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TRICYCLO[4.2.1.$0^{1,6}$]NON-3-ENE(I) AND TRICYCLO[4.2.1.$0^{1,6}$]NONANE(II) -TWO NEW STRAINED PROPELLANES[1]

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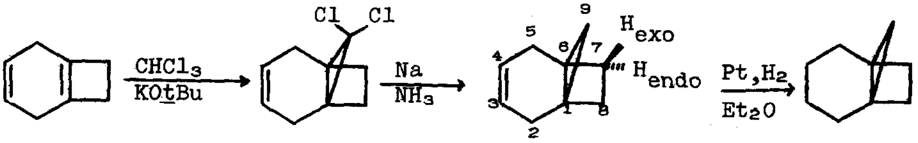
Considerable effort is being expended toward the understanding of the nature of strained carbon-carbon single bonds.[2] In this respect, strained propellanes are very instructive.[3] We wish to report syntheses for and reactivities of two new [4.2.1] propellanes;[4] we feel the results contribute to an understanding of the relationship between strain and reactivity.

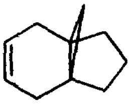
The title compounds, I and II, were synthesized as outlined below, beginning with the known 3,6-dihydrobenzocyclobutene, IV:[5]



IV III I II

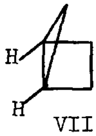
Thus the dichlorocarbene addition to IV resulted in the production of a single adduct, III, as judged by the nmr spectrum [narrow absorptions at τ4.45 (2 vinyl H's), 7.78 (4 allylic H's) and 7.94 (4 cyclobutyl H's)]. The instability[6] of III precluded its purification; however, the mass spectrum indicated two chlorines and gave a parent ion at m/e = 188 for the species having only ^{35}Cl. Reduction of III with Na/NH_3 gave I in reasonable yield.[7]

After purification by gas chromatography, I (which remains unchanged after 22 hrs at 180° and is insensitive to oxygen) gave satisfactory analysis and the correct mass spectral parent ion (m/e = 120). The nmr spectrum was particularly definitive [narrow absorption at τ4.60 (2 vinyl H's), broad singlet at 7.74 (4 allylic H's), AA'BB' system centered at 8.17 (4 cyclobutyl H's), perturbed by long-range coupling of the low field cyclobutyls (H_{endo}) with the cyclobutyl proton *syn* to the six-membered ring (J = 2 Hz), half of an AB quartet at 9.31 (1 cyclopropyl H *syn* to four-membered ring (J_{AB} = 4 Hz), and half of an AB quartet at 9.48 (1 cyclopropyl H *syn* to six-membered ring)], resembling that found for tricyclo[4.3.1.$0^{1,6}$]deca-3-ene(V).[8] Catalytic hydrogenation of I (Pt/C in ether) gave II {analysis, mass spectrum, ir and nmr [τ8.32 (center of multiplets for 8 H's adjacent to the cyclopropane ring), 8.84 (center of multiplet for 4 H's remote from the cyclopropane ring), 9.27 (half of an AB quartet representing the cyclopropyl H *syn* to the four-membered ring, J_{AB} = 5 Hz), and 9.55 (half of an AB quartet representing the cyclopropyl H *syn* to the six-membered ring, and further perturbed by long-range coupling, as for I, J = 2 Hz)] as expected}.



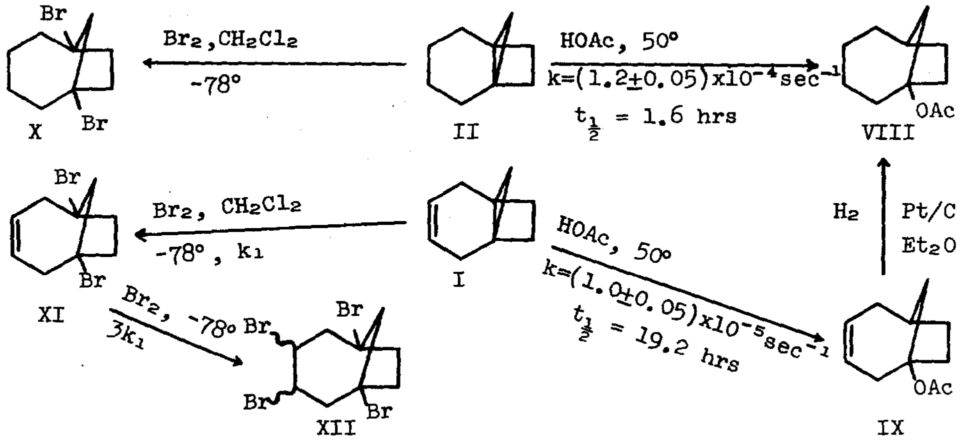
V

VI



VII

The reactivity of the "propellane bonds" (central or 1,6 bonds) of I and II are of paramount interest. It is known[3d] that VI rapidly adds acetic acid across the central bond, at room temperature (reaction completed in <5 min). In contrast, bicyclo[2.1.0]pentane, VII, takes 24 hrs at 48° to react completely with acetic acid.[9] The question of whether or not the increase in reactivity of VI over VII is partly due to alkyl substitution at the reacting centers was heretofore unresolved. We find that II reacts cleanly with acetic acid at 50°, with $t_{\frac{1}{2}}$ = 1.6 hrs,[10] to yield IX[11] (we take the production of IX as further support for our structural assignments). Thus, II is 1.5 to 3 times as reactive as VII toward acetic acid, an amount attributable to alkyl substitition. However, II is still between 3900 and 20,000 times less reactive than VI. This difference, which corresponds to 5-6 kcal/mole, can be partly attributed to the difference in strain between II and VI.[12] Surprisingly, I reacted 12 times slower with acetic acid ($t_{\frac{1}{2}}$ = 19.2 hrs[10] at 50°) than II. The difference may be due to a combination of inductive and conformational factors.



Perhaps more interesting is the reaction of I and II with Br_2. In contrast to the relatively slow rate of Br_2 addition to the [4.2.2] and [3.2.2] propellanes of Eaton[3g,13] and Applequist,[3a,13] II took up Br_2 instantaneously at -78°. The product contained no cyclopropyl protons and no protons on carbon bearing bromine; the mass spectrum indicated the presence of 2 Br atoms. Therefore, we assign it the structure X. The reaction of I with Br_2 was more complex. We consistently obtained product mixtures (when <2 equiv. of Br_2 were used) which mass spectral analysis showed to contain a tetrabromide (XII); on the other hand, nmr showed olefinic protons (τ4.57), protons on carbon bearing bromine (τ5.60) and <u>no</u> cyclopropyl protons.[15] When <1 equivalent of Br_2 was used, some tetrabromide was again produced, indicating that XI reacts some three times faster with Br_2 than does I.[16] This is, to our knowledge, the first example of an isolated σ-bond reacting more rapidly than an isolated π-bond with a reagent as electrophilic[17] as Br_2.

We are continuing our study of the chemistry of I and II.

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1) We thank the donors of the Petroleum Research Fund and Iowa State University for support of this work.

2)(a) K.B. Wiberg, G.M. Lampman, R.P. Ciula, D.S. Connor, P. Schertler and J. Lavanish, *Tetrahedron*, *21*, 2749 (1965); (b) K.B. Wiberg and D.S. Connor, *J. Amer. Chem. Soc.*, *88*, 4437 (1966); (c) N.C. Baird and M.J.S. Dewar, *ibid.*, *89*, 3966 (1967); (d) K.B. Wiberg and R. A. Fenoglio, *ibid.*, *90*, 3395 (1968); (e) P. Schleyer, J.E. Williams and K.R. Blanchard, *ibid.*, *92*, 2377 (1970);(f) N.L. Allinger, M.T. Tribble, M.A. Miller and D.H. Wertz, *ibid.*, *93*, 1637 (1971) and references cited therein; (g) M.H. Delton and D.J. Cram, *ibid.*, *94*, 1699 (1972) and references cited therein.

3)(a) D.E. Applequist and R. Searle, *ibid.*, *86*, 1389 (1964); (b) D. Ginsburg, *Accts. Chem. Res.*, *2*, 121 (1968); (c) K.B. Wiberg, J.E. Hiatt and G.J. Burgmaier, *Tetrahedron Lett.*, 5855 (1968); (d) K.B. Wiberg and G.J. Burgmaier, *ibid.*, 317 (1969); (e) P.G. Gassman, A. Topp, and J.W. Keller, *ibid.*, 1093 (1969); (f) K.B. Wiberg, E. C. Lupton, Jr., and G.J. Burgmaier, *J. Amer. Chem. Soc.*, *91*, 3372 (1969); (g) P.E. Eaton and K. Nyi, *ibid.*, *93*, 2786 (1971); (h) L.A. Paquette and R.W. Houser, *ibid.*, *93*, 4522 (1971).

4)For an explanation of the propellane nomenclature, see J. Altman, E. Babad, J. Itzchaki and D. Ginsburg, *Tetrahedron Suppl.*, *8*(1), 279 (1966).

5)J.M. Garrett and G.J. Fonken, *Tetrahedron Lett.*, 191 (1969).

6)We will soon report on the novel product derived from labile III.

7)Our yields are comparable to the 30% reported by Wiberg and Burgmaier[3d] in the [3.2.1]propellane series.

8)W. Rosen, *Diss. Abstracts*, *28*, 4506-B(1968). We thank Professor Radlick for a copy of the thesis. See also E. Vogel, W. Wiedemann, H. Kiefer and W. Harrison, *Tetrahedron Lett.*, 673 (1963).

9)R.T. LaLonde and L.S. Forney, *J. Amer. Chem. Soc.*, *85*, 3767 (1963).

10)The rates were measured by nmr spectroscopy.

11)IX was identified by comparing its ir and nmr spectrum with those of an authentic sample. We thank Professor W. Dauben for supplying the spectra.

12)We defer a more quantitative discussion for our full paper.

13)Eaton states[3g] that both [4.2.2] and [3.2.2]propellane react with Br_2 in 10-20 min at room temperature. We find it remarkable that *both* propellanes react at about the same rate. Applequist's[3a] [4.2.2]propellane derivative, 9,10-dehydrodianthracene, reacts only 50% with Br_2 after 30 min in refluxing CCl_4. This is noteworthy since this generally overlooked[3g,3h] propellane may be more strained[14] than Eaton's.[3g]

14)The fusing of 2 cyclobutane rings causes them both to be flat, thereby increasing the torsional strain in the rings; this may be as much or more than the strain caused by unsaturation to the cyclobutenoid system.

15)That we should expect the cyclopropyl protons of 3,4-dibromo-tricyclo-[4.2.1.$0^{1,6}$]nonane in the normal cyclopropyl region is indicated by the analogous [4.3.1]propellane derivative.[8] However, we reduced a sample of XI + XII mixture to the hydrocarbons with $(\underline{n}Bu)_3SnH$. Neither the reduced mixture nor the hydrogenated bicyclo[4.2.1]nonane showed any cyclopropyl protons. Rather, the spectra were analogous to those of acetates VIII and IX. Importantly, I does not react with $(\underline{n}Bu)_3SnH$.

16)Kinetic analysis taken from S.W. Benson, "The Foundations of Chemical Kinetics" (McGraw-Hill Book Co., New York, 1960) p. 45.

17)Br_2 addition to Applequist's[3a] propellane is largely free radical in nature; however, we doubt this is the case for I and II.