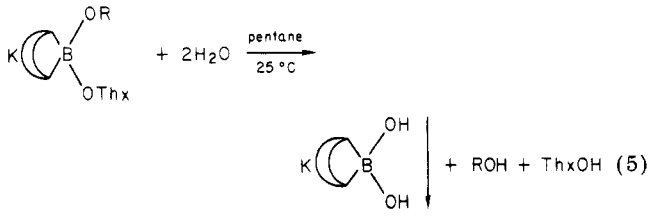
relatively difficult to remove from the reaction mixture. Usually they must be oxidized by alkaline hydrogen peroxide, following reduction, to convert them into the corresponding alcohols and boric acid. This might be an undesirable procedure, particularly in cases where the compound being reduced is itself sensitive to oxidation.

Fortunately, the use of reagent 1 overcomes this problem, while achieving comparable stereoselectivity. The byproduct of the reaction, K9-OThx-9-BBNOR, is readily converted into the hydroxy ate complex by treatment with a slight excess over the theoretical amount of water (eq 5). This simple isolation procedure provides a major



advantage for this reagent in stereoselective reductions where it is desirable to avoid the presence of higher trialkylboranes in the reaction mixture.

The following procedure served to prepare B-OThx-9-BBN. An oven-dried, 250-mL, round-bottomed flask, equipped with a side arm, a condenser, and an adaptor connected to a mercury bubbler, was cooled to room temperature under a stream of nitrogen and maintained under a static pressure of nitrogen. To this flask was added 12.2 g of 9-BBN (100 mmol) and 30 mL of THF; 10.7 g of 2,3-dimethyl-2-butanol (105 mmol) was added to the slurry of 9-BBN and THF dropwise with vigorous stirring at room temperature. After the addition was completed, the reaction mixture was brought to a gentle reflux to ensure completion of hydrogen evolution (1 h). Evaporation of the solvent, followed by distillation from a small piece of potassium metal, yielded 20 g of pure B-OThx-9-BBN (89% yield): bp 95–96 °C (1.3 mm), n^{20}_D 1.4785, ^{11}B NMR δ 55.1 ppm (neat).[5]

The following procedure served for the preparation of the reagent. Into a 100-mL flask was placed 6.4 g of potassium hydride (160 mmol) as an oil suspension by using a double-ended needle. Potassium hydride was washed with THF (3 × 10 mL) to remove the oil medium.[6] To this oil-free potassium hydride was added 50 mL of freshly distilled THF, followed by 18.0 g of B-OThx-9-BBN (80 mmol). The reaction mixture was stirred vigorously at room temperature. The reaction was complete within 24 h, producing the addition compound, K9-OThx-9-BBNH, in pure form: ^{11}B NMR δ −2.8 (d, J_{BH} = 60.3 Hz), IR ν 2000 cm^{-1} (B–H), 1355 cm^{-1} (B–O).

The following procedure was used to explore the stereoselectivity of this reagent. In a 50-mL, round-bottomed flask was placed 2.2 mL of a 0.92 M solution of the reagent in THF (2.0 mmol). The flask was maintained at 0 °C by immersion in an ice–water bath. To the flask was added 1.0 mL of precooled 2-methylcyclohexanone solution in THF (1.0 M in ketone) and the reaction mixture was stirred at 0 °C for 3 h. The reaction was then quenched by addition of 2 mL of 2 N HCl, and the aqueous layer was saturated with anhydrous potassium carbonate. GC analysis of the organic layer showed the presence of a quantitative yield of 2-methylcyclohexanol, containing 98.5% of the cis isomer.

The use of such a large excess of reagent is not necessary, as shown by the following larger scale reaction. In the usual assembly, 5.6 g of 2-methylcyclohexanone (50 mmol) was added dropwise as the neat liquid to 60 mL of the reagent solution in THF (55 mmol) at 0 °C. The reaction was complete in 1 h and the mixture was hydrolyzed with 2.5 mL (140 mmol) of water for 0.5 h at room temperature. All THF was then pumped off by using an aspirator. Then 50 mL of pentane was added to the residue and the mixture was stirred. A white solid precipitated out. The pentane solution was separated and subjected to fractional distillation: 4.8 g of 2-methylcyclohexanol (84%), bp 166–168 °C (753 mm), containing by GC analysis 98.5% of the cis isomer.

Registry No. 1, 89999-86-0; *B*-OThx-9-BBN, 89999-87-1; 9-BBN, 280-64-8; 2-methylcyclohexanone, 583-60-8; 3-methylcyclohexanone, 591-24-2; 4-methylcyclohexanone, 589-92-4; 4-*tert*-butylcyclohexanone, 98-53-3; 3,3,5-trimethylcyclohexanone, 873-94-9; norcamphor, 497-38-1; camphor, 76-22-2; thexyl alcohol, 594-60-5; *cis*-2-methylcyclohexanol, 7443-70-1.

(5) The chemical shifts are reported relative to BF_3·OEt_2 with chemical shifts downfield from BF_3·OEt_2 assigned as positive.
(6) Brown, C. A. *J. Org. Chem.* **1974**, *39*, 3913.

(7) Postdoctoral research associate on Grant ARO DAAG-29-79-C-0027, supported by the U.S. Army Research Office.

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Photoinitiated Additions of Ketones to Bicyclo[1.1.0]butanes. The Existence of Diverse Reaction Pathways

Summary: A radical chain process has been established for the addition of a series of ketones across the C1–C3 bond of bicyclo[1.1.0]butane and its methylated derivatives. For certain ketones, capture of an acyl radical intermediate, generated in a Norrish type I cleavage of the ketone, competes effectively with the radical chain process.

Sir: Recently, we reported the addition of a variety of nucleophiles across the C1–C7 bond of tricyclo[4.1.0.0^{2,7}]heptane in a photoinitiated reaction that involved initial electron transfer to excited state 1-cyanonaphthalene.[1] We have also described the addition of acetone across this same carbon–carbon σ bond.[2] We now report that a variety of different photoinitiated reaction paths can be observed for the addition of ketones across the C1–C3 σ bond of bicyclo[1.1.0]butane and its methylated derivatives.

Table I lists a series of reactions involving the photoinitiated addition of ketones across carbon–carbon single bonds of strained hydrocarbons. Yields appear to depend on the type of methyl substitution on the parent hydrocarbon and on the nature of the ketone. In those cases where methyl substitution was present at the C1(bridgehead) position, only "anti-Markovnikov" addition was observed and the yields were low.[3] Thus, while 1 gave 2

(1) Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977. Gassman, P. G.; Olson, K. D. *Ibid.* **1982**, *104*, 3740.
(2) Gassman, P. G.; Smith, J. L. *J. Org. Chem.* **1983**, *48*, 4438.

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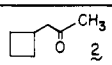
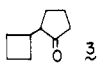
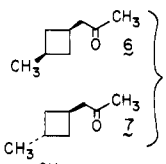
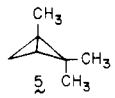
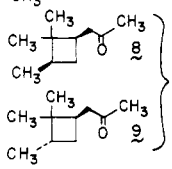
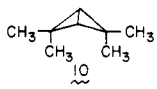
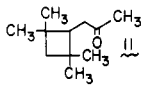
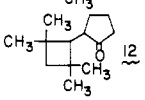
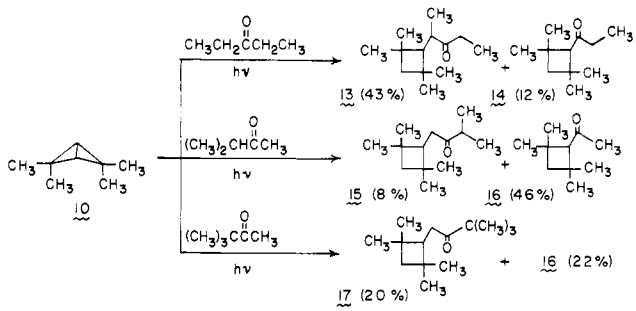
Table I. Products Obtained in the Photoinitiated Addition of Ketones to Bicyclo[1.1.0]butane and Its Methylated Derivatives

hydrocarbon	ketone	product	% yield
 1	acetone	 2	36
	cyclopentanone	 3	38
 4	acetone	 6 + 7	21
 5	acetone	 8 + 9	25
 10	acetone	 11	68
	cyclopentanone	 12	76

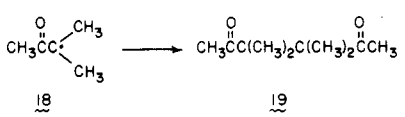
and **3** with acetone[4,5] and cyclopentanone, respectively, **4** and **5** gave mixtures of **6** and **7** and of **8** and **9**, respectively, but in substantially lower yield.[6] For **10**, which has no hydrogens β to C1 or C3, both acetone and cyclopentanone added in good yield to give **11** and **12**, respectively.

Mechanistically, we view the addition reactions listed in Table I as involving a photoinitiated radical chain process. The photoinitiated addition of cyclopentanone to **10** (0.2 M) occurred with a quantum yield of 8.3, which indicated the chain nature of the process.[7] Inhibition of the addition by oxygen pointed to a radical intermediate. Ample evidence exists for the photoconversion of ketones into α-keto radicals.[8] Thus, it would appear that the initially photogenerated radical adds to the C1–C3 bond of the bicyclo[1.1.0]butane moiety to produce a cyclobutyl radical, which, in turn, can abstract a hydrogen from the ketone and continue the chain.

In contrast to the results presented above, the photoinitiated addition of pentan-3-one, 3-methylbutan-2-one, and 3,3-dimethylbutan-2-one to **10** gave products that indicated the presence of diverse reaction paths. In addition to the anticipated products **13**, **15**, and **17**, the reaction with pentan-3-one gave 12% of **13** while the reactions of **10** with 3-methylbutan-2-one and 3,3-dimethylbutan-2-one gave **16** in 46% and 22% yields, respectively. The ketones, **14**



and **16**, appear to be derived from capture of the acyl radicals generated by Norrish type I cleavage of the solvent.[9] It is clear that this photochemical cleavage process and capture of the resulting radical competes quite well with the photoinitiated radical chain reactions that are indicated for the formation of **13**, **15**, and **17**. The reaction of **10** with 3-methylbutan-2-one is of particular interest because the yield of product due to capture of the acetyl radical far exceeds that from addition of the α-keto radical. We believe that this results from the quenching of the radical chain process by the ketone, since abstraction of a hydrogen from C3 of 3-methylbutan-2-one would produce **18**. No product that would correspond to the addition of **18** to **10** has been detected. However, the dimerization of **18** would be expected to produce **19**, which has been isolated in substantial quantities.[10,11]



18 19

Acknowledgment. We are indebted to the National Science Foundation for Grant CHE81-14772, which supported this investigation.

Registry No. **1**, 157-33-5; **2**, 13027-76-4; **3**, 90046-35-8; **4**, 30494-08-7; **5**, 28569-96-2; **6**, 90046-36-9; **7**, 90046-37-0; **8**,

(3) In addition to the observed products, substantial quantities of nonvolatile, intractable materials were formed, presumably by oligomerization of either the bicyclo[1.1.0]butyl moiety or of olefins formed subsequent to ketone addition.

(4) In a typical experiment, the strained hydrocarbon (10–100 mg) was dissolved in the ketone (as solvent) in Pyrex. The solution was degassed, since the presence of oxygen inhibited the reaction, and then the reaction mixture was irradiated for 1–5 h with a bank of 16 15-W, 300-nm ultraviolet lamps. The reaction progress was monitored by VPC analysis. For all of the reactions reported in Table I, the concentration of the strained hydrocarbon was 0.2 M.

(5) Satisfactory elemental analyses and/or exact mass molecular weights were obtained for all new compounds. All products had IR and NMR spectra that were consistent with the assigned structures.

(6) The ratio of isomers in the addition to **4** was 1.5:1 while for **5** the ratio was 1.6:1. On the basis of data currently available, we cannot rigorously define which isomer has which stereochemistry. The relatively low yields obtained in the additions to **4** and **5** are thought to result from oligomerization of olefins resulting from β-hydrogen loss with the intermediate radical species or from radical-promoted oligomerization of starting hydrocarbon. If this were correct, yields should be a function of hydrocarbon concentration. In support of this concept we have found that decreasing the concentration of **5** in acetone from 0.2 to 0.05 and 0.005 M resulted in the yield changing from 25% to 30% and 43%, respectively. Since all yields reported in this communication are for the same concentration,[4] the given yields are comparable.

(7) Radical chain additions to bicyclo[1.1.0]butane derivatives and radical-induced polymerization of the system have been previously recognized. For early references, see: Wiberg, K. B.; Ciula, R. P. *J. Am. Chem. Soc.* **1959**, *81*, 5261. Blanchard, E. P., Jr.; Cairncross, A. *Ibid.* **1966**, *88*, 487. Swartz, T. D.; Hall, H. K., Jr. *Ibid.* **1971**, *93*, 137. Hall, H. K., Jr.; Baldt, J. H. *Ibid.* **1971**, *93*, 140. It should be noted that the radical chain processes cited in the literature generally involve bicyclo[1.1.0]butanes bearing conjugating groups at the bridgehead position.

(8) Numerous examples of the photoinduced addition of acetone and of other ketones *to olefins* exist in the literature. These additions to olefins have been postulated to occur via radical chain processes. For leading references, see: Bartlett, P. D.; Roof, A. A. M.; Winter, W. J. *J. Am. Chem. Soc.* **1981**, *103*, 6520. Reusch, W. *J. Org. Chem.* **1962**, *27*, 1882. de Mayo, P. "Advances in Organic Chemistry"; Interscience: New York, 1960; Vol. 2, p 367. Elad, D. In "Organic Photochemistry"; Chapman, O., Ed.; Marcel Dekker: New York, 1969; Vol. 2, p 190. See also de Mayo, P.; Stothers, J. B.; Templeton, W. *Can. J. Chem.* **1961**, *30*, 488. Vaish, S. P.; McAlpine, R. D.; Cocivera, M. *J. Am. Chem. Soc.* **1974**, *96*, 1683. See also Haget, M; Malek, J. *Synthesis* **1976**, 315.

(9) For selected references, see: Blank, B; Henne, A.; Fischer, H. *Helv. Chim. Acta* **1974**, *57*, 920. Roberts, B. P.; Singh, K. *J. Chem. Soc., Perkin Trans. 2* **1981**, 866. Abuin, E.; Lissi, E. A. *J. Photochem.* **1976**, *6*, 1.

(10) Addition of both the acetyl radical and the photogenerated 3-methylbutan-2-on-1-yl radical to **10** would produce radicals that could react with 3-methylbutan-2-one to produce **18** and subsequently **19**. On a molar ratio basis the ratio of 15:16:19 was 0.11:0.66:0.22.

(11) For the formation of **19** from **18**, see: Chkir, M.; Lelandais, D.; Bacquet, C. *Can. J. Chem.* **1981**, *59*, 945.

90046-38-1; 9, 90046-39-2; 10, 30494-12-3; 11, 90046-40-5; 12, 90046-41-6.

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Intramolecular Photocycloaddition–Cyclobutane Fragmentation: A Highly Stereoselective Total Synthesis of (±)-Pentalenic Acid

Summary: An efficient total synthesis of pentalenic acid has been accomplished by utilizing an intramolecular photocycloaddition–cyclobutane fragmentation as the key reaction sequence.

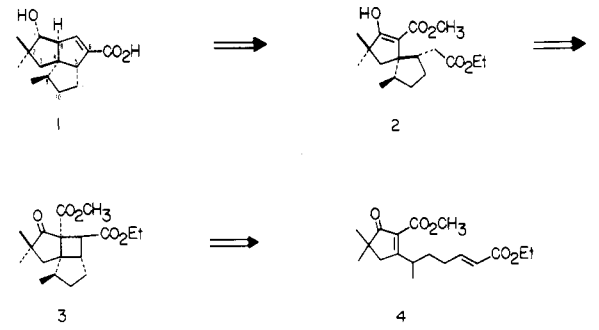
Sir: Several variously substituted triquinane natural products have recently been isolated and characterized.[1-5] One of the more important and more highly functionalized members of this growing class of compounds has been identified as a key intermediate in the biosynthesis of the biologically important pentalenolactones and has been designated pentalenic acid (1).[5,6] Pentalenic acid has previously been prepared through a biogenetic-like synthesis from humulene.[5b]

This report describes an efficient, highly stereoselective total synthesis of pentalenic acid by utilizing an intramolecular photocycloaddition–cyclobutane fragmentation[7] to introduce three of the necessary stereocenters. The effectiveness of intramolecular photocycloadditions in synthesis has previously been demonstrated by Pirrung's[1b] synthesis of isocomene and Oppolzer's synthesis of α-acoradiene[8] and longifolene.[9]

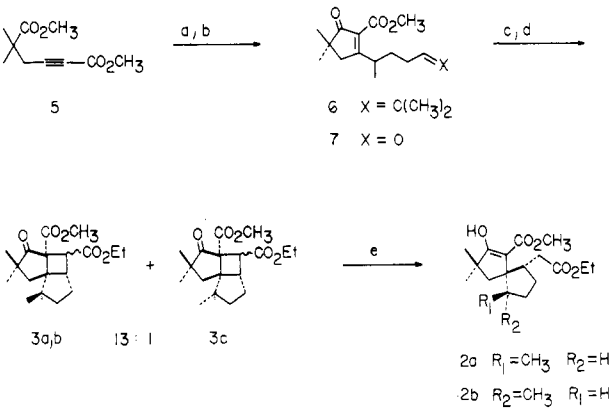
Retrosynthetically, **1** was seen as being accessible from β-keto ester **2** (Scheme I). In turn, **2** could be produced through a reductive cleavage of the tricyclic cyclobutane diester **3**, the product of an intramolecular [2 + 2] photocycloaddition of diene **4**.

Our plan for the construction of **4** centered around a new conjugate addition–cycloacylation[10] sequence on acetylenic diester **5** which was prepared from methyl isobutyrate in

Scheme I

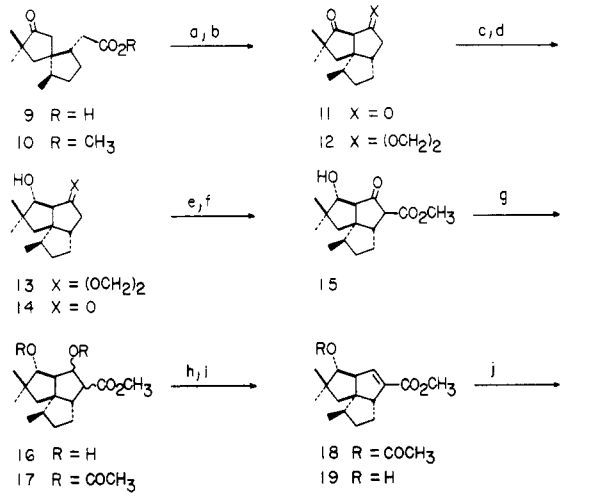


Scheme II[a]



[a] (a) $CH_3CHMgClCH_2CH_2CH{=}C(CH_3)_2$, CuI, THF, TMEDA, −78 °C, 2 h to 25 °C, 2 h. (b) O_3, CH_2Cl_2, −78 °C, then $(CH_3)_2S$, 25 °C; (c) $Ph_3P{=}CHCO_2Et$, CH_2Cl_2, 40 °C, 6 h; (d) 1 h, hexane, 366 nm; (e) Li, NH_3, Et_2O, −78 °C.

Scheme III[a]



[a] (a) CH_3OH, H_2SO_4, $(CH_3O)_3CH$, reflux, 4 h; (b) t-BuO^-K^+, C_6H_6, reflux; (c) p-TSA, C_6H_6, $(CH_2OH)_2$, reflux, 4 h; (d) Li, NH_3OH, −33 °C; (e) 10% HCl, acetone, 5 h; (f) LDA, THF, −78 °C; CO_2; 10% HCl, −20 °C; CH_2N_2, CH_2Cl_2, 40 °C; (g) $NaBH_4$, CH_3OH, 2 h; (h) Ac_2O, DMAP, Et_3N; (i) DBU, C_6H_6; (j) KOH, CH_3OH, 25 °C, 3 h.

(1) Isocomene. (a) Isolation: Zalkow, L. H.; Harris, R. N., III; Van Derveer, D.; Bertand, J. A. *J. Chem. Soc., Chem. Commun.* **1977**, 456. Zalkow, L. H.; Harris, R. N., III; Burke, N. I. *J. Natl. Prod.* **1979**, *42*, 96. Bohlmann, F.; LeVan, N.; Pickhardt, J. *Chem. Ber.* **1977**, *110*, 3777. (b) Synthesis: Paquette, L. A.; Han, Y. K. *J. Org. Chem.* **1979**, *44*, 4014; *J. Am. Chem. Soc.* **1981**, *103*, 1835. Oppolzer, W.; Battig, K.; Hudlicky, T. *Helv. Chim. Acta* **1979**, *62*, 1493; *Tetrahedron* **1981**, *37*, 4359. Pirrung, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 7130; **1981**, *103*, 82. Dauben, W. G.; Walker, D. M. *J. Org. Chem.* **1981**, *46*, 1103. Wender, P. A.; Dreyer, G. B. *Tetrahedron* **1981**, *37*, 4445.

(2) Silphenene. (a) Isolation: Bohlmann, F.; Jakupovic, J. *Phytochemistry* **1980**, *19*, 259. (b) Synthesis: Paquette, L. A.; Leone-Bey, A. *J. Org. Chem.* **1982**, *47*, 4173. Tsunoda, T.; Kodama, M.; Ito, S. *Tetrahedron Lett.* **1983**, *24*, 83.

(3) Senoxydene. (a) Isolation: Bohlmann, F.; Zdero, C. *Phytochemistry* **1979**, *18*, 1747. (b) Attempted Synthesis: Paquette, L. A.; Galemmo, R. A., Jr.; Springer, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 6975.

(4) Pentalenene. (a) Isolation: Seto, H.; Yonehara, H. *J. Antibiot.* **1980**, *33*, 92. (b) Synthesis: Paquette, L. A.; Annis, G. D. *J. Am. Chem. Soc.* **1982**, *104*, 4504. Misumi, S.; Ohtsuka, T.; Ohfune, Y.; Sugita, K.; Shirahama, H.; Matsumoto, T. *Tetrahedron Lett.* **1979**, 31. Crimmins, M. T., manuscript in preparation.

(5) Pentalenic Acid. (a) Isolation: Seto, H.; Sasaki, T.; Uzawa, J.; Takeuchi, S.; Yonehara, H. *Tetrahedron Lett.* **1978**, 4411. (b) Synthesis: Sakai, K.; Ohtsuka, T.; Misumi, S.; Shirahama, H.; Matsumoto, T. *Chem. Lett.* **1981**, 355.

(6) Cane, D. E.; Rossi, T.; Pachlatko, J. P. *Tetrahedron Lett.* **1979**, 3639. Cane, D. E.; Rossi, T.; Tillman, A. M.; Pachlatko, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 1838.

(7) For a recent review, see: Oppolzer, W. *Acc. Chem. Res.* **1982**, *15*, 135.

(8) Oppolzer, W.; Zutterman, F.; Battig, K. *Helv. Chim. Acta* **1983**, *66*, 522.

(9) Oppolzer, W.; Godel, T. *J. Am. Chem. Soc.* **1978**, *100*, 2583.

(10) Crimmins, M. T.; Mascarella, S. W.; DeLoach, J. A. *J. Org. Chem.*, in press.

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