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endo - FREE RADICAL ADDITION TO NORBORNADIENE

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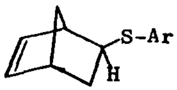
Attack of a free-radical on norbornene or norbornadiene is generally thought to occur from the *exo* side (1,2), although exceptions have been reported (3). There are many examples of *exo*-addition to norbornene by free-radicals (1), but few studies have been made on the sterochemistry of free-radical addition to norbornadiene (2). Cristol, Brindell, and Reeder (2a) were primarily concerned with the question of non-classical free radicals, but they also noted that only *exo*-2-*p*-tolylbicyclo[2.2.1]hept-5-en-2-yl sulfide (**1a**) and the corresponding nortricyclene (**2a**) were formed when p-toluenethiol added to norbornadiene. None of *endo* sulfide **3a** was reported. Similar



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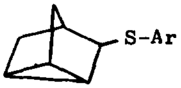

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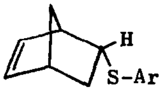

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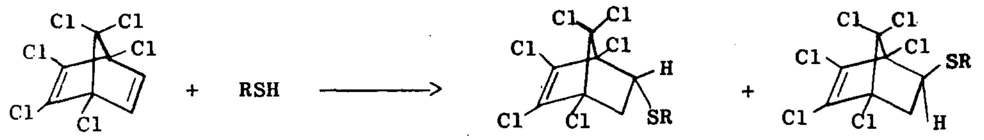
a Ar = p-CH_3-C_6H_4-

b Ar = C_6H_5-

results have been reported (2) with benzenethiol. These results are frequently quoted (1a,1b,2b), and theoretical discussions (2b) normally assume initial free-radical attack will take place from the *exo* side of norbornadiene. The addition of several thiols to 1,2,3,4,7,7-hexachloronorbornadiene (**4**) has recently been reported (4) to produce *endo*-substituted norbornenes (**5**) as well as the *exo*-substituted products (**6**), and in some cases, rearranged products. *Endo* attack on hexachloronorbornadiene was attributed to the directive effects of the steric bulk of the chlorine atoms on C-7.



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These results suggested, however, the possibility that free radical attack on the endo side of norbornadiene might occur more extensively than generally assumed. This has proved to be the case. Addition of thiolacetic acid to an equimolar quantity or to an excess of norbornadiene at -8° to 25° gives a mixture of mono-addition products composed of 35-43% exo-2-thioacetoxybicyclo[2.2.1]hept-5-ene (7), 17-21% endo-2-thioacetoxybicyclo[2.2.1]hept-5-ene (8) and 37-50% 3-thioacetoxytricyclo[2.2.1.0^{2,6}]heptane (9). These isomeric thioacetates were separated by distillation and preparative gas chromatography. The assigned structures were determined by elemental analyses, by infrared spectra, and n.m.r. spectra (Figure 1). The n.m.r. coupling constants (Table I) between the protons on C-2 and on adjacent positions are those expected (5) for the geometries assigned. These assignments are further supported by the widely separated vinyl proton signals and the very high field

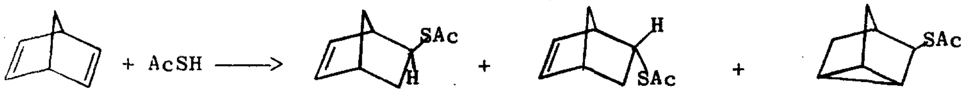

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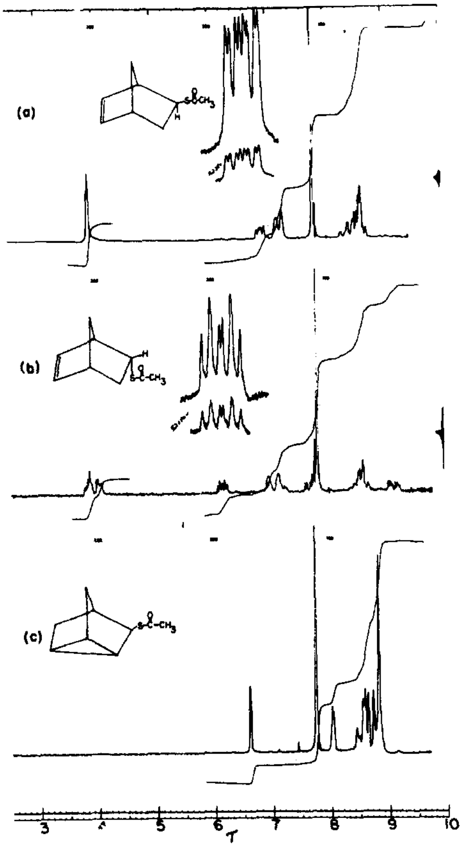
TABLE I. N.M.R. COUPLING CONSTANTS (c.p.s.)[a]

Compound	$J_{1,2x}$	$J_{2x,3x}$	$J_{2n,3n}$	$J_{2x,3n}$	$J_{2n,3x}$	$J_{2n,7s}$
7	--	--	7.8	--	4.4	1.6
8	3.7[b]	9.0	--	3.9[b]	--	--

[a] The terminology is that used in Ref. 5. These values were determined by direct measurement from the spectrum and high accuracy (6) is not implied.

[b] These assignments are tentative.



Nmr spectra (100 Mc.) of (a) exo-2-thioacetoxybicyclo[2.2.1]hept-5-ene (**7**), (b) endo-2-thioacetoxybicyclo[2.2.1]-hept-5-ene (**8**), and (c) 3-thioacetoxytricyclo[2.2.1.$0^{2,6}$]-heptane (**9**).

(τ 9.2) signal of the 3-*endo*-proton of compound **8**. These are characteristic features of the n.m.r. spectra of *endo*-2-substituted bicyclo[2.2.1]hept-5-enes (5). The n.m.r. spectrum of nortricyclene **9** is similarly characteristic of 3-substituted nortricyclenes.

Monitoring of the reaction by gas chromatography showed that the *endo*-substituted isomer **8** appears at very low conversion, and that the *endo*/*exo* ratio does not increase as the reaction proceeds to completion. Thus it is highly probable that *endo*-thioacetate **8** is a direct product of addition, and not the product of subsequent rearrangement.

Other thiols add to norbornadiene in a similar manner, although the amount of *endo* isomer formed is generally smaller. Preliminary results have shown that addition of benzenethiol to norbornadiene results in formation of some *endo* adduct **3b** as well as the reported (2) *exo* (**1b**) and nortricyclyl (**2b**) adducts.

These findings should not be taken as aspersing the work of Cristol, Brindell, and Reeder (2a) as their study was executed prior to the advent of gas chromatography--an essential tool in this study.

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