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COPPER(I) TRIFLATE A SUPERIOR CATALYST FOR OLEFIN PHOTODIMERIZATION

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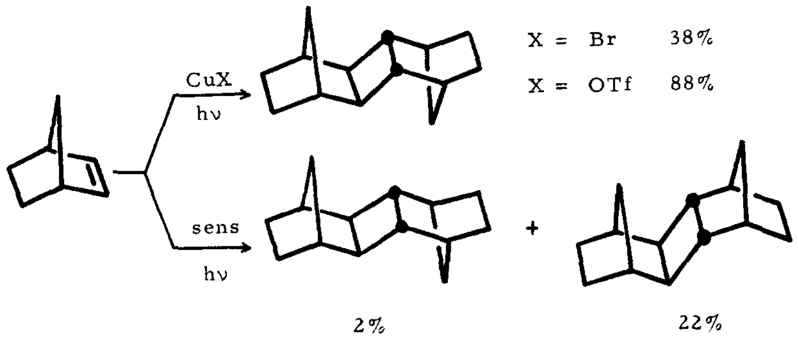
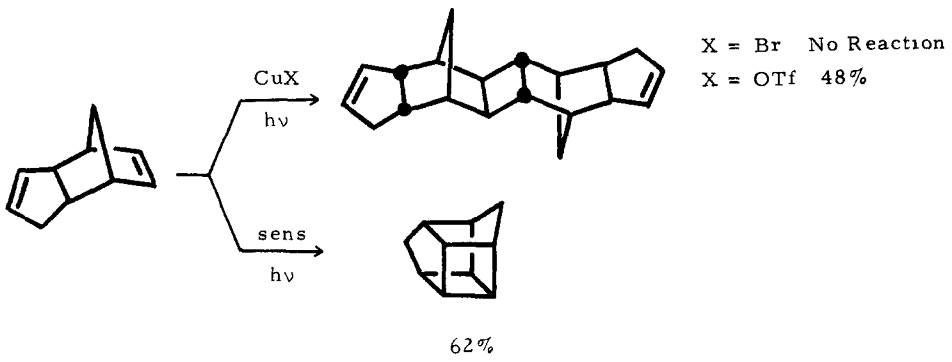
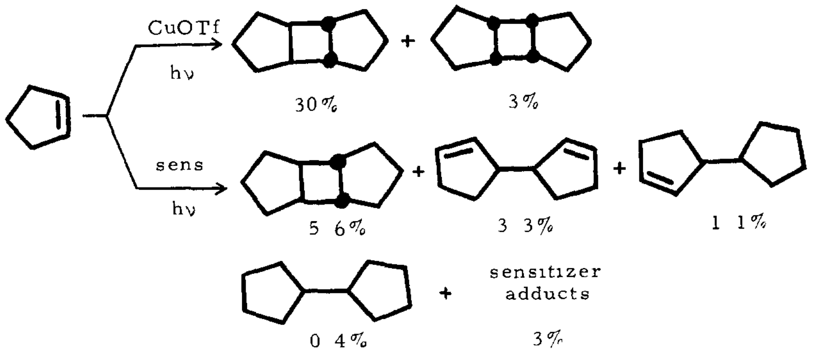
We have discovered an excellent catalyst for the copper(I) induced photodimerization of isolated monoolefins Earlier, Trecker, Henry, and McKeon reported that Cu(I) halides catalyze the photodimerization of norbornene and related strained monoolefins [1] However, the Cu(I) halide catalysts have several shortcomings, including insolubility and instability The latter is especially troublesome since Cu(I) halides are transformed under ultraviolet irradiation into an opaque insoluble deposit on the walls of the reaction vessel [2] The solid must be repeatedly and tediously removed manually, and additional Cu(I) halide replenished during the course of the photodimerization

In contrast to the insolubility of the olefin complexes of Cu(I) halides, olefin complexes of Cu(I) trifluoromethanesulfonate (CuOTf) are readily soluble in a variety of polar organic solvents [3] All olefin-CuOTf-complexes examined exhibit two strong u v absorption bands, one at 233-241 nm (ε_{max} 2500-3600) and one at 272-282 nm (ε_{max} 1500-2100) These properties suggested the possible utility of CuOTf as a catalyst for olefin photodimerization The preliminary results communicated herein demonstrate the superiority of this new catalyst

The catalyst is introduced into the reaction mixture either as an isolated olefin-CuOTf complex[4] or as $(CuOTf)_2 \cdot C_6H_6$ from which the weakly coordinated benzene is readily displaced by olefins to afford olefin-CuOTf complexes <u>in situ</u> For example, a solution of $(CuOTf)_2 \cdot C_6H_6$ (1 2 g) in norbornylene (30 g) and THF (15 ml) was irradiated for 6 days in a quartz vessel with a medium pressure mercury vapor lamp (450 watt Hanovia) The reaction mixture remained light and clear Pentane (30 ml) was added and the mixture was washed with aqueous KCN to remove the catalyst Distillation afforded dimer (26 4 g) in 88% yield,


CuX
hν
X = Br 38%
X = OTf 88%
sens
hν
+
2%
22%

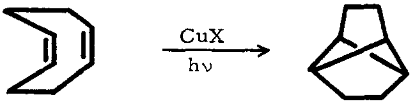

CuX
hν
X = Br No Reaction
X = OTf 48%
sens
hν
62%


CuOTf
hν
+
30%
3%
sens
hν
+
+
5.6%
3.3%
1.1%
+
sensitizer
adducts
0.4%
3%

which is a substantial improvement on the 38% yield reported for the same reaction catalyzed by CuBr [2] The product is almost pure exo-trans-exo isomer with either catalyst

Similarly, a solution of (endo-dicyclopentadiene)$_2$ CuOTf (0 4 g) and endo-dicyclopentadiene (13 g) in THF (7 ml) was irradiated for 1 week in a quartz tube at 254 nm in a Rayonet RPR-100 photochemical reactor Cyclohexane (300 ml) was added and the resulting mixture washed with aqueous KCN Solvents and unreacted olefin were removed under reduced pressure by distillation and the residue triturated with pentane to give dimer (6 3 g) in 48% yield Recrystallization from ethanol gave white flakes, mp 180-184° An exo-trans-exo-structure is assumed for this dimer in analogy with the norbornene dimer * Analysis of the recovered dicyclopentadiene by gas chromatography revealed about 2% yield of pentacyclo[5 2 1 0 ^{2,6}0^{4,8}]decane by comparison with an authentic sample [5] These results contrast with the failure of CuBr to catalyze inter- or intramolecular photocycloaddition reactions of endo-dicyclopentadiene

The intramolecular photocycloaddition reaction of 1,5-cyclooctadiene to give tricyclo-[3 3 0 0^{2,6}]octane requires 1 liter of ether for 14 g of diene with CuCl as catalyst [6] The use of CuOTf as catalyst obviates the necessity of intermittent addition of fresh catalyst and cleaning of the reaction vessel The catalyst is recovered quantitatively in the form of (1,5-cyclooctadiene)$_2$ CuOTf With an equal volume of 1·1 THF-MeOH, the catalyst is soluble in 1,5-cyclooctadiene However, yields obtained in initial preparative experiments (23%) were slightly lower than reported for CuCl as catalyst Optimization of the reaction conditions may overcome this disadvantage, since a smaller run irradiated in a sealed quartz tube at 254 nm in the Rayonet photochemical reactor for three weeks gave 53% of the tricyclic hydrocarbon, and even under these conditions appreciable diene remains unreacted



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*New compounds were characterized by spectral (nmr and mass) and elemental analyses

Especially significant is the finding that CuOTf catalyzes photodimerization of cyclopentene (see figure) Thus, with CuOTf as the catalyst, photodimerization is not limited to strained olefins such as norbornene derivatives The products of CuOTf catalyzed photoreactions are often different from those of the corresponding high energy triplet sensitized photoreactions[7] (see figure), and products due to allylic hydrogen abstraction and sensitizer adducts are avoided by the use of CuOTf as catalyst

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