great facility, through formation of labile palladium hydrides.[31] It is our contention that these hydrides in decomposing change the metal crystallite morphology to reduce surface area.

These observations strongly support our hypothesis that the poisons used to deactivate palladium catalysts do not block active sites but act to rearrange the surface structure of the palladium.

That the catalyst poisons are not involved in the actual reductions is also supported by the observed transformation of benzoyl chloride (429 mg) to benzaldehyde with ultrapure palladium powder[32] (29 mg) at 0 °C (7% conversion after 16 h). The same, untreated palladium powder also catalyzes the transformation of 5-decyne (10 mL) to *cis*-5-decene (after 22 h, complete conversion to 70% *cis*-, 8% *trans*-5-decene, 12% decane, and 10% unidentified isomers was obtained).

However, the "Lindlar"-active palladium foil showed no activity for the conversion of benzoyl chloride to benzaldehyde under various conditions. This experiment demonstrates that despite similar catalyst preparation procedures, the two reactions are catalyzed by different active sites; the active site for semihydrogenation being the "metallic" palladium, the nature of the active site for acid chloride hydrogenolysis is not identified yet. A detailed investigation with defined palladium surfaces is actively being pursued.[33]

Acknowledgment. W.F.M. thanks the College of Chemistry at Berkeley and the Research Corporation for their support. R.M.L. and Y.S. thank the National Science Foundation and the Army Research Office for support through NSF Chem. Eng. Grant No. 82-19541 and ARO contract no. DAAG29-81-k-0086.

Registry No. BuC≡CH, 693-02-7; PhC≡CPh, 501-65-5; BuC≡CBu, 1942-46-7; Me$_2$OCC≡CCO$_2$Me, 762-42-5; BuCH=CH$_2$, 592-41-6; (*Z*)-PhCH=CHPh, 645-49-8; (*Z*)-BuCH=CHBu, 7433-78-5; (*Z*) Me$_2$OCCH=CHCO$_2$Me, 624-48-6; palladium, 7440-05-3; triethylamine, 121-44-8; benzoyl chloride, 98-88-4; benzaldehyde, 100-52-7.

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(31) Rosenhall, G. *Ann. Phys. (Paris)* **1935**, *24*, 297 and references cited therein.

(32) Purchased from Thiocol, 0.25–0.55 μm, purity 99.95%.

(33) W.F.M., work in progress.

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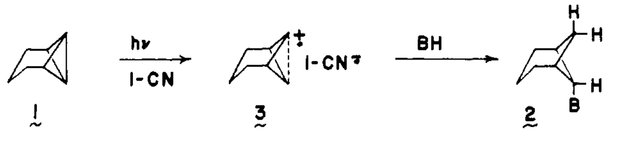
Photoinduced Additions to Carbon-Carbon σ Bonds. Addition of Acetone, Acetonitrile, and Ethyl Acetate to Bicyclo[1.1.0]butanes

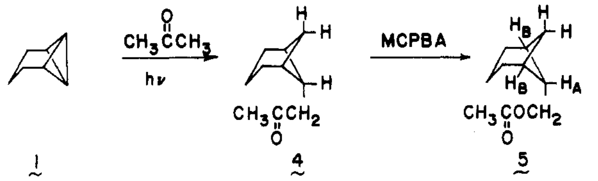
Summary: Acetone, acetonitrile, and ethyl acetate have been photochemically added across the C1–C7 σ bond of tricyclo[4.1.0.0^{2,7}]heptane. This photoinitiated radical chain reaction was shown to occur in an anti-Markovnikov manner.

Sir: Recently, we presented evidence for the addition of nucleophiles across carbon–carbon σ bonds under conditions where photoexcited sensitizers first removed an electron from the carbon–carbon σ bond to produce a cation radical–anion radical pair.[1,2] In this manner, tricyclo[4.1.0.0^{2,7}]heptane (1) was readily converted into 2 via

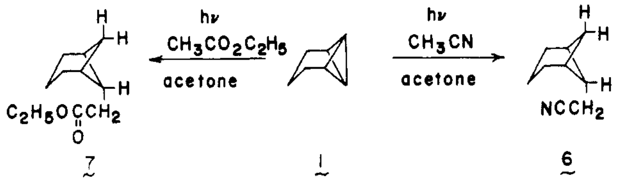


the intermediacy of the cation radical 3, which was generated through electron transfer to excited-state 1-cyanonaphthalene (1-CN). This proceeded in high yield, where B was hydroxyl, methoxyl, and cyano. We now report on the photoinitiated addition of acetone, acetonitrile, and ethyl acetate across strained carbon–carbon σ bonds.

When a solution of 0.74 g of 1 in 41 mL of acetone was irradiated for 5.5 h in a Pyrex vessel under argon in a Rayonet photochemical reactor equipped with 16 300-nm lamps, 0.42 g (35% yield) of a pure, colorless liquid was obtained after distillation:[3] bp 100–103 °C (12 mm); ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.53–2.42 (3 H, m), 2.33–2.27 (2 H, m), 2.13 (3 H, s), 1.88–1.60 (6 H, m), 1.60–1.50 (2 H, m); ^{13}C NMR (CDCl$_3$) δ 208.78 (s), 41.50 (t), 37.45 (d), 36.01 (d), 30.04 (q), 27.99 (t), 22.78 (t), 13.88 (t); IR (neat) 2930, 2865, 1715, 1355, 1175, 1150 cm^{-1}. The spectral data indicated that acetone had added across the C1–C7 bond of the bicyclo[1.1.0]butyl moiety of 1 to give either 4 or its epimer. In order to establish the stereochemistry of the addition, 4 was treated with *m*-chloroperbenzoic acid to give an 84% yield of 5. Examination of 5 by ^{1}H NMR at 300 MHz in the presence of a lanthanide shift reagent showed H$_A$ to be a pentet, which collapsed to a triplet ($J_{H_A-H_B}$ = 6.0 Hz) when the methylene protons adjacent to the acetoxyl group were decoupled. The observed coupling constant between H$_A$ and H$_B$ established the stereochemistry of the addition as shown in 4.[1,2,4]



Under similar photochemical conditions, a 0.2 M solution of 1 in acetonitrile containing 0.2% acetone (v/v) was irradiated for 100 h, with an amount of acetone equivalent to 0.2% of the solution being added every 20 h. Workup by chromatography on silica gel gave a 42% isolated yield of 6.[5] Irradiation of 1 in ethyl acetate containing 0.2% acetone for 120 h, with an amount of acetone equivalent to 0.2% of the solution being added at 20-h intervals, gave



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(1) Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977.

(2) Gassman, P. G.; Olson, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 3740.

(3) Satisfactory elemental analyses and/or exact mass molecular weights were obtained on all new compounds.

(4) Abraham, R. J.; Cooper, M. A.; Indyk, H.; Siverns, T. M.; Wittaker, D. *Org. Magn. Reson.* **1973**, *5*, 373. Abraham, R. J.; Cooper, M. A.; Salmon, J. R.; Wittaker, D. *Ibid.* **1972**, *4*, 489.

(5) In addition, a small amount (0.4–0.6%) of 4 was obtained in this reaction.

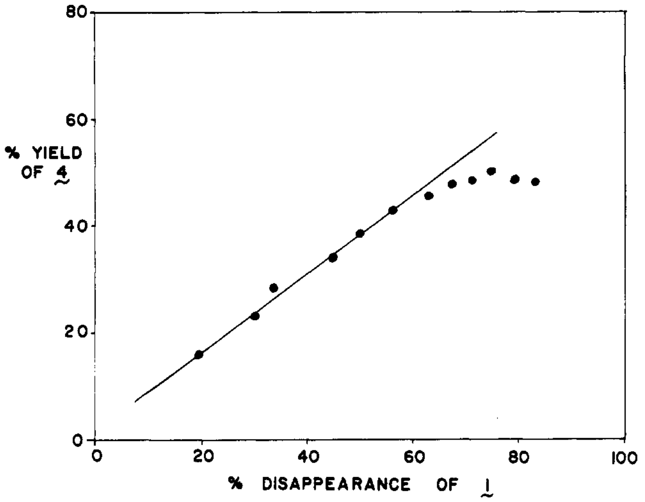


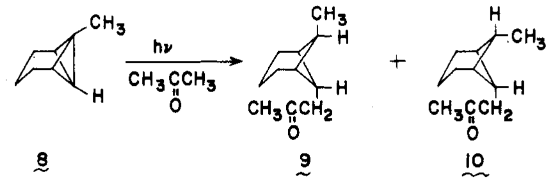
Figure 1. Plot of appearance of the photoproduct 4 vs. the disappearance of tricyclo[4.1.0.$0^{2,7}$]heptane (1).

a 34% isolated yield of 7.[5] Analysis of the crude reaction mixture by VPC after 120 h indicated the presence of 46% of 7 and 12% of 1.[6] The structures of 6 and 7 were established through a comparison of their spectral properties with those of 4 and 5.

Mechanistically, we believe that the addition of acetone, acetonitrile, and ethyl acetate across the C1–C7 bond of 1 occurs via a photoinitiated radical chain reaction.[7] Since no reaction occurs in the dark, the addition was certainly photoinitiated. Numerous factors point to the radical nature of the addition. The addition was inhibited by the presence of oxygen. With toluene as solvent, 1,2-diphenylethane was the major product with only trace amounts of acetone adduct being observed.[8] In addition, the formation of the acetonitrile adduct in the presence of small amounts of the photoactive acetone provided convincing evidence for a radical chain process.

The ability to obtain high yields of 4 from 1 was limited by the stability of 4 under the reaction conditions. Figure 1 shows a plot of disappearance of 1 vs. appearance of 4. As can be seen from this plot, a reasonably linear relationship exists for the conversion of 1 into 4 up to about 60% reaction. At this point, the product concentration leveled off, even though the starting material continued to be used up. At 60% reaction, the yield of 4 was 75%, based on unreacted starting material.[9]

Lastly, the photoinduced addition of acetone to 1-methyltricyclo[4.1.0.$0^{2,7}$]heptane (8) was studied. This reaction gave a 42% yield of a 4.3:1 mixture of 9 and 10, respectively.[10] The anti-Markovnikov nature of the addition to 8 is significant in that it is consistent with the intermediacy of a radical chain process.



We are continuing to study photoinitiated additions to strained carbon–carbon σ bonds.

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

Registry No. 1, 287-13-8; 4, 87568-92-1; 5, 87568-93-2; 6, 87568-95-4; 7, 87568-94-3; 8, 32348-63-3; 9, 87568-96-5; 10, 87638-00-4; $CH_3C(O)CH_3$, 67-64-1; $CH_3CO_2C_2H_5$, 141-78-6; CH_3CN, 75-05-8.

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[6] Direct irradiation of 1 in ethyl acetate (which contained no acetone) in a quartz cell with a 450-W Hanovia medium-pressure mercury lamp also gave 7, but in lower yield (16%).

[7] Numerous examples of the photoinduced addition of acetone and of other ketones *to olefins* have appeared 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. deMayo, P. "Advances in Organic Chemistry"; Interscience: New York, 1960; Vol. II; p 367. Elad, D. In "Organic Photochemistry"; Chapman, O., Ed.; Marcel Dekker: New York, 1969, Vol. II, p 190.

[8] Heating of 1 in acetone containing α,α′-azobis(isobutyronitrile) gave low yields of 4.

[9] We do not know the nature of the products formed in the photodecomposition of 4.

[10] The structures of 9 and 10 were established on the basis of their 300-MHz ^{1}H NMR spectra and their 20-MHz ^{13}C NMR spectra.[3]

[11] Sohio Fellow, 1979–1980; Amoco Foundation Fellow, 1980–1981.

A Versatile Synthesis of α-Pyrones

Summary: The α-oxoketene dithioacetal functionality is exploited in a versatile and efficient synthesis of annulated and simple α-pyrones. The alkyl substitution pattern about the α-pyrone ring can be modified at all four olefinic carbon atoms in a systematic manner.

Sir: We report an efficient and versatile synthesis of alkyl-substituted α-pyrones from α-oxoketene dithioacetals. The α-pyrone ring system[1] is found in several types of natural products and is an important synthetic intermediate. Steroidal,[2] nor- and dinorditerpenoid,[3] and monocyclic[4] α-pyrones constitute important classes of natural products that exhibit a wide range of biological activity. The steroidal bufadienolides show cardiotonic[2c] and antineoplastic[2b] properties while several nor- and dinorditerpenoid α-pyrones isolated from *Podocarpus* plants function as insect larvae toxins[3e] and cytotoxic agents.[3a–c] Synthetically, the Diels–Alder reaction of α-pyrones with acetylene[5] or olefin[6] dienophiles affords preparative routes to benzene and cyclohexadiene derivatives, respectively.

The synthesis of α-pyrones from α-oxoketene dithioacetals requires a sequence of operations involving organocopper conjugate addition, 1,2-nucleophilic addition of ester enolates, and subsequent ester hydrolysis and enol lactonization. The method is applicable for the synthesis of both simple and annulated α-pyrones, and, in principle,

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[1] For a discussion of the chemistry of α-pyrones see: Staunton, J. In "Comprehensive Organic Chemistry"; Sammes, P. G., Ed.; Pergamon Press: Oxford, England, 1979; Vol. 4, Part 18.2, pp 629–646. 2*H*-Pyran-2-one and its derivatives are commonly referred to as 2-pyrones or α-pyrones.

[2] (a) Goetz, M. A.; Meinwald, J.; Eisner, T. *Experientia* **1981**, *37*, 679 and references cited therein. (b) Kupchan, S. M.; Moniot, J. L.; Sigel, C. W.; Hemingway, R. J. *J. Org. Chem.* **1971**, *36*, 2611 and references cited therein. (c) Chem, K. K.; Kovarikova, A. *J. Pharm. Sci.* **1967**, *56*, 1535.

[3] (a) Hayashi, Y.; Matsumoto, T.; Sakan, T. *Heterocycles* **1978**, *10*, 123. (b) Hayashi, Y.; Yuki, Y.; Matsumoto, T.; Sakan, T. *Tetrahedron Lett.* **1977**, 3637. (c) Hayashi, Y.; Yuki, Y.; Matsumoto, T.; Sakan, T. *Ibid.* **1977**, 2953. (d) Loder, J. W.; Nearn, R. H. *Ibid.* **1975**, 2497. (e) Russell, G. B.; Fenemore, P. G.; Singh, P. *J. Chem. Soc., Chem. Commun.* **1973**, 166.

[4] Adityachaudhury, N.; Das, A. K. *J. Sci. Ind. Res.* **1979**, *38*, 265.

[5] (a) Bryson, T. A.; Donelson, D. M. *J. Org. Chem.* **1977**, *42*, 2930. (b) Reed, J. A.; Schilling, C. L., Jr.; Tarvin, R. F.; Rettig, T. A.; Stille, J. K. *Ibid.* **1969**, *34*, 2188.

[6] Kozikowski, A. P.; Corey, E. J. *Tetrahedron Lett.* **1975**, 2389.

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