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A NEW STRATEGY FOR CONSTRUCTION OF ANGULARLY FUSED TRICYCLIC RING SYSTEMS. TRANSANNULAR BOND FORMATION OF BICYCLIC ENONES VIA PHOTOCHEMICAL INTRAMOLECULAR HYDROGEN ABSTRACTION

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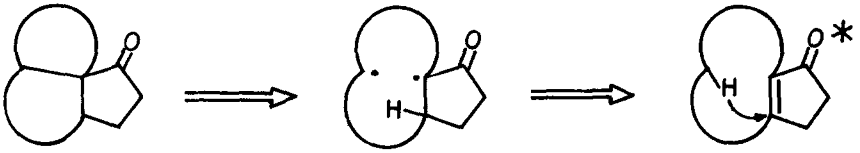
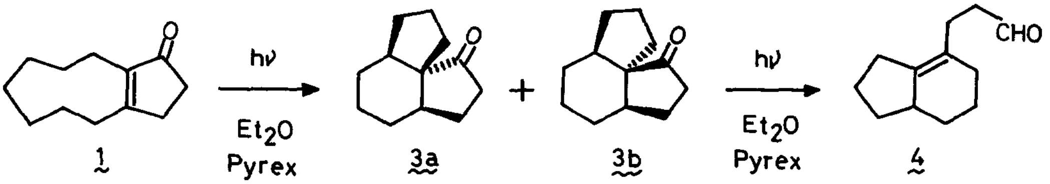
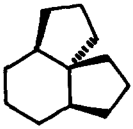
Summary: Tricyclic ketones 3a, b and 7a-c having angularly fused 5-6-5 or 5-7-5 ring system have been efficiently prepared by irradiation of bicyclic enones 1 and 2.

Angularly fused tricyclic ring systems have been attracted increasing interest because many natural products which possess this new type of carbon frameworks composed of a variety of constituent rings have been found in recent years.[1] We report herein a new strategy for construction of angularly fused 5-6-5 and 5-7-5 ring systems from reasily available bicyclic enones 1 and 2.[2] Namely, the above systems could be formed by transannular C-C bond formation in the diradical intermediate generated by photochemical intramolecular hydrogen abstraction at β-carbon atom[3] of enones 1 and 2 as shown below.



As expected, irradiation of 1 in ether (5×10^{-2} M) through a Pyrex filter gave successfully two tricyclic ketones 3a[4] and 3b in 55% and 19% yields, respectively.[5] The 5-6-5 ring system of 3a and 3b was readily proved by conversion of them into the same aldehyde 4[6] (60-65% yields) by irradiation under similar conditions. The stereochemistry about the ring junction of 3a and 3b was unambigously established on the basis of the following reactions. (i) Since reduction of the carbonyl groups of both 3a and 3b (3a; N_2H_4, K_2CO_3, 49%. 3b; (i) $LiAlH_4$, (ii) $ClPO(NMe_2)_2$, (iii) Li, $EtNH_2$, 49% overall yield) afforded the same unsymmetric cis-trans hydrocarbon 5 (twelve signals in ^{13}C NMR spectrum),[4] 3a and 3b should be either trans-cis or cis-trans isomer. (ii) Oxidative degradations of 3a ((i) $TsNHNH_2$, (ii) MeLi, (iii) O_3, (iv) H_2CrO_4, (v) CH_2N_2, 41% overall yield) gave cis-hydrindane 6 having trans ester side chains whose stereochemical arrangement was determined by the identity with an authentic sample prepared independently.[7]





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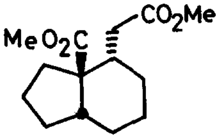

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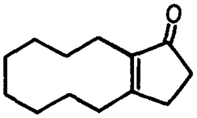

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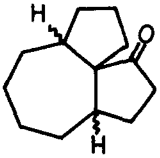
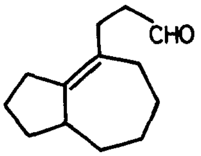


7a-c



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Consequently, **3a** should have trans-cis junction and, therefore, **3b** should be cis-trans isomer.

In a similar fashion, enone **2** afforded three stereoisomers of 5-7-5 tricyclic ketones **7a-c** in a ratio of 2:1:1 as the major products.^{5} Though the stereochemistry of **7a-c** was undetermined as yet, the 5-7-5 ring system was elucidated by conversion of all of them into the same aldehyde **8**^{6} by UV irradiation. Thus a new efficient entry to angularly fused 5-6-5 and 5-7-5 ring systems was exploited based on photochemical transannular bond formation of bicyclic enones **1** and **2**.

References and Notes

(1) 5-5-5 ring system: triquinane sesquitepenes, for reviews; L. A. Paquette, *Top. Curr. Chem.*, *79*, 41 (1979); *119*, 1 (1983). 4-5-6 ring system: panasinsene; K. Yoshihara and Y. Hirose, *Bull.Chem. Soc. Jpn.*, *48*, 2078 (1975). 6-6-6 ring system: aflavinine; R. T. Gallagher, T. McCabe, K. Hirotsu, J. Clardy, J. Nicholson, and B. J. Wilson, *Tetrahedron Lett.*, *21*, 243 (1980).

(2) S. Hirano, S. Takagi, T. Hiyama, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, *53*, 169 (1980); S. Kulkowit and M. A. McKervey, *J. Chem. Soc., Chem. Commun.*, *1978*, 1069. See also Y. Tobe A. Doi, A. Kunai, K. Kimura, and Y. Odaira, *J. Org. Chem.*, *42*, 2523 (1977).

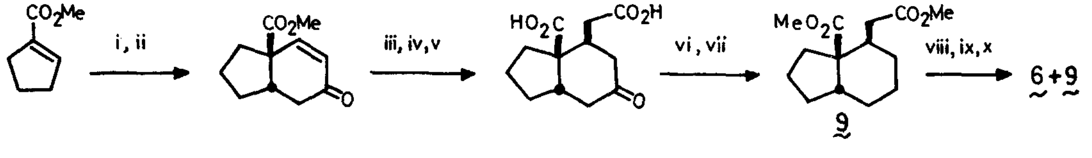
(3) S. Wolff, W. L. Schreiber, A. B. Smith, III, and W. C. Agosta, *J. Am. Chem. Soc.*, *94*, 7797 (1972).

(4) All new compounds gave satisfactory analytical and spectral properties. ^{13}C NMR data (δ in $CDCl_3$) for selected compounds are listed: **3a**; 219.2(s), 59.2(s), 43.0(d), 40.3(d), 35.4(t), 30.1(t), 29.4(t), 25.9(t), 25.2(t, 2C), 23.3(t), 20.2(t). **3b**; 219.9(s), 60.3(s), 45.7(d), 44.2(d), 34.4(t), 33.9(t), 29.5(t), 27.7(t), 26.5(t), 26.4(t), 24.5(t), 20.4(t). **5**; 52.8(s), 46.3(d), 45.6(d), 37.2(t), 30.2(t), 29.3(t), 29.1(t), 26.9(t), 25.5(t), 25.0(t), 20.2(t), 20.1(t). **7a**; 222.5(s), 62.4(s), 46.7(d), 44.4(d), 40.3(t), 36.5(t), 35.1(t), 32.8(t), 28.9(t), 27.8(t), 27.3(t), 24.9(t), 21.9(t). **7b**; 221.4(s), 62.7(s), 44.6(d), 39.0(d), 35.2(t), 32.4(t), 31.8(t), 31.0(t), 29.9(t), 29.3(t), 27.0(t), 23.7(t), 23.1(t). **7c**; 222.0(s), 65.6(s), 48.3(d), 43.8(d), 37.3(t), 35.9(t), 35.5(t), 35.0(t), 33.5(t), 31.1(t), 30.6(t), 29.2(t), 23.1(t).

(5) Since (i) the reaction was quenched by 1,3-pentadiene and (ii) **1** and **2** showed broad phosphorescence spectra (λ_{max} in EPA at 77K **1**; 442 nm, **2**; 439 nm) with long lifetimes ($\tau_{1/2}$ **1**; 98 msec, **2**; 93 msec), it is deduced that the reaction proceeds from a π,π^* triplet state of **1** and **2**.^{3}

(6) The structures of **4** and **8** were confirmed by the identity with the respective authentic samples prepared by (i) reaction of bicyclo[4.3.0]nonan-1-one or bicyclo[5.3.0]decan-1-one with allylmagnesium chloride, (ii) dehydration by $SOCl_2$, (iii) hydroboration with 9-BBN followed by H_2O_2 oxidation, (iv) PCC oxidation.

(7) An authentic sample of **6** was prepared as shown below: (i) 1-methoxy-3-trimethylsilyloxy-1,3-butadiene (S. Danishefski and T. Kitahara, *J. Am. Chem. Soc.*, *96*, 7807 (1974).), Δ, (ii) HCl, (iii) $NaCH(CO_2Me)_2$, (iv) NaOH, (v) H_2SO_4, Δ, (vi) N_2H_4, KOH, (vii) CH_2N_2, (viii) LDA, PhSeCl, (ix) H_2O_2, (x) H_2, Pd/C.



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