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Copper(I)-Catalyzed Intramolecular Diene–Diene Cycloaddition Reactions and Rearrangements[1,7]

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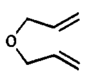
Abstract: The intramolecular cycloaddition reactions of the tetraene ethers **10** and **17** and the triene ether **28** were investigated. Acetone-sensitized excitation of **10** led to three intramolecular [2 + 2] cycloadducts **11–13**. However, CuOTf-catalyzed photolysis of **10** gave two rearranged products **15** and **16** via copper(I)-catalyzed, photoinduced [1, 3] and [3, 3] rearrangement reactions of the divinylcyclobutane intermediates **11–13**. The Cope product **14** is the precursor of the tetracyclic product **16** in a photocatalytic process. All photochemical products contain cis-fused rings. By analogy with the photochemical reactions of **10**, acetone-sensitized photolysis of the tetraene ether **17** afforded four intramolecular [2 + 2] cycloadducts **18–21**. The dipropenylcyclobutanes **18–21** were formed as intermediates under CuOTf-catalyzed irradiation of **17** as well. However, longer irradiation times led to four rearranged products **22–25**. Two cyclooctadiene intermediates **26** and **27** are the precursors of the tetracyclic products **24** and **25**. Acetone-sensitized or CuOTf-catalyzed photolysis of the triene ether **28** gave two vinylcyclobutanes **29** and **30**, but no copper(I)-catalyzed ring expansion reactions were found. Thermolysis of **10** in toluene at 150 °C produced a mixture of four isomeric vinylcyclohexenes **31**, **32**, **15**, and **33**, whereas the CuOTf-catalyzed intramolecular Diels–Alder reaction in THF at 80 °C showed an improved selectivity, the trans-fused hexahydroisobenzofuran derivative **31** being the main product. Thermolysis of **17** in toluene at 150 °C gave two cyclohexene derivatives **22** and **34**. Thermolysis of **28** at 150 °C resulted in formation of two bicyclic cyclohexenes **35** and **36**. Also, the thermal rearrangement reactions of the divinylcyclobutanes **11–13** and the dipropenylcyclobutanes **18–21** were studied. Initial experiments concerning the activity of copper(II) triflate as catalyst for the described intramolecular cycloaddition reactions were carried out.

Introduction

In the field of cycloaddition reactions, copper catalysis has been applied to several intermolecular Diels–Alder reactions. Cupric tetrafluoroborate,[8a–d] copper zeolites,[8e] or cuprous chloride/ammonium chloride[8f] are frequently used catalysts.

The first example of a copper(I)-catalyzed olefin photocycloaddition was the photolysis of *cis,cis*-1,5-cyclooctadiene in the presence of cuprous chloride reported by Srinivasan in 1963.[9a] In 1973, the bis(copper(I) trifluoromethanesulfonate)–benzene complex [$(CuSO_3CF_3)_2C_6H_6$] (CuOTf)[10] was introduced by Salomon and Kochi as an efficient catalyst for photodimerizations of cyclic alkenes.[11] Later Evers and Mackor found that CuOTf catalyzed the photoinduced [4 + 2] cycloaddition between cyclohexene and 1,3-dienes.[12] They also discovered the catalytic influence of CuOTf in the area of photoinduced intramolecular [2 + 2]-cycloaddition reactions of 1,6-dienes.[13] This method, which provides the basis for the synthesis of *cis*-bicyclo[3.2.0]heptane derivatives, has been thoroughly studied by Salomon et al.[11,14] For example, the CuOTf-catalyzed photobicyclization of diallyl ether (**1**) leads to *cis*-3-oxabicyclo[3,2,0]heptane (**2**) in 52% yield.[14c] Salomon also showed that several allyl 2,4-hexadienyl ethers **3a–c** afford bicyclic vinylcyclobutanes **4a–c** (yield 80–87%) upon irradiation in the presence of CuOTf.[14a,c]



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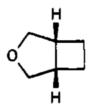

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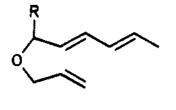
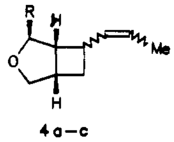


3a–c



4a–c

a: R=H b: R=Me c: R=n-Bu

It is known[10] that CuOTf is an excellent reagent for the preparation of copper(I)–olefin complexes. In the presence of olefins, benzene, a rather weak π ligand, is quickly displaced from copper(I). Cationic complexes are formed, which are soluble in various organic solvents. The poorly coordinating triflate anion does not compete with the olefin for the ligand sites on Cu(I), in contrast to strongly coordinating halides in copper(I) halide–olefin complexes.

Copper(I) catalysis has not been applied to cycloaddition reactions of bis(dienes). However, acid-catalyzed formal intra-

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(1) The series Thermal Reactions of Donor–Acceptor Systems (A, ref 2) has now been combined with parts of the series Radical Ions and Photochemical Charge Transfer Phenomena (B, ref 3) and with three single papers cited in refs 4–6. This paper now counts as part 30 of our new series Cycloadditions.

(2) Last number of A: Mattay, J.; Kneer, G.; Mertes, J. *Synlett* **1990**, 145.

(3) Last number of B: Mattay, J.; Rumbach, T.; Runsink, J. *J. Org. Chem.* **1990**, *55*, 5691.

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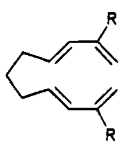
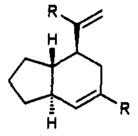
Table I. Sensitized and CuOTf-Catalyzed Photolysis of the Tetraene Ether **10**[a]

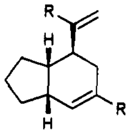
sens[b]/catalyst	solvent	filter	time, h	product ratio[c] **10**	**11**	**12**	**13**	**14**	**15**	**16**	yield,[d] %
Me_2CO[e]	Me_2CO	Pyrex	3		34	58	3	4	<1		88
CuOTf[f]	THF	quartz	3	58	18	18	1	2	3		
			6	4	38	36	3	4	14	1	
			16		40	6	1	4	42	7	
			43		32	2	1	3	46	16	
			120						71	29	63

[a] Conditions: **10**, 0.1 M; argon; 85-mL photoreactor; lamp, Philips HPK 125 W. [b] sens, sensitizer. [c] Product ratios determined by ^{13}C NMR (CH_2O signals). Traces of **15** detected by GLC analysis. [d] Isolated. [e] See ref 19: Benzophenone-sensitized excitation of **10** gave, after 16 h, cycloadducts **11** and **12** (ratio 1:1, yield 50%). [f] CuOTf, 2 mol %.

molecular Diels–Alder reactions[15] of 2,10-dialkyl-substituted 1,3,8,10-undecatetraenes **5a,b** were described by Gassman in 1984.[16] In the presence of trifluoromethanesulfonic acid at −23 °C, the bisdienes **5a,b** underwent rapid intramolecular cyclization to the hexahydroindene derivatives **6a,b** and **7b** in high yields. Williams[17] used the intramolecular Diels–Alder reaction of substrates bearing two dienic components as a strategy to synthesize substituted trans-fused decalins.



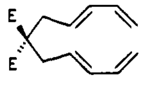


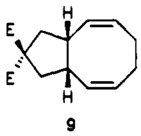


5a,b 6a,b 7b

a : R=Me b : R=t-Bu

Investigating the synthesis of eight-membered ring systems, Wender reported on the thermally and photochemically induced intramolecular [4 + 4]- and [2 + 2]-cycloaddition reactions of various tetraenes;[18,19] for instance, he prepared the cis-fused bicyclic cyclooctadiene **9**, starting from the bis(diene) **8**, under Ni(O)-catalytic conditions at 60 °C.[18] Benzophenone-sensitized excitation of the tetraene ether **10** led to the formation of the divinylcyclobutanes **11** and **12** in a ratio of 1:1 in 50% yield.[19] Thermolysis of the photochemically obtained [2 + 2] cycloadducts **11** and **12** at 210 °C afforded the cis-fused, heterobicyclic product **14** in 75% yield.[19]





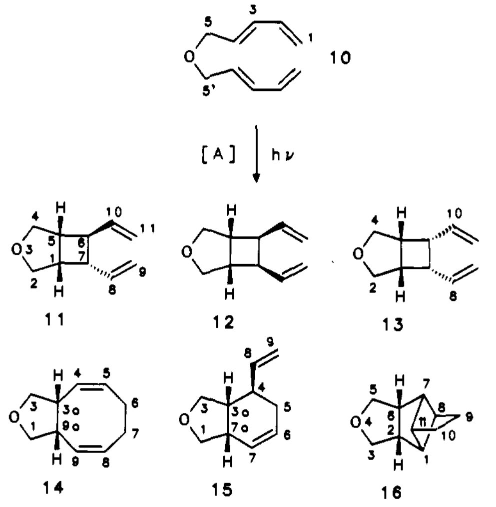
8 $E=CO_2Et$ 9

In the course of our investigations concerning copper(I)-catalyzed cycloadditions, we encountered various interesting bicyclic ring systems. We now report on our recent results in the field of intramolecular cycloaddition reactions of the tetraene ethers **10** and **17** as well as the triene ether **28** under homogeneous copper(I) catalysis.

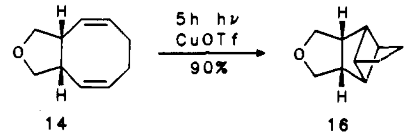
Photoreactions

Photolysis of 5,5′-Oxybis[(*E*)-1,3-pentadiene] (10). The tetraene ether **10** was synthesized in 80% yield from 2,4-pentadienol[20] and 2,4-pentadienyl bromide[20] under phase-transfer catalysis using tetra-*n*-butylammonium chloride as catalyst.

Scheme I



Scheme II



Irradiation of **10** (3h), using acetone as sensitizer, led to the divinylcyclobutanes **11** and **12**, the exo-6,7-divinyl isomer **12** being the main product. As minor products, we also found the endo-6,7-divinyl isomer **13**, the cyclooctadiene derivative **14**, and traces of the vinylcyclohexene **15**. All products were obtained in a combined yield of 88% (Scheme I and Table I).

The intramolecular [2 + 2] cycloadducts **11–13** were formed as intermediates under copper(I)-catalyzed photolysis using 2 mol % CuOTf as well. However, longer irradiation times (5 days) gave two rearranged products **15** and **16** in 63% yield in a ratio of 2.5:1. All products contain cis-fused rings (Scheme I and Table I). The stereochemical course during the irradiation is shown in Table I. The *exo*-6,7-divinylcyclobutane **12** and the cyclooctadiene intermediate **14** are quickly converted, while the *exo,endo*-6,7-divinylcyclobutane **11** rearranges very slowly and therefore causes long irradiation times.

Copper(I)-catalyzed photolysis of the mixture of [2 + 2] cycloadducts **11–13**, isolated from the acetone-sensitized reaction of the tetraene ether **10**, led to the same products. Thus, after 51 h, **15** and **16** were obtained in 73% yield.

The cyclooctadiene **14** is the precursor of the tetracyclic product **16** under copper(I)-photocatalytic conditions, as was shown in an independent experiment with pure isolated **14** (90% yield after 5 h; Scheme II). This reaction step corresponds to the well-known cuprous chloride catalyzed photoisomerization of *cis,cis*-1,5-cyclooctadiene to tricyclo[3.3.0.0^{2,6}]octane (**37**),[9] first reported by Srinivasan in 1963.[9a]

Further studies on the photocatalytic behavior of the separated divinylcyclobutane isomers **11** and **12** indicated that they interconvert through epimerization at C-7 during irradiation in the

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(15) For reviews of intramolecular Diels–Alder reactions, see: (a) Taber, D. F. *Intermolecular Diels–Alder and Alder Ene Reactions*; Springer-Verlag: Berlin, Heidelberg, 1984. (b) Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63. (c) Oppolzer, W. *Angew. Chem.* **1977**, *89*, 10.

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Table II. Irradiation of the Pure Divinylcyclobutane Isomers **11** and **12** in the Presence of CuOTf[a]

			product ratio[b]					
compd	time, h	conversn, %	**11**	**12**	**14**	**15**	**16**	yield,[c] %
11	3	21	79	4	2	12	3	
	40	100				68	32	68
12	3	77	12	23	12	35	18	
	10	100				56	44	80

[a] Conditions: **11** or **12**, 0.1 M; CuOTf, 2 mol %; argon; 45-mL photoreactor; filter, quartz; solvent, THF; lamp, Philips HPK 125 W. [b] Product ratios determined by ^{13}C NMR (CH_2O signals). [c] Isolated.

Table III. Acetone-Sensitized Photolysis of the Tetraene Ether **17**[a]

	product ratio[b]					
time, h	**18**	**19**	**20**	**21**	others[c]	yield,[d] %
3	7	30	31	22	10	87

[a] Conditions: **17**, 0.1 M; argon; 85-mL photoreactor; filter, Pyrex; acetone neat; lamp, Philips HPK 125 W. [b] Product ratio determined by ^{13}C NMR (CH_2O signals). [c] Several not identified, minor products. [d] Isolated.

Table IV. CuOTf-Catalyzed Photolysis of the Tetraene Ether **17**[a]

	product ratio[b]					
time, h	**22**	**23**	**24**	**25**	others[c]	yield,[d] %
120	18	23	32	12	15	45

[a] Conditions: **17**, 0.1 M; argon; 85-mL photoreactor; filter, quartz; solvent, THF; CuOTf, 2 mol %; lamp, Philips HPK 125 W. [b] Product ratio determined by ^{13}C NMR (CH_2O signals, for the ratio of **24** to **25** CH_3 signals). [c] Several not identified, minor products. [d] Isolated.

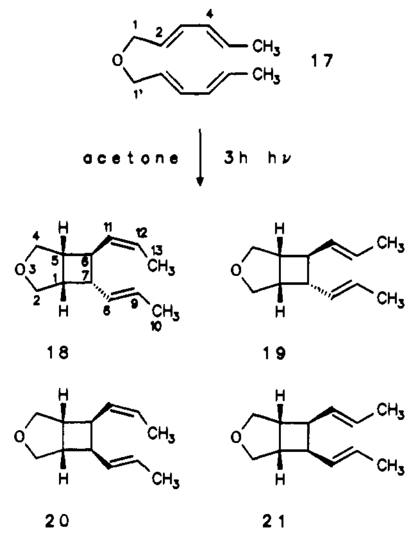
presence of CuOTf. Both isomers irreversibly formed the ring-enlarged products **14** and **15**. The described transformations of the [2 + 2] cycloadducts **11** and **12** are exclusively copper(I)-catalyzed and photoinduced processes, as was proven by control experiments.[21] The formation of the cyclooctadiene intermediate **14** corresponds to a Cope rearrangement, whereas the cis-fused bicyclic vinylcyclohexene **15** results from a formal [1, 3] migration of the cyclobutane bond. Compared to **11**, the *exo*-6,7-divinylcyclobutane **12** rearranged more efficiently in the Cope manner and afforded greater amounts of the tetracyclic product **16** (deriving from the Cope product **14**), which can be explained as a consequence of a more favorable geometry in **12** for the Cope rearrangement. The results are summarized in Table II.

We also found that the described photobicyclization of **10** and the [3, 3] and [1, 3] rearrangements of the divinylcyclobutanes **11**–**13** can be catalyzed by copper(II) trifluoromethanesulfonate. In the presence of $Cu(OTf)_2$ (3 mol %), photolysis of **10** led after 5 days to the rearranged products **15** and **16** in 40% yield. We suggest that the reduction of copper(II) to catalytically active copper(I) is a key step in the photocatalytic process. Further studies on the mechanistic aspects of these findings are in progress.

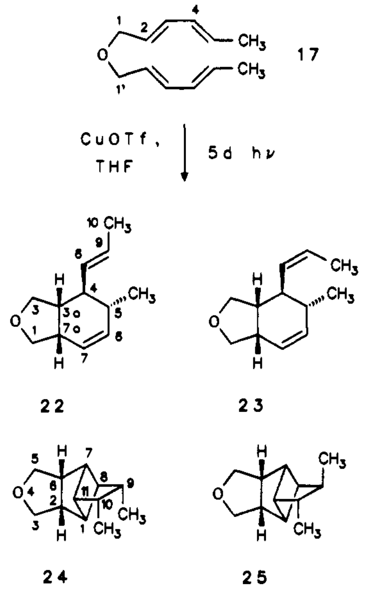
Photolysis of 1,1′-Oxybis[(*E*,*E*)-2,4-hexadiene] (17). In order to examine the copper(I)-catalyzed photoreactions of another bis(diene) we synthesized the tetraene ether **17**, which, in contrast to **10**, has two methyl-substituted double bonds. **17** was obtained in 80% yield from sorbyl alcohol[20] and sorbyl bromide[20] under phase-transfer catalysis.

The acetone-sensitized photolysis of **17** gave a mixture of products (yield 87%) with four intramolecular [2 + 2] cycloadducts **18**–**21** as main compounds (Scheme III and Table III). **18** and **19** possess a *trans*- and **20** and **21** a *cis*-6,7-dipropenylcyclobutane unit. Two isomers, **18** and **20**, have one cis- and one trans-propenyl configuration due to a photochemical cis–trans isomerization of one double bond.

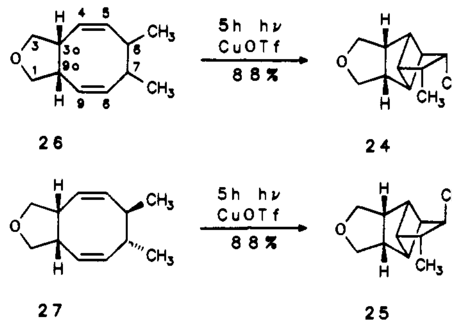
Scheme III



Scheme IV



Scheme V



The CuOTf-catalyzed irradiation (5 days) of **17** mainly led to two methylpropenylcyclohexene derivatives **22** and **23** and two tetracyclic products **24** and **25** (Scheme IV and Table IV). All products show a cis ring junction. During the Cu(I)-catalyzed photolysis of **17** we observed the formation of the [2 + 2] cycloadducts **18**–**21** as intermediates. The CuOTf-catalyzed, photoinduced [1, 3] rearrangement of the primarily formed dipropenylcyclobutanes **18**–**21** gave two cyclohexene derivatives **22** and **23**, which only differ in the configuration of the propenyl side chain. **22** has a trans- and **23** a cis-propenyl unit. The Cope rearrangement of **18**–**21** led to two cyclooctadiene intermediates

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[21] Photolysis without CuOTf gave no rearrangement of **11** and **12**. The same product ratios of **15** to **16** were obtained when the CuOTf-catalyzed photoreactions were carried out at room temperature or at −24 °C (At room temperature **12** rearranges to **14** within several weeks but is stable at −24 °C.). Therefore a thermal process can be excluded. Tetra-*n*-butylammonium triflate[22] showed no catalytic activity.

Scheme VI

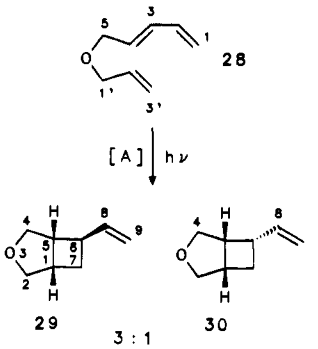

Table V. Sensitized and CuOTf-Catalyzed Intramolecular [2 + 2] Photocycloaddition of the Triene Ether **28**[a]

sens[b]/catal	solv	filter	time, h	prodt ratio[c] 29	prodt ratio[c] 30	yield,[d] %
Me_2CO	Me_2CO	Pyrex	8	72	28	77
CuOTf[e]	THF	quartz	12	75	25	65

[a] Conditions: **28**, 0.1 M; argon; 45-mL photoreactor; lamp, Philips HPK 125 W. [b] sens, sensitizer. [c] Product ratios determined by ^{13}C NMR (CH_2O signals). [d] Isolated. [e] CuOTf, 2 mol %.

Table VI. Thermolysis of the Tetraene Ether **10**[a]

catalyst	solvent	T, °C	time, h	product ratio[b] 31	product ratio[b] 32	product ratio[b] 15	product ratio[b] 33	yield,[c] %
none	none	150	1	polymerization				
none	toluene	150	11	58	12	26	4	80
none	THF	80	29					
CuOTf	THF	80	29	87	<1	<1	12	87
$Cu(OTf)_2$	THF	80	40	87	<1	<1	12	42
$Cu(BF_4)_2$	THF	80	120	87	<1	<1	12	80
$Cu(ClO_4)_2$	THF	80	56	87	<1	<1	12	31
CF_3SO_3H	CH_2Cl_2	−25	2					
R_4NOTf[d]	THF	80	29					

[a] Conditions: **10**, 0.1 M; catalysts, 6 mol %; argon; 20 mL of solution in a 50-mL glass autoclave. [b] Product ratios determined by ^{13}C NMR (CH_2O signals). Traces of **15** and **32** detected by GLC analysis. [c] Isolated. [d] R = *n*-Bu, OTf = $CF_3SO_3^-$.

26 and **27**, which are converted to the tetracyclic products **24** and **25** in the presence of CuOTf, Two independent experiments with pure isolated **26** and **27** showed that the tetracyclic product **24** with cis-methyl groups is efficiently formed from the *cis*-6,7-dimethylcyclooctadiene **26** and the tetracyclic product **25** with trans-methyl groups from the *trans*-6,7-dimethylcyclooctadiene **27** (Scheme V).

Photobicyclization of 5-(2'-Propenyloxy)-(*E*)-1,3-pentadiene (28). In order to test the scope and limits of the present ring-expansion reactions, we also investigated the photochemistry of the triene ether **28**, prepared from 2,4-pentadienol[20] and allyl bromide under phase-transfer catalysis in 74% yield.

As shown in Scheme VI and Table V, the acetone-sensitized excitation and the copper(I)-catalyzed photolysis gave comparable results. In both cases, the [2 + 2] cycloadducts **29** and **30** were formed in a ratio of 3:1. Longer irradiation times in the presence of CuOTf did not result in formation of ring-enlarged products. In conclusion, vinylcyclobutanes were found to be inactive under copper(I)-photocatalytic conditions in contrast with divinylcyclobutanes.

Thermal Reactions

Thermolysis of 5,5'-Oxybis[(*E*)-1,3-pentadiene] (10) and the [2 + 2] Cycloadducts 11–13. The uncatalyzed thermolysis of the tetraene ether **10** in toluene at 150 °C afforded a mixture of four intramolecular Diels–Alder products **31**, **32**, **15**, and **33** in 80% yield after 11 h (Scheme VII and Table VI).

Scheme VII

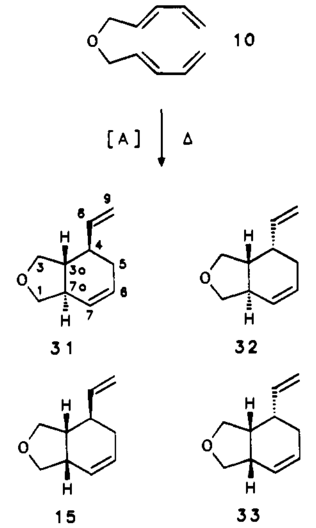

Table VII. Thermolysis of the Divinylcyclobutane Derivatives **11–13**[a]

compd	T, °C	time, h	product ratio[b] 14	product ratio[b] 31	product ratio[b] 32	product ratio[b] 15	product ratio[b] 33	yield,[c] %
12	80	3	100					87
11	190	25	44	3	5	36	12	77
11–13[d,e]	190	16	80	2	2	12	4	82

[a] Conditions: 0.5 g; argon; 10-mL glass autoclave. [b] Product ratios determined by ^{13}C NMR (CH_2O signals). [c] Isolated. [d] The mixture of [2 + 2] cycloadducts, which was obtained from the acetone-sensitized excitation of **10**, was used; see Table I. [e] See ref 19: A mixture of **11** and **12** (1:1) afforded **14** in 75% yield upon thermolysis (200 °C, 22 h).

The stereoselectivity was remarkably enhanced by using CuOTf as catalyst in tetrahydrofuran at 80 °C. In this case, the trans-fused vinylcyclohexene **31** was favored over the cis-fused product **33** by a factor of 7. Only traces of the other two [4 + 2] cycloadducts **15** and **32** could be detected by GLC analysis (Table VI). The rate of the catalyzed Diels–Alder reaction depended on the catalyst concentration; 6 mol % of CuOTf led to complete conversion after 29 h, whereas the use of 12 mol % halved the reaction time needed (100% conversion after 16 h).

Copper(II) salts with weekly coordinating anions were also tested as catalysts. The copper(II) triflate, copper(II) tetrafluoroborate hydrate, and copper(II) perchlorate hexahydrate catalyzed Diels–Alder reaction of **10** also gave **31** and **33** in a ratio of 7:1, but was less efficient. No cyclization was found under the catalytic influence of trifluoromethanesulfonic acid or tetra-*n*-butylammonium triflate[22] (Table VI). In the presence of Cu(II) salts, the Diels–Alder reaction was significantly accelerated by the use of catalytic amounts of hydroquinone, which acts as reducing agent [Cu(II) → Cu(I)].[8a] These experiments demonstrated that the described stereoselective intramolecular [4 + 2] cycloaddition of the unactivated bis(diene) ether **10** is indeed a copper(I)-catalyzed process.

Thermal rearrangement reactions of divinylcyclobutanes to *cis,cis*-1,5-cyclooctadienes and 4-vinylcyclohexenes are well-known.[19,23] As expected, thermolysis of the *exo*-6,7-divinylcyclobutane **12** exclusively produced the cyclooctadiene derivative **14** under mild conditions (80 °C, 3 h) in high yield (87%). Rearrangement of the *exo,endo*-6,7-divinyl isomer **11** required quite drastic reaction conditions (190 °C, 25 h) to result in formation of the bicyclic cyclooctadiene **14** and four isomeric 4-vinylcyclohexenes **31**, **32**, **15**, and **33**. The products of a [3, 3] and [1, 3] rearrangement pathway were equally favored. The thermal rearrangement of **11** was not induced by CuOTf catalysis

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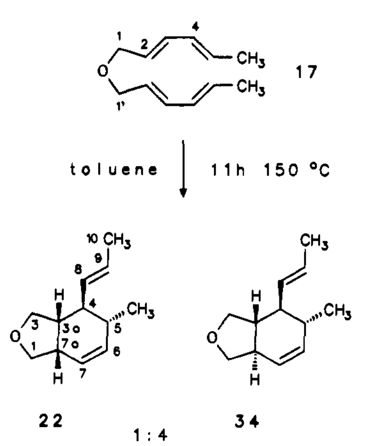
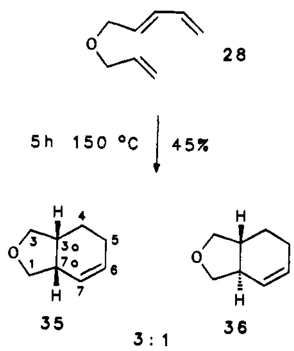
(22) Rousseau, K.; Farrington, G. C.; Dolphin, D. *J. Org. Chem.* **1972**, *37*, 3968.

(23) For examples, see: (a) Vogel, E. *Justus Liebigs Ann. Chem.* **1958**, *615*, 1. (b) Hammond, G. S.; DeBoer, C. D. *J. Am. Chem. Soc.* **1964**, *86*, 899. (c) Trecker, D. J.; Henry, J. P. *J. Am. Chem. Soc.* **1964**, *86*, 902. (d) Berson, J. A.; Dervan, P. B.; Malherbe, R.; Jenkins, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5937.

Scheme VIII



Scheme IX



in tetrahydrofuran at 80 °C. Thermolysis of a mixture of [2 + 2] cycloadducts **11–13**, which was obtained from the acetone-sensitized irradiation of the tetraene ether **10**, led to the cyclooctadiene **14** as major product ([3, 3]:[3, 1] = 4;1) (Table VII).

Thermolysis of 1,1′-Oxybis[(*E*,*E*)-2,4-hexadiene] (17) and the [2 + 2] Cycloadducts 18–21. The thermolysis of the tetraene ether **17** in toluene at 150 °C produced a mixture of intramolecular Diels–Alder adducts (yield 81% after 11 h) with the cis-fused cyclohexene derivative **22** and the trans-fused isomer **34** (ratio 1;4) as main products (Scheme VIII).

Thermolysis (200 °C, 14 h) of a mixture of dipropenylcyclobutanes **18–21**, which was obtained from the acetone-sensitized photolysis of **17**, gave a mixture of products (yield 86%) with two cyclooctadiene derivatives **26** and **27** (ratio 1.3:1) as main compounds.[24]

Thermolysis of 5-(2′-Propenyloxy)-(*E*)-1,3-pentadiene (28). Thermolysis of the triene ether **28** at 150 °C gave two bicyclic cyclohexenes **35** and **36** in 45% yield after 5 h. The cis-fused isomer **35** was the main product (cis;trans = 3:1; Scheme IX). With toluene as solvent, the intramolecular [4 + 2] cycloaddition was complete after 11 h at 150 °C but the isolated cycloadducts were contaminated with the solvent. No bicyclization of the triene ether **28** was achieved in tetrahydrofuran at 80 °C in the presence of CuOTf. Increase of the reaction temperature led to decomposition of the catalyst.

NMR Studies

The structures of all intramolecular cycloadducts of **10**, **17**, and **28** were determined by NMR analysis including COSY, HETCOR, and proton-decoupling studies. Some characteristic features of the NMR spectra are discussed here. For spectroscopic data, see Experimental Section.

The coupling constants of the cyclobutane protons of the [2 + 2] cycloadducts **12** and **13** reveal a typical small trans coupling in the case of **12** ($^3J_{1,7} = {}^3J_{5,6}$ = 3.7 Hz) and a large cis coupling in the case of **13** ($^3J_{1,7} = {}^3J_{5,6}$ = 9.6 Hz). The ^{13}C NMR spectra of **11**, **13**, and **30** show remarkable shifts of sterically interacting C atoms (**11**, C-2/C-8; **13**, C-2/C-8 and C-4/C-10; **30**, C-4/C-8) to lower ppm values according to a γ effect. The NMR data of the dipropenylcyclobutanes **18–21** are comparable to the data of the divinyl compounds **11** and **12**. The methyl groups of a cis- or trans-propenyl configuration show characteristic chemical shifts (cis-CH$_3$: δ ^{1}H = 1.47–1.55 ppm, δ ^{13}C = 13.0–13.5 ppm. trans-CH$_3$: δ ^{1}H = 1.63–1.65 ppm, δ ^{13}C = 17.6–18.0 ppm) in accordance with NMR data given by Berson.[23d]

The structure of the tetracyclic product **16** was confirmed by comparing the ^{1}H NMR data with those of a ^{1}H–^{13}C satellite spectrum of the unsubstituted analogue **37**. The coupling constants of the rigid four-membered-ring structure (**16**, H-1, H-7, H-8, H-11; **37**, H-1, H-2, H-5, H-6) are characteristic. $^4J_{\mathrm{CH,CH}}$ was found to be 6.8 Hz, whereas $^3J_{\mathrm{CH,CH}}$ is near zero.

The structures of the cyclohexenes **31**, **32**, **15**, **33**, **35**, and **36** were determined by comparison of their ^{1}H and ^{13}C NMR spectra. The CH$_2$O protons show characteristic coupling schemes depending on the ring fusion. In the trans-fused compounds **31**, **32**, and **36** the dihedral angle between 1-H′ and 7a-H or 3-H′ and 3a-H is 180°. Therefore, large vicinal coupling constants (>11 Hz) occur. However, the CH$_2$O protons of the cis-fused bicyclic cyclohexenes **15**, **33**, and **35** have medium-sized coupling constants up to 9 Hz. Protons 3a of the trans-fused compounds **31** and **36** have three neighboring axial H atoms (3-H′, 4-H$_{\mathrm{ax}}$, 7a-H; dihedral angle 180°), which characteristically results in three large vicinal coupling constants (>10 Hz). Proton 3a of the vinylcyclohexene **32** with an axial vinyl group only has two axial H neighbors so that the number of large ^3J's is reduced to two (**31**, $^3J_{3\mathrm{a},4\mathrm{ax}}$ = 11.2 Hz; **32**, $^3J_{3\mathrm{a},4\mathrm{eq}}$ = 4.2 Hz). The complete structures of the methylpropenylcyclohexene derivatives **22**, **23**, and **34** were tentatively assigned by comparison of the observed NMR data with those of the vinylcyclohexenes **15** and **31** and with reported ^{1}H NMR data of 3-methyl-4-propenylcyclohexenes.[23d]

Summary

As a result, CuOTf-catalyzed thermally and photochemically induced intramolecular cycloaddition reactions of the bis(diene) ether **10** mainly led to vinylcyclohexene derivatives. The thermal reaction at 80 °C directly gave the trans-fused compound **31** as the major product. The photochemical pathway produced the [2 + 2] cycloadducts **11–13** as intermediates, which interconvert through epimerization at C-6 and C-7 during the irradiation in the presence of CuOTf. The divinylcyclobutanes **11–13** irreversibly formed the ring-enlarged products **14** and **15** via copper(I)-catalyzed, photoinduced [3, 3]- and [1, 3]-rearrangement reactions. The Cope product **14** is the precursor of the tetracyclic product **16** in a photocatalytic process. The cis-fused vinylcyclohexene **15** and the tetracyclic compound **16** were formed in a ratio of 2.5;1. The results are summarized in Scheme X.

The copper(I)-catalyzed, photoinduced [1, 3]- and [3, 3]-rearrangement reactions of the divinylcyclobutanes **11–13** can be applied to dipropenylcyclobutanes, as was shown for the [2 + 2] cycloadducts **18–21** of the bis(diene) ether **17**. **18–21** rearranged to the cis-fused methylpropenylcyclohexene derivatives **22** and **23** via formal [1, 3] migration of the cyclobutane bond and to the cyclooctadiene intermediates **26** and **27** via Cope rearrangement. **26** and **27** are the precursors of the tetracyclic products **24** and **25** under CuOTf-photocatalytic conditions. The products of a [1, 3]- and [3, 3]-rearrangement pathway were equally favored.

The CuOTf-catalyzed photolysis of the triene ether **28** resulted in formation of two [2 + 2] cycloadducts **29** and **30**, but no rearranged products were obtained. In conclusion, vinylcyclobutanes were found to be inactive under copper(I) catalysis in contrast with divinyl- and dipropenylcyclobutanes.

Experimental Section

Materials. Tetrahydrofuran and toluene for photolyses and thermolyses were purified by boiling over NaH and distillation under argon. Tricyclo[3.3.0.0^{2,6}]octane,[9b] 2,4-pentadienol,[20] 2,4-pentadienyl bromide,[20] sorbyl alcohol,[20] sorbyl bromide,[20] CuOTf,[10b] and (n-Bu)$_4$NOTf[22] were prepared according to reported procedures. Cu(OTf)$_2$, CF$_3$SO$_3$H, and acetone (UV-spectroscopic grade) were purchased from Fluka, (n-

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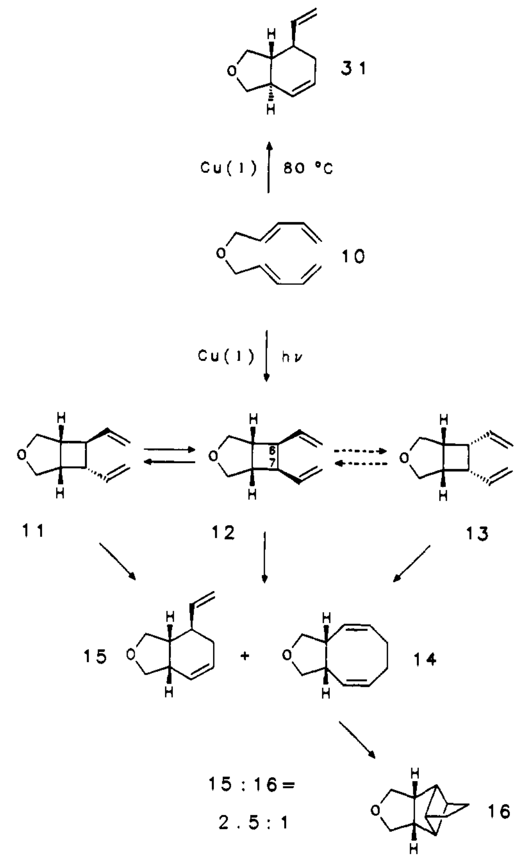
(24) For thermal rearrangement reactions of 1,2-dipropenylcyclobutanes, see ref 23d.

Scheme X



Bu)$_4$NCl and Cu(ClO$_4$)$_2$·6H$_2$O from Janssen; allyl bromide was from Merck-Schuchardt and Cu(BF$_4$)$_2$·6H$_2$O from Strem Chemicals.

Instrumental Analysis. ^{1}H NMR and ^{13}C NMR spectra: Varian VXR 300 (300 MHz/75 MHz), Bruker WM300 (300 MHz/75 MHz); TMS as internal standard; ^nJ with n = 1–5: coupling constant over n bonds; $\sum J$, distance (in hertz) between the first and last peak of a signal. IR spectra: Perkin-Elmer 1700; Perkin-Elmer 257 grating infrared spectrophotometer. MS: Varian MAT 212, Varian MAT CH7A, Finnigan MAT 8230. Microanalyses were performed by Mikroanalytisches Laboratorium der RWTH Aachen and Analytisches Labor des Organisch-Chemischen Institutes der WWU Münster.

Chromatographic Equipment. HPLC: Kontron HPLC pump 420 and LiChrosorb Si 60-5 columns (250 × 20 mm). GLC: Siemens Sichromat 3 or Sichromat 1-4; capillary column 25-m HP-Ultra 2; integrator Spectra Physics 4290. Column chromatography: ICN Alumina B, activity 1.

5,5′-Oxybis[(*E*)-1,3-pentadiene] (10). A mixture of 13.3 g (0.09 mol) of 2,4-pentadienyl bromide, 6.3 g (0.075 mol) of 2,4-pentadienol, 1.1 g (0.004 mol) of tetra-*n*-butylammonium chloride, 30 g of 50% aqueous sodium hydroxide, and 30 mL of dichloromethane was vigorously stirred at room temperature for 4 h. The reaction mixture was poured into 100 mL of water. The layers were separated, and the aqueous phase was extracted with five 50-mL portions of pentane. The combined organic extracts were washed with brine and dried over MgSO$_4$. After evaporation of the solvent, the residue was distilled to give 9.9 g (80%) of **10**: bp 37–38 °C (0.4 mmHg); IR (neat) ν 3085 (=CH$_2$); 3040, 3010 (=CH); 2980, 2920, 2850 (CH); 1660, 1605 (C=C); 1355, 1110, 1050, 1005, 955, 905 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.02 (d/m, $^3J_{4,5}$ = 6.0 Hz, 4 H, 5-H), 5.09 (d/m, $^3J_{1c,2}$ = 10.1 Hz, 2 H, 1-H$_{cis}$), 5.20 (d/m, $^3J_{1t,2}$ = 16.1 Hz, 2 H, 1-H$_{trans}$), 5.77 (d/tr, $^3J_{3,4}$ = 14.4 Hz/$^3J_{4,5}$ = 6.0 Hz, 2 H, 4-H), 6.2–6.41 (m, 4 H, 2-H, 3-H); ^{13}C NMR (CDCl$_3$) δ 70.21 (C-5); 117.46 (C-1); 130.03, 133.21, 136.35 (C-2, C-3, C-4); MS (70 eV) m/z (%) 150 (0.23) [M$^{\bullet+}$], 68 (10.8), 67 (100), 65 (12.8), 55 (6.3), 41 (31.4). Anal. Calcd for C$_{10}$H$_{14}$O: C, 79.96; H, 9.39. Found: C, 79.81; H, 9.30.

1,1′-Oxybis[(*E*,*E*)-2,4-hexadiene] (17). **17** was prepared in the same way as **10** by using 14.5 g (0.09 mol) of sorbyl bromide, 7.4 g (0.075 mol) of sorbyl alcohol, 1.1 g (0.004 mol) of (n-Bu)$_4$NCl, 30 g of 50% aqueous NaOH, and 30 mL of CH$_2$Cl$_2$: yield 11.8 g (80%); bp 52 °C (0.03 mmHg); IR (neat) ν 3020 (=CH); 2960, 2930, 2915, 2880, 2850 (CH); 1660 (C=C); 1450, 1360, 1115, 1080, 1050, 990, 930 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.75 (d/d, $^3J_{5,6}$ = 6.7 Hz/$^4J_{4,6}$ = 1.4 Hz, 6 H, 6-H), 3.96 (d, $^3J_{1,2}$ = 6.5 Hz, 4 H, 1-H), 5.62 (d/tr, $^3J_{2,3}$ = 15.0 Hz/$^3J_{1,2}$ = 6.5 Hz, 2 H, 2-H), 5.69 (d/q, $^3J_{4,5}$ = 14.9 Hz/$^3J_{5,6}$ = 6.7 Hz, 2 H, 5-H), 6,05 (d/d/q, $^3J_{4,5}$ = 14.9 Hz/$^3J_{3,4}$ = 10.4 Hz/$^4J_{4,6}$ = 1.4 Hz, 2 H, 4-H), 6.20 (d/d, $^3J_{2,3}$ = 15.0 Hz/$^3J_{3,4}$ = 10.4 Hz, 2 H, 3-H); ^{13}C NMR (CDCl$_3$) δ 17.56 (C-6); 69.79 (C-1); 126.45, 129.00, 130.59, 132.47 (C-2, C-3, C-4, C-5); MS (70 eV) m/z (%) 178 (0.85) [M$^{\bullet+}$], 82 (15.0), 81 (100), 79 (29.5), 69 (5.1), 67 (17.4), 53 (12.5), 41 (27.5). For a different preparation method for **17**, see ref 25.

5-(2′-Propenyloxy)-(*E*)-1,3-pentadiene (28). **28** was prepared in the same way as **10** by using 27.2 g (0.225 mol) of allyl bromide, 12.6 g (0.15 mol) of 2,4-pentadienol, 2.1 g (0.0075 mol) of (n-Bu)$_4$NCl, 60 g of 50% aqueous NaOH, and 60 mL of CH$_2$Cl$_2$: yield 13,8 g (74%); bp 70–71 °C (40 mmHg); IR (neat) ν 3085 (=CH$_2$); 3040, 3015 (=CH); 2980, 2920, 2850 (CH); 1660, 1650, 1605 (C=C); 1355, 1110, 1075, 1055, 1005, 955, 925, 905 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.98 (d/tr, $^3J_{1',2'}$ = 5.7 Hz/^4J = 1.3 Hz, 2 H, 1′-H), 4.02 (d/m, $^3J_{4,5}$ = 6.0 Hz, 2 H, 5-H), 5.09 (d/m, $^3J_{1c,2}$ = 10.1 Hz, 1 H, 1-H$_{cis}$), 5.17 (d/m, $^3J_{2',3'c}$ = 10.4 Hz, 1 H, 3′-H$_{cis}$), 5.20 (d/m, $^3J_{1t,2}$ = 16.1 Hz, 1 H, 1-H$_{trans}$), 5.28 (d/m, $^3J_{2',3't}$ = 17.1 Hz, 1 H, 3′-H$_{trans}$), 5.77 (d/tr, $^3J_{3,4}$ = 14.4 Hz/$^3J_{4,5}$ = 6.0 Hz, 1 H, 4-H), 5.91 (d/d/tr, $^3J_{2',3'1}$ = 17.1 Hz/$^3J_{2',3'c}$ = 10.4 Hz/$^3J_{1',2'}$ = 5.7 Hz, 1 H, 2′-H), 6.2–6.41 (m, 2 H, 2-H, 3-H); ^{13}C NMR (CDCl$_3$) δ 70.17, 71.10 (C-1′, C-5); 116.95, 117.43 (C-1, C-3′); 130.06, 133.13, 134,74, 136.35 (C-2, C-2′, C-3, C-4); MS (70 eV) m/z (%) 124 (0.13) [M$^{\bullet+}$], 83 (6.8), 81 (7.3), 80 (16.7), 68 (12.3), 67 (73.7), 66 (10.6), 65 (11.9), 57 (8.9), 56 (5.0), 55 (100), 54 (15.4), 53 (13.9), 42 (5.5), 41 (86.5). Anal. Calcd for C$_8$H$_{12}$O: C, 77.38; H, 9.74. Found: C, 77.12; H, 9.63.

Irradiation, Thermolysis, and Product Isolation. Irradiations were carried out under argon in Pyrex photoreactors (45 and 85 mL) with a water-cooled immersion well (quartz or Pyrex glass). The reaction mixtures were stirred magnetically and irradiated internally with a high-pressure mercury lamp HPK 125 W (Philips). All thermolyses were carried out with magnetic stirring under argon in glass autoclaves (10 or 50 mL). Product formation and conversion of starting material were monitored by GLC analysis combined with ^{13}C NMR spectroscopy. After completion of the reaction, the solvent was removed by rotary evaporation and the residue purified by filtration over basic alumina (3% ethyl acetate in cyclohexane as eluent) or distillation under reduced pressure. Product ratios were determined by ^{13}C NMR (CH$_2$O signals). The product mixtures were separated by HPLC with 3% ethyl acetate in cyclohexane as eluting solvent (flow 10 mL/min). All products were isolated as colorless liquids.

Acetone-Sensitized Photolysis of 10. A 1.28-g sample (8.5 mmol) of **10** in 85 mL of acetone (0.1 M) was irradiated for 3 h under argon by using a Pyrex immersion well. After removal of the solvent, the residue was distilled: bp 29–30 °C (0.7 mmHg); yield 1.13 g (88%). For product ratio, see Table 1. Products **11–14** were separated by HPLC.

(1α,5α,6α,7β)-6,7-Diethenyl-3-oxabicyclo[3,2,0]heptane (11): IR (neat) ν 3080 (=CH$_2$); 2960, 2920, 2845 (CH); 1640 (C=C); 1085, 1040, 995, 910 cm^{-1}; NMR analysis by COSY, HETCOR, and proton decoupling at 5.9 ppm; ^{1}H NMR (CDCl$_3$) δ 2.55 ("q", $\sum J$ = 21 Hz, 1 H, 6-H), 2.73 ("tr"/d, $\sum J$ = 18 Hz, $^3J_{4,5}$ = 4.4 Hz, 1 H, 5-H), 2.80 ("q", $\sum J$ = 24 Hz, 1 H, 7-H), 2.91 ("q", $\sum J$ = 22.8 Hz, 1 H, 1-H), 3.39 (d/d, $^2J_{4,4H'}$ = 8.9 Hz/$^3J_{4,5}$ = 4.4 Hz, 1 H, 4-H), 3.43 (d/d, $^2J_{2,2H'}$ = 9.8 Hz/$^3J_{1,2}$ = 6.5 Hz, 1 H, 2-H), 3.79 (d, $^2J_{4,4H'}$ = 8.9 Hz, 1 H, 4-H′), 4.06 (d/d, $^2J_{2,2H'}$ = 9.8 Hz/$^3J_{1,2H'}$ = 1.4 Hz, 1 H, 2-H′), 4.95 (d/tr, $^3J_{10,11c}$ = 10.2 Hz/$^2J_{11c,11t}$ = $^4J_{6,11c}$ = 1.5 Hz, 1 H, 11-H$_{cis}$), 4.98 (d/tr, $^3J_{10,11t}$ = 17.2 Hz/$^2J_{11c,11t}$ = $^4J_{6,11t}$ = 1.5 Hz, 1 H, 11-H$_{trans}$), 5.01 (d/d/d, $^3J_{8,9t}$ = 17.2 Hz/$^2J_{9c,9t}$ = 2.0 Hz/$^4J_{7,9t}$ = 1.2 Hz, 1 H, 9-H$_{trans}$), 5,06 (d/d/d, $^3J_{8,9c}$ = 10.4 Hz/$^2J_{9c,91}$ = 2.0 Hz/$^4J_{7,9c}$ = 1.2 Hz, 1 H, 9-H$_{cis}$), 5.86 (d/d/d, $^3J_{8,9t}$ = 17.2 Hz/$^3J_{8,9c}$ = 10.4 Hz/$^3J_{7,8}$ = 7.1 Hz, 1 H, 8-H), 5,92 (d/d/d, $^3J_{10,11t}$ = 17.2 Hz/$^3J_{10,11c}$ = 10.2 Hz/$^3J_{6,10}$ = 6.8 Hz, 1 H, 10-H); ^{13}C NMR (CDCl$_3$) δ 39.51 (C-1), 42.21 (C-5), 42.69 (C-7), 45,78 (C-6), 68.67 (C-2), 72.51 (C-4), 113.04 (C-11), 115.61 (C-9), 137.07 (C-8), 140.81 (C-10); MS (70 eV) m/z (%) 150 (0.02) [M$^{\bullet+}$], 91 (7.9), 80 (5.1), 79 (19.8), 78 (6.8), 77 (7.9), 69 (11.8), 68 (14.3), 67 (100), 66 (7.0), 65 (14.3), 55 (10.8), 53 (5.8), 41 (30.7). Anal. Calcd for C$_{10}$H$_{14}$O; C, 79.96; H, 9.39. Found: C, 79.68; H, 9.52.

(1α,5α,6α,7α)-6,7-Diethenyl-3-oxabicyclo[3,2,0]heptane (12); IR (neat) ν 3080 (=CH$_2$); 2980, 2960, 2920, 2845 (CH); 1640, (C=C); 1075, 1055, 1030, 995, 910 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 2,43 (m, $\sum J$ = 8,9 Hz, $^3J_{1,7}$ = $^3J_{5,6}$ = 3.7 Hz, 2 H, 1-H, 5-H), 2.73 (m, $\sum J$ = 11.4 Hz, $^3J_{1,7}$ = $^3J_{5,6}$ = 3.7 Hz, 2 H, 6-H, 7-H), 3,27 (d/d/m, $^2J_{2,2H'}$ = $^2J_{4,4H'}$ = 9.7 Hz/$^3J_{1,2}$ = $^3J_{4,5}$ = 5.2 Hz, 2 H, 2-H, 4-H), 3.73 (d, $^2J_{2,2H'}$ = $^2J_{4,4H'}$ = 9,7 Hz, 2 H, 2-H′, 4-H′), 4.90 (d/m, $^3J_{8,9t}$ = $^3J_{10,11t}$ = 17.1 Hz, 2 H, 9-H$_{trans}$, 11-H$_{trans}$), 4.98 (d/m, $^3J_{8,9c}$ = $^3J_{10,11c}$ = 10.4 Hz, 2 H, 9-H$_{cis}$, 11-H$_{cis}$), 5.76–5.89 ("d/d/d", $^3J_{8,9t}$ = $^3J_{10,11t}$ = 17,1 Hz/$^3J_{8,9c}$ = $^3J_{10,11c}$ = 10.4 Hz/$^3J_{7,8}$ = $^3J_{6,10}$ = 7.7 Hz, 2 H, 8-H, 10-H); ^{13}C NMR (C$_6$D$_6$) δ 41.80, 45.01 (C-1/C-5, C-6/C-7); 73.34 (C-2, C-4); 114.19 (C-9, C-11); 139.30 (C-8, C-10); MS (70 eV) m/z (%) 150 (0.42) [M$^{\bullet+}$], 119 (7.8), 117

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(25) Stepanova, O. S.; Ganin, E. V. *Ukr. Khim. Zh.* **1977**, *43*, 168.

(6.7), 106 (7.5), 105 (13.8), 92 (8.8), 91 (17.8), 83 (7.3), 82 (5.5), 80 (9.3), 79 (27.4), 78 (9.3), 77 (9.7), 69 (8.0), 68 (14.9), 67 (100), 66 (11.6), 65 (13.2), 55 (8.2), 53 (5.6), 41 (29.4). Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.67; H, 9.24.

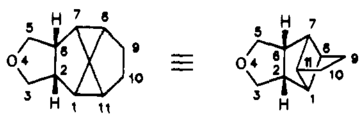
(1α,5α,6β,7β)-6,7-Diethenyl-3-oxabicyclo[3.2.0]heptane (13): IR (neat) ν 3075 (=CH$_2$); 2960, 2925, 2845 (CH); 1635 (C=C); 1080, 1005, 915 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.04 (m, $\sum J$ = 15.4 Hz, $^3J_{1,7} = {}^3J_{5,6}$ = 9.6 Hz, 2 H, 1-H, 5-H), 3.22 (m, $\sum J$ = 19.6 Hz, $^3J_{1,7} = {}^3J_{5,6}$ = 9.6 Hz, 2 H, 6-H, 7-H), 3.36 (d/d/m, $^2J_{2,2H'} = {}^2J_{4,4H'}$ = 10.2 Hz/$^3J_{1,2} = {}^3J_{4,5}$ = 5.8 Hz, 2 H, 2-H, 4-H), 4.05 (d, $^2J_{2,2H'} = {}^2J_{4,4H'}$ = 10.2 Hz, 2 H, 2-H′, 4-H′), 4.94 (d/d, $^3J_{8,9t} = {}^3J_{10,11t}$ = 17.0 Hz/$^2J_{9c,9t} = {}^2J_{11c,11t}$ = 2.4 Hz, 2 H, 9-H$_{trans}$, 11-H$_{trans}$), 5.02 (d/d, $^3J_{8,9c} = {}^3J_{10,11c}$ = 10.2 Hz/$^2J_{9c,9t} = {}^2J_{11c,11t}$ = 2.4 Hz, 2 H, 9-H$_{cis}$, 11-H$_{cis}$), 6.07 ("d/tr", $^3J_{8,9t} = {}^3J_{10,11t}$ = 17.0 Hz/$^3J_{8,9c} = {}^3J_{10,11c} = {}^3J_{7,8} = {}^3J_{6,10}$ = 10.2 Hz, 2 H, 8-H, 10-H); ^{13}C NMR (CDCl$_3$) δ 40.61, 42.07 (C-1/C-5, C-6/C-7); 69.47 (C-2, C-4); 116.94 (C-9, C-11); 135.56 (C-8, C-10); MS (70 eV) *m/z* (%) 150 (0.09) $[M^{\bullet+}]$; 106 (6.5), 105 (5.2), 91 (10.9), 80 (6.6), 79 (21.3), 78 (7.3), 77 (7.6), 69 (17.9), 68 (15.3), 67 (100), 66 (6.8), 65 (14.2), 55 (11.1), 53 (5.0), 41 (25.3). Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 80.11; H, 9.48.

1,3,3a,6,7,9a-Hexahydro-*cis*-cycloocta[*c*]furan (14): IR (neat) ν 3010 (=CH); 2960, 2930, 2890, 2860 (CH); 1650 (C=C); 1080, 1060, 1020, 1005, 920, 760, 695 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.06 (m, 2 H, 6-H, 7-H), 2.61 (m, 2 H, 6-H′, 7-H′), 3.32 (m, 2 H, 3a-H, 9a-H), 3.61 (d/d/m, $^2J_{1,1H'} = {}^2J_{3,3H'}$ = 8.0 Hz/$^3J_{1,9a} = {}^3J_{3,3a}$ = 6.1 Hz, 2 H, 1-H, 3-H), 4.02 (d/d/m, $^2J_{1,1H'} = {}^2J_{3,3H'}$ = 8.0 Hz/$^3J_{1H',9a} = {}^3J_{3H',3a}$ = 6.9 Hz, 2 H, 1-H′, 3-H′), 5.40 (d/m, $^3J_{4,5} = {}^3J_{8,9}$ = 11.1 Hz, 2 H) and 5.59 (m, 2 H, 4-H, 9-H and 5-H, 8-H); ^{13}C NMR (CDCl$_3$) δ 27.99 (C-6, C-7); 43.61 (C-3a, C-9a); 73.98 (C-1, C-3); 128.99, 129.54 (C-4/C-9, C-5/C-8); MS (70 eV) *m/z* (%) 150 (1.5) $[M^{\bullet+}]$, 132 (6.3), 121 (8.1), 119 (15.6), 117 (12.1), 109 (5.1), 106 (8.2), 105 (31.1), 104 (6.4), 93 (8.8), 92 (27.4), 91 (47.4), 84 (5.6), 83 (28.0), 82 (15.2), 81 (11.1), 80 (22.2), 79 (64.1), 78 (14.2), 77 (19.6), 69 (12.5), 68 (9.8), 67 (100), 66 (33.3), 65 (13.9), 55 (8.6), 53 (8.6), 51 (6.6), 41 (31.7). Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.50; H, 9.40.

CuOTf-Catalyzed Photolysis of 10. A homogeneous solution of the tetraene ether **10** (1.28 g, 8.5 mmol) in 85 mL of THF (0.1 M) with 43 mg (0.17 mmol, 2 mol %) of CuOTf was irradiated for 5 days under argon by using a quartz immersion well. Evaporation of the solvent gave a brown, oily residue, which was purified by filtration over basic alumina. Yield 0.81 g (63%). **15** and **16** (ratio 2.5:1; see Table I) were separated by HPLC.

(3aα,4α,7aα)-4-Ethenyl-1,3,3a,4,5,7a-hexahydroisobenzofuran (15): IR (neat) ν 3080 (=CH$_2$); 3020 (=CH); 2970, 2920, 2880, 2860 (CH); 1650, 1640 (C=C); 1080, 995, 915, 720 cm^{-1}; NMR analysis by proton decoupling at 2.75 ppm; ^{1}H NMR (CDCl$_3$) δ 1.90 (m, $\sum J$ = 35 Hz, 1 H, 5-H′), 2.12 (m, $\sum J$ = 35 Hz, 3 H, 3a-H, 4-H, 5-H), 2.75 (m, 1 H, 7a-H), 3.39 (d/d, $^3J_{1H',7a}$ = 9.0 Hz/$^2J_{1,1H'}$ = 8.0 Hz, 1 H, 1-H′), 3.78 (d/d, $^2J_{3,3H'}$ = 8.9 Hz/$^3J_{3H',3a}$ = 2.7 Hz, 1 H, 3-H′), 3.91 (d/d, $^2J_{3,3H'}$ = 8.9 Hz/$^3J_{3,3a}$ = 6.2 Hz, 1 H, 3-H), 4.01 (tr, $^2J_{1,1H'} = {}^3J_{1,7a}$ = 8.0 Hz, 1 H, 1-H), 5.02 (d/d, $^3J_{8,9c}$ = 10.2 Hz/$^2J_{9c,9t}$ = 1.7 Hz, 1 H, 9-H$_{cis}$), 5.07 (d/d, $^3J_{8,9t}$ = 17.3 Hz/$^2J_{9c,9t}$ = 1.7 Hz, 1 H, 9-H$_{trans}$), 5.66 (d/d/d, $^3J_{8,9t}$ = 17.3 Hz/$^3J_{8,9c}$ = 10.2 Hz/$^3J_{4,8}$ = 7.4 Hz, 1 H, 8-H), 5.68 (d/d/d/d, $^3J_{6,7}$ = 10.0 Hz/$^3J_{7,7a}$ = 3.8 Hz/$^4J_{5,7}$/$^4J_{5H',7}$ = 2.7 Hz/1.2 Hz, 1 H, 7-H), 5.82 (d/d/tr, $^3J_{6,7}$ = 10.0 Hz/$^3J_{5,6}$, $^3J_{5H',6}$ = 5.1, 2.1 Hz/$^4J_{6,7a}$ = 2.1 Hz, 1 H, 6-H); ^{13}C NMR (CDCl$_3$) δ 30.21 (C-5); 39.14, 39.25, 41.20 (C-3a, C-7a, C-4); 72.13, 72.76 (C-1, C-3); 115.04 (C-9); 125.67, 127.22 (C-6, C-7); 141.75 (C-8); MS (70 eV) *m/z* (%) 150 (1.2) $[M^{\bullet+}]$, 132 (8.1), 131 (6.0), 129 (7.5), 121 (6.2), 120 (5.3), 119 (18.9), 118 (6.3), 117 (22.9), 115 (8.5), 108 (7.8), 107 (7.9), 106 (21.3), 105 (100), 104 (15.9), 103 (16.1), 94 (7.8), 93 (15.4), 92 (33.1), 91 (81.1), 83 (6.0), 82 (10.7), 81 (5.8), 80 (28.4), 79 (93.3), 78 (35.9), 77 (68.8), 74 (6.9), 71 (6.9), 69 (18.1), 68 (8.1), 67 (31.9), 66 (27.8), 65 (25.9), 63 (10.4), 58 (5.2), 55 (8.8), 53 (8.8), 52 (6.9), 51 (26.0), 50 (11.9), 44 (18.2), 43 (7.1), 41 (24.4). Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.70; H, 9.45.

(2α,6α)-4-Oxatetracyclo[6.3.00^{2,6},0^{7,11}]undecane (16): IR (neat) ν 2950, 2875, 2845 (CH); 1095, 910, 720 cm^{-1}; NMR analysis by proton decoupling at 2.47 ppm; ^{1}H NMR (C$_6$D$_6$) δ 1.50 (m ("tr"), $^3J_{9,10}$ = 6.5 Hz, 2 H, CH$_2$), 1.53 (s, 2 H, 1-H, 7-H), 1.68 (m ("tr"), $^3J_{9,10}$ = 6.5 Hz, 2 H, CH$_2$), 1.85 (d/tr, $^4J_{8,11}$ = 6.7 Hz/$^3J_{10,11}$ = 1.3 Hz, 1 H, 11-H), 2.47 (m, 2 H, 2-H, 6-H), 2.61 (d, $^4J_{8,11}$ = 6.7 Hz, 1 H, 8-H), 3.49 (d/d/m, $^2J_{3,3H'} = {}^2J_{5,5H'}$ = 9.1 Hz/$^3J_{2,3} = {}^3J_{5,6}$ = 6.4 Hz, 2 H, 3-H, 5-H), 3.62 (d, $^2J_{3,3H'} = {}^2J_{5,5H'}$ = 9.1 Hz, 2 H, 3-H′, 5-H′); ^{13}C NMR (CDCl$_3$) δ 23.40, 25.18 (C-9, C-10); 44.40, 44.99, 53.66, 55.06 (C-2/C-6, C-1/C-7, C-8, C-11); 71.73 (C-3, C-5); MS (70 eV) *m/z* (%) 150 (1.7) $[M^{\bullet+}]$, 132 (8.0), 121 (9.8), 120 (5.9), 119 (30.5), 118 (5.8), 117 (29.0), 109 (9.5), 106 (9.5), 105 (38.7), 104 (12.7), 103 (7.0), 93 (12,8), 92 (41.2), 91 (84.9), 84 (7.8), 83 (25.5), 82 (19.1), 81 (14.7), 80 (31.4), 79 (100), 78 (25.5), 77 (34.6), 69 (19.4), 68 (6.3), 67 (78.9), 66 (47.6), 65 (14.5), 55 (8.6), 54 (12.2), 53 (11.3), 52 (5.8), 51 (12.2). Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.62; H, 9.29.



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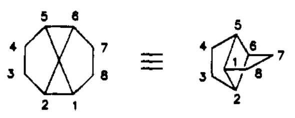
Tricyclo[3.3.0.0^{2,6}]octane (37): ^{1}H NMR (CDCl$_3$) δ 1.71 (s, 8 H, CH$_2$), 1.81 (s, 4 H, CH); ^{1}H NMR ^{13}C satellite spectrum (CDCl$_3$) 1.71 (d/"tr", $^1J_{C,H}$ = 133 Hz/$^3J_{CH_2,CH_2}$ = 6.5 Hz, 8 H, CH$_2$), 1.81 (d/d, $^1J_{C,H}$ = 148 Hz/$^4J_{CH,CH}$ = 6.8 Hz, $^3J_{CH,CH} \leq 1$ Hz/$^3J_{CH,CH_2} \leq 1$ Hz, 4 H, CH); ^{13}C NMR (CDCl$_3$) δ 25.49 (CH$_2$), 50.76 (CH); ^{13}C NMR proton-coupled spectrum (CDCl$_3$) δ 25.49 (tr/m, $^1J_{C,H}$ = 133 Hz, CH$_2$), 50.76 (d/m, $^1J_{C,H}$ = 148 Hz, CH).



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Acetone-Sensitized Photolysis of 17. A 1.51-g sample (8.5 mmol) of **17** in 85 mL of acetone (0.1 M) was irradiated for 3 h under argon by using a Pyrex immersion well. After removal of the solvent, the residue was distilled: bp 40 °C (0.02 mmHg); yield 1.31 g (87%). For product ratio, see Table III. The main products **18–21** were separated by HPLC and isolated in purities greater than 80%. Anal. of the product mixture Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.66; H, 10.18.

(1α,5α,6α,7β)-6,7-(*Z*,*E*)-Dipropenyl-3-oxabicyclo[3.2.0]heptane (18): IR (neat) ν 3010 (=CH); 2960, 2920, 2850 (CH); 1080, 970, 910, 710 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.55 (d/d, $^3J_{12,13}$ = 6.6 Hz/$^4J_{11,13}$ = 1.5 Hz, 3 H, 13-H), 1.65 (d, $^3J_{9,10}$ = 5.7 Hz, 3 H, 10-H), 2.56 ("tr"/d, $\sum J$ = 18 Hz/$^3J_{4,5}$ = 4.7 Hz, 1 H, 5-H), 2.69 (m, 2 H, 6-H, 7-H), 2.87 ("q", $\sum J$ = 22.5 Hz, 1 H, 1-H), 3.37 (d/d, $^2J_{4,4H'}$ = 9.1 Hz/$^3J_{4,5}$ = 4.7 Hz, 1 H, 4-H), 3.40 (d/d, $^2J_{2,2H'}$ = 9.7 Hz/$^3J_{1,2}$ = 6.5 Hz, 1 H, 2-H), 3.79 (d, $^2J_{4,4H'}$ = 9.1 Hz, 1 H, 4-H′), 4.06 (d, $^2J_{2,2H'}$ = 9.7 Hz, 1 H, 2-H′), 5.29–5.55 (m, 4 H, 8-H, 9-H, 11-H, 12-H); ^{13}C NMR (CDCl$_3$) δ 13.50 (C-13); 18.01 (C-10); 39.96, 41.06, 43.24, 43.77 (C-1, C-5, C-6, C-7); 68.86 (C-2); 72.87 (C-4); 123.56, 126.19, 130.22, 134.53 (C-8, C-9, C-11, C-12); MS (70 eV) *m/z* (%) 178 (0.4) $[M^{\bullet+}]$, 163 (1.4), 93 (10.0), 91 (8.5), 82 (20.2), 81 (100), 79 (26.0), 77 (9.0), 69 (10.5), 67 (17.5), 65 (5.0), 55 (5.5), 53 (12.0), 43 (5.8), 41 (24.0).

(1α,5α,6α,7β)-6,7-(*E*,*E*)-Dipropenyl-3-oxabicyclo[3.2.0]heptane (19): IR (neat) ν 3010 (=CH); 2960, 2920, 2850 (CH); 1075, 970, 910, 710 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.63 (d, ^3J = 5.5 Hz, 3 H, CH$_3$), 1.65 (d, ^3J = 5.5 Hz, 3 H, CH$_3$), 2.38 ("q", $\sum J$ = 21 Hz, 1 H, 6-H), 2.62 (m, 2 H, 5-H, 7-H), 2.82 ("q", $\sum J$ = 22.5 Hz, 1 H, 1-H), 3.35 (d/d, $^2J_{4,4H'}$ = 9.1 Hz/$^3J_{4,5}$ = 4.3 Hz, 1 H, 4-H), 3.39 (d/d, $^2J_{2,2H'}$ = 9.6 Hz/$^3J_{1,2}$ = 6.8 Hz, 1 H, 2-H), 3.74 (d, $^2J_{4,4H'}$ = 9.1 Hz, 1 H, 4-H′), 4.03 (d, $^2J_{2,2H'}$ = 9.6 Hz, 1 H, 2-H′), 5.29–5.55 (m, 4 H, 8-H, 9-H, 11-H, 12-H); ^{13}C NMR (CDCl$_3$) δ 17.85, 18.01 (C-10, C-13); 39.78, 42.37, 42.81, 45.94 (C-1, C-5, C-6, C-7); 68.75 (C-2); 72.56 (C-4); 123.74, 126.19, 130.22, 134.18 (C-8, C-9, C-11, C-12); MS (70 eV) *m/z* (%) 178 (0.6) $[M^{\bullet+}]$, 163 (1.8), 93 (10.5), 91 (8.0), 82 (19.5), 81 (100), 79 (27.0), 77 (9.5), 69 (9.0), 67 (17.5), 65 (5.5), 55 (5.5), 53 (11.0), 41 (22.5).

(1α,5α,6α,7α)-6,7-(*Z*,*E*)-Dipropenyl-3-oxabicyclo[3.2.0]heptane (20): IR (neat) ν 3015 (=CH); 2960, 2915, 2840 (CH); 1075, 1030, 970, 910, 705 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 1.47 (d/d $^3J_{12,13}$ = 6.5 Hz/$^4J_{11,13}$ = 1.2 Hz, 3 H, 13-H), 1.63 (d, $^3J_{9,10}$ = 6.4 Hz, 3 H, 10-H), 2.37 (m, 1 H, CH), 2.48 (m, 1 H, CH), 2.79 (m, 1 H, CH), 3.11 (tr/d, ^3J = 9.5, 4.7 Hz, 1 H, CH), 3.35 (m, 2 H, 2-H, 4-H), 3.85 (d, ^2J = 9.1 Hz, 1 H) and 3.87 (d, ^2J = 9.1 Hz, 1 H, 2-H′, 4-H′), 5.31 (d/q, $^3J_{8,9}$ = 15.2 Hz/$^3J_{9,10}$ = 6.4 Hz, 1 H, 9-H), 5.49 (d/q, $^3J_{11,12}$ = 10.9 Hz/$^3J_{12,13}$ = 6.5 Hz, 1 H, 12-H), 5.60 (m, 2 H, 8-H, 11-H); ^{13}C NMR (CDCl$_3$) δ 13.06 (C-13); 17.67 (C-10); 38.54, 42.24, 43.57, 43.60 (C-1, C-5, C-6, C-7); 73.42, 73.49 (C-2, C-4); 123.93, 124.49, 131.28, 131.67 (C-8, C-9, C-11, C-12); MS (70 eV) *m/z* (%) 178 (0.8) $[M^{\bullet+}$, 163 (2.2), 105 (6.0), 93 (8.5), 91 (12.5), 82 (19.5), 81 (100), 80 (7.0), 79 (36.5), 77 (13.0), 69 (14.0), 67 (21.0), 65 (8.0), 55 (7.5), 53 (17.0), 41 (36.0).

(1α,5α,6α,7α)-6,7-(*E*,*E*)-Dipropenyl-3-oxabicyclo[3.2.0]heptane (21): IR (neat) ν 3015 (=CH); 2960, 2915, 2850 (CH); 1075, 1030, 970, 910, 705 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 1.63 (d/d, $^3J_{9,10} = {}^3J_{12,13}$ = 6.4 Hz/$^4J_{8,10} = {}^4J_{11,13}$ = 1.5 Hz, 6 H, 10-H, 13-H), 2.47 (m, 2 H, 1-H, 5-H), 2.78 (m, 2 H, 6-H, 7-H), 3.35 (d/d/m, $^2J_{2,2H'} = {}^2J_{4,4H'}$ = 9.4 Hz/$^3J_{1,2} = {}^3J_{4,5}$ = 5.1 Hz, 2 H, 2-H, 4-H), 3.85 (d, $^2J_{2,2H'} = {}^2J_{4,4H'}$ = 9.4 Hz, 2 H, 2-H′, 4-H′), 5.32 (d/q, $^3J_{8,9} = {}^3J_{11,12}$ = 15.2 Hz/$^3J_{9,10} = {}^3J_{12,13}$ = 6.4 Hz, 2 H, 9-H, 12-H), 5.59 (d/m, $^3J_{8,9} = {}^3J_{11,12}$ = 15.2 Hz, 2 H, 8-H, 11-H); ^{13}C NMR (CDCl$_3$) δ 17.67 (C-10, C-13); 42.18, 43.96 (C-1/C-5, C-6/C-7); 73.31 (C-2, C-4); 124.55, 131.74 (C-8/C-11, C-9/C-12); MS (70 eV) *m/z* (%) 178 (1.3) $[M^{\bullet+}]$, 163 (1.9), 147 (5.0), 105 (5.5), 93 (8.5), 91 (9.0), 82 (21.5), 81 (100), 80 (6.0), 79 (27.0), 77 (9.5), 69 (12.0), 67

(17.0), 67 (17.0), 65 (5.0), 55 (5,5), 53 (12.0), 41 (27.0).

CuOTf-Catalyzed Photolysis of 17. A homogeneous solution of the tetraene ether **17** (1.51 g, 8.5 mmol) in 85 mL of THF (0.1 M) with 43 mg (0.17 mmol, 2 mol%) of CuOTf was irradiated for 5 days under argon by using a quartz immersion well. Evaporation of the solvent gave a brown, oily residue, which was purified by bulb-to-bulb distillation at 50 °C (0.02 mmHg). Yield 0.68 g (45%). For product ratio, see Table IV. The main products **22–25** were separated by HPLC and isolated in purities greater than 80%. Anal. of the product mixture Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.84; H, 10.12.

(3aα,4α,5β,7aα)-5-Methyl-4-(*E*)-propenyl-1,3,3a,4,5,7a-hexahydroisobenzofuran (22): IR (neat) ν 3020 (=CH); 2960, 2930, 2870 (CH); 1650 (C=C); 1095, 1075, 1060, 1030, 970, 910 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (d, $^3J_{5,CH_3}$ = 7.2 Hz, 3 H, CH_3), 1.55 (m, 1 H, CH), 1.67 (d/d, $^3J_{9,10}$ = 6.4 Hz/$^4J_{8,10}$ = 1.6 Hz, 3 H, 10-H), 1.89 (m, 1 H, CH), 2.03 (m, 1 H, CH), 2.71 (m, 1 H, CH), 3.31 (d/d, $^2J_{1,1H'}$ = 8.0 Hz/$^3J_{1H',7a}$ = 9.8 Hz, 1 H, 1-H′), 3.74 (d/d, $^2J_{3,3H'}$ = 8.8 Hz/$^3J_{3H',3a}$ = 2.4 Hz, 1 H, 3-H′), 3.81 (d/d, $^2J_{3,3H'}$ = 8.8 Hz/$^3J_{3,3a}$ = 6.1 Hz, 1 H, 3-H), 3.98 (tr, $^2J_{1,1H'}$ = $^3J_{1,7a}$ = 8.0 Hz, 1 H, 1-H), 5.02 (d/d/q, $^3J_{8,9}$ = 15.2 Hz/$^3J_{4,8}$ = 9.2 Hz/$^4J_{8,10}$ = 1.6 Hz, 1 H, 8-H), 5.45 (d/q, $^3J_{8,9}$ = 15.2 Hz/$^3J_{9,10}$ = 6.4 Hz, 1 H, 9-H), 5.59 (m, 2 H, 6-H, 7-H); ^{13}C NMR ($CDCl_3$) δ 17.91, 19.76 (CH_3); 34.35, 39.61, 41.82, 46.71 (C-3a, C-4, C-5, C-7a); 72.51, 72.78 (C-1, C-3); 124.09, 127.39, 133.42, 134.47 (C-6, C-7, C-8, C-9); MS (70 eV) *m/z* (%) 178 (5.2) [$M^{•+}$], 163 (3.4), 149 (7.8), 147 (6.4), 134 (5.3), 133 (6.0), 122 (8.0), 121 (5.0), 119 (8.5), 107 (5.5), 106 (7.0), 105 (17.0), 95 (6.5), 94 (6.0), 93 (10.0), 91 (19.0), 82 (25.0), 81 (100), 80 (8.5), 79 (21.5), 77 (13.0), 69 (10.5), 67 (19.5), 65 (6.0), 55 (8.5), 53 (8.5), 41 (17.5).

(3aα,4α,5β,7aα)-5-Methyl-4-(*Z*)-propenyl-1,3,3a,4,5,7a-hexahydroisobenzofuran (23): IR (neat) ν 3020 (=CH); 2960, 2920, 2870 (CH); 1650 (C=C); 1090, 1065, 1030, 970, 910, 730, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (d, $^3J_{5,CH_3}$ = 7.0 Hz, 3 H, CH_3), 1.62 (d/d, $^3J_{9,10}$ = 6.9 Hz/$^4J_{8,10}$ = 1.8 Hz, 3 H, 10-H), 1.63 (m, 1 H, CH), 1.88 (m, 1 H, CH), 2.02 (m, 1 H, CH), 2.71 (m, 1 H, CH), 3.38 (d/d, $^2J_{1,1H'}$ = 8.0 Hz/$^3J_{1H',7a}$ = 9.8 Hz, 1 H, 1-H′), 3.63 (d/m, $^2J_{3,3H'}$ = 8.7 Hz, 1 H, 3-H′), 3.81 (d/d, $^2J_{3,3H'}$ = 8.7 Hz/$^3J_{3,3a}$ = 5.6 Hz, 1 H, 3-H), 4.00 (tr, $^2J_{1,1H'}$ = $^3J_{1,7a}$ = 8.0 Hz, 1 H, 1-H), 5.02 ("d/d/q", $^3J_{8,9}$ = 11.0 Hz/$^3J_{4,8}$ = 9.5 Hz/$^4J_{8,10}$ = 1.8 Hz, 1 H, 8-H), 5.41 (m, 1 H, 9-H), 5.63 (m, 2 H, 6-H, 7-H); ^{13}C NMR ($CDCl_3$) δ 17.30, 19.50 (CH_3); 34.83, 39.54, 40.40, 42.54 (C-3a, C-4, C-5, C-7a); 72.67, 72.83 (C-1, C-3); 124.28, 125.92, 133.28, 134.37 (C-6, C-7, C-8, C-9); MS (70 eV) *m/z* (%) 178 (8.0) [$M^{•+}$], 163 (3.6), 149 (8.9), 147 (20.0), 145 (5.8), 134 (5.8), 133 (10.8), 131 (9.0), 122 (5.3), 121 (7.1), 120 (7.7), 119 (21.9), 117 (6.9), 107 (11.0), 106 (9.1), 105 (29.8), 95 (11.1), 94 (6.8), 93 (21.2), 92 (8.7), 91 (45.3), 82 (22.8), 81 (100), 80 (11.5), 79 (35.6), 78 (6.1), 77 (20.2), 69 (16.8), 68 (6.6), 67 (25.5), 65 (12.0), 55 (23.6), 53 (17.4), 51 (6.7), 41 (62.1).

(2α,6α)-*cis*-9,10-Dimethyl-4-oxatetracyclo[6.3.0.0^{2,6}.0^{7,11}]undecane (24): IR (neat) ν 2950, 2870, 2840 (CH); 1090, 910, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.82 (d, ^3J = 7.5 Hz, 3 H, CH_3), 0.87 (d, ^3J = 7.5 Hz, 3 H, CH_3), 1.77 (d/d, $^4J_{1,7}$ = 7.0 Hz/^3J = 1.4 Hz, 1 H, 1-H), 1.80 (d, $^4J_{8,11}$ = 7.4 Hz, 1 H, 11-H), 2.08 (d/d, $^4J_{1,7}$ = 7.0 Hz/^3J = 1.2 Hz, 1 H, 7-H), 2.09 (quint, $^3J_{10,CH_3}$ = $^3J_{9,10}$ = 7.5 Hz, 1 H, 10-H), 2.17 (d, $^4J_{8,11}$ = 7.4 Hz, 1 H, 8-H), 2.25 (quint, $^3J_{9,CH_3}$ = $^3J_{9,10}$ = 7.5 Hz, 1 H, 9-H), 2.71 (m, 1 H) and 2.76 (m, 1 H, 2-H, 6-H), 3.61 (d/d, $^2J_{3,3H'}$ = $^2J_{5,5H'}$ = 7.0 Hz/$^3J_{2,3}$ = $^3J_{5,6}$ = 2.5 Hz, 2 H, 3-H, 5-H), 3.62 (d, $^2J_{3,3H'}$ = $^2J_{5,5H'}$ = 7.0 Hz, 2 H, 3-H′, 5-H′); ^{13}C NMR ($CDCl_3$) δ 14.61, 14.69 (CH_3); 33.05, 34.78, 44.05, 44.54, 47.26, 51.25, 54.23, 61.84 (CH); 71.69, 71.82 (C-3, C-5); MS (70 eV) *m/z* (%) 178 (1.9) [$M^{•+}$], 163 (5.4), 149 (9.4), 148 (5.9), 147 (18.4), 145 (10.8), 136 (5.1), 133 (16.4), 131 (8.6), 121 (5.7), 120 (6.1), 119 (11.2), 117 (6.8), 109 (25.3), 108 (17.6), 107 (27.4), 106 (12.6), 105 (29.2), 95 (33.5), 94 (28.7), 93 (22.6), 92 (21.7), 91 (53.1), 82 (7.5), 81 (16.0), 80 (11.3), 79 (100), 78 (10.7), 77 (24.9), 69 (33.2), 67 (11.2), 65 (9.4), 55 (18.1), 53 (11.1), 51 (6.4).

(2α,6α)-*trans*-9,10-Dimethyl-4-oxatetracyclo[6.3.0.0^{2,6}.0^{7,11}]undecane (25): IR (neat) ν 2950, 2860, 2840 (CH); 1090, 910, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (d, ^3J = 6.8 Hz, 3 H, CH_3), 0.98 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.45 (q/d, $^3J_{10,CH_3}$ = 6.8 Hz/$^3J_{9,10}$ = 3.5 Hz, 1 H, 10-H), 1.59 (m, 1 H, 9-H), 1.77 (d, $^4J_{8,11}$ = 7.4 Hz, 1 H, 11-H), 2.01 (s, 2 H, 1-H, 7-H), 2.15 (d, $^4J_{8,11}$ = 7.4 Hz, 1 H, 8-H), 2.72 (m, 2 H, 2-H, 6-H), 3.60 (m, 4 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 18.79, 18.87 (CH_3); 39.70, 41.51, 44.19, 44.41, 50.71, 52.04, 52.12, 61.20 (CH); 71.61, 71.77 (C-3, C-5); MS (70 eV) *m/z* (%) 178 (3.1) [$M^{•+}$], 163 (4.8), 149 (8.6), 148 (5.3), 147 (18.0), 145 (10.3), 136 (5.3), 133 (15.9), 131 (8.1), 121 (5.4), 120 (6.1), 119 (9.7), 117 (6.3), 109 (23.1), 108 (17.0), 107 (25.4), 106 (11.4), 105 (26.4), 95 (41.8), 94 (25.8), 93 (22.1), 92 (21.9), 91 (51.2), 82 (8.1), 81 (15.0), 80 (11.4), 79 (100), 78 (11.0), 77 (23.1), 69 (32.0), 67 (11.6), 65 (9.2), 55 (18.1), 53 (11.9), 51 (6.3).

Acetone-Sensitized Photolysis of 28. A 0.56-g sample (4.5 mmol) of **28** in 45 mL of acetone (0.1 M) was irradiated for 8 h under argon by using a Pyrex immersion well. After removal of the solvent, the residue was distilled: bp 58–59 °C (38 mmHg); yield 0.43 g (77%). Products **29** and **30** (ratio 3:1); see Table V) were separated by HPLC.

(1α,5α,6α)-6-Ethenyl-3-oxabicyclo[3.2.0]heptane (29); IR (neat) ν 3080 (=CH_2); 2960, 2930, 2845 (CH); 1640 (C=C); 1080, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.85–2.04 (m, 2 H, 7-H, 7-H′), 2.63 (m, 1 H) and 2.70–2.88 (m, 2 H, 1-H, 5-H, 6-H), 3.46 ("d/d", ^2J = 9.2 Hz/^3J = 4.8 Hz, 1 H) and 3.52 ("d/d", ^2J = 9.2 Hz/^3J = 5.5 Hz, 1 H, 2-H, 4-H), 3.87 (d/m, ^2J = 9.2 Hz, 2 H, 2-H′, 4-H′), 4.94 (d/m, $^3J_{8,9c}$ = 10.1 Hz, 1 H, 9-H_{cis}), 4.96 (d/m, $^3J_{8,91}$ = 17.1 Hz, 1 H, 9-H_{trans}), 5.98 (d/d/d, $^3J_{8,9t}$ = 17.1 Hz/$^3J_{8,9c}$ = 10.1 Hz/$^3J_{6,8}$ = 7.1 Hz, 1 H, 8-H); ^{13}C NMR ($CDCl_3$) δ 29.73 (C-7), 35.16, 40.40, 44.92 (C-1, C-5, C-6); 73.68, 74.43 (C-2, C-4); 112.18 (C-9); 142.41 (C-8); MS (70 eV) *m/z* (%) 124 (0.6) [$M^{•+}$], 79 (12.9), 69 (100), 67 (9.8), 65 (5.5), 55 (31.6), 54 (41.5), 53 (12.7), 51 (6.4), 42 (28.2), 41 (54.7). Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9,74. Found: C, 76.89; H, 10.06.

(1α,5α,6β)-6-Ethenyl-3-oxabicyclo[3.2.0]heptane (30); IR (neat) ν 3080 (=CH_2); 2970, 2940, 2850 (CH); 1640 (C=C); 1085, 915 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.67 ("d/tr", $^2J_{7,7H'}$ = 12.2 Hz/$^3J_{1,7}$ = $^3J_{6,7}$ = 6.4 Hz, 1 H, 7-H), 2.30 ("d/tr", $^2J_{7,7H'}$ = 12.2 Hz/$^3J_{1,7H'}$ = $^3J_{6,7H'}$ = 8.4 Hz, 1 H, 7-H′), 2.88 (m, 1 H) and 3.00 (m, 2 H, 1-H, 5-H, 6-H), 3.38 (m, 2 H, 2-H, 4-H), 3.73 (d, $^2J_{2,2H'}$ = 9.1 Hz, 1 H, 2-H′), 4.03 (d, $^2J_{4,4H'}$ = 9.7 Hz, 1 H, 4-H′), 4.96 (d/m, $^3J_{8,9t}$ = 17.1 Hz, 1 H, 9-H_{trans}), 5.04 (d/m, $^3J_{8,9c}$ = 10.4 Hz, 1 H, 9-H_{cis}), 5.90 ("d/d/d", $^3J_{8,9t}$ = 17.1 Hz/$^3J_{8,9c}$ = 10.4 Hz/$^3J_{6,8}$ = 7.1 Hz, 1 H, 8-H); ^{13}C NMR ($CDCl_3$) δ 29.32 (C-7); 35.86, 36.03, 42.69 (C-1, C-5, C-6); 69.17 (C-4); 73.64 (C-2); 114.99 (C-9); 138.56 (C-8); MS (70 eV) *m/z* (%) 124 (0.7) [$M^{•+}$], 91 (5,6), 82 (9.2), 81 (5.1), 80 (9.5), 79 (16.6), 77 (9.4), 70 (15.3), 69 (100), 68 (6.3), 67 (10.1), 55 (23.8), 54 (52.4), 53 (10.5). Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 76.22; H, 9.71.

CuOTf-Catalyzed Photolysis of 28. A homogeneous solution of the triene ether **28** (0.56 g, 4.5 mmol) in 45 mL of THF (0.1 M) with 23 mg (0.09 mmol, 2 mol %) of CuOTf was irradiated for 12 h under argon by using a quartz immersion well. Evaporation of the solvent gave a yellow residue, which was purified by filtration over basic alumina. Yield 0.36 g (65%). Products **29** and **30** were obtained in a ratio of 3:1; see Table V.

Thermolysis of 10. A solution of 0.3 g (2 mmol) of **10** in 20 mL of toluene (0.1 M) was heated to 150 °C for 11 h under argon in a 50-mL glass autoclave. After evaporation of the solvent, the residue was filtered over basic alumina. Yield 0.24 g (80%). For product ratio; see Table VI. Products **31**, **32**, **15**, and **33** were separated by HPLC. For spectroscopic data of **15**, see under CuOTf-Catalyzed Photolysis of **10**.

(3aα,4α,7aβ)-4-Ethenyl-1,3,3a,4,5,7a-hexahydroisobenzofuran (31): IR (neat) ν 3080 (=CH_2); 3020 (=CH); 2975, 2930, 2855 (CH); 1650, 1640 (C=C); 1035, 1000, 915, 890, 695 cm^{-1}; NMR analysis by COSY and HETCOR; ^{1}H NMR ($CDCl_3$) δ 1.83 (q/d, $^3J_{3a,7a}$ = $^3J_{3a,3H'}$ = $^3J_{3a,4}$ = 11.2 Hz/$^3J_{3a,3}$ = 7.4 Hz, 1 H, 3a-H), 2.01 (m, 1 H, 5-H′), 2.37 (m, 3 H, 4-H, 5-H, 7a-H), 3.36 (d/d, $^3J_{1H',7a}$ = 11.5 Hz/$^2J_{1,1H'}$ = 7.2 Hz, 1 H, 1-H′), 3.40 (d/d, $^3J_{3a,3H'}$ = 11.2 Hz/$^2J_{3,3H'}$ = 7.4 Hz, 1 H, 3-H′), 3.97 (tr, $^2J_{3,3H'}$ = $^3J_{3a,3}$ = 7.4 Hz, 1 H, 3-H), 4.07 (tr, $^2J_{1,1H'}$ = $^3J_{1,7a}$ = 7.2 Hz, 1 H, 1-H), 4.96 (d/m, $^3J_{8,9c}$ = 10.2 Hz, 1 H, 9-H_{cis}), 5.04 (d/m, $^3J_{8,9t}$ = 17.1 Hz, 1 H, 9-H_{trans}), 5.70 (d/m, $^3J_{6,7}$ = 9.6 Hz, 1 H, 6-H), 5.72 (d/d/d, $^3J_{8,9t}$ = 17.1 Hz/$^3J_{8,9c}$ = 10.2 Hz/$^3J_{4,8}$ = 7.6 Hz, 1 H, 8-H), 5.79 (d/m, $^3J_{6,7}$ = 9.6 Hz, 1 H, 7-H); ^{13}C NMR ($CDCl_3$) δ 33.29 (C-5); 41.75, 44.04 (C-4, C-7a); 47.58 (C-3a); 70.68 (C-3); 71.01 (C-1), 114.00 (C-9); 124.37 (C-7); 128.55 (C-6); 141.56 (C-8); MS (70 eV) *m/z* (%) 150 (2.8) [$M^{•+}$], 119 (14.2), 117 (13.2), 106 (17.3), 105 (37.1), 104 (8.0), 93 (9.5), 92 (19.5), 91 (41.8), 83 (7.9), 82 (18.0), 81 (7.9), 80 (16.3), 79 (59.6), 78 (21.6), 77 (23.9), 69 (28.0), 68 (19.2). 67 (100), 66 (24.1), 65 (16.4), 55 (11.7), 53 (11.2), 51 (8.7), 41 (34.5). Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.80; H, 9.58.

(3aβ,4α,7aα)-4-Ethenyl-1,3,3a,4,5,7a-hexahydroisobenzofuran (32): IR (neat) ν 3080 (=CH_2); 3020 (=CH); 2975, 2930, 2880 (CH); 1650, 1640 (C=C); 1030, 1000, 920, 890, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2,06 (tr/d/d, $^3J_{3a,7a}$ = $^3J_{3a,3H'}$ = 11.2 Hz/$^3J_{3a,3}$ = 7.4 Hz/$^3J_{3a,4}$ = 4.2 Hz, 1 H, 3a-H), 2.17 (d/m, $^2J_{5,5H'}$ = 18.5 Hz, 1 H, 5-H′), 2.37–2.52 (m, 2 H, 5-H, 7a-H), 2.76 (m, 1 H, 4-H), 3.33 (d/d, $^3J_{1H',7a}$ = 11.0 Hz/$^2J_{1,1H'}$ = 7.0 Hz, 1 H, 1-H′), 3.44 (d/d, $^3J_{3a,3H'}$ = 11.2 Hz/$^2J_{3,3H'}$ = 7.4 Hz, 1 H, 3-H′), 3.87 (tr, $^3J_{3a,3}$ = $^3J_{3,3H'}$ = 7.4 Hz, 1 H, 3-H), 4.03 (tr, $^3J_{1,7a}$ = $^3J_{1,1H'}$ = 7.0 Hz, 1 H, 1-H), 5.03 (d/m, $^3J_{8,9t}$ = 17.1 Hz, 1 H, 9-H_{trans}), 5.10 (d/m, $^3J_{8,9c}$ = 10.1 Hz, 1 H, 9-H_{cis}), 5.70 (d/m, $^3J_{6,7}$ = 10.0 Hz, 1 H, 6-H), 5.79 (d/m, $^3J_{6,7}$ = 10.0 Hz, 1 H, 7-H), 5.84 (d/d/d, $^3J_{8,9t}$ = 17.1 Hz/$^3J_{8,9c}$ = 10.1 Hz/$^3J_{4,8}$ = 8.0 Hz, 1 H, 8-H); ^{13}C NMR ($CDCl_3$) δ 31.98 (C-5); 35.53, 37.72, 45.91 (C-3a, C-4, C-7a); 68.62, 70.56 (C-1, C-3); 116.26 (C-9); 124.44, 127.75 (C-6, C-7); 137.04 (C-8); MS (70 eV) *m/z* (%) 150 (6.5) [$M^{•+}$], 135 (9.7), 122 (8.9), 121 (24.1), 120 (15.3), 119 (11.6), 117 (14.3), 108 (27.9), 107 (15.7), 106 (29.1), 105 (54.6), 103 (10.2), 96 (8.7), 95 (17.0), 94 (11.7), 93 (26.5), 92 (38.4), 91 (81.4), 83 (11.4), 82 (14.0), 81 (13.6), 80 (23.3), 79 (100), 78 (30.6), 77 (42.4), 69 (30.0), 68 (23.0), 67 (89.9), 66 (37.2), 65 (24.0), 55 (18.4), 54 (7,6), 53 (18.7), 51 (14.3), 41 (52,7). Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.75; H, 9.52.

(3aα,4β,7aα)-4-Ethenyl-1,3,3a,4,5,7a-hexahydroisobenzofuran (33): IR (neat) ν 3080 (=CH$_2$); 3020 (=CH); 2965, 2920, 2860 (CH); 1650, 1640 (C=C); 1070, 915, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.03 (m, 2 H) and 2.63 (m, 2 H, 3a-H, 4-H, 5-H′, 5-H), 2.84 (m, 1 H, 7a-H), 3.58 (tr, $^{2}J_{1,1H'} = {}^{3}J_{1H',7a}$ = 8.3 Hz, 1 H, 1-H′), 3.60 (d/d, $^{2}J_{3,3H'}$ = 8.4 Hz/$^{3}J_{3H',3a}$ = 2.0 Hz, 1 H, 3-H′), 3.78 (tr, $^{2}J_{3,3H'} = {}^{3}J_{3,3a}$ = 8.4 Hz, 1 H, 3-H), 3.83 (d/d, $^{2}J_{1,1H'}$ = 8.3 Hz/$^{3}J_{1,7a}$ = 6.1 Hz, 1 H, 1-H), 4.97 (d/m, $^{3}J_{8,9c}$ = 10.0 Hz, 1 H, 9-H$_{cis}$), 5.02 (d/m, $^{3}J_{8,9t}$ = 17.0 Hz, 1 H, 9-H$_{trans}$), 5.55 (d/m, $^{3}J_{6,7}$ = 10.1 Hz, 1 H) and 5.67–5.83 (m, 2 H, 6-H, 7-H, 8-H); ^{13}C NMR (CDCl$_3$) δ 25.16 (C-5); 37.12, 40.05, 41.26 (C-3a, C-4, C-7a); 67.20, 73.04 (C-1, C-3); 113.78 (C-9); 126.89, 128.50 (C-6, C-7); 141.68 (C-8); MS (70 eV) *m/z* (%) 150 (3.3) [M$^{\bullet+}$], 121 (9.7), 120 (8.0), 119 (17.9), 118 (7.8), 117 (18.4), 108 (10.3), 107 (9.3), 106 (33.0), 105 (78.0), 104 (19.1), 103 (10.8), 96 (10.0), 94 (9.4), 93 (20.6), 92 (47.8), 91 (77.1), 82 (9.1), 80 (17.0), 79 (100), 78 (37.6), 77 (39.3), 69 (15.5), 68 (9.0), 67 (26.2), 66 (32.9), 65 (17.3), 55 (8.7), 53 (11.0), 51 (12.2), 41 (30.6). Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 80.08; H, 9.39.

CuOTf-Catalyzed Thermolysis of 10. A homogeneous solution of **10** (0.3 g, 2 mmol) in 20 mL of THF (0.1 M) with 30 mg (0.12 mmol, 6 mol %) of CuOTf was heated to 80 °C for 29 h under argon in a 50-mL glass autoclave. After removal of the solvent, the residue was filtered over basic alumina. **31** and **33** (ratio 7:1; see Table VI) were obtained in 87% (0.26 g) yield.

Thermolysis of 17. A solution of 0.53 g (3 mmol) of **17** in 30 mL of toluene (0.1 M) was heated to 150 °C for 11 h under argon in a 50-mL glass autoclave. After evaporation of the solvent, the residue was distilled: bp 39 °C (0.02 mmHg); yield 0.43 g (81%). The main products **22** and **34** were obtained in a ratio of 4:1 and were separated by HPLC. Anal. of the product mixture Calcd for $C_{12}H_{18}O$: C, 80.85, H, 10.18. Found: C, 80.28; H, 10.25. For spectroscopic data of **22**, see under CuOTf-Catalyzed Photolysis of **17**.

(3aα,4α,5β,7aβ)-5-Methyl-4-(*E*)-propenyl-1,3,3a,4,5,7a-hexahydroisobenzofuran (34): IR (neat) ν 3020 (=CH); 2970, 2930, 2860 (CH); 1630 (C=C); 1090, 1050, 1020, 970, 890, 730 cm^{-1}; NMR analysis by COSY; ^{1}H NMR (CDCl$_3$) δ 0.93 (d, $^{3}J_{5,CH_3}$ = 6.7 Hz, 3 H, CH$_3$), 1.63 (d, $^{3}J_{9,10}$ = 4.7 Hz, 3 H, 10-H), 1.88 (q/d, $^{3}J_{3a,3H'} = {}^{3}J_{3a,4} = {}^{3}J_{3a,7a}$ = 11.0 Hz/$^{3}J_{3a,3}$ = 7.3 Hz, 1 H, 3a-H), 2.26–2.48 (m, 3 H, 4-H, 5-H, 7a-H), 3.29 (d/d, $^{3}J_{3a,3H'}$ = 11.0 Hz/$^{2}J_{3,3H'}$ = 7.3 Hz, 1 H, 3-H′), 3.33 (d/d, $^{3}J_{1H',7a}$ = 11.4 Hz/$^{2}J_{1,1H'}$ = 7.1 Hz, 1 H, 1-H′), 3.88 (tr, $^{2}J_{3,3H'} = {}^{3}J_{3a,3}$ = 7.3 Hz, 1 H, 3-H), 4.01 (tr, $^{2}J_{1,1H'} = {}^{3}J_{1,7a}$ = 7.1 Hz, 1 H, 1-H), 5.41 (m, 2 H, 8-H, 9-H), 5.60 (d/tr, $^{3}J_{6,7}$ = 9.8 Hz/$^{3}J_{5,6} = {}^{4}J_{6,7a}$ = 2.8 Hz, 1 H, 6-H), 5.70 (d/m, $^{3}J_{6,7}$ = 9.8 Hz, 1 H, 7-H); ^{13}C NMR (CDCl$_3$) δ 16.28, 17.49 (CH$_3$); 36.00, 42.38, 44.07, 44.91 (C-3a, C-4, C-5, C-7a); 70.13, 70.42 (C-1, C-3); 122.56, 125.04, 131.64, 135.34 (C-6, C-7, C-8, C-9); MS (70 eV) *m/z* (%) 178 (4.4) [M$^{\bullet+}$], 163 (2.8), 149 (5.5), 147 (6.0), 106 (5.0), 105 (10.0), 95 (6.0), 93 (8.0), 91 (16.0), 82 (28.0), 81 (100), 80 (8.5), 79 (22.0), 77 (11.0), 69 (11.5), 67 (19.5), 65 (6.0), 55 (8.0), 53 (9.5), 41 (21.5).

Thermolysis of a Mixture of [2 + 2] Cycloadducts 18–21. A 1.0-g sample of a mixture of dipropenylcyclobutanes **18–21**, which was obtained from the acetone-sensitized photolysis of **17** (for product ratio, see Table III), was heated to 200 °C for 14 h under argon in a 10-mL glass autoclave. The yellow oil was purified by filtration over basic alumina. Yield 0.86 g (86%). The main products **26** and **27** (ratio 1.3:1) were separated by HPLC. Anal. of the product mixture Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.55; H, 10.11.

***cis*-6,7-Dimethyl-1,3,3a,6,7,9a-hexahydro-*cis*-cycloocta[*c*]furan (26)**: IR (neat) ν 3010 (=CH); 2960, 2925, 2860 (CH); 1650 (C=C); 1080, 1065, 1040, 910, 770, 730, 710 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.96 (d, $^{3}J_{6,CH_3} = {}^{3}J_{7,CH_3}$ = 6.7 Hz, 6 H, CH$_3$), 2.90 (m, 2 H, 6-H, 7-H), 3.29 (m, 2 H, 3a-H, 9a-H), 3.57 (d/d, $^{2}J_{1,1H'} = {}^{2}J_{3,3H'}$ = 8.1 Hz/$^{2}J_{1,9a} = {}^{3}J_{3,3a}$ = 6.4 Hz, 2 H, 1-H, 3-H), 3.98 (d/d, $^{2}J_{1,1H'} = {}^{2}J_{3,3H'}$ = 8.1 Hz/$^{3}J_{1H',9a} = {}^{3}J_{3H',3a}$ = 6.9 Hz, 2 H, 1-H′, 3-H′), 5.29 (m, 4 H, 4-H, 9-H and 5-H, 8-H); ^{13}C NMR (CDCl$_3$) δ 16.85 (CH$_3$); 37.75, 43.63 (C-6/C-7, C-3a/C-9a); 74.04 (C-1, C-3); 126.8, 135.89 (C-4/C-9, C-5/C-8); MS (70 eV) *m/z* (%) 178 (1.3) [M$^{\bullet+}$], 163 (2.1), 147 (5.4), 105 (8.8), 95 (5.2), 93 (8.2), 91 (12.8), 82 (19.6), 81 (100), 80 (6.8), 79 (25.9), 77 (8.8), 69 (8.4), 67 (18.1), 65 (5.2), 55 (6.6), 53 (10.5), 41 (26.4).

***trans*-6,7-Dimethyl-1,3,3a,6,7,9a-hexahydro-*cis*-cycloocta[*c*]furan (27)**: IR (neat) ν 3010 (=CH); 2960, 2925, 2870 (CH); 1650 (C=C); 1080, 1065, 1040, 915, 755, 740, 710 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1,00 (d, ^{3}J = 6.3 Hz, 3 H, CH$_3$), 1.07 (d, ^{3}J = 6.9 Hz, 3 H, CH$_3$), 1.84 (d/quint, ^{3}J = 11.2, 6.9 Hz, 1 H, 6-H or 7-H), 2.65 (m, 1 H, 6-H or 7-H), 3.13 (m, 1 H, 3a-H or 9a-H), 3.34 (m, 2 H, CH$_2$O), 3.75 (m, 1 H, 3a-H or 9a-H), 4.00 (m, 2 H, CH$_2$O), 5.11 (d/d, ^{3}J = 11.5, 7.5 Hz, 1 H, =CH), 5.30 (m, 2 H, =CH), 5.62 (d/d/d, ^{3}J = 11.5, 7.3 Hz/^{4}J = 1.7 Hz, 1 H, =CH); ^{13}C NMR (CDCl$_3$) δ 17.51, 19.43 (CH$_3$); 38.77, 42.27, 42.43, 44.25 (C-3a, C-6, C-7, C-9a); 72.13; 75.27 (C-1, C-3); 125.06, 127.37, 136.84, 137.38 (C-4, C-5, C-8, C-9); MS (70 eV) *m/z* (%) 178 (4.3) [M$^{\bullet+}$], 163 (2.0), 147 (11.5), 136 (6.5), 105 (8.0), 95 (7.5), 93 (8.0), 91 (16.5), 82 (21.0), 81 (100), 80 (7.0), 79 (29.5), 77 (16.0), 69 (13.5), 67 (14.0), 65 (6.0), 55 (9.5), 53 (13.0), 41 (31.5).

Thermolysis of 28. A 1-g sample (8.1 mmol) of **28** was heated to 150 °C for 5 h under argon in a 10-mL glass autoclave. The yellow oil was purified by filtration over basic alumina. Yield 0.45 g (45%). The cyclohexenes **35** and **36** were formed in a ratio of 3:1 and were separated by HPLC. For a different preparation method for **35**, see ref 26.

1,3,3a,4,5,7a-Hexahydro-*cis*-isobenzofuran (35): IR (neat) ν 3020 (=CH); 2930, 2860 (CH); 1650 (C=C); 1085, 1050, 910, 735, 710 cm^{-1}; NMR analysis by COSY, HETCOR, and proton decoupling at 2.02 ppm; ^{1}H NMR (CDCl$_3$) δ 1.54 (d/d/d/d, *J* = 13.1, 9.4, 7.7, 6.1 Hz, 1 H, 4-H$_{ax}$), 1.70 (d/q, *J* = 13.1, 5.2 Hz, 1 H, 4-H$_{eq}$), 1.98–2.06 (m, 2 H, 5-H′, 5-H), 2.37 (d/tr/tr, *J* = 9.6, 7.2, 4.6 Hz, 1 H, 3a-H), 2.69 (q/d/q, *J* = 7.5, 4.0, 2.0 Hz, 1 H, 7a-H), 3.46 (d/d, *J* = 7.9, 7.3 Hz, 1 H, 1-H′), 3.61 (d/d, *J* = 8.4, 4.5 Hz, 1 H, 3-H′), 3.95 (d/d, *J* = 8.4, 7.1 Hz, 1 H, 3-H), 3.96 (tr, *J* = 7.9 Hz, 1 H, 1-H), 5.64 (d/d/tr, *J* = 10.1, 4.0, 2.0 Hz, 1 H, 7-H), 5.82 (d/tr/d, *J* = 10.1, 3.9, 1.8 Hz, 1 H, 6-H); coupling constants $^{2}J_{4eq,4ax}$ = 13.1 Hz, $^{3}J_{3a,4ax}$ = 9.5 Hz, $^{3}J_{4ax,5}$, $^{3}J_{4ax,5H'}$ = 7.7, 6.1 Hz, $^{3}J_{4eq,5} = {}^{3}J_{4eq,5H'}$ = 5.2 Hz, $^{3}J_{3a,4eq}$ = 4.9 Hz, $^{3}J_{3,3a}$ = 7.1 Hz, $^{3}J_{3H',3a}$ = 4.5 Hz, $^{3}J_{3a,7a}$ = 7.3 Hz, $^{3}J_{1,7a}$ = 7.9 Hz, $^{3}J_{1H',7a}$ = 7.3 Hz, $^{3}J_{7,7a}$ = 4.0 Hz, $^{5}J_{5,7a} = {}^{5}J_{5H',7a}$ = 2.0 Hz, $^{4}J_{6,7a}$ = 1.8 Hz, $^{2}J_{1,1H'}$ = 7.9 Hz, $^{2}J_{3,3H'}$ = 8.4 Hz, $^{3}J_{6,7}$ = 10.1 Hz, $^{3}J_{5,6} = {}^{3}J_{5H',6}$ = 3.9 Hz, $^{4}J_{5,7} = {}^{4}J_{5H',7}$ = 2.0 Hz; ^{13}C NMR (CDCl$_3$) δ 22.79 (C-5); 23.42 (C-4); 36.61 (C-3a); 38.89 (C-7a); 72.90, 72.94 (C-1, C-3); 126.51 (C-7); 128.36 (C-6); MS (70 eV) *m/z* (%) 124 (4.7) [M$^{\bullet+}$], 94 (10.2), 93 (10.3), 91 (12.8), 82 (12.8), 80 (12.0), 79 (100), 78 (15.8), 77 (28.0), 66 (11.1), 53 (10.5), 51 (10.6), 41 (14.1). Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.27; H, 9.72.

1,3,3a,4,5,7a-Hexahydro-*trans*-isobenzofuran (36): IR (neat) ν 3020 (=CH$_2$); 2930, 2860 (CH); 1650 (C=C); 1090, 1025, 990, 890, 685 cm^{-1}; NMR analysis by COSY, HETCOR, and proton decoupling at 5.69 and 5.80 ppm; ^{1}H NMR (CDCl$_3$) δ 1.48 (tr/d/d, $^{2}J_{4ax,4eq}$, $^{3}J_{4ax,5a}$, $^{3}J_{3a,4ax}$ = 12.2, 12.2, 10.1 Hz, $^{3}J_{4ax,5eq}$ = 7.1 Hz, 1 H, 4-H$_{ax}$), 1.86 (m, 1 H, 3a-H), 1.96 (m, 1 H, 4-H$_{eq}$), 2.26 (m, 2 H, 5-H$_{ax}$, 5-H$_{eq}$), 2.32 (m, 1 H, 7a-H), 3.32 (d/d, $^{3}J_{1H',7a}$ = 11.4 Hz/$^{2}J_{1,1H'}$ = 7.1 Hz, 1 H, 1-H′), 3.38 (d/d, $^{3}J_{3H',3a}$ = 11.2 Hz/$^{2}J_{3,3H'}$ = 7.2 Hz, 1 H, 3-H′), 3.98 (tr, $^{2}J_{3,3H'} = {}^{3}J_{3,3a}$ = 7.2 Hz, 1 H, 3-H), 4.04 (tr, $^{2}J_{1,1H'} = {}^{3}J_{1,7a}$ = 7.1 Hz, 1 H, 1-H), 5.69 (d/q, $^{3}J_{6,7}$ = 9.7 Hz/$^{3}J_{5,6} = {}^{4}J_{6,7a}$ = 3.1 Hz, 1 H, 6-H), 5.80 (d/q, $^{3}J_{6,7}$ = 9.7 Hz/$^{3}J_{7,7a} = {}^{4}J_{5,7}$ = 2.0 Hz, 1 H, 7-H); ^{13}C NMR (CDCl$_3$) δ 23.65 (C-4), 26.24 (C-5), 43.45 (C-3a), 43.85 (C-7a), 70.83 (C-1), 71.47 (C-3), 124.62 (C-7), 128.90 (C-6); MS (70 eV) *m/z* (%) 124 (5.0) [M$^{\bullet+}$], 95 (12.2), 94 (17.3), 93 (11.5), 92 (7.3), 91 (12.0), 82 (19.3), 80 (16.8), 79 (100), 78 (11.3), 77 (24.6), 69 (15.5), 67 (10,5), 66 (11.4), 55 (7.4), 53 (8.1), 41 (17.7). Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 76.90; H, 9.83.

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