

HEXACYCLO(5.4.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{8,10})UNDECANE: A NEW C₁₁H₁₂ HYDROCARBON

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Recent interest in the chemistry of the trishomocubyl system¹⁻³ and other highly strained cage hydrocarbon systems prompts us to communicate some preliminary results of our investigation of the reaction of the ditosylate (2) derived from pentacyclo(5.4.0.0^{2,6}.0^{3,10}.0^{5,9})undecane-endo,endo-8,11-diol (1)⁴ with sodium iodide in hexamethylphosphoramide (HMPA) solvent. This reaction affords five products, (see Scheme).⁵ The isomeric diiodides (3, 4, and 5) were isolated in a total 43.4% yield. Nmr analysis of the product mixture which contained 3, 4, and 5 was performed via integration of the broad singlets corresponding to the protons geminal to the iodine atoms in these three compounds. This analysis revealed the presence of the diiodides in the ratio 3 : (4 + 5) = ca. 1 : 1.5. Separation of the three isomeric diiodides was effected via elution chromatography on silica gel (hexane eluant); the diiodides were eluted in the order 3 - 5 - 4. The isomeric C₁₁H₁₂ hydrocarbons (6 and 7) were isolated via preparative vpc techniques in a total 11.6% yield. Vpc analysis of the product mixture containing 6 and 7 revealed their presence in the ratio 1 : 2.5.

Dehalogenation of diiodide 3 with tri-n-butyltin hydride afforded the corresponding hydrocarbon (8)⁶. Dehalogenation of diiodides 4 and 5 with either zinc-acetic acid^{2,3} or with tri-n-butyltin hydride afforded trishomocubane, (9). Comparison of spectral and physical properties of the products of these dehalogenation reactions with the corresponding literature values for 8⁶ and 9^{2,3} permitted our assigning the carbon skeletons of 3 and of 4 and 5, respectively.

The carbon-iodine bond stereochemistries in 3, 4, and 5 were determined via analysis of their ¹³C nmr spectra. The proton noise-decoupled ¹³C nmr spectrum of 3 displayed six peaks: 73.9, 78.3, 79.3, 86.4, 97.1, and 97.2 ppm upfield from benzene. The off-resonance decoupled ¹³C nmr spectrum of 3 displayed five doublets and one triplet. These spectra are consistent with 3 having the C-I bonds either endo,endo or exo,exo; sterically and mechanistically (i.e., S_N2 displacement of the endo-tosylate groups in 2 by iodide), the latter would appear to be the more likely of the two choices.

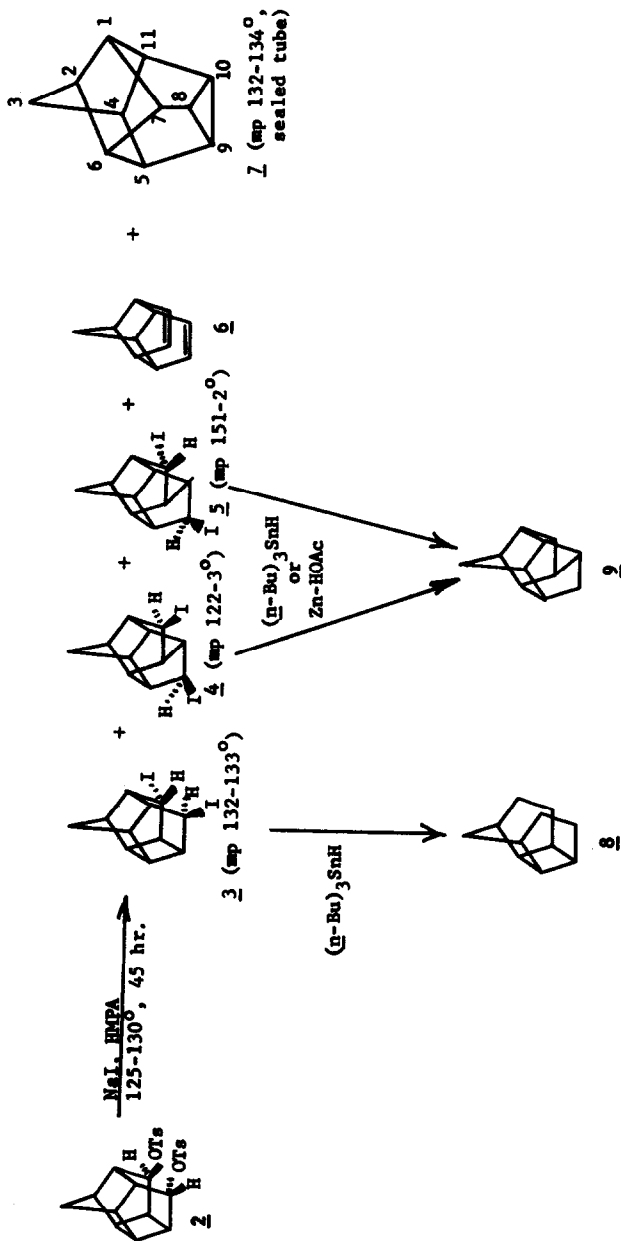
The proton noise-decoupled ^{13}C nmr spectrum of 4 displayed eleven peaks: 69.2, 70.7, 71.8, 75.1, 79.1, 79.9, 87.2, 88.0, 95.9, 98.1, and 98.6 ppm upfield from benzene. This result requires the endo, exo configuration of the C-I bonds in 4. The corresponding off-resonance decoupled ^{13}C nmr spectrum of 5 displayed only six peaks: 68.9, 72.2, 81.9, 87.7, 94.3, and 99.2 ppm upfield from benzene. This result is consistent with either the endo,endo or exo,exo configuration of the C-I bonds in 5. Sterically and mechanistically, the latter would appear to be the more likely of the two choices. Assignment of the structure of diene 6 was made via analysis of its proton noise-decoupled ^{13}C nmr spectrum (four peaks: 96.8, 79.5, 63.6, and -8.6 ppm from benzene), its ^1H nmr spectrum, and by comparison of its physical properties with literature values^{1,2}.

The title compound (7) was identified via analysis of its ^{13}C nmr spectrum. The proton noise-decoupled ^{13}C -FT nmr spectrum of 7 displayed eight lines, five arising from distinct carbon atoms (C2, C3, C4, C7, and C8- see Scheme) and three arising from pairs of equivalent carbon atoms (C1-C6, C5-C11, and C9-C10). The chemical shifts (ppm upfield from benzene) are: 66.4(1C), 71.2(2C), 75.8(2C), 79.8(1C), 87.6(1C), 88.5(2C), 88.7(1C), and 92.4(1C). The off-resonance decoupled ^{13}C -FT nmr spectrum of 7 displayed seven doublets and one triplet (the latter occurring 88.7 ppm upfield from benzene). That 7 contains only one cyclopropane ring is suggested by the fact that it reacts with $\text{Br}_2/\text{CHCl}_3$ solution to afford a mixture of isomeric dibromides ($\text{C}_{11}\text{H}_{12}\text{Br}_2$, mol. wt. (by mass spectrometry) 302/304/306, with the intensity profile characteristic of the Br_2 multiplet)⁷.

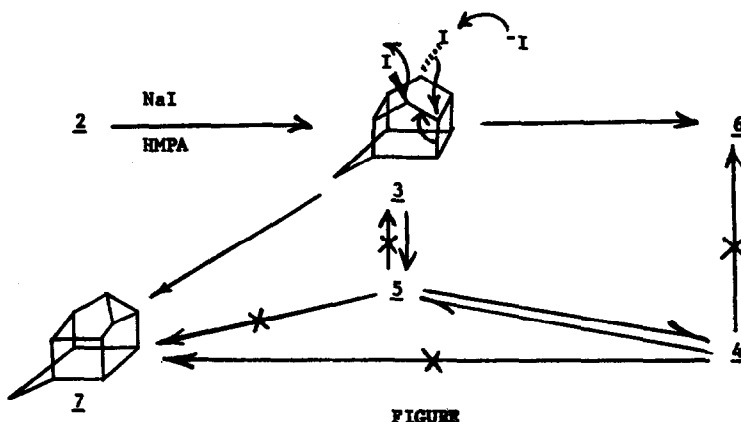
There are two points which come out of this study which merit additional comment. First, Schleyer and coworkers² have reported the synthesis of 4 and 5 as a "mixture of trishomocubyl diiodides" having mp 82-84°. The foregoing ^{13}C nmr spectral evidence suggests that our materials are the stereochemically pure exo,endo and exo,exo diiodides, respectively.

The second point relates to the mechanism of formation of products 4 - 7. Control experiments were performed by subjecting each of the products 3, 4, and 5 in turn to the reaction conditions, (i.e., NaI in HMPA solvent, 125-130°, 45 hr). The results of these control experiments, indicated in the Figure, suggest that 7 must be formed from 3 and not from either 4 or 5. Indeed, compounds 4 - 7 are all formed irreversibly from 3. Products 4 and 5 mutually equilibrate when either pure compound is subjected to the reaction conditions.

A particularly salient feature of the mechanism shown in the Figure is that an iodide-promoted 1,4-dehalogenation leading to the formation of a new, highly strained carbon-carbon sigma bond via reductive cyclization is required to account for the formation of 7 from 3. Such reductive cyclizations of α, ω -dihalides are commonly encountered when promoted either electrolytically or by powerful nucleophiles.⁸ However, it is unusual to encounter iodide-promoted reductive cyclization in



SCHEME



FIGURE

a 1,4-dihalide which must necessarily lead to the formation of such a highly strained cage system as **7**

We are presently studying some aspects of the chemistry of **7**. We hope to report the results of these studies shortly.

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