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Propellanes. XVIII. Free Radical Bromination in the Dark

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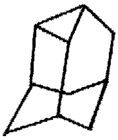
Skell[2] has found that the low temperature (-78°) photoinduced bromination of various alkyl-cyclopropanes proceeds via a radical mechanism. Particularly convincing was the inhibition of bromination in the presence of *iso*-amyl-nitrite (iAmONO). In the case of **1**, bromination proceeded slowly in the dark at -78°, but was inhibited by added iAmONO. Lambert[3] recently reported that methylcyclopropanes brominate in the dark at 0° via an ionic process, although radical pathways do play a small role when uninhibited. We now report studies on propellanic cyclopropanes which further implicate free radical chains in dark, low temperature brominations.

Wiberg[4] has already implicated radicals in the bromination of [3.2.1]propellane (**2**), wherefrom a mixture of halides **3a** and **3b** was obtained. We have



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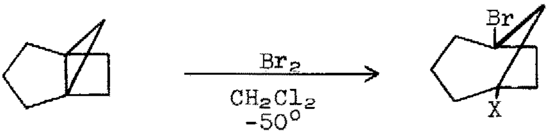

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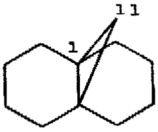
3a, X=Br
b, X=Cl

studied the bromination of [4.4.1]propellane (**4**),[5] [4.3.1]propellane (**5**),[6] [3.3.1]propellane (**6**),[7] [4.3.1]propell-3-ene (**7**)[6] and cyclohexene (**8**).



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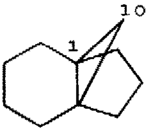

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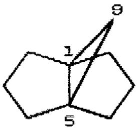

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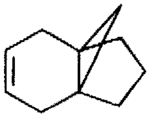

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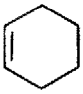

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In order to show that **4**, **5** and **6** brominate in the dark, experiments were performed, in a dark room, in which Br$_2$/CH$_2$Cl$_2$ (1 eq.) was added to the propellane in CH$_2$Cl$_2$, the resulting mixture shaken for 1 minute, and 10 eq. **8** then added to quench any excess Br$_2$, all at -78°. Pmr examination of the consequent reaction mixture revealed that each propellane had completely disappeared. In qualitative experiments in a dimly lit room, **4**, **5** and **6** each appeared to react instantaneously with Br$_2$. The bromides resulting from **4**, **5** and 6 were only briefly investigated; pmr analysis indicated that 4 and 5 reacted mainly by side bond (C_1-C_{11} and C_1-C_{10}) cleavage, whereas 6 apparently underwent both side (C_1-C_9) and central bond (C_1-C_5) cleavage. Of course 7 brominates at the double bond.[6]

Since a radical mechanism was suspected, iAmONO was utilized as an inhibitor. Typically, 4, 5 or 6 was dissolved in CH_2Cl_2 ([propellane] = 0.06-0.25M) along with 2 to 4 eq. iAmONO.[8] One eq. Br_2 was then added to the cold (-78°) solution. After ca. 3 min., excess 8 was added to quench the reaction. In every case, the propellane was largely or wholly recovered. Contrariwise, when the bromination of 7 was performed in the presence of 3 eq. iAmONO, followed by a cyclohexene quench, no 7 was recovered. Thus (if 7 does not brominate much faster than 8, vide infra) the bromination of the double bond of 7 is *mechanistically distinct* from that of the cyclopropane rings of 4-6.

Further evidence for a radical chain bromination was uncovered during initial attempts to measure relative bromination rates. Thus when 4 was treated with 0.19 eq. Br_2 or when 5 was treated with 0.17 eq. Br_2 in CH_2Cl_2 (-78°), no propellane remained when the reaction mixture was examined by pmr. In the case of 6, reaction with 0.48 eq. Br_2 left only 46% 6, which is not too different from the expected 52%. The chains are apparently quite short for 6. These results are in accord with Wiberg's findings for 2.

Competitive brominations (at -78°) were conveniently carried out in CS_2 solution. The disappearance of starting materials was analyzed by pmr (p-dibromobenzene as internal standard). The relative rates measured (or estimated) are given in Table I. As expected, 8 reacted slightly faster than 7. The reactivity order of 4, 5 and 6 was in accord with predictions based on consideration of eclipsing interactions as a bromine atom approaches the three-membered ring.

We lastly explored the possibility that iAmONO prevented bromination by inhibiting the formation of a catalytic amount of HBr, which might otherwise initiate a cationic chain reaction. Skell[10] has found that HBr can be involved in cyclopropane to propylene conversions in dark brominations at higher temperatures (0°). We found that when Br_2 was added to ca. 1 eq. HBr (as an HBr/CH_2Cl_2 solution), 5 and 2 eq. iAmONO (CH_2Cl_2, -78°), followed by a cyclohexene quench, the propellane was recovered, but the cyclohexene was brominated. Again, a clear dichotomy between olefin and cyclopropane bromination was apparent. It also seems unlikely that HBr is involved in these low temperature propellane brominations.

In conclusion, propellanes **4**, **5** and **6**, as well as the smaller ones studied by us[9] and Wiberg,[4] undergo rapid, thermally initiated, low temperature radical chain addition of bromine to their cyclopropane rings.

Table I. Some relative bromination rates (CS_2, -78°).

Compound	k_{rel}	k_{rel}	k_{rel}
8	2.17±0.77		
7	(1.00)		2-≥10[b]
4		>10[a]	
5		(1.00)	(1.00)
6		0.47±0.11	

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a **4** brominated too rapidly to be measured vs. **5**;

b this rate was not measured (peak overlap makes pmr analysis difficult), but is a guess based on the fact that the double bond of **7** must react at least 10 times faster than its cyclopropane ring, but the cyclopropane ring of **5** may react faster than that of **7** due to an inductive effect of the double bond in **7**.

References and Notes

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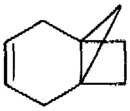
8. Smaller amounts of iAmONO produced a slower reaction, but not complete inhibition. Indeed, for **i**,[9] even 5 eq. iAmONO did not prevent bromination of the cyclopropane ring!



i

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