboxylation gave the olefin (II) in 30 - 40% yield. Although the yields are comparable for the two routes, the lead tetraacetate procedure is more convenient for large scale preparation due to difficulties encountered in large scale electrolyses. Tricyclo[3.2.2.$0^{2,4}$]nona-6,8-diene (IV)[3,4] was prepared by the electrolytic decarboxylation of the diacids obtained from adducts of cycloheptatriene, maleic anhydride and dimethyl fumarate. In both cases the yield was comparable to that reported[3] but only on a small scale procedure (ca. 1. g). Scaleup resulted in increasingly smaller yields and reasonable quantities of the diene were obtained only through repetition of the small scale electrolyses. The saturated hydrocarbon, tricyclo[3.2.2.$0^{2,4}$] nonane (III) was prepared by catalytic hydrogenation of either I or II. The

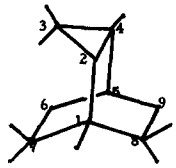
spectral and physical properties of III and IV coincided with those reported.[4] Compounds I - III are white volatile solids and are easily purified by distillation, sublimation or preparative g.l.p.c. The infrared spectra of all three compounds had a band at 3030 cm^{-1} characteristic of cyclopropane rings in addition to the olefinic band at 3050 cm^{-1} present in I and II. The ultraviolet absorption spectra of I - III showed no absorption down to 220 nm. (hexane solvent). The chemical shifts[5] of the protons of I - III are listed in the table. The n.m.r. spectrum of the diene was identical with that previously reported.[4]



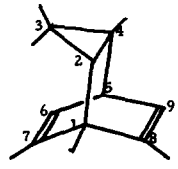
I



II



III



IV

	δ (ppm)[a]			
$H_{1,5}$	2.67	2.61	1.82	3.60
$H_{2,4}$	0.77 (+0.04)[b]	0.96 (-0.15)[b]	0.81.	1.10
H_{3a}	-0.10 (+0.56)[b]	0.85 (-0.39)[b]	0.46	0.60
H_{3b}	-0.10 (+0.30)[b]	0.53 (-0.33)[b]	0.20	0.60
$H_{6,7}$	5.72	6.44	1.26,1.54	5.90
$H_{8,9}$	1.19,1.49	0.92,1.36		6.45

[a] δ in ppm. downfield from internal TMS; solutions are 15% (v/v) in CCl_4. [b] Δδ values as compared to the saturated compound, III; positive sign is an upfield shift.

The chemical shifts of the protons were measured from the 220 MHz spectra of compounds I - III.[5] The secondary cyclopropyl protons in compounds II and III were cleanly resolved and were identified by their different coupling constants with the tertiary cyclopropyl protons[6] (J_{cis} = 7.5 Hz, J_{trans} = 3.5 Hz). In compounds I and IV the secondary cyclopropyl protons are nearly degenerate and not individually resolvable, but appear as a sharp line in the 220 MHz spectra and as an irregular multiplet in the 60 MHz spectra centered about a sharp intense center line. This phenomenon is also observed in the similar compounds obtained from addition of maleic anhydride and dimethyl fumarate to cycloheptatriene and the related cis- and trans-diacids. The diamagnetic anisotropic effect of the cyclopropane ring[7] is seen in the shielding of the olefinic protons of I and the aliphatic ring protons ($H_{8,9}$) of II. This serves to establish the identity of the olefinic protons of the

diene IV. The individual resonances of the aliphatic ring protons $H_{8,9}$ of I and II and $H_{6,7,8,9}$ of III cannot be established at this time.

The identification of the cyclopropyl proton chemical shifts and the fact that these protons are positioned rigidly in a rather wide variety of angles and distances from the perturbing π-clouds make them particularly interesting in regard to analysis of the double bond anisotropy. The geometrical changes in compounds I - III are very small and charge densities should be similar. Thus chemical shift differences are chiefly attributable to the anisotropy of the double bond. Qualitatively, it is seen that the aliphatic ring protons $H_{8,9}$ of I and II are little affected by the presence of the double bond when compared to the corresponding protons in III. The fact that the olefinic protons of IV are similar to those of I and II indicates that there is no anisotropic effect of one double bond on the other. In addition the tertiary cyclopropyl protons $H_{2,4}$ of I and II are only slightly affected by the double bond. Comparison of the geometrical orientation of these protons with the calculated values[1] indicates that these protons are all located near the nodal surface of the shielding-deshielding regions of the double bond. Thus the chemical shift changes are small and unpredictable in sign similar to those noted for the 7-norbornenyl protons.[8]

The secondary cyclopropyl protons all lie in the yz plane[1] bisecting the molecules through the center of the double bond and the cyclopropane ring. The geometrical orientation of these protons to the double bond and the observed chemical shift differences exhibit the greatest variation. The geometrical parameters (θ, the angle of incidence of a line, r (in Å) from the proton to the center of the double bond with the plane of the σ-framework of the double bond) were measured from Dreiding models: proton, $\Delta\delta_{obs'd.}$ (θ, r in Å); H_{3a}(I), +0.56 (84°, 2.02); H_{3b}(I), +0.30 (64°, 3.63); H_{3b}(II), -0.33 (22°, 4.51); H_{3a}(II), -0.39 (-2°, 3.74). Thus the region directly above the double bond is strongly shielding and the region in the plane of the double bond is strongly deshielding with an extreme difference of 0.95 ppm. Qualitatively the agreement with theory[1] is good. Using the geometrical parameters for all of the cyclopropane protons, comparison of the experimental shift differences with the contour maps for the shielding affect of the double bond calculated by Tillieu and Pople and with Jackman's calculations reveals that the Pople and Jackman treatments (centered at carbon and point dipoles at the center of the double bond, respectively) are in better agreement. The Tillieu values, especially for the protons most distant from and near the plane of the double

bond are far off in magnitude and of opposite sign. While the Pople and Jackman calculated values[1] give the best agreement they considerably underestimate the magnitudes of these shifts. The chemical shift differences of the diene IV relative to the saturated hydrocarbon III do not show an additive relationship with the spectra of I - III and are considerably deshielded compared to the spectra of I and II indicating the presence of some other factor in this molecule.

The literature abounds with simple systems which should possess the criteria for this type of analysis: rigid and varied geometries, identifiable resonances and the lack of complicating perturbations. Unfortunately, much of the needed spectral data is unreported or unavailable or incomplete. An intensive literature search is underway and other available compounds are being studied.

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5. NMR spectra were taken on a Varian A-60 spectrometer and on a Varian 220 MHz spectrometer through the generous cooperation of Dr. Dinshaw Patel of the Bell Laboratories.

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