

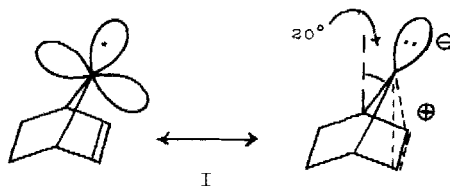
7-NORBORNENYLIDENE--STERESELECTIVITY OF THE ADDITION
REACTION AS A TEST FOR BRIDGE-BENDING

Robert A. Moss* and Chi-Tang Ho

Wright and Risman Laboratories, School of Chemistry,
Rutgers, The State University of New Jersey,
New Brunswick, New Jersey 08903

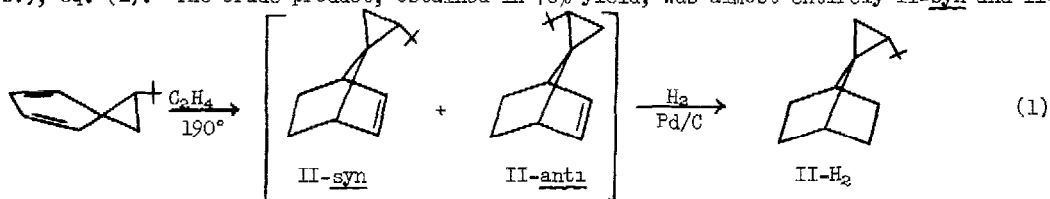
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Calculations indicate that 7-norbornenylidene, I, is a "singlet, stabilized, nonclassical methylene," with its carbenic bridge bent $\sim 20^\circ$ away from the vertical, toward the π bond.¹ Because of the bending, it was suggested that "sterically bulky substituents on the addend should prefer the side anti to the double bond" during olefinic addition of I.¹ Having characterized



the intramolecular chemistry of I,² and reported the initial examples of its intermolecular addition reactions,³ we have now examined the stereoselectivity of its reaction with t-butylethylene⁴ as a test of the stereochemical prediction.⁵

The adducts of I and t-butylethylene were presynthesized by Diels-Alder addition of ethylene to 1-t-butylspiro[2.4]heptadiene⁶ (neat, degassed, excess ethylene solvent, steel bomb, 190° , 20 hrs.), eq. (1). The crude product, obtained in 70% yield, was almost entirely II-syn and II-

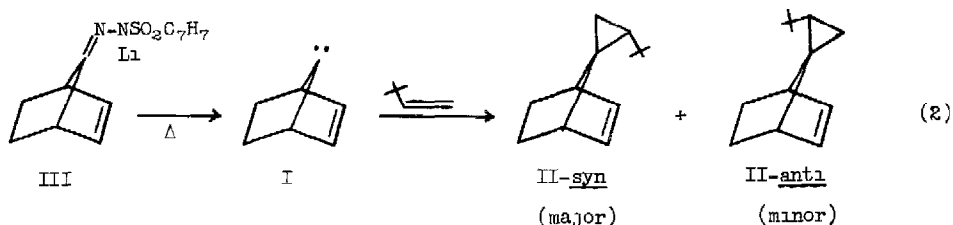


anti, in a ratio of 7.86:1 (gc, 150 ft. fluorosilicone Golay column).⁷ After gc purification (SE-30 column), the adduct mixture afforded a satisfactory elemental analysis, showed m/e 176 (M^+) in its mass spectrum, and could be reduced to II- H_2 which was characterized by nmr and mass

spectroscopy Consistent ir and nmr^e spectra of the adduct mixture were obtained; t-butyl resonances appeared at δ 0.79 (II-anti) and 0.76 (II-syn) One might have expected the t-butyl protons of II-syn to lie in the shielding zone of the π -bond,⁹ and their resonance to appear up-field from that of II-anti,¹⁰ but the small differential chemical shift necessitates further substantiation of the stereochemical assignments

By itself, the stereoselectivity of the Diels-Alder reaction is strongly supportive of these assignments The syn adduct would be expected to predominate whether the observed product ratio reflected kinetic control^{11a} or equilibrium control.^{11b} Moreover, the gc retention time of II-syn on a saturated AgNO₃-ethylene glycol column was, as expected, much shorter than that of II-anti,¹² providing further support for the stereochemical assignments¹³

With preliminary work secure, the dry Li salt of 7-norbornenone tosylhydrazone, III,² was pyrolyzed in dry, degassed, excess t-butylethylene at 200-220° for 20 min. The complex product mixture was largely derived from intramolecular chemistry of I,² but capture products II-syn and II-anti (~0.1 %) were observed by gc on the 150 ft fluorosilicone Golay column,¹⁴ eq (2) Reduction of this product mixture converted both adducts to II-H₂, identical in capillary gc retention time to the authentic sample Duplicate pyrolyses of III in t-butylethylene contained in



glass ampoules (sealed in a steel bomb, half-filled with pentane, 220°, 20 or 80 min) gave (II-syn/II-anti) = 7.02 ± 0.06 Duplicate pyrolyses conducted directly in the steel bomb (200°, 20 min.) gave this ratio as 2.57 ± 0.12, unchanged after resubmission of the mixture to the pyrolysis conditions in the presence of lithium p-toluenesulfinate The altered product ratios observed in the latter pyrolyses are suggestive of metal-catalyzed (carbenoid) decompositions Indeed, pyrolysis of 0.5 g of III in 2.5 g of t-butylethylene containing 20 mg of anhydrous CuSO₄ (glass ampoule) afforded (II-syn/II-anti) = 3.19.

Experimentally, then, syn addition of I to t-butylethylene is the dominant mode of cyclopropanation, in contrast to the anti selectivity anticipated because of the calculated bridge-bending in I⁴ The experimental results neither negate the possibility of such bending, nor vitiolate the strength of the calculations But if the predicted carbene- π interaction in I (for which we have adduced circumstantial evidence^{2,3}) does lead to bridge-bending, then such bending does not itself dominate the stereoselectivity of addition, *cf.*, eq (2) Assumption of a Hoffmann-like transition state¹⁵ for the addition of I to t-butylethylene, together with a study of molecular models, predict the observed dominance of II-syn, in that less steric hindrance would be experienced by an alkene during syn approach over the in-plane vinyl protons of I than during anti approach over its exo-ethano protons¹⁶ Indeed, if 7-norbornenone is considered a model for singlet I (both have "electrophilic" p orbitals at C₇), then the stereoselectivity of olefin

addition to I is analogous to that of the attack of various nucleophiles at C₇ of the ketone¹⁷

It is worth noting that carbene I clearly differs from the analogous 7-norbornenyl cation, for which anti addition of nucleophiles is rigorously controlled by homoallylic π -participation¹⁸. Presumably, the interaction is, as expected,¹ weaker in the carbene¹⁹.

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- (19) A referee has suggested that our conclusion concerning bridge-bending is too mild, and that the results negate such bending. We find this view too exclusive. Our results definitely establish as incorrect the prediction of anti-stereoselectivity which Hoffmann and Glenter¹ extrapolated from the 20° bridge-bending indicated by their calculations. However, there is no standard by which to measure what degree of bridge-bending would be consistent with our observed 7.02 syn/anti product ratio. Perhaps this ratio is consistent with a 20° bending. Perhaps, if there were no bridge-bending in I, the observed syn/anti ratio would have been 20:1 or even 50:1. In the absence of any way to quantitatively correlate bridge-bending with product ratio, we feel our results are best interpreted as telling against both the published stereochemical prediction¹ and the domination of stereoselectivity by bridge-bending, but not as definitively excluding either bridge-bending or chemically significant carbene- π bond interaction.³