Table V

Compd reduced, mg	Dimethyl sulfoxide, ml	Chromous acetate, mg	*n*-Butanethiol, ml	Product, %
17, 602	34	1400	1.0	**18**, 78
19, 600	35	1400	1.0	**20**, 74
21, 571	60	1260	1.05	**22**, 80
23, 555	34	1400	1.0	**24**, 35
25, 275	25	780	1.0	**26**, 67
27, 522	35	1400	1.5	**28**, 65[a]

[a] M. Akhtar, D. H. R. Barton, and P. G. Sammes, *J. Am. Chem. Soc.*, **87**, 4601 (1965).

In a control experiment the bromo fluoride **29** (100 mg) in dimethyl sulfoxide (9 ml) was treated with chromous acetate (300 mg) as in the above experiment. The homogeneous product (thin layer chromatography), crystallized from methylene dichloride–methanol, gave only 9(11)-anhydrocortisol acetate.

Mild alkaline hydrolysis as for the 16α-methyl steroid described below gave 11β-fluoro-17α,21-dihydroxypregn-4-ene-3,20-dione. Recrystallized from methylene dichloride–methanol, this compound had mp 235–240°, $[\alpha]_D$ +170° (*c* 0.33, 11 methanol–methylene dichloride); λ_{max}^{MeOH} 239 mμ (ϵ 16,000); ν_{max}^{KBr} 3400 (s), 1710 (s), 1660 (vs), and 1610 (m) cm^{-1}.

Anal. Calcd for $C_{21}H_{29}FO_4$: C, 69.21; H, 8.02; F, 5.21. Found: C, 69.03; H, 8.05; F, 5.28.

Preparation of 11β-Fluoro-17α,21-dihydroxypregna-1,4-diene-3,20-dione 21-Acetate (32). The bromofluoride **31** (200 mg) in dimethyl sulfoxide (10 ml) containing *n*-butanethiol (0.5 ml) was treated with chromous acetate (750 mg) overnight at room temperature. Chromatography of the product over acid-washed alumina afforded 11β-fluoro-17α,21-dihydroxypregna-1,4-diene-3,20-dione 21-acetate (**32**, 52 mg). Crystallized from acetone–cyclohexane, this compound had mp 206–209°, $[\alpha]_D$ +103°, λ_{max}^{MeOH} 241 mμ (ϵ 14,500); ν_{max}^{KBr} 3500 (m), 1740 (s), 1710 (s), 1660 (vs), 1630 (m), and 1610 cm^{-1}.

Anal. Calcd for $C_{23}H_{29}FO_5$: C, 68.30; H, 7.23; F, 4.70. Found: C, 68.40; H, 7.42; F, 4.07.

Preparation of 11β-Fluoro-16α-methylpregna-1,4-diene-17α,21-diol-3,20-dione. The bromofluoride **33** (1.91 g) in dimethyl sulfoxide (35 ml) containing *n*-butanethiol (5.0 ml) was treated with chromous acetate (4.6 g) overnight at room temperature. Chromatography of the product over acid-washed alumina (50 g) gave the fluoro steroid **34** (750 mg). Crystallized from methanol, this compound had mp 176–178°, $[\alpha]_D$ +80°, λ_{max}^{MeOH} 242 mμ (ϵ 14,700); ν_{max}^{KBr} 3500 (s), 175 (s), 1730 (s), 1660 (vs), 1620 (m), and 1600 (m) cm^{-1}.

Anal. Calcd for $C_{25}H_{33}FO_6$: C, 66.95; H, 7.42; F, 4.24. Found: C, 66.76; H, 7.32; F, 3.97.

This ester **34** in methylene dichloride and methanol (20 ml) was treated with aqueous sodium hydroxide (2.75 ml of 1.0 *N*) for 1 hr at room temperature. Chromatography of the product over acid-washed alumina giave 11β-fluoro-16α-methylpregna-1,4-diene-17α,21-diol-3,20-dione (410 mg). Crystallized from acetone–cyclohexane, this compound had mp 175–189°, $[\alpha]_D$ +64°, λ_{max}^{MeOH} 241 mμ (ϵ 15,000); λ_{max}^{KBr} 3600 (s), 1700 (s), 1660 (vs), and 1620 (m) cm^{-1}.

Anal. Calcd for $C_{22}H_{29}FO_4$: C, 70.19; H, 7.76; F, 5.05. Found: C, 70.04; H, 7.80; F, 5.20.

Comparative Reduction of 9α-Bromo-11β-acyloxy Compounds. For this study 9α-bromo-11β-formyloxyprogesterone was prepared by standard methods.[31] Recrystallized from methylene dichloride–ether, this compound had mp 160–173° dec, $[\alpha]_D$ +208°, ν_{max}^{KBr} 3000, 1735, 1710, 1660, and 1150 cm^{-1}.

Anal. Calcd for $C_{22}H_{29}BrO_4$: C, 60.42; H, 6.68; O, 14.63; Br, 18.27. Found: C, 60.32; H, 6.90; O, 14.55; Br, 18.02.

The following compounds (a) 9α-bromo-11β-hydroxyprogesterone (163 mg), (b) 9α-bromo-11β-formyloxyprogesterone (172 mg), and (c) 9α-bromo-11β-trifluoroacetoxyprogesterone (200 mg) were each separately reduced with chromous acetate (240 mg) in dimethyl sulfoxide (10 ml) for 45 min. The reaction mixtures were diluted with ether (70 ml) and washed with water (25 ml). Standardized aliquots of each organic extract were scanned for ultraviolet absorption at 240 mμ. The balance was dried and the solvent was removed *in vacuo*. The residue was assayed by thin layer chromatography and the major product crystallized. Compound a gave mainly cyclosteroid; b and c gave largely 9(11)-dehydroprogesterone. The relative amounts of the latter for a, b, and c were 0.23, 0.83, and 1.0 as determined by ultraviolet measurements and checked by thin layer chromatography.

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[31] C. H. Robinson and L. E. Finckenor, U. S. Patent 2,986,564 (1965).

Photochemical Reactions of Metal-Complexed Olefins. II. Dimerization of Norbornene and Derivatives[1]

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Abstract: The cuprous halide catalyzed photodimerization of norbornene has been studied in detail. In all instances the reaction was highly stereoselective to the cyclobutane-fused *exo,trans,exo* dimer. Quantum-yield measurements suggest that the mechanism involves attack of a photoexcited norbornene–cuprous halide complex on two uncomplexed ground-state norbornenes, with the dimerization proceeding *via* a transient 3:1 olefin–CuX tetrahedral intermediate. Spectral data have been gathered in an effort to elucidate the nature of the metal-olefin complex.

Until quite recently, examples of photochemical reactions involving metal–olefin complexes were few.[2] In 1959, Pettit reported[3] the light-catalyzed dimerization of norbornadiene in the presence of pentacarbonyliron(0). However, subsequent work showed that the reaction also proceeded in the dark.[4] More recently, Srinivasan reported[5] a variety of intramolecular rearrangements of dienes, both acyclic and cyclic. These photoinduced reactions required the presence of

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[1] For part I, see D. J. Trecker, J. P. Henry, and J. E. McKeon, *J. Am. Chem. Soc.*, **87**, 3261 (1965).

[2] For a review, see W. Strohmeier, *Angew. Chem. Intern. Ed. Engl.*, **3**, 730 (1964).

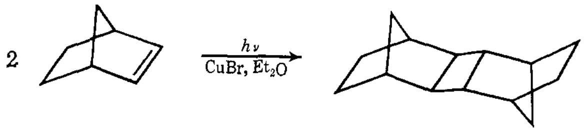
[3] R. Pettit, *J. Am. Chem. Soc.*, **81**, 1266 (1959).

[4] C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Letters*, 373 (1961).

[5] (a) R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 3048 (1963); (b) R. Srinivasan, *ibid.*, **86**, 3318 (1964).

certain metal salts, but apparently involved a preformed metal–olefin complex in only one instance—the rearrangement of di-μ-chlorobis(1,5-cyclooctadiene)dirhodium (I) to 1,3-cyclooctadiene.[5]

The first intermolecular photoreactions involving olefin–metal complexes were recently reported for ferrocene–isoprene[6] and for cuprous bromide–norbornene.[1] In the latter case, ultraviolet irradiation of ether solutions of norbornene in the presence of cuprous halides led to the stereoselective formation (97%) of one dimer—the *exo,trans,exo* form (I). The involvement of a preformed complex in this sequence was strongly suggested. In the absence of cuprous halides no photodimerization occurred. Likewise, when each olefin was heated with CuBr in the dark, no reaction took place. Thus, the requisite of both cuprous salts and ultraviolet radiation was established. We now wish to report the results of further studies on this and related systems, with the purpose of defining the nature of the complex and its role in the mechanism.

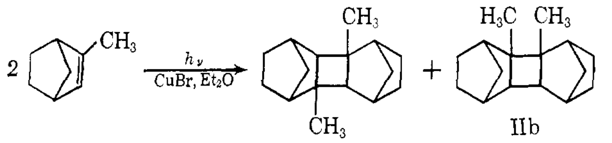


(1)

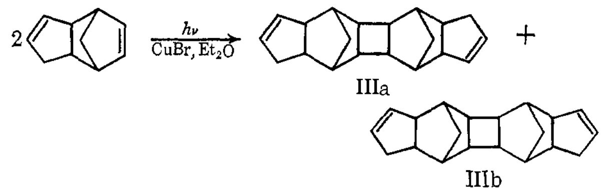
Results

The cuprous halide catalyzed photodimerization of norbornene has been studied in detail. Under conditions of widely varying olefin and cuprous halide concentrations and light intensity, the reaction proceeded to give *exo,trans,exo* dimer I in high stereoselectivity. The rigorous structure proof of dimer I has been described in previous reports.[1,7]

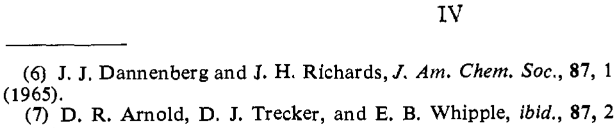
The scope of the reaction was tested with various derivatives of norbornene. Irradiation of 2-methyl-2-norbornene and *exo*-dicyclopentadiene in the presence of cuprous halides gave rise to dimers tentatively assigned structures II and III. Rigorous structural assignments of these complex dimers are not possible by the spectroscopic methods employed to establish the structure of I.[7] Tentative assignments of II and III were based on analogy to reaction 1 and on spectroscopic data which were compatible with, but not necessarily conclusive for, the cyclobutane-centered systems.



IIa IIb (2)



IIIa IIIb (3)



IV (4)

Other norbornene derivatives followed different reaction paths or resisted reaction altogether. Norbornadiene, for example, did not dimerize in the presence of cuprous halides, but underwent its usual internal cyclization to quadricyclene.[8] *endo*-Dicyclopentadiene and 3,6-epoxy-1-cyclohexene underwent no detectable reaction whatsoever. These results are summarized in Table I.

Table I. Preparative-Scale Irradiations of Norbornene Derivatives and Cuprous Bromide[a]

Olefin	Concn, M[b]	Irradiation time, hr	Yield of dimer, %[c]
Norbornene	7.2	142[d]	38.4
exo-Dicyclopentadiene	3.9	120[d]	26.6
2-Methyl-2-norbornene	5.0	231[d]	39.1
Norbornadiene	6.2	22[e]	None[f,g]
endo-Dicyclopentadiene	3.5	33[e]	None[g]
3,6-Epoxy-1-cyclohexene	1.3	67[e]	None[g]

[a] For details, see the Experimental Section. [b] Cuprous bromide concentrations ranged between 0.02 and 0.03 M. [c] Yields were those of isolated dimers. [d] Irradiations were carried out with a 450-w medium-pressure mercury arc. [e] 100-w medium-pressure arcs were used. [f] Quadricyclene was formed instead. [g] Yields of $\geq$0.5% would have been detectable by vpc.

The Complex. Cuprous halide–olefin complexes have been known for many years.[9] A variety of metal salts,[10] including copper(I),[11] have been shown to form metal–olefin coordination complexes with norbornadiene with ease. While no analogous norbornene–metal complex had been isolated, the likelihood of facile coordination was evident from equilibrium studies with silver nitrate.[12] The apparent ease of metal coordination with these bicyclic olefins has been related[12] to the strain inherent in their double bonds.[13]

The norbornene–cuprous halide complexes relevant to this work were studied by ultraviolet (Figure 1) and infrared (Figure 2) spectroscopy. A detailed spectral examination of the norbornene–CuBr system is summarized in Table II. Benesi-Hildebrand treatment of the spectral data[14] showed that it was best accommodated by a simple Beer's law relationship. The usual [CuX]/OD *vs.* 1/[NB] plot[14] gave a horizontal straight line with a [CuX]/OD intercept of 8.9×10^{-4}, the result of absorption intensities remaining constant over the range of olefin concentrations 0.29–0.77 M,[15] with cuprous bromide concentration being kept unchanged. Thus, if equilibria such as 5 or 6 did exist in

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[6] J. J. Dannenberg and J. H. Richards, *J. Am. Chem. Soc.*, **87**, 1626 (1965).

[7] D. R. Arnold, D. J. Trecker, and E. B. Whipple, *ibid.*, **87**, 2956 (1965).

[8] W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961).

[9] For a general review, see G. E. Coates, "Organometallic Compounds," 2nd ed, Butler and Tanner Ltd., London, 1960.

[10] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).

[11] (a) H. L. Haight, J. R. Doyle, N. C. Baenziger, and G. F. Richards, *Inorg. Chem.*, **2**, 1301 (1963); (b) G. N. Schrauzer and S. Eichler, *Chem. Ber.*, **95**, 260 (1962).

[12] J. G. Traynham and J. R. Olechowski, *J. Am. Chem. Soc.*, **81**, 571 (1959); M. A. Muhs and F. T. Weiss, *ibid.*, **84**, 4697 (1962).

[13] R. B. Turner, W. R. Meador, and R. E. Winkler, *ibid.*, **79**, 4116 (1957); R. C. Lord and R. W. Walker, *ibid.*, **76**, 2518 (1954).

[14] L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 15 ff.

[15] Solutions of lower norbornene concentration, which were measured in 1.0-cm cells, gave erratic and irreproducible results, perhaps due to the limited solubility of cuprous bromide in ether. Reliable data were obtained at higher norbornene concentrations with 0.1-cm cells.

Table II. Ultraviolet Spectral Data[a]

[Norbornene], *M*	[CuBr] × 10^{-4} *M*	Cell, cm[b]	Solvent	Optical density at λ, mμ[c]				
				230	239	250	260	270
0.29	6.97	0.1	Ether	0.63	0.72	0.57	0.36	0.21
0.35	6.97	0.1	Ether	0.68	0.79	0.62	0.39	0.23
0.41	6.97	0.1	Ether	0.68	0.79	0.62	0.39	0.23
0.45	6.97	0.1	Ether	0.67	0.78	0.62	0.39	0.23
0.58	6.97	0.1	Ether	0.66	0.77	0.60	0.37	0.22
0.72	6.97	0.1	Ether	0.66	0.75	0.59	0.37	0.22
0.77	6.97	0.1	Ether	0.67	0.77	0.60	0.38	0.22
0.64	6.97	0.1	Ether	0.69	0.78	0.62	0.40	0.24
0.64	5.58	0.1	Ether	0.57	0.64	0.52	0.34	0.21
0.64	4.18	0.1	Ether	0.45	0.49	0.40	0.27	0.18
0.64	2.79	0.1	Ether	0.31	0.33	0.28	0.19	0.15
5.4×10^{-3}	0.33	1.0	Methanol	0.37	0.36	0.17	0.09	0.07
				(λ_{max} 234 mμ; OD, 0.39)				
4.6×10^{-3}	0.29	1.0	*n*-Heptane	0.16	0.17	0.22	0.30	0.23
				(λ_{max} 262 mμ;[d] OD, 0.33)				

[a] Measurements were made on a Beckman DU and on a Cary 14 recording spectrophotometer. [b] Sealed cells were employed to minimize errors due to evaporation. [c] Each solution was rechecked after standing for 20 hr and was found to have changed less than 3% at each wavelength. [d] Submaxima in the form of fine structure appeared at 248, 255, and 268 mμ.

solution, they would appear to be singly or together far to the right. Consistent with this picture, increasing quantities of cuprous bromide resulted in nearly linear

$$\text{NB} + \text{CuX} \underset{}{\overset{k_5}{\rightleftarrows}} (\text{CuX})(\text{NB}) \tag{5}$$

$$\text{NB} + (\text{CuX})(\text{NB}) \overset{k_6}{\rightleftarrows} (\text{CuX})(\text{NB})_2 \tag{6}$$

increases in absorption. Thus, the molar extinction coefficient for the complex was calculated with the assumption that essentially all of the cuprous salt was incorporated into the absorbing complex. On this basis,

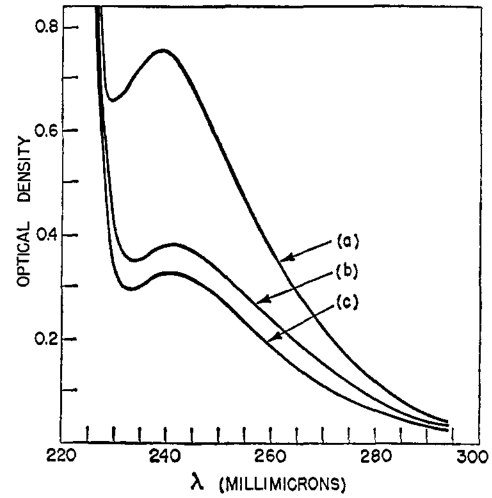

Figure 1. The ultraviolet spectra of (a) norbornene (7.19 × 10^{-1} *M*) and CuBr (7.0 × 10^{-4} *M*) in ether, (b) *exo*-dicyclopentadiene (6.44 × 10^{-1} *M*) and CuBr (7.0 × 10^{-4} *M*) in ether, and (c) 2-methyl-2-norbornene (7.88 × 10^{-1} *M*) and CuBr (8.4 × 10^{-4} *M*) in ether. Measurements were made in sealed, 1-mm cells.

ϵ_{max} was found to be 1.12 ± 0.03 × 10^4. Utilizing an expression modified for unsymmetrical absorption bands[16]

$$f = 1.62 \times 10^{-8}\epsilon_{max}(\tilde{\nu}_{max} - \tilde{\nu}_1)$$

the oscillator strength (f) was calculated as 0.32. This indicates a strongly allowed transition. The approximate mean radiative lifetime (τ) of the excited complex was calculated to be *ca.* 2.6 × 10^{-9} sec from the attendant relationship

$$f = \frac{1.500}{\tilde{\nu}_{max}^{\,2}}$$

As indicated in the preliminary communication of this work,[1] a 1:1 (or x:x) norbornene–cuprous chloride compound was isolated by the method of Haight, *et al.*[11a] Its infrared spectrum is shown in Figure 2.

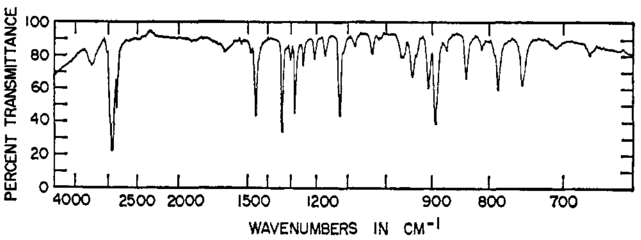

Figure 2. The infrared spectrum (in KBr) of the isolated norbornene–cuprous chloride complex.

It will be noted that the characteristic norbornene double-bond absorptions at 1563 and 707 cm^{-1} [13] are absent. The band at 752 cm^{-1} may correspond to the metal-perturbed =C—H deformation observed in Cu_2Cl_2-cycloocta-1,5-diene spectra.[17] The expected shift of the norbornene C=C band from 1563 to 1480–1450 cm^{-1} [11b] was not detected, perhaps due to masking by the absorption at 1455 cm^{-1}.

While the isolated 1:1 complex does not necessarily correspond to the absorbing species in solution, there is reason to believe that the two may be identical. An ether solution of the solid complex, without added norbornene, afforded the same ultraviolet absorption curve (Figure 2) as complexes prepared and analyzed *in situ*. The only variation was that of intensity. While no firm assignment can be made from this limited evidence, it should be noted that precedent favors this interpreta-

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(16) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961. $\tilde{\nu}_{max}$, and $\tilde{\nu}_1$ are the wavenumbers at the maximum and at the long wavelength side of the peak at half-band width, respectively.

(17) J. H. Van den Hende and W. C. Baird, Jr., *J. Am. Chem. Soc.*, **85**, 1009 (1963).

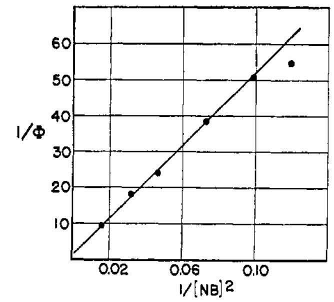

Figure 3. Plot of quantum yields of I at varying norbornene concentrations. The slope (493) and the intercept (1.56) were determined by least-squares calculations, omitting the last point.

tion. Reported examples of anything other than 1:1 monoolefin–metal compounds are few.[11b]

Whatever the stoichiometry in solution, spectral evidence suggests that there is but a *single* complex present. Over a wide range of norbornene concentrations (0.29–4.60 *M*)[18] there was no detectable variation in either the position of the maximum or the essential shape of the curve. Thus, the presence of a second absorbing species, such as 2:1 complex, appears unlikely.

Quantum Yields. The strong absorption of the complex in the lower ultraviolet region prompted a study of the dimerization with 2537-A light. As expected, the reaction proceeded readily under these conditions, each dimerization following apparent zero-order kinetics, regardless of the initial olefin concentration. Such observations are consistent with rates being limited by initial light absorption, and, in turn, by intensity, provided sufficient complex is present to absorb all of the incident radiation. Each run was limited to 1 hr, or no more than 0.2% conversion from quantum outputs of 2.0 ± 0.1 × 10^{18} quanta/sec. Extended reaction periods led to coating of the lamp surface, with attendant decreases in rate.

Quantum yields of dimer formation are compiled in Table III. In all determinations light intensity and initial cuprous bromide concentrations were kept constant, and sufficient complex was present in each case to absorb over 97% of the emitted light. It is seen that, over a twofold range of increasing norbornene concentrations, quantum yields increased by a factor of nearly 6.

Table III. Quantum Yields of Dimer Formation[a]

Olefin	Concn, *M*[b]	Quantum yield
Norbornene	2.90	0.019 ± 0.001
Norbornene	3.18	0.020 ± 0.003
Norbornene	3.72	0.026 ± 0.002
Norbornene	4.65	0.045 ± 0.005
Norbornene	5.59	0.054 ± 0.001
Norbornene	7.93	0.107 ± 0.002
2-Methyl-2-norbornene	4.62	0.080 ± 0.006
exo-Dicyclopentadiene	4.09	0.013 ± 0.002

[a] See the Experimental Section for details. [b] Cuprous bromide concentration was 3.2 ± 0.2 × 10^{-3} *M* in each determination.

Discussion

Involvement of the Complex. It seems clear that the complex plays a necessary role in the dimerization process. Without added cuprous halide, there was no absorption beyond 220 mμ in the ultraviolet, and no reaction took place. Moreover, dimerization occurred even when the actinic light was filtered with Pyrex, which ordinarily transmits above 290 mμ. In that region only the complex absorbed appreciably.

Evidence that a true metal–olefin complex, and not merely the free cuprous salt, was necessary for the reaction came as a result of experiments with the isolated complex. When ether solutions of norbornene were irradiated in the presence of trace amounts of added complex, but no additional CuCl, the dimerization proceeded at a rapid rate. Such results do not, of course, preclude the possibility that the complex partially dissociated in solution to give free CuCl and olefin, in accord with the equilibrium concept mentioned earlier.

Finally, it should be noted that the role of the cuprous halide is that of a catalyst, not a stoichiometric coreactant. Dissociative participation, resulting in one molecule of dimer formed per molecule of CuX destroyed, was ruled out by the experimental fact that over 40 molecules of dimer were formed per molecule of cuprous salt initially present.[19] The best alternative to such sequences would appear to be a process catalytic in CuX, involving the formation of an intermediate norbornene–cuprous halide complex which itself participates directly in dimer formation.

Mechanism. The quantum yield data presented above best support a mechanism such as that outlined in Scheme I. In this simplified scheme, a photoactivated complex of unspecified stoichiometry interacts with two uncomplexed, unactivated, ground-state norbornene molecules in an unspecified manner to form dimer. With the assumption explicit that the photoactivated complex (C*) exists in a photochemical steady state—that is, with the rate of excitation approximately equaling the rate of energy loss by all routes—a standard kinetic treatment of these steps gives expression 10.

Scheme I

$$\mathrm{C} + h\nu \xrightarrow{\phi} \mathrm{C}^* \quad \text{excitation} \tag{7}$$

$$\mathrm{C}^* \xrightarrow{k_8} \mathrm{C} + \Delta H \text{ (and/or } h\nu'\text{)} \quad \text{energy loss} \tag{8}$$

$$\mathrm{C}^* + 2\mathrm{NB} \xrightarrow{k_9} \mathrm{I} + \mathrm{C} \text{ (or NB + CuX)} \quad \text{reaction} \tag{9}$$

$$\mathrm{C} = (\mathrm{C_7H_{10}})(\mathrm{CuX});\ \mathrm{NB} = \text{norbornene}$$

$$\frac{1}{\Phi_\mathrm{I}} = \frac{1}{\phi} + \frac{k_8}{\phi k_9[\mathrm{NB}]^2} \tag{10}$$

Figure 3 accommodates this derivation over the range of norbornene concentrations 3.2–7.9 *M*. The intercept, $1/\phi$, of 1.6 establishes an upper limit for the quantum yield (0.62), based on the quantum efficiency of attaining the reactive complex in step 7. Subsequent intramolecular energy crossovers, if any, from the initial excited state would be extremely rapid and to a first approximation may be included in step 7. The

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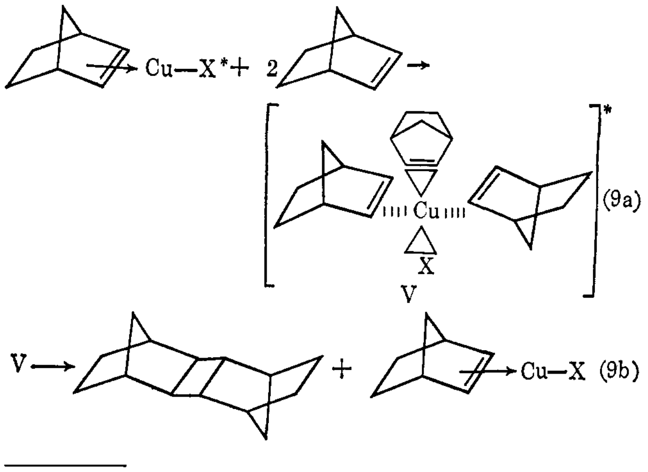
[18] A 0.019-mm cell was employed at the higher concentrations.

[19] The possibility of halide atoms from CuX participating in a radical chain process to form I was eliminated by independent experiments in which norbornene was irradiated in the presence of chlorine, bromine, iodine, and NBS.

ratio of rate constants k_8/k_9 calculated from this treatment was 308. Thus, at an initial norbornene concentration of 7.9 M, the rate of decay of the excited complex would be about 39 times faster than the rate of dimerization. This strongly suggests a short-lived intermediate—possibly the same excited state attained in the initial excitation.[20] The low quantum yields and the sharp dependence of quantum yield on norbornene concentration reflect the inefficient nature of the dimerization step 9.

Reaction pathways other than Scheme I appear to be at variance with the experimental facts. For example, a dimerization involving two olefins *both* of which are complexed to the metal in the ground state[21] would demand that the quantum yield be independent of norbornene concentration and vary only with light intensity.[22] A second alternative, involving the interaction of a single ground-state olefin with the excited complex requires a first-order olefin relationship—again incompatible with the experimental results. Similarly, a photosensitized dimerization, where the excited complex simply acts as an energy-transfer agent,[6] would require an expression unimolecular in olefin. It should be noted, moreover, that a conventional photosensitized dimerization would not afford the striking stereoselectivity observed here and, in fact, does lead to an altogether different isomer, the *exo,trans,endo* form, as the major product.[7]

A somewhat disturbing feature of Scheme I is the requirement that the dimerization step involve a termolecular interaction of two ground-state olefins with an excited complex. This may be reconciled in terms of a new transient complex, existing only in the excited state, which comprises three olefins coordinated to a single cuprous halide. Ample precedent does exist for the photochemical exchange of ligands in solution.[2] For example, cyclopentadienylmanganese tricarbonyl under the influence of ultraviolet irradiation exchanges a molecule of carbon monoxide for a π-electron donor such as ethylene.[23] Similar photochemically induced exchanges have been carried out with olefins and the carbonyls of osmium, iron, chromium, molybdenum, and tungsten.[2]



Although no analogous reaction has been reported for copper(I), a similar sort of explanation may be invoked here to account for the quantum yield data and the stereoselectivity of the reaction. Hence, the dimerization may occur through the expansion of an electronically excited, linear 1:1 complex to a very short-lived tetrahedral complex of three norbornenes and one cuprous halide, which instantaneously collapses to product (9a and b). As the lifetime of V decreases, it would begin to approach the actual transition state of the dimerization. In either case, the metal template would establish a favorable disposition for *exo,trans,exo* dimer formation.[24]

Experimental Section[25]

Irradiation of 2-Methyl-2-norbornene. A solution of 2-methyl-2-norbornene (330 g, 3.05 moles) and cuprous bromide (2 g, 0.014 mole) in anhydrous ether (200 ml) was added to a tubular reactor which was fitted with a concentric, water-jacketed Vycor immersion finger containing a 450-w Hanovia medium-pressure mercury arc. The solution was irradiated, with continuous sparging of nitrogen, for 231 hr. The lamp finger was cleaned five times during this period, and ether was twice added to make up for evaporation losses. After the irradiation period, the reaction mixture was filtered, and the filtrate was distilled to remove the ether and unreacted olefins. Continued distillation on a 36-in. spinning-band column afforded ten cuts of dimer (bp 134–139° (1.2–1.5 mm), $n^{20}\text{D}$ 1.5240–1.5262, 139 g, 0.49 mole, 39.1% yield).

Anal. Calcd for $C_{16}H_{24}$: C, 88.89; H, 11.11; parent mass, 216. Found: C, 88.84; H, 11.16; parent mass, 216.

Vpc analysis (10-ft poly(diethanolamine succinate)–PDEAS on Chromosorb W column, 180°, helium gas) showed the presence of two major isomers (80.7 and 12.9%) and three minor isomers (total 6.4%). The infrared spectrum of the mixture of dimers was consistent for saturated hydrocarbons, with characteristic cyclobutane absorption at 958, 910, and 889 cm^{-1}.[26] Maxima indicative of the norbornene double bond (3050, 1653, and 707 cm^{-1})[13] were absent.

Further distillation provided no better separation of the isomers. The major products were collected by preparative-scale vpc (20-ft column of 15% Versamid 900 on Chromosorb W, 230°, 50 lb of helium). The collected samples were shown to be essentially 100% pure. The nmr spectrum of IIb revealed a sharp singlet (six methyl protons) at τ 9.06 and a partially resolved multiplet (ten protons) centered at 8.72. IIa gave an nmr spectrum consisting of a sharp singlet (six methyl protons) at τ 9.02, a multiplet (ten protons) centered at 8.74, and a multiplet (eight protons) centered at 8.32.

Irradiation of *exo*-Dicyclopentadiene. A solution of *exo*-dicyclopentadiene (320 g, 2.42 moles) and cuprous bromide (1.0 g, 0.007 mole) in anhydrous ether (300 ml) was irradiated in the fashion described above for 120 hr. Vpc analysis (5-ft silicone column, 208°, helium gas) of the reaction mixture indicated the presence of dimers.[27] Ether and unreacted starting diene were rapidly distilled away, leaving a crystalline residue (95 g). Sublimation (~120° (0.5 mm)) afforded white crystals of III (85 g, 0.32 mole, 26.6% yield), which were recrystallized from ethanol to yield silver plates melting at 171–174° cor.

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[20] This observation is qualitatively in accord with the high oscillator strength (0.32) calculated from the spectral data.

[21] *Cf.* ref 17, which describes a 2:2 complex of two olefins to a Cu_2X_2 species.

[22] This alternate scheme would accommodate the quantum yield data if increased norbornene concentration merely provided more complex (*via* equilibria 5 and 6), which would, in turn, absorb a larger portion of the actinic light. However, constant light intensity was maintained throughout all runs, and >97% of the incident light was absorbed by the complex at even the *lowest* norbornene concentration.

[23] H. P. Kögler and E. O. Fischer, *Z. Naturforsch.*, **15b**, 676 (1960).

[24] The preference for metal coordination with norbornene from the *exo* direction has been previously noted: *cf.* T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, **85**, 2746 (1963), and ref 11b and 12.

[25] Melting points and boiling points are uncorrected unless otherwise specified. We are indebted to Dr. H. E. Fritz, Olefins Division, Union Carbide Corp., for generous samples of 2-methyl-2-norbornene and *exo*-dicyclopentadiene.

[26] *Cf.* C. Valentine, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 5202 (1964); L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, pp 30, 31.

[27] We are indebted to Dr. E. A. Rick of this department for carrying out the initial analysis and for pointing out the presence of III, which he independently synthesized by a different route (unpublished results).

Anal. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15; mol wt, 264. Found: C, 90.97; H, 9.10; mol. wt, 263.

Hydrogen uptake was 1.99 equiv/mole (theoretical, 2.00). The infrared spectrum of III showed bands at 3050, 1615, and 695 cm^{-1} characteristic of cyclopentene absorptions[13] and maxima at 940, 917, and 824 cm^{-1} assigned to cyclobutane ring vibrations.[26] Peaks diagnostic of norbornene double bonds (1563 and 707 cm^{-1})[13] were absent. The nmr spectrum of III exhibited a set of mirror-image proton signals (two protons each; each containing two closely grouped sets of triplets; centers at τ 4.35 and 4.59) identical with those found in the nmr spectrum of *exo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene. The differences in olefinic proton signals in norbornene and cyclopentene derivatives were recently noted by Bartlett.[28]

A sample of III was hydrogenated over palladium on charcoal to IV. Recrystallized from ethanol, the white crystals melted at 216–217°.

Anal. Calcd for $C_{20}H_{28}$: C, 89.49; H, 10.51. Found: C, 89.31; H, 10.43.

The infrared spectrum showed no double-bond character. Cyclobutane ring vibrations appeared at 1010, 975, 935, and 917 cm^{-1}.[26]

Mass Spectral Analyses.[29] The tentative identity of each major isomer as the *exo,trans,exo* form was suggested by the similarity of the cracking patterns of II and III to that of the known compound I. In contrast with the *exo,trans,endo* isomer of I, which was shown[7] to give a tropylium ion as the base peak (92), I, II, and III all gave major masses which could most reasonably result from scission of the cyclobutane ring to give the original monomers, with subsequent loss of the ethylene bridge (or, in the case of III, a cyclopentadiene fragment). A list of the major masses and their relative intensities, based on 100 as the base peak, is given as shown: (I) 66 (100), 91 (64), 67 (31.6), 41 (31.5), 79 (29.6), 39 (27.9), 80 (24.7), 159 (24.1), 27 (20.9); (II) 80 (100), 108 (18.6), 41 (11.7), 79 (10.1), 91 (7.0); (III) 66 (100), 67 (38.9), 132 (30.1), 131 (29.6), 91 (27.3), 197 (23.9), 28 (23.7).

Irradiation of Norbornadiene. A solution of norbornadiene (92 g, 1.0 mole) and cuprous chloride (0.5 g) in anhydrous ether (135 ml) was irradiated with a 100-w medium-pressure mercury arc for 20 hr. Vpc analysis (5-ft silicone column, 190°, helium gas; 10-ft Ucon polar on Chromosorb W column, 100°, helium gas) showed that no dimer had been formed. Quadricyclene[8] was the only detectable product.

Irradiation of *endo*-Dicyclopentadiene. A solution of *endo*-dicyclopentadiene (298 g, 2.26 moles) and cuprous bromide (0.5 g) in anhydrous ether (250 ml) was irradiated with a 450-w medium-pressure mercury arc for 78 hr. Vpc analysis (10-ft Ucon polar on Chromosorb W column, 120°, helium gas) showed that no pentacyclo[5.2.1.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decane[30] had been formed. Analysis for dimer (5-ft silicone column, 200°, helium gas) indicated that none was present.

Irradiation of 3,6-Epoxy-1-cyclohexene. Synthesized by the procedure of Nudenberg and Butz,[31] 3,6-epoxy-1-cyclohexene (1 g) and cuprous bromide (0.004 g) were taken up in anhydrous ether (7 ml), placed in a quartz tube, and irradiated with a 100-w medium-pressure mercury arc for 66.5 hr. Vpc analysis showed that no dimer had been formed.

Control Runs. Irradiation of each norbornene derivative was carried out in a fashion similar to that described above, except that the cuprous halide was omitted. Careful vpc analysis indicated that no dimer whatsoever had been formed in any of these runs. Similar controls were run with cuprous bromide, but without light. Each olefin in question was refluxed in the dark in ether solution containing cuprous bromide. Vpc analysis again showed the absence of any dimer.

To test the possibility that copper metal or cupric salts may actually be the active species in the dimerization, solutions containing norbornene (88 g), anhydrous ether (50 ml), and copper powder (0.2 g) in one, and cupric chloride (0.2 g) in the other, were irradiated with a 100-w medium-pressure mercury arc for 16 hr each. Careful vpc analysis of the irradiated solutions revealed no dimer in either case.

Irradiations of the Isolated Complex. A norbornene–cuprous chloride complex of approximately 1:1 composition[1] was isolated by the procedure of Haight, *et al.*[11a] Three quartz tubes were filled as follows: (A) the solid complex (0.1 g) alone; (B) a solution of the complex (0.1 g) in ether (10 ml); (C) a solution of the complex (0.1 g) and norbornene (5 g) in ether (5 ml). The three tubes were irradiated simultaneously with a 100-w medium-pressure mercury arc at a distance of 10 cm for 66 hr. Following the reaction period, tube A was washed with benzene, and the solutions in each tube were analyzed by vpc. A showed only the most minute traces of dimer, B showed none whatsoever, and C showed copious amounts of dimer I.

Irradiation of Norbornene in The Presence of Halogen Sources. Ether solutions (120 ml) of norbornene (80 g) and (A) iodine (0.3 g) and (B) chlorine (slow ebullition through the solution) were irradiated for 42 hr each with a 100-w medium-pressure mercury arc. Vpc analysis showed that no dimer whatsoever had been formed in either case. Quartz tubes containing (C) norbornene (5 g), ether (12 ml), and bromine (0.2 g) (where the active intermediate was dibromonorbornane) and (D) norbornene (5 g), ether (12 ml), and N-bromosuccinimide (0.1 g) were irradiated simultaneously from a distance of 10 cm with a 100-w medium-pressure mercury arc for 24 hr. Vpc analysis of the irradiated solutions revealed that no dimer had been formed.

Quantum-Yield Determinations. The apparatus consisted of a quartz-spiral, low-pressure mercury arc (Nester and Faust, 12 turns, 16-cm length) inside the center chamber of a tubular quartz reactor made up of two concentric quartz chambers—the outer tube, 12 cm in length and 75 mm outer diameter, holding a 350-ml volume; and the inner tube, 15 cm in length and 48 mm outer diameter, holding a 215-ml volume. The outer jacket served as the actinometer chamber. It contained two outlet arms near the top; through one of these was passed and sealed into place a 23-cm long, 1-mm diameter Teflon sample-withdrawal tube. The inner jacket served as the reaction cell. It was equipped with a side arm leading to a −78° reflux condenser and a small outlet arm, through which was passed and sealed into place a Teflon tube 20 cm long and 1 mm in diameter, used for sample withdrawal. Sample withdrawal from each jacket was accomplished by syringe. The entire outer surface of the apparatus was wrapped with optical black tape.

The electrical train was made up of the arc leading to a Nester and Faust Model 400 0–5000 ac step-up transformer (set on 70 v), then to a Sola constant-voltage transformer (CVS-1, primary 95–130/secondary 123), and finally to the house line.

Uranyl oxalate served as the actinometer.[32] The quantum output, determined by irradiating both cells filled with actinometer solution, was found to be $2.00 \pm 0.08 \times 10^{18}$ quanta/sec. In each case the inner jacket absorbed >97% of the light.

Quantum yields were obtained by irradiating the reaction mixture in the inner jacket and the actinometer solution in the outer jacket. Both solutions were stirred magnetically throughout. A slight positive pressure of purified nitrogen was maintained on the reaction chamber. The reaction mixture consisted of the norbornene derivative in varying amounts, anhydrous ether in amounts sufficient to make *ca.* 220 ml of solution, cuprous bromide (0.10 ± 0.01 g), and *exo,trans,endo*-dodecahydro-1,4:5,8-dimethanobiphenylene (*ca.* 0.2 g), an internal standard. For the quantum yield determination of III, IV was employed as the internal standard. Vpc measurements (5-ft 15% PDEAS on Chromosorb W column, 165–225°, helium gas) determined the amount of dimer formed *vs.* the constant quantity of the internal standard. The thermal stabilities of the dimers to vpc conditions were demonstrated by independent experiments. Previous calibration related relative peak areas to relative molar quantities of dimer and the internal standard. At least five points were taken for each determination. Initial runs showed that >97% of the light was absorbed by the reaction medium, with only about 3% passing through to the outer jacket. Thus, for subsequent runs water was metered through the outer jacket; a constant reaction temperature of 30.0 ± 0.5° was maintained.

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(29) We are indebted to Mr. J. E. Richardson of this department for carrying out the mass spectral analyses and for aiding in their interpretation.

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(31) W. Nudenberg and L. W. Butz, *J. Am. Chem. Soc.*, **66**, 307 (1944).

(32) W. G. Leighton and G. S. Forbes, *ibid.*, **52**, 3139 (1930).