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COPPER(I) CATALYZED $2\pi + 2\pi$ PHOTOCYCLOADDITIONS OF ALLYL ALCOHOL

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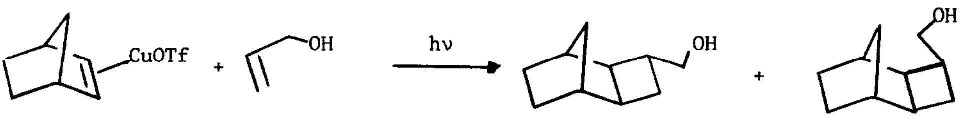
Copper(I) salts promote a large array of photoreactions of simple alkenes. Previous studies have shown that five, six, and seven membered cycloalkenes undergo $2\pi + 2\pi$ photocycloadditions,[1] methylenecyclopropanes undergo rearrangements and fragmentation,[2] and acyclic olefins as well as cyclooctene, cyclododecene, and 1,5,9-cyclododecatrienes undergo cis-trans isomerization upon photolysis in the presence of copper(I).[3] However, synthetically interesting applications of copper(I) catalyzed photoreactions to functionally substituted olefins remain unexplored. We now report the first examples of copper(I) promoted photocycloadditions involving (1) an acyclic alkene, and (2) a functionally substituted olefin.

Since allyl alcohol forms isolable complexes with Cu(I),[4] we explored the possibility that copper(I) trifluoromethanesulfonate[5] (CuOTf) might promote photoreactions involving allyl alcohol. As observed previously with other acyclic olefins,[3] allyl alcohol does <u>not</u> dimerize by $2\pi + 2\pi$ cycloaddition upon photolysis in the presence of CuOTf. However, irradiation (254 nm) of the 1:1 complex 1 of norbornene and CuOTf in allyl alcohol as solvent produces two epimeric cyclobutanes 2 and 3 (4:1) in 76% yield. The structures assigned are in accord with

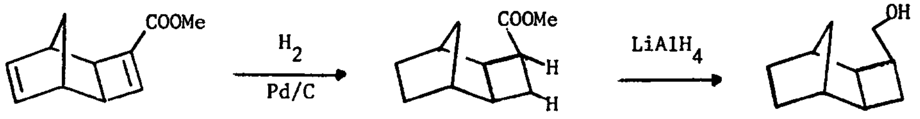


1

2

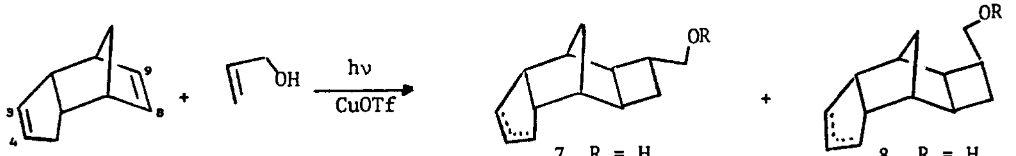
3

the ^1H nmr and mass spectra of 2 and 3.[6] The structure 3 assigned to the minor isomer was firmly established by unambiguous stereospecific synthesis from methyl *exo*-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene-3-carboxylate (4). Catalytic hydrogenation to 5, followed by reduction with $LiAlH_4$ gave 3: ^1H nmr ($CDCl_3$)δ3.67(dd,H,J = 8.5, 10.6Hz), 3.55(dd,H,J = 6.8, 10.6Hz), 1.8-3.0(7H), 0.9-1.7(7H). A 0.12ppm difference in chemical shift is found for the diastereotopic hydrogens of the sterically congested hydroxymethyl group in 3. The corresponding protons in 2 appear as a simple doublet at δ3.55(J = 6.4Hz).



4 5 3

Photolysis of *endo*-dicyclopentadiene (6) in the presence of CuOTf with allyl alcohol as solvent results in regiospecific cross-reaction between allyl alcohol and the 8,9 double bond of 6. Two epimeric cyclobutanes 7 and 8 (4:1) are obtained in 96% yield.[6,8] The corresponding acetates 7' and 8' were separated by glpc (2' x 1/4" 10% DC710 on Chromosorb W).[6] The ^1H nmr spectra (CCl_4) of the major and minor isomers (rel. retention times 1.00 and 1.15 respectively) have doublets at δ3.94(J = 6.5Hz) and δ4.04(J = 7Hz) respectively due to the acetoxymethyl CH_2 group, and both exhibit a multiplet at δ5.5 corresponding to the vinyl hydrogens at positions 3 and 4. A similar multiplet is found in the ^1H nmr spectrum of 6. A vinylic hydrogen absorption at δ5.95 corresponding to the 8 and 9 hydrogens in 6 is absent in the spectra of 7 and 8 and the derived acetates. Thus, the 8, 9 double bond of 6 is not present in 7 and 8. The *exo* configuration of the cyclobutane ring and the stereochemistry of the hydroxymethyl group in 7 and 8 is assumed by analogy with 2 and 3. Photolysis of 6 in the presence of CuOTf, but in the absence of allyl alcohol, results in intermolecular photocycloaddition which is also regiospecific, involving the 8,9 double bond, in spite of the intimate juxtaposition of the 3,4 and 8,9 double bonds in 6.[1e] Acetone sensitized photolysis of 6 gives intramolecular photocyclo-

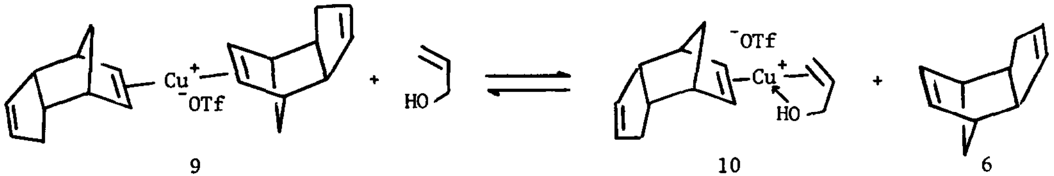


6

7, R = H
7', R = OAc

8, R = H
8', R = OAc

addition.[9] The regiospecific reactivity of 6 in the copper(I) promoted reaction is explained by a preference for coordination of the 8,9 double bond of 6 with copper,[10] and a requirement for coordination to copper of both carbon-carbon double bonds undergoing photodimerization.[1e] In fact, 6 and CuOTf form an isolable 2:1 complex 9. A mixed complex 10 is the pivotal intermediate in the cross-reaction between allyl alcohol and 6. It is reasonable that the equilibrium between 9 and 10 strongly favors the latter in allyl alcohol as reaction solvent. This results in the remarkable selectivity for cross-reaction even though allyl alcohol cannot photocycloadd to itself.

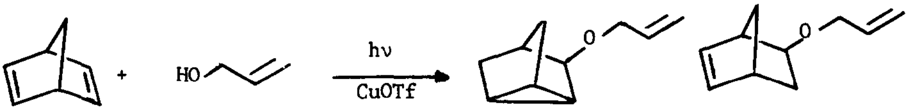


9 10 6

Cyclohexene photodimerizes in the presence of CuOTf.[1f] In allyl alcohol as reaction solvent, dimerization is blocked, but no cross-reaction is observed either. Apparently cyclohexene, which is a relatively poor ligand, cannot compete with allyl alcohol for coordination sites on copper. The 2:1 complex 12 of allyl alcohol and CuOTf is strongly favored in allyl alcohol as reaction solvent over the mixed complex 11 required for cross-reaction.

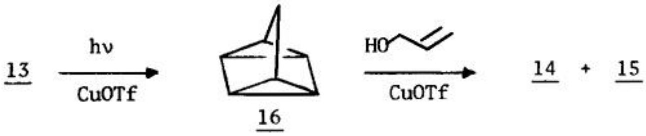
11 12

In contrast, irradiation (254nm) of a solution of norbornadiene (13) in allyl alcohol in the presence of CuOTf results in addition of allyl alcohol to afford the ethers 14 and 15 (7:3)



13 14 15

Since the same products are obtained in high yield from thermal reaction of quadricyclane (16) with allyl alcohol in the presence of CuOTf, the photochemical reaction probably involves Cu(I) catalyzed intramolecular photocycloaddition of 13 to give 16 followed by a dark reaction between 16 and allyl alcohol promoted by CuOTf.[11] Analogous reactions of 16 promoted by silver salts are known.[12]



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6. Satisfactory elemental analyses were obtained for these new compounds. Mass spectra (70eV) m/e (rel intensity): 2-152(6), 134(47), 121(53), 94(47), 93(47), 80(50), 79(49), 66(100); 3-152(3), 134(31), 121(39), 94(46), 93(44), 80(46), 79(50), 66(100); 14-150(18), 132(52), 121(29), 117(42), 109(54), 93(80), 92(51), 91(78), 83(68), 81(87), 80(51), 79(100), 77(68), 66(66); 15-150(23), 109(38), 81(49), 79(31), 77(28), 66(100). ^{1}H nmr($CDCl_3$): 6'-δ5.5(2H, m), 3.94(2H,d,J=6.5), 2.8-3.2(1H), 1.3-2.8(12H), 1.96(3H,s); 7'-δ5.5(2H,m), 4.03(2H,d,J=7Hz), 2.0-3.2(11H), 1.96(3H,s), 1.5(2H,m); 14-δ5.7-6.3(1H,m), 5.0-5.5(2H,m), 3.96(2H,d,J=5Hz), 3.57(1H,m), 1.7-2.1(2H), 1.0-1.7(6H); 15-δ5.7-6.4(3H),5.0-5.5(2H), 4.00(2H,d,J=5Hz), 3.6(1H), 2.9(2H), 1.0-2.0(4H).

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8. A solution of $(CuOTf)_2 \cdot C_6H_6$ (2.4g, 9.5mequiv) and 6 (9.5mmole) in allyl alcohol (40mL) in a cylindrical quartz vessel with an internal water-cooled cold finger is irradiated in a Rayonet photochemical reactor (RPR-100) with 254nm lamps for 40 hrs. A second portion of 6 (9.5mmole) is added and irradiation continued for 40 hrs, after which a third portion of 6 (9.5mmole) is added. After a final 40 hrs irradiation, the reaction mixture is poured into 20% NH_4OH (100mL) and extracted into pentane (2 x 100mL). The organic extract is washed with water (100mL), dried (Na_2SO_4) and concentrated. Distillation under reduced pressure gives 7 + 8; bp 110-113°/1.5mm (5.2g).

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