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METAL-CATALYZED ORGANIC PHOTOREACTIONS. PHOTOREACTION OF OLEFINS WITH 2-CHLOROACETOPHENONE IN THE PRESENCE OF SILVER TRIFLUOROMETHANESULFONATE

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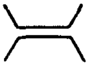
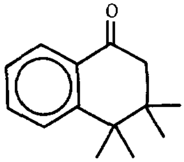
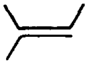
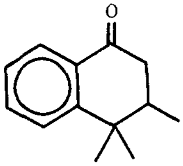
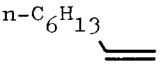
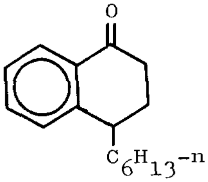
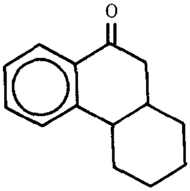
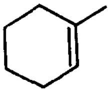
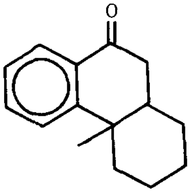
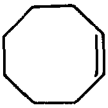
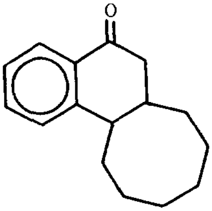
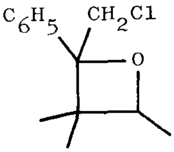
Abstract: Under UV irradiation with 2-chloroacetophenone in the presence of silver trifluoromethanesulfonate in acetonitrile, acyclic olefins gave naphthalenone derivatives, while cyclic olefins gave phenanthrenone derivatives in moderate yields.

In the course of our investigations on the metal-catalyzed photoreactions, we have observed a unique effect of metal compounds upon the photoreaction pattern of organic molecules. For instance, titanium(IV) chloride induced a cross coupling between ketone and alcohol molecules,1) while iron(III) chloride or uranyl acetate induced a photooxidation of olefins to produce β-substituted hydroperoxides.2) These reactions have been schemed as involving interligand electron transfer upon photoexcitation, and we proposed a term "long-range electron transfer" for this process.3) In order to verify the mechanism, we have adopted a strategy of trying to discover new reactions which are consistent with the proposed mechanism, rather than trying to find direct evidence for the mechanism. Recently we found a novel coupling reaction between olefins and 2-chloroacetophenone by the UV irradiation in acetonitrile in the presence of silver trifluoromethanesulfonate (triflate), which was schemed most reasonably by the long-range electron transfer mechanism.

When acetonitrile solutions of 2-chloroacetophenone 1 (1 eq), olefins 2 (1.5 eq), and silver triflate (1 eq) were irradiated with Pyrex-filtered light for 1 - 6 h, cyclized ketones 3 were obtained as major products. The precipitate of silver chloride which separated during the irradiation coagulated mostly at the bottom of the reaction tubes, and did not cause any appreciable disturbance for the light absorption by the reactants. The results are shown in the Table. The prolonged irradiation (10 - 24 h) did not increase the yields of the products, although the starting material 1 disappeared completely. The structures of the products were assigned by spectroscopic data.4) In case of unsymmetrical olefins, the reaction proceeded to give compounds having more substituents on the 4-position of the naphthalenone nucleus, as shown by the formation of 3b, 3c, and 3e. The NMR spectrum of 3b coincided with the reported datum, which differed definitely from that of the alternative isomer of 3,3,4-trimethyl-3,4-

Table. Ag(I)-Catalyzed Photoreaction of Olefins with 2-Chloroacetophenone

Entry	Starting olefin 2	Product 3	Reaction time (h)	Yield (%)	Recovery of 1 (%)
a			1.3 4.0	61 72	22 0
b			1.7	46	24
c			1.7	36	24
d			5.6	39	0
e			1.0	45	28
f			3.0	30	30



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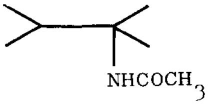

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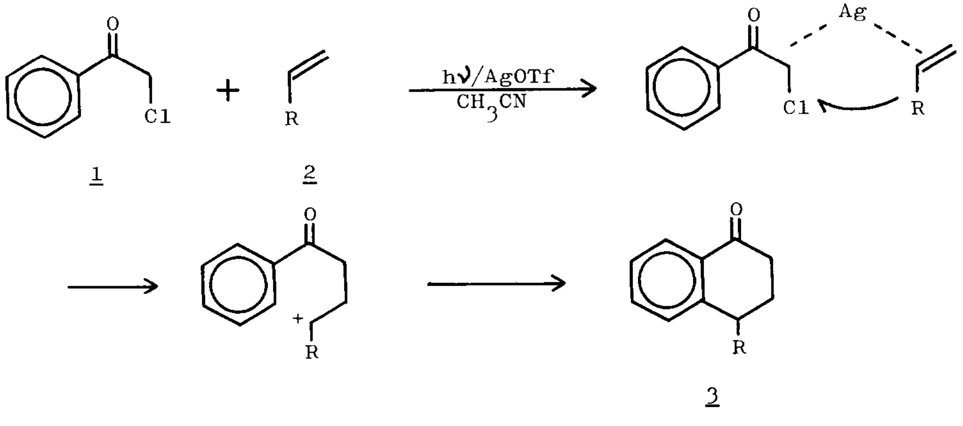
dihydro-1(2H)-naphthalenone.5) The structure of 3e was assigned by the coupling pattern of the methylene α to the carbonyl group. The position of the hexyl group in 3c was assigned by analogy. The IR spectrum of 3d coincided with that of the cis isomer, which was distinguishable from that of the trans isomer.6) The GLC analysis showed a small shoulder ($<5\%$) presumably of the trans isomer. Since the methyl signal of 3e on the NMR spectrum showed a single singlet and did not split further even upon the addition of a shift reagent, we concluded that the product is stereochemically pure. The cis junction was assigned on the analogy of 3d. The product 3f showed two peaks (∼1 : 1) on the GLC analysis. Since both fractions (Fr 1 and Fr 2) gave almost identical MS spectra, we concluded that the product was a mixture of cis and trans isomers.

The present reaction proceeded only under the irradiation. A quantitative amount of 1 was recovered when a mixture of 1, 2f, and silver triflate was refluxed in acetonitrile for 10 h. The effect of silver triflate is characteristic. Although the products 3a and 3e were obtained upon irradiation of the corresponding olefins with the chloro ketone 1 in acetonitrile even in the absence of the metal compound, the presence of silver triflate was requisite for the formation of the other products. In case of the olefin 2b, the irradiation without the metal compound gave another product, for which we assigned the structure of an oxetane 4, while in cases of olefins 2c, 2d, and 2f, no identifiable products except acetophenone were isolated under the metal-free conditions. The present reaction is generally clean, the major byproducts being acetophenone and polymers of olefins which can be removed easily by distillation. In case of the reaction of 2a, a small amount of an amide 5 was identified as a byproduct.

The fact that the coupling reaction under silver-free irradiation proceeded only with electron-rich olefins 2a and 2e indicates that an electron transfer from olefin to ketone is an important step. The revival of the same type reaction with less-substituted olefins by the presence of silver ion would be an evident indication that the silver ion assists the interligand electron transfer. The electron donation from the olefin molecules during the irradiation is evident because the rate of formation of silver chloride is very slow when



2-chloroacetophenone alone was irradiated with silver triflate in acetonitrile. In view of these facts, we formulated the reaction as shown in the Scheme.

The present reaction is characteristic in forming two carbon-carbon bonds in a single step, and promisible as a synthetic method of preparation of naphthalenone and phenanthrenone nuclei.

References and footnotes

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4) 3a: MS,7) m/e 202(13, M^+), 187(110, 146(100), 131(97); IR,8) 1688, 1298, 766 cm^{-1}; NMR,8) δ 1.00(s, 6H), 1.33(s, 6H), 2.49(s, 2H), 7.1 - 7.5(m, 3H), 7.8 - 8.0(m, 1H). 3b: MS, m/e 188(26, M^+), 173(96), 145(83), 131(100), 117 (67), 115(51), 91(49); IR, 1685, 1302, 767 cm^{-1}; NMR, δ 1.00(d, J = 7 Hz, 3H), 1.22(s, 3H), 1.37(s, 3H), 1.7 - 2.9(m, 3H), 7.0 - 7.5(m, 3H), 7.8 - 8.0(m, 1H). 3c: MS, m/e 230(18, M^+), 145(100), 117(30); IR, 1686, 1286, 764 cm^{-1}; NMR, δ 0.89(t, J = 6 Hz, 3H), 1.1 - 1.8(b, 10H), 1.9 - 3.0(m, 5H), 7.0 - 7.5 (m, 3H), 7.8 - 8.0(m, 1H). 3d: MS, m/e 200(82, M^+), 158(100), 131(35), 118 (36), 115(38); IR, 1684, 1295, 763 cm^{-1}; NMR, δ 1.2 - 2.1(b, 8H), 2.2 - 3.0 (m, 4H), 7.1 - 7.5(m, 3H), 7.8 - 8.0(m, 1H). 3e: MS, m/e 214(31, M^+), 199 (100), 158(34), 131(58); IR, 1684, 765 cm^{-1}; NMR, δ 1.30(s, 3H), 1.3 - 2.5 (m, 9H), 2.28 and 2.95(ABq, J = 17 Hz, upper and lower halves split into doublets, J = 4 and 5 Hz, respectively), 7.0 - 7.5(m, 3H), 7.8 - 8.0(m, 1H). The ABq pattern became more obvious upon the addition of $Eu(fod)_3$. 2,4-Dinitrophenylhydrazone, mp 180 - 181°C (lit:9) mp 182.5 - 184°C). 3f-Fr 1: MS, m/e 228(24, M^+), 158(100), 145(37), 144(64), 131(84), 129(43), 118(70), 115 (88), 77(41); 3f-Fr 2: MS, m/e 228(25, M^+), 158(83), 145(48), 144(56), 131 (100), 129(51), 118(54), 115(59); 3f (mixture): IR, 1683, 1299, 759 cm^{-1}; NMR, δ 1.4 - 1.9(b, 12H), 2.0 - 3.0(m, 4H), 7.0 - 7.5(m, 3H), 7.8 - 8.0 (m, 1H). 4: MS, m/e 179(1.4) and 181(0.5)(M^+ - CH_3CHOH), 154(8) and 156(3)(M^+ - $(CH_3)_2CCHCH_3$), 70(100); IR, 2962, 1448, 1003, 702 cm^{-1}; NMR, δ 0.67(s, 3H), 1.15(d, J = 7 Hz, 3H), 1.23(s, 3H), 3.79 and 4.06(ABq, J = 11 Hz, 2H), 4.59 (q, J = 7 Hz, 1H), 7.16(s, 5H). 5: mp 65 - 66°C (lit:10) mp 62 - 64°C). IR(CCl_4), 3300, 1675, 1545 cm^{-1}; NMR, δ 0.88(d, J = 7 Hz, 6H), 1.22(s, 6H), 1.85(s, 3H), 2.41(heptet, J = 7 Hz, 1H), 6.63(b, 1H).
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