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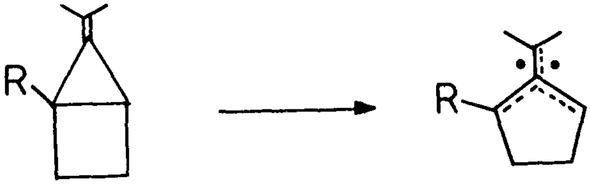
NEW TRIMETHYLENEMETHANE CYCLOADDITION MECHANISMS. CHEMISTRY OF 1-t-BUTYL-5-ISOPROPYLIDENEBICYCLO[2.1.0]PENTANE[1]

Anthony D. Sabatelli, Richard F. Salinaro, James A. Mondo, and Jerome A. Berson*

Department of Chemistry, Yale University, Box 6666, New Haven, CT 06511

Abstract: Substitution of a t-butyl group for hydrogen at the bridgehead position of 5-isopropylidenebicyclo[2.1.0]pentane changes the cycloaddition chemistry, and several new pathways emerge.

The planar singlet trimethylenemethane(TMM)-type biradical, 2-isopropylidenecyclopentan-1,3-diyl 2a,



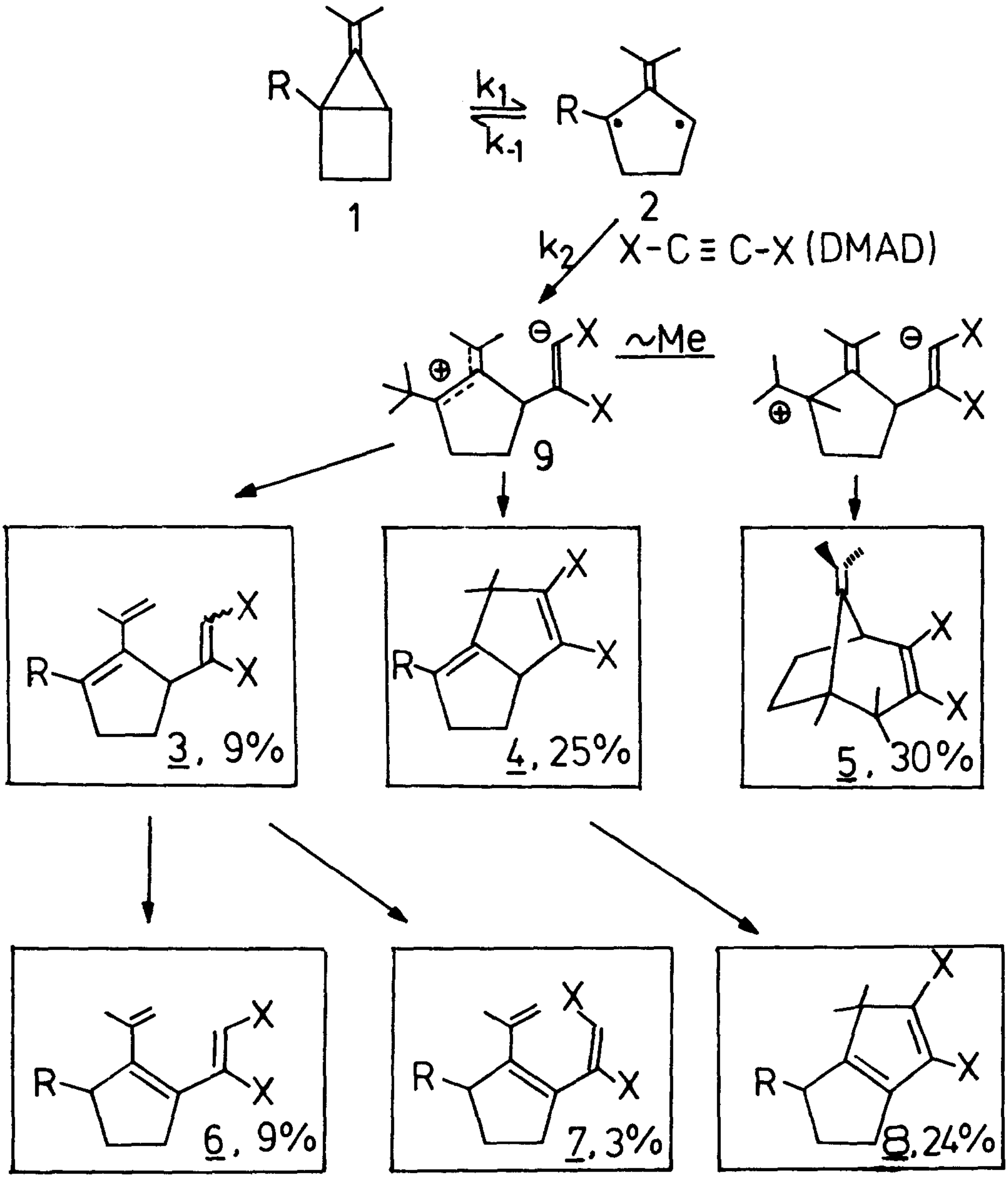
1a: R = H
b: R = t-Bu

2a: R = H
b: R = t-Bu

seems to be implicated in the cycloaddition chemistry of 5-isopropylidenebicyclo[2.1.0] pentane 1a[2], but the formation of the biradical is much more difficult when a t-butyl group is present at C_1[3]. Differences in chemical behavior between the bicyclic hydrocarbons 1a and 1b therefore might be expected[3]. We report here several mechanistically significant types of cycloaddition chemistry of 1b not previously observed in TMM systems.

A de-gassed benzene or acetonitrile solution of dimethyl acetylenedicarboxylate (DMAD), $\sim$1M, was added to freshly distilled 1b[3], and after reaction for about 12 h at 25°C, the six products 3b-8b were identified (Scheme I). The minor products 6b and 7b were obtained as a 3:1 mixture, whereas 3b-5b and 8b were isolated[4] by gas chromatography (GC). Although none of the products interconverted under the GC conditions, 8b and the 6b/7b pair probably are derived from 4b and 3b, respectively, in secondary reactions.

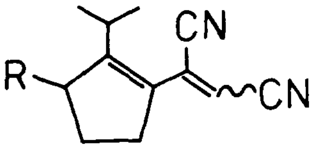
Product 4b is a fused adduct of a type frequently observed in TMM-olefin cycloadditions[2], but 3b, formally an ene adduct of 1b and DMAD, and the secondary products 6b and 7b, have no counterparts in the previous work. To determine whether the ene reaction pathway which produces 3b is a consequence of the use of an acetylenic rather than an olefinic trapping agent, Scheme I: X = CO_2CH_3; R = H(a), R = t-Bu(b)



we studied the reaction of the hydrocarbon 1a, lacking the bridgehead *t*-butyl group, with DMAD. The products were 85% of the fused adduct 4a (85%) and dimers of biradical 2a (10%). The bridged adduct, 7-isopropylidene-2,3-dicarbomethoxynorborn-2-ene, constituted <1% of the mixture. A third product, formed in <1% yield, has not been characterized but may be the ene adduct 3a. These results suggest that it is *t*-butyl substitution on the hydrocarbon 1 rather than the nature of the trapping agent that causes the emergence to visibility of the ene reaction pathway.

Product 5 contains no *t*-butyl group and results from a retropinacolic rearrangement. In Scheme I, we have formulated this as a carbonium ion process in the zwitterionic intermediate 9 (rather than in its biradical counterpart) on the assumption that 1,2-alkyl shifts in radicals are unlikely[7]. Whether 9 is formed by intramolecular electron-transfer in the adduct biradical or by another pathway is not known. For the sake of economy, 9 is shown as a common intermediate on the pathways to 3b, 4b, and 5b, although this point has not been established.

With either of the olefinic trapping agents fumaronitrile or maleonitrile, 1b gives a complex mixture of adducts. Two of the major products, 10 and 11 (each formed in ∿20% yield), appear to result from successive ene reaction and hydrogen shift involving the olefin and one or more double bond position-isomers of 1-*t*-butyl-2-isopropylcyclopentadiene. The latter hydrocarbon series presumably is entered by a hydrogen shift in the biradical 2b[3].



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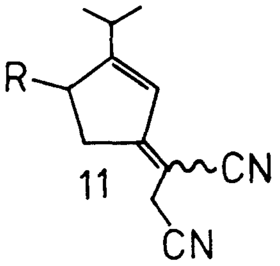

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We have used the previously described[8] kinetic technique to distinguish between the mechanism of Scheme I (reversible unimolecular ring-cleavage followed by bimolecular capture of the intermediate) and an alternative bimolecular process (direct reaction between bicyclic hydrocarbon 1b and the trapping agent). Plots of $1/k_{obs}$ *vs.* 1/[trap], where k_{obs} is the pseudo-first-order rate coefficient for disappearance of the ^{1}H NMR *t*-butyl resonance of 1b, are linear in experiments with either DMAD-d_6 or fumaronitrile in benzene-d_6 or CH_3CN solvent at 296K. The slopes, k_{-1}/k_1k_2, of the plots for the two trapping agents are different but the intercepts, $1/k_1$, are the *same* within experimental error. These results are incompatible with a direct bimolecular reaction of 1b with trapping agent and support the hypothesis that a common intermediate, plausibly biradical 2b, is formed in the reactions with either trapping agent[9].

The effect of the *t*-butyl group in altering the reactivity of 2b compared to that of 2a may be exerted not only through its impediment to the achievement of planarity of the biradical but also through retardation of the rate of the biradical's concerted cycloaddition. This may give normally unfavorable side-reactions a better chance to compete.

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REFERENCES AND NOTES

1. This paper is dedicated to Professor Harry Wasserman on the occasion of his 65th birthday.
2. For a review, see Berson, J.A. in "Diradicals," Borden, W.T., ed., Wiley, New York, 1982, Chapter 4 and references cited therein.
3. Salinaro, R.F.; Berson, J.A. *Tetrahedron Lett.* **1982**, *23*, 1447, 1451.
4. Products 3a-8a all showed MS parent peaks at m/e = 306 as well as concordant ^{1}H NMR spectra[5,6]. Compound 5a was obtained in sufficient quantity for ^{13}C NMR spectroscopy (125.8 MHz, CDCl$_3$): δ23.50, 23.63, 25.09, 28.59, 29.08, 30.59, 31.22, 45.56, 51.79, 52.15, 60.1, 85.1, 112.0, 138.6, 145.1, 152.9, 164.2, 170.8. Exact mass determinations for 3a-5a and 8a were within 2 millimass units of the calculated value 306.1817. Compound 8 showed UV(MeOH): λ_{max} 306 nm.
5. Salinaro, R.F. Ph.D. Thesis, Yale University, 1982.
6. Sabatelli, A.D. Ph.D. Thesis, Yale University, 1984.
7. See Wilt, J.W. in "Free Radicals," Kochi, J.K., ed., Wiley-Interscience, New York, 1973, Vol. I, p. 340.
8. Mazur, M.R.; Berson, J.A. *J. Am. Chem. Soc.* **1981**, *103*, 684; **1982**, *104*, 2217.
9. (a) From an extensive study[6] of the temperature dependences of k_1, we find for 1a, E_a = 12.9 ± 1.0 kcal/mol, log A = 9.8 ± 0.9 (A in s^{-1}), and for 1b, E_a = 13.7 ± 1.3 kcal/mol, log A = 10.4 ± 0.9 (A in s^{-1}). The log A terms are surprisingly low for the reaction 1 → singlet 2; (b) In a formal sense, the role of the reactive intermediate could be played by the rearranged isomer of 1b, 2-*t*-butyl-6,6-dimethylbicyclo[3.1.0]hex-1-ene. This hypothesis does not provide obvious explicative advantages over that of biradical 2b.

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