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The $[M(cod)(PPh_3)_2]PF_6$ (M = Rh, Ir; cod = 1,5-cyclooctadiene) Mediated Activation of Aldehyde C-H Bond

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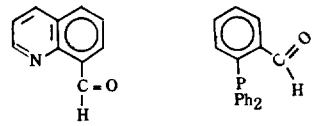
Acetone solution of quinoline-8-carbaldehyde reacts with $[Rh(cod)(PPh_3)_2]PF_6$ and $[Ir(cod)(PPh_3)_2]PF_6$ to yield $[Rh(NC_9H_6CO)(H)(PPh_3)_2(CH_3COCH_3)]PF_6$ (1) and $[Ir(NC_9H_6CO)(H)(PPh_3)_2(CH_3COCH_3)]PF_6$ (2), respectively. The compound $[Ir(cod)(PPh_3)_2]PF_6$ also reacts with $Ph_2PC_6H_4$-o-CHO in the acetone/H_2O mixture to give $[Ir(Ph_2PC_6H_4\text{-o-}CO)(H)(PPh_3)_2(CH_3COCH_3)]PF_6$ (3). Compounds 1, 2, and 3 were characterized by infrared, ^1H NMR, ^{31}P NMR spectra and conductivity measurement. The ^1H NMR spectra of 1, 2, and 3 support the presence of a terminal hydride that is cis to the phosphine. The IR band of 3 at 2185 cm^{-1}, which is assigned to ν(Ir-H), and the hydride cleavage reaction of 3 with CCl_4, provide evidence for the Ir-H bond.

Introduction

Transition metal acyl hydride compounds are known or postulated to be key intermediates in catalyzed hydroformylation reaction[1] and metal-catalyzed carbonylation processes[2]. In addition, formation of coordinatively unsaturated acyl metal hydride intermediates through the oxidative addition of aldehydes to metal centers is thought to be involved in metal catalyzed decarbonylations of aldehydes.

Recently, we reported the Pt $PCy_3(C_2H_4)$[3] and $Ir(PPh_3)_2(CO)OClO_3$[4] mediated activation of aldehyde C-H bonds, which led to transition metal acyl hydride compounds. The stable transition metal acyl hydrides have been obtained through reactions involving the scission of C-H bonds in cases where a coordinating group on the metal is available to form a five-membered chelate and where the transition metal precusor is strongly nucleophilic. In an extension of these works, $[M(cod)(PPh_3)_2]PF_6$ (M = Rh, Ir; cod = 1,5-cyclooctadiene) were selected as candidates, because they are coordinatively unsaturated, and provide a nucleophilic metal center. The complexes $[M(cod)(PPh_3)_2]PF_6$ also show different features from those of previously used iridium (1) and platinum (0) compounds due to the bidentate character of the cod group. Readily available aldehydes able to form a chelate are quinoline-8-carbaldehyde (A) and o-diphenylphosphinobenzaldehyde (B), which stabilize intermediates in the reactions of the aldehyde group with metal ions.



A B

We describe here the reactions between $[M(cod)(PPh_3)_2]PF_6$ and A, B, which lead to C-H activation through formation of stable five-coordinate rhodium(III) and iridium acyl hydride compounds.

Experimental

All synthetic procedures were carried out with use of standard Schlenk tube under a dry and oxygen free atmosphere of N_2. The $[Ir(cod)(PPh_3)_2]PF_6$[5], $[Rh(cod)(PPh_3)_2]PF_6$[6], quinoline-8-carbaldehyde[7], and $Ph_2PC_6H_4$-o-CHO[8] were prepared according to literature methods. Solvents were reagent grade and were distilled from the appropriate drying agents. Infrared spectra were recorded on a Shimazu IR-440 spectrophotometer from KBr pellet. ^1H NMR spectra were recorded on a Bruker WP 80 spectrometer. ^{31}P NMR spectra

were recorded on a Bruker WP 200 spectrometer operating 81M Hz with broad-band proton decoupling. The ^{31}P chemical shifts are reported relative to 85% H_3PO_4. Conductivity measurement was conducted with an Industrial Instruments Model RC216B2. Melting points were measured on a Wagner U. Munz Co., capillary type. Elemental analyses were performed at the center of instrumental analysis, College of Engineering, Seoul National University, Seoul, Korea.

Preparation of complexes

$[Rh(NC_9H_6CO)(H)(PPh_3)_2(CH_3COCH_3)]PF_6$ (1). To a stirred acetone(3 m*l*) solution of $[Rh(cod)(PPh_3)_2]PF_6$ (0.8 m mol) quinoline-8-carbaldehyde (0.8 m mol) dissolved in acetone (2 m*l*) was added dropwise under nitrogen at room temperature. Upon addition, the color was immediately changed into pale yellow. After the solution was stirred for 30 minutes, ether (8 m*l*) was added to initiate precipitation of a pale yellow power, which was collected on a frit. The solid was recrystallized from acetone/pentane, and dried under vacuum. Yield: 90%. M.P.: 208-212°C(dec.). (ohm^{-1} cm^2 mol^{-1}): 118. Anal. Calcd for $RhP_3F_6NO_2C_{49}H_{43}$: C, 55.03; H, 4.88. Found: C, 54.79; H, 4.71. ^1H NMR ($CDCl_3$): δ 8.2-6.8 (36H), δ 2.04(6H), δ -10.38 (d of t, J_{Rh-H} = 22.79, J_{P-H} = 6Hz, 1H). $^{31}P\{H\}$ NMR($CDCl_3$): δ 38.51 (d, J_{Rh-P} = 125.55 Hz), δ -92.27 (septet, J_{P-E} = 712.8 Hz). IR(KBr pellet): 2007(m), 1692(m), 1657(s), 1630(m), 1572(m), 1498(m), 1397(w), 1308 (w), 1238(w), 1216(m), 1180(w), 1158(w), 1091(s), 1050(w), 1020(w), 994(w), 890(s), 830(vs), 782(s), 748(s), 690(s), 610(w), 554(s), 509(s), 492(m).

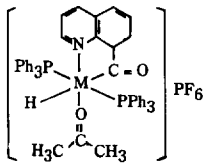
$[Ir(NC_9H_6CO)(H)(PPh_2)(CH_3COCH_3)]PF_6$ (2). To a stirred acetone(5 m*l*) solution of $[Ir(cod)(PPh_3)_2]PF_6$ (0.7 m mol) quinoline-8-carbaldehyde (0.7 m mol) dissolved in acetone (2 m*l*) was added under nitrogen. The reaction was continued for 40 minutes at room temperature. The volume was reduced to ca.3 m*l* and ether (5 m*l*) was added. The solution was left at room temperature for 1 hour and the supernatant liquid was decanted from the solid. The resulting pale yellow solid was dried in vacuum overnight. Yield: 78%. M.P.: 214-216°C. (ohm^{-1} cm^2 mol^{-1}): 123.. Anal. Calcd for $IrP_3F_6NO_2C_{49}H_{43}$: C, 54.60; H, 3.99. Found: C, 54.22; H, 3.83. ^1H NMR ($CDCl_3$): δ 8.4-6.8(36H), δ 2.09(6H), δ -13.42(t, J_{P-H} = 14.50 Hz. 1H). $^{31}P\{H\}$ NMR ($CDCl_3$): δ 40.21 (s), δ -99.25(septet, J_{P-F} = 708.21 Hz). IR(KBr pellet): 2140(m), 1698(m), 1654(s), 1627(m), 1580(m), 1496(m), 1354(m), 1237 (w), 1220(m), 1154(w), 1090(s), 840(vs), 780(s), 746(s), 686(s), 560(s), 510(s), 488(m).

$[Ir(Ph_2PC_6H_4\text{-}o\text{-}CO)(H)(PPh_3)_2(CH_3COCH_3)]PF_6$ (3). To a mixture of $[Ir(cod)(PPh_3)_2]PF_6$ (0.8m mol) and $Ph_2PC_6H_4$-o-CHO (0.8 m mol) was added acetone (8 m*l*) and H_2O (2 m*l*) at room temperature. The reaction was continued for 24 hours. The solvents were stripped off. The resulting light yellow compound was recrystallized with CH_2Cl_2/hexane and dried in vacuum overnight. Yield: 85%. M.P.: 198-202°C (dec.). Λ_M(ohm^{-1} cm^2 mol^{-1}): 120.. Anal Calcd for $IrP_4O_2F_6C_{58}H_{51}$: C, 57.57; H, 4.25. Found: C. 57.21; H, 4.32. ^1H NMR($CDCl_3$): δ 8.0-7.6(54H), δ 2.11(6H), δ -2.12 (d of t, J_{P-H} = 7.21, equatorial phosphine to the hydride, J_{P-H} = 14.82, axial phosphine to the hydride, 1H). $^{31}P\{H\}$ NMR ($CDCl_3$): δ 38.83(d), δ 18.25(t, J_{P-P} = 306.2 Hz), δ -107.34(septet, J_{P-F} = 710.2 Hz). IR(KBr pellet): 2185(m), 1683(s), 1634(vs), 1622(s), 1588(m), 1492(m), 1384(w), 1306 (w), 1260(w), 1182(w), 1158(w), 998(m), 868(w), 838(vs), 742 (s), 692(vs), 621(s), 542(m), 515(vs), 492(m).

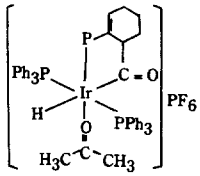
$[Ir(Ph_2PC_6H_4\text{-}o\text{-}CO)(Cl)(PPh_3)_2]PF_6$ (4). To a stirred CH_2Cl_2(3 m*l*) solution of 3 was added CCl_4 (5 m*l*) at room temperature. The solution was slowly changed from pale yellow to yellow. After the solution was stirred for 3 hours, the volume was reduced to ca. 3 m*l* and ether (3 m*l*) was added. The resulting yellow solid was filtered off and dried in vacuum overnight. Yield: 95%, M.P.: 218-222°C. Λ_M(ohm^{-1} cm^2 mol^{-1}): 123.. Anal. Calcd for $IrO_2P_4C_{58}H_{50}ClF_6$: C, 55.97; H, 4.02. Found: C. 56.63; H, 4.14. ^1H NMR($CDCl_3$): δ 8.43-6.50 (44H), δ 1.88(6H). $^{31}P\{H\}$ NMR($CDCl_3$): δ 42.36 (d), δ 24.87(t, J_{P-P} = 304.9 Hz), δ -104.23(septet, J_{P-F} = 709.2 Hz). IR(KBr pellet): 1702(m), 1645(vs), 1631(s), 1586(m), 1494(m), 1310(w), 1192(w), 1164(w), 996(m), 840 (vs), 744(s), 696(vs), 625(s), 548(m), 520(vs), 438(m), 335(m).

Results and Discussion

Synthesis. The rhodium and iridium acyl hydrides have been prepared through reactions between $[M(cod)(PPh_3)_2]PF_6$ (M = Rh, Ir) and a molar equivalent amount of ligands A, B. $[M(cod)(PPh_3)_2]PF_6$ + RCHO + CH_3COCH_3 $[M(EC_nH_mCO)(PPh_3)_2(H)(CH_3COCH_3)]PF_6$ where: M = Rh, Ir, cod = cyclooctadiene, R = $Ph_2PC_6H_4$-o, 8-quinolinecarboxyl, E = P, N. The addition of equimolar quantity of A or B to a stirred acetone solution of $[M(cod)(PPh_3)_2]PF_6$ affords a pale yellow solution. The resulting pale yellow complexes, $[Rh(NC_9H_6CO)(H)(PPh_3)_2(CH_3COCH_3)]PF_6$(1), $[Ir(NC_9H_6CO)(H)(PPh_3)_2(CH_3COCH_3)]PF_6$(2), were isolated as air stable solids in 78-90% yields. The structure of compounds 1, and 2 were deduced from their IR, ^1H NMR, ^{31}P NMR and conductivity measurements. In contrast to the reaction of $[Rh(cod)(PPh_3)_2]PF_6$ and A, treatment of B with $[Ir(cod)(PPh_3)_2]PF_6$ in acetone results in oxidative addition, affording $[Ir(Ph_2PC_6H_4\text{-}o\text{-}CO)(H)(PPh_3)_2(CH_3COCH_3)]PF_6$ (3) only in the presence of a small amount of H_2O.



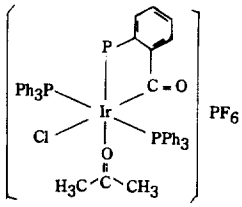
1. M = Rh
2. M = Ir



3

The role of H_2O is supposed to be kicked a coordinated cod up, giving rise to a vacant site for an oxidative addition reaction. It may be attributable to the difference of nitrogen and phosphine ligands in strength for displacing a strongly coordinated cod on metal site.

In an attempt to cleave a terminal metal hydride, compound 3 was reacted with CCl_4. The reaction produced the yellow chlorine-substituted iridium complex 4 in 95% yield.



4

Table 1. Infrared Data, and Molar Conductivity

Complex	IR absorption band(cm^{-1})[a]				Molar Conductivity[b]
	ν(M-H)	ν(C=O)	ν(C=C)	ν(P-F)	(ohm^{-1} cm^2 mol^{-1})
1	2007	1692, 1657, 1630	1572	830	118.
2	2140	1698, 1654, 1627	1580	840	123.
3	2185	1683, 1634, 1622	1588	838	120.
4		1702, 1645	1586	840	123.

[a] KBr pellet. [b] 3.8×10^{-4}M in acetone at 25°C.

The structure of compound 4 was deduced from its IR, ^{1}H NMR, elemental analysis, and conductivity measurement.

IR spectra. The key infrared features and molar conductivity of compounds 1, 2, 3, and 4 are presented in Table 1. The infrared spectrum of 1 in KBr pellet clearly indicates the presence of the Rh-H bond. The intense peak at 2007 cm^{-1} is assigned to a Rh-H stretching mode, which is expected a band with stretching frequency in the region 2200-1900 cm^{-1}.[9-11] The value is very close to that of compound $\overline{Rh(NC_9H_6CO)}(PPh_3)_2(H)(Cl)$[12], which appears at 2020 cm^{-1}. The infrared spectrum of 2 shows the Ir-H stretching mode at 2140 cm^{-1}. It may be related to the difference of mucleophilicity in Rh complex and Ir complex. On the other hand, the infrared spectrum of 3 gave a high value (2185 cm^{-1}) for the hydride stretching frequency compared with that of compound 2. It may be attributable to the decrease of electron density on Ir site by substituting the π-acceptor phosphine ligand for σ-donor nitrogen ligand. The peak at 1692 cm^{-1} of 1 is assigned to ν(C = O) of acetone, which is shifted to a lower frequency than that found for the free acetone (1708 cm^{-1}) due primarily to the coordination on a nucleophilic metal complex. The peaks at 1657 and 1630 of 1 is assigned to the ν(C = O) of chelation ligand. The two bands in the acyl region appear in other instances[12-13] in acylrhodium(III) complexes. The compounds of 2, 3 and 4 are similarly assigned as that of 3 in C = O region. The disappearance of band at 2185 cm^{-1} of 3 and the appearance of one band at 335 cm^{-1} of 4, which is assigned to the Ir-Cl stretching mode, imply that the Ir-H bond is substituted into the Ir-Cl bond. The peak at 830 cm^{-1} of 1 is assigned to ν(P-F)[14] (see Table 1).

The conductance measurements (118-123 ohm^{-1} cm^2 mol^{-1} for 1-4) indicate that the complexes are 1:1 electrolytes.

NMR spectra. The ^{1}H NMR and ^{31}P NMR spectral data of compounds 1, 2, and 3 are presented in Table 2. The ^{1}H NMR spectrum of 1 taken in $CDCl_3$ exhibits resonances of Rh-H centered at -10.38. Its pattern consists of doublets of triplets(see Figure 1), due to the spin coupling between the phosphorus, rhodium, and hydride, corresponding to the

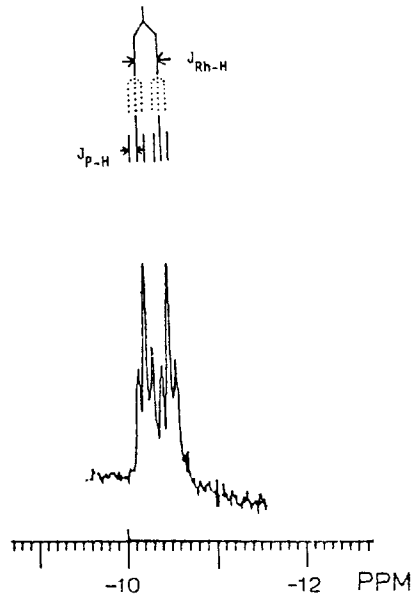


Figure 1. The ^{1}H NMR spectrum of $[\overline{Rh(NC_9H_6CO)}(H)(PPh_3)_2(CH_3COCH_3)]$ PF_6 in the hydride region.

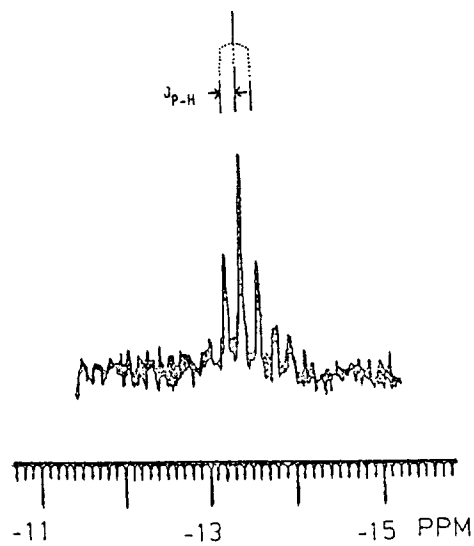


Figure 2. The ^{1}H NMR spectrum of $[\overline{Ir(CN_9H_6CO)}(H)(PPh_3)_2(CN_3COCH_3)]$ PF_6 in the hydride region.

AMX_2 spin system. The value is very close to that of the compound $\overline{Rh(NC_9H_6CO)}(PPh_3)_2(H)(Cl)$[12], which occurs at -11.93 (J_{Rh-H} = 15, J_{P-H} = 6Hz). The spin system indicates that two phosphorus ligands are made equivalent by a molecular mirror plane. The ^{1}H NMR spectrum of 2 shows reson-

Table 2. ^{1}H NMR, and ^{31}P[H] Spectral Data

Complex	^{1}H NMR[a] M-H	^{1}H NMR[a] CH_3	^{31}P NMR[d] PPh_3	^{31}P NMR[d] PF_6
1	-10.38(d of t, J_{Rh-H} = 22.79, J_{P-H} = 6 Hz)	2.04	38.51(d, J_{Rh-P} = 125.55 Hz)	-92.27(septet, J_{P-F} = 712.8 Hz)
2	-13.42(t, J_{P-H} = 14.50 Hz)	2.09	40.21	-99.25(septet, J_{P-F} = 708.2 Hz)
3	-2.12 (d of t, J_{P-H}^b = 7.21, J_{P-H} = 14.82 Hz)	2.11	32.83(d), 18.25(t, $J_{P_1-P_2}^e$ = 306.2 Hz)	-107.34(septet, J_{P-F} = 710.2 Hz)

[a] In P.P.M. relative to $SiMe_4$ in $CDCl_3$, J values in Hz. [b] Equatorial phosphine to the hydride. [c] Axial phosphine to the hydride. [d] Reported in ppm from 85% H_3PO_4 at 80.96 MHZ. [e] Axial phosphine to the equatarial phosphine.

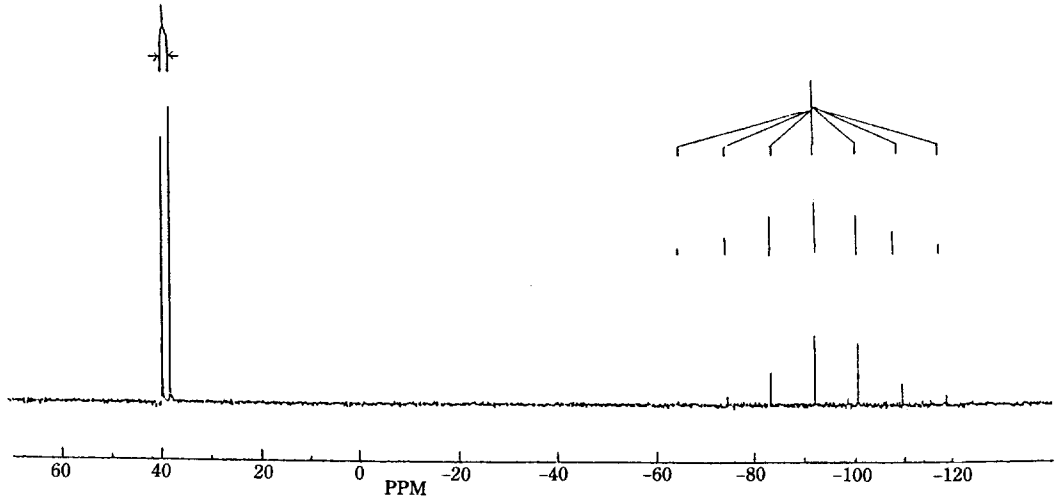
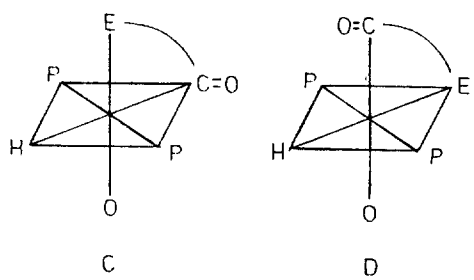


Figure 3. The $^{31}P\{H\}$ NMR spectrum of $[Rh(NC_9H_6CO)(H)(PPh_3)_2(CH_3COCH_3)]PF_6$.

ances of Ir-H centered at δ -13.42(see Figure 2). The value is comparable to that of compound $Ir(Ph_2PC_6H_4CO)(PPh_3)(CO)(Cl)(H)$[15], which occurs at -7.5(J_{P-H} = 14-15 Hz). The pattern and value of 3 is very close to that of compound $[Ir(Ph_2PC_6H_4\text{-}o\text{-}CO)(PPh_3)_2(CO)(H)]ClO_4$. These data are best explained by two possible octahedral structure C and D in which two phosphorus ligands have the trans configuration. Based on



the data of compounds 1 and 3, the structures C and D are both acceptable. However, the spectral data of compound 3 may be helpful in deciding a correct structure. If the correct structure in compound 3 is D, in which the hydride and chelating phosphine ligand have trans configuration, the coupling constant between them is expected to be relatively large (50-150 Hz)[16-17] compared with that between hydride and cis phosphorus (3-20 Hz). The small coupling constant of 3 indicates that the hydride is cis to the phosphorus. Therefore, the structure of D will be eliminated. Analogously, the structure of compounds 1 and 2 may be assigned as C, because the compound of 1 is same as 3, except the nitrogen ligand replacing one axial phosphine.

The $^{31}P\{\mathbf{H}\}$ NMR spectrum of compound 1 is shown in Figure 3. Its pattern consists of one doublet with almost equal intensity and one septet due to the spin coupling between the chemically equivalent two phosphine ligands and rhodium, one phosphine and six fluoride, respectively. The chemical shifts and coupling constants of Rh-P and PF_6 are very similar to those of compound $Ir(Ph_2PC_6H_4CO)(PPh_3)(CO)(Cl)(H)$ and $[Ir_2(\mu\text{-}CNR)(CNR)_4(PMe_2CH_2PMe_2)_2](PF_6)_2$[18], respectively. Accordingly, from our experimental observations, the correct geometry of compounds 1, 2, and 3 appears to favor the structure C.

Conclusion

The rhodium and iridium metal-acyl hydrides were isolated through the reaction between a strongly basic metal compounds and a corresponding aldehyde which is able to form a five membered chelate ring. In order to achieve the activation of C-H bond, we propose that the metal center should be basic, have easily displaceable ligands, and coordinatively unsaturated.

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Photochemical C_4-Cycloadduct Formation between 5(E)-Styryl-1,3-dimethyluracil and Some Olefins-Via Photochemical Diels-Alder Type [4 + 2] Adduct

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The cyclobutane forming photocycloaddition reaction of 5(E)-styryl-1,3-dimethyluracil with some olefins occurs on the 5,6-double bond of uracil ring rather than the expected central double bond via an intermediate, probably the photochemical Diels-Alder type adduct. This intermediate formed on short term irradiation of 5(E)-styryl-1,3-dimethyluracil and 2,3-dimethyl-2-butene solution is converted into the C_4-cycloadduct on the prolonged irradiation. Quantum yield of the intermediate formation is not linear with the concentration of 2,3-dimethyl-2-butene probably due to the secondary reaction accompanied with the complex reaction kinetics. The intermediate is formed from the lowest excited singlet state.

Introduction

The photophysical and photochemical behaviors of stilbene have been extensively studied and the results have contributed prominently to the development of a mechanistic theory of photochemical reactions.[1] The mechanistic details of the photochemical E⇌Z isomerization[2] and photodehydrocyclization[3] of stilbene are well established. Photocycloaddition of stilbene to numerous olefins[4,5] has been thoroughly studied and is known to undergo via a relatively nonpolar singlet exciplex intermediates formed between the electronically excited stilbene and ground state olefins and not via a radical ion pair.[6]

Heterocyclic compounds containing both (n, π^*) and (π, π^*) excited states behave differently from stilbene because of the participation of (n, π^*) states in the decay and/or reaction processes.[7,8] Our laboratory has been interested in the photochemical and photophysical behavior of stilbene derivatives containing hetero-atoms for some time and reported previously that both unimolecular and bimolecular reactions of 1,2-bispyrazinylethylene are very different from those of stilbene because of the high intersystem crossing efficiency.[9-14]

The photocycloaddition reaction of the stilbene derivatives which contain hetero-atoms or are unsymmetrically substituted has been paid little attention until now. 5(E)-Styryl-1,3-dimethyluracil, in which one phenyl ring in stilbene is replaced with a pyrimidine base,[15] is unsymmetrically substituted around the central C = C bond and has both (n, π^*) and (π, π^*) excited states resulting in the different photochemical and photophysical properties from stilbene. It was previously reported that E⇌Z photoisomerization[16] and photocyclization[17] of 5(E)-styryl-1,3-dimethyluracil occur via the excited singlet state as those of stilbene. The photocycloaddition reaction of 5(E)-styryl-1,3-dimethyluracil with some olefins is investigated.

Experimental

Materials. 5(E)-Styryl-1,3-dimethyluracil was prepared by palladium-catalyzed reaction[18,19] of styrene and 1,3-dimethyluracil.[20] 2,3-Dimethyl-2-butene(Aldrich Chemical Co., Milwaukee, USA) was purified by distillation. Dimethyl maleate, methyl crotonate, and dimethyl ethylidenemalonate (Aldrich) were used without further purification. Fumaronitrile (Aldrich) were recrystallized twice from ethanol. Azulene (Aldrich) was purified by vacuum sublimation. Benzophenone (Sigma Chemical Co., St. Louis, USA) was recrystallized from cyclohexane. Kiesel Gel 60 (70-230 mesh, Merck, D-6100 Darmstadt, F.R. Germany) and Kiesel Gel GF_{254} (Merck) were used for silica gel column chromatography and thin layer chromatography, respectively.

Instruments. Ultraviolet-visible spectra were recorded on Cary 17 spectrophotometer. Infrared spectra were measured on a Perkin Elmer 267 spectrophotometer using potassium bromide pellet or sodium chloride cell. Nuclear magnetic resonance spectra were measured on Varian T-60A, Varian FT-80A at 79.542 MHz, and Bruker AM-200-SY spectrometers. Mass spectra were determined with a Hewlett Packard 5985 A GC/MS system by electron impact method. Elemental analysis was carried out on a F&M Scientific Cooperation C.H.N. Analyzer Model 180. High performance liquid chromatography was performed on a Waters Associates Model 244 liquid chromatograph equipped with Model 600A solvent delivery system, Model 440 UV absorbance detector fixed at 254 nm and 280 nm, Model U 6K universal injector. μ-Bondapak CN, Radialpak C_8, and Lichrosorb Si 60 columns were used for purpose of analysis and separation. Fluores-