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PHOTOCYCLOADDITION OF 1,3-DIPHENYL-*N*-METHYL ENAMINOKETONATOBORON DIFLUORIDE WITH SIMPLE OLEFINS

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Abstract- The photoaddition of some cyclic and acyclic olefins to (N-B)-*Z*-1-difluoroboryloxy-1,3-diphenyl-3-methylimino-1-propene (BF_2-complex (**1**)) is discussed. Some of the resulting [2+2] photoadducts produce cyclobutane derivatives having *cis* configurations. The rearrangements of the cyclobutanes give pyridinium salts and 1,5-diketones. Reaction schemes for the formation of the cyclobutanes are presented. The dimer of the BF_2-complex (**1**) is also formed in a reaction which is in competition with the olefins photoaddition.

INTRODUCTION

It is well known that the photocycloaddition of 1,3-diketones to olefins yields versatile intermediates that can be useful in natural product synthesis.[1] Beginning with the researchs of Corey *et al*.[2] and De Mayo,[3] many reports[4] attempting to explain the regio- and stereoselectivity of the photoaddition, have appeared. On the basis of these results, we were led to anticipate that the photoaddition of the corresponding carbonyl compounds (β-enaminoketones) containing a β-enamine group, to olefins might provide a useful route to compounds containing a nitrogen atom. However, irradiation of mixtures of such enaminoketones with some olefins gave no photoadducts, and hence the reaction has hardly been investigated.[5] However, Chow[6] demonstrated that

the reactivity of 1,3-diketones towards olefins was enhanced by complex formation with boron trifluoride, and that the boron difluoride derivatives react with olefins and aromatic compounds to give products in good yields. Therefore, we prepared some enaminoketonatoboron difluorides (BF_2-complexes) by reaction with boron trifluoride and confirmed that, in line with the 1,3-diketones, the BF_2-complexes of enaminoketone have lower reduction potentials[7] than the parent compounds.[8] We have also examined the reaction of some BF_2-complexes with olefins. However, only (N-B)-*Z*-1-difluoroboryloxy-1,3-diphenyl-3-methylimino-1-propene (**1**) yielded products with reasonably good yields.

RESULTS AND DISCUSSION

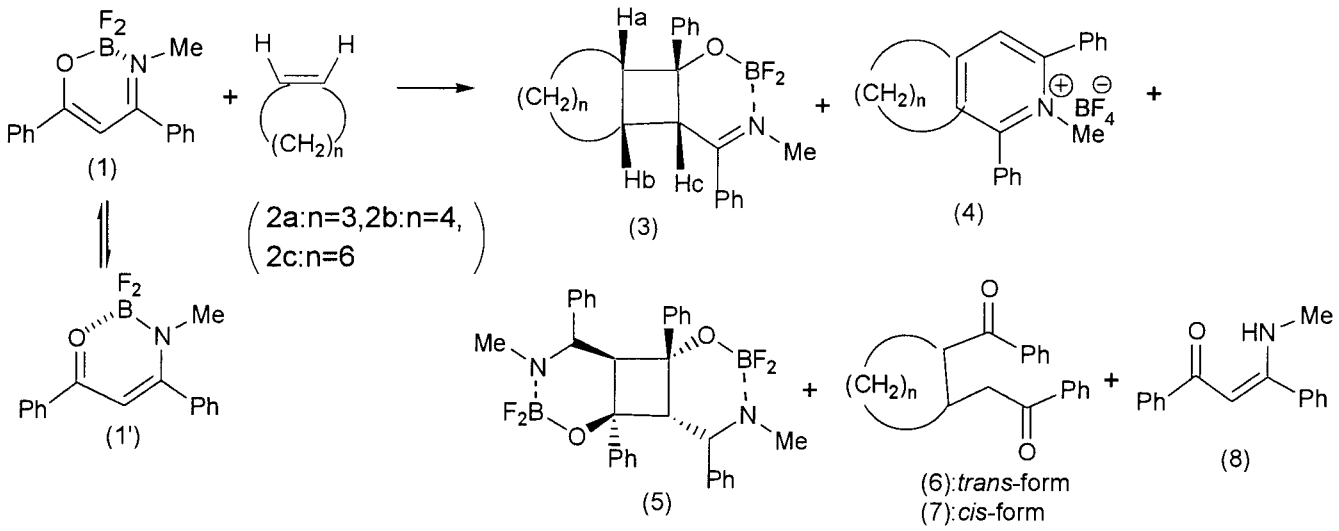
Photocycloaddition of the BF_2-complex (1) to cyclic olefins (2a ~ c)

Irradiation of the BF_2-complex (**1**) with cyclic olefins (**2**) as solvent by a high pressure mercury lamp for 10 h in a Pyrex test tube gave the cyclobutane derivative (**3**), the pyridinium salt (**4**), the dimer (**5**), the 1,5-diketones (*trans* form: **6**, *cis* form: **7**), and the enaminoketone (**8**) as a minor product (Scheme 1). Each of the photoadducts and their derivatives were obtained in pure form by column chromatography, followed by recrystallization. The cyclic olefins used were cyclopentene (**2a**), cyclohexene (**2b**), and cyclooctene (**2c**). The results are shown in Table 1. Despite the increasing ring-size, the products were all formed in similar yields. A possible slight dependence of yields on ring size might, however, be perceived. The structures of the products were determined on the basis of the spectral data. Specifically, the structure of the pyridinium salt (**4**) was determined by X-Ray analysis of a single crystal (Figure 1).[9] In the cyclobutane (**3**), the molecular ion peak (M^+) in the MS spectrum indicated the addition of cyclic olefin (**2**) to the BF_2-complex (**1**). Its ^{1}H-NMR spectra showed the signals due to three methine protons (Hb:δ=2.44 ~ 2.51 (m), Ha:2.69 ~ 2.77 (m), Hc:4.09 (d, *J*=9Hz) ppm) characteristic of cyclobutanes, and the relation of these methine protons is assigned by H-H COSY spectra. A ^{13}C-NMR signal for the imine carbon atom was observed at 181.1 ppm. The structure was confirmed by alkaline hydrolysis of **3** to 1-benzoyl-2-benzoyl- methylcycloalkane by a retro-aldol ring cleavage. The stereochemistry of the cyclobutane (**3**) was mainly determined by the NOESY experiment. The cross peaks appeared between the Ha-Hb-Hc-Ph

configuration, which is assigned as a *cis-syn-cis* orientation (Scheme 1). It is well known that 1,3-enaminoketones exist in ketoamine-enolimine tautomeric equilibrium.[10] (**1 ⇌ 1'**) The X-Ray analysis of the BF_2-complex (**1**) has proven that the 6-membered chelate ring shows a shift to the enol form ((O)-C=C-:1.37 Å, (N)-C=C- : 1.40 Å).[11] The structures of the products suggest that the excited BF_2-complex reacts in the enol form. The MS spectrum of the photoproduct (**4**) revealed that the peak of the highest mass number (M^+-BF_2OH) arose from the loss of BF_2OH from the adduct. Its ^{1}H- and ^{13}C-NMR spectra showed signals based on a ring-fused cycloalkane, an aromatic ring and a methyl group. The product (**4**) is insoluble in organic solvents so we were unable to obtain additional information useful to assign the structure. However, the single crystal structure analysis by X-Ray diffraction showed that the photoproduct (**4**) is the cycloalkane-fused pyridinium salt depicted in Figure 1. The NMR spectra of photoproduct (**5**) revealed no cycloalkane signal and, in contrast to other photoproducts, no further useful structural information could be obtained from its MS spectra (no M^+). The same product was obtained by irradiation of a hexane solution of the neat BF_2-complex (**1**). (78% yield for 10 h).[12] The structure was reported by us using the X-Ray analysis.[12] The product (**5**) is the dimer of the BF_2-complex (**1**), having a sterically *anti* head-to-tail form. The ^{1}H-NMR spectra of the photoproducts (**6, 7**) showed signals due to a cycloalkane and aromatic rings, and the ^{13}C-NMR spectra showed not only these rings but also two carbonyl groups (200, 204 ppm). Further, their IR spectra indicated carbonyl groups (1680, 1600 cm^{-1}). The stereochemistry of the products (**6, 7**) were determined from the H-H COSY and NOESY spectra. Also, on treatment with alkaline solution, the cyclobutane (**3)** underwent retro-aldol ring cleavage to produce a mixture of **6** and **7**. The ratio of the diketones (**6, 7**) changed during the photoreaction and isolation leading to difficulties in purification. The parent compound (**8**) (enaminoketone) of the BF_2-complex (**1**) was obtained as the minor product.

Photocycloaddition of the BF_2-complex (1) to acyclic olefins (2d ~ f)

Irradiation of the acyclic olefins (**2d ~ f**) with the BF_2-complex (**1**) using the similar conditions as that of the cyclic olefins gave the cyclobutane derivative (**9**) ([2 + 2]



Scheme 1

Table 1. Photocycloaddition of BF_2-complex (**1**) with cyclic olefins (**2**)

	cyclobutane (**3**)%	py.salt (**4**)%	dimer (**5**)%	diketone (**6**)(*cis*)%	(**7**)(*trans*)%	enaminone (**8**)%
Cyclopentene (**2a**)	21	21	16	8	6	6
Cyclohexene (**2b**)	24	18	19	3	2	11
Cyclooctene (**2c**)	28	22	18	---	3	15
(**2a**) + H_3PO_4	11	33	6	16	---	8

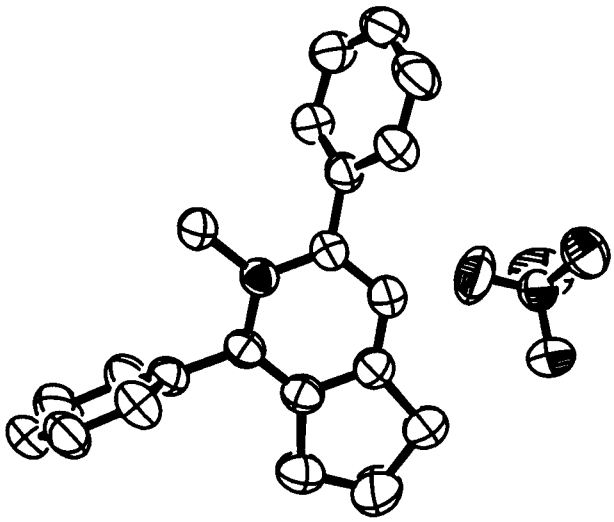
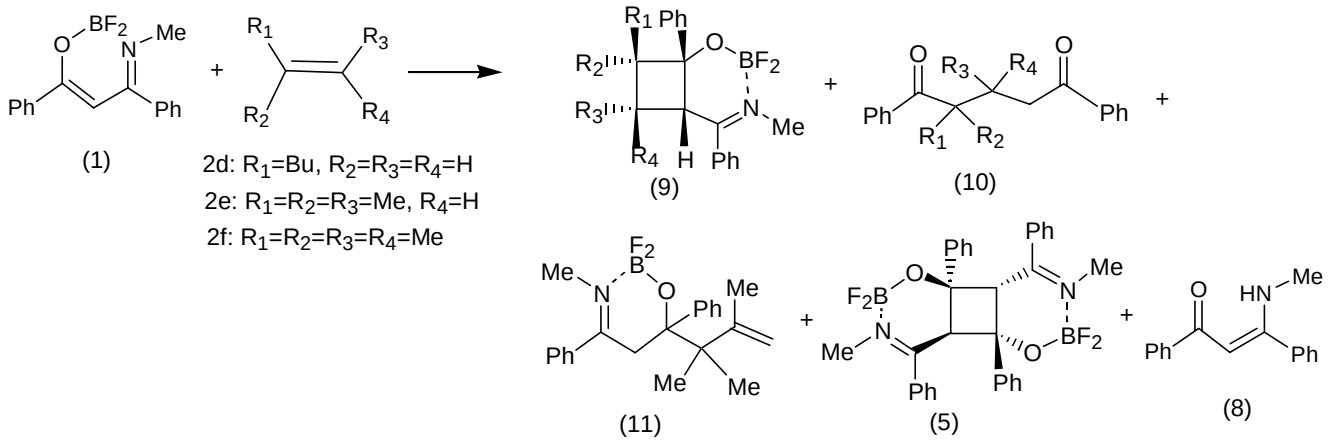


Figure 1. The structure of the pyridinium salt (**4**)

photoadduct), the 1,5-diketone (**10**), its rearrangement compound (**11**), and the dimer (**5**) (Scheme 2). The photoproducts were separated by column chromatography, followed by recrystallization. The products and yields are shown in Table 2. The structures of the products were determined from the spectral data. Product yields depended on the configuration of the olefins (**2d ~ f**).

In the reaction of hexene (**2d**), 2-butyl-1,5-diphenyl-1,5-pentanedione (**10d**) was obtained as the main product. It is produced by a retro-aldol ring cleavage from [2+2] photoadduct (**9d**). The dimer (**5**) was obtained in high yield.



Scheme 2

Table 2. Photocycloaddition of BF_2-complex with acyclic olefins

	cyclobutane (**9**)%	1,5-diketone (**10**)%	rearrangement (**11**)%	dimer (**5**)%	enaminone (**8**)%
1-hexene(2d)	----	15	----	40	5
2-methyl-2-butene(2e)	29	16	----	27	16
2,3-dimethyl-2-butene(2f)	40	----	10	19	3

In the reaction of 2-methyl-2-butene (**2e**), the cyclobutane (**9e**) and its ring cleavage product (1,5-diketone) (**10e**) were obtained. The dimer (**5**) and the enaminoketone (**8**) were also formed. The stereochemistry of **9e** was determined by the cross peak between the two methines (2.27 and 4.29 ppm) at the cyclobutane ring in H-H COSY and NOESY spectra. It showed that the stereochemistry takes head-to-head form (H-H) and the *cis*-to-*cis* conformation indicated.

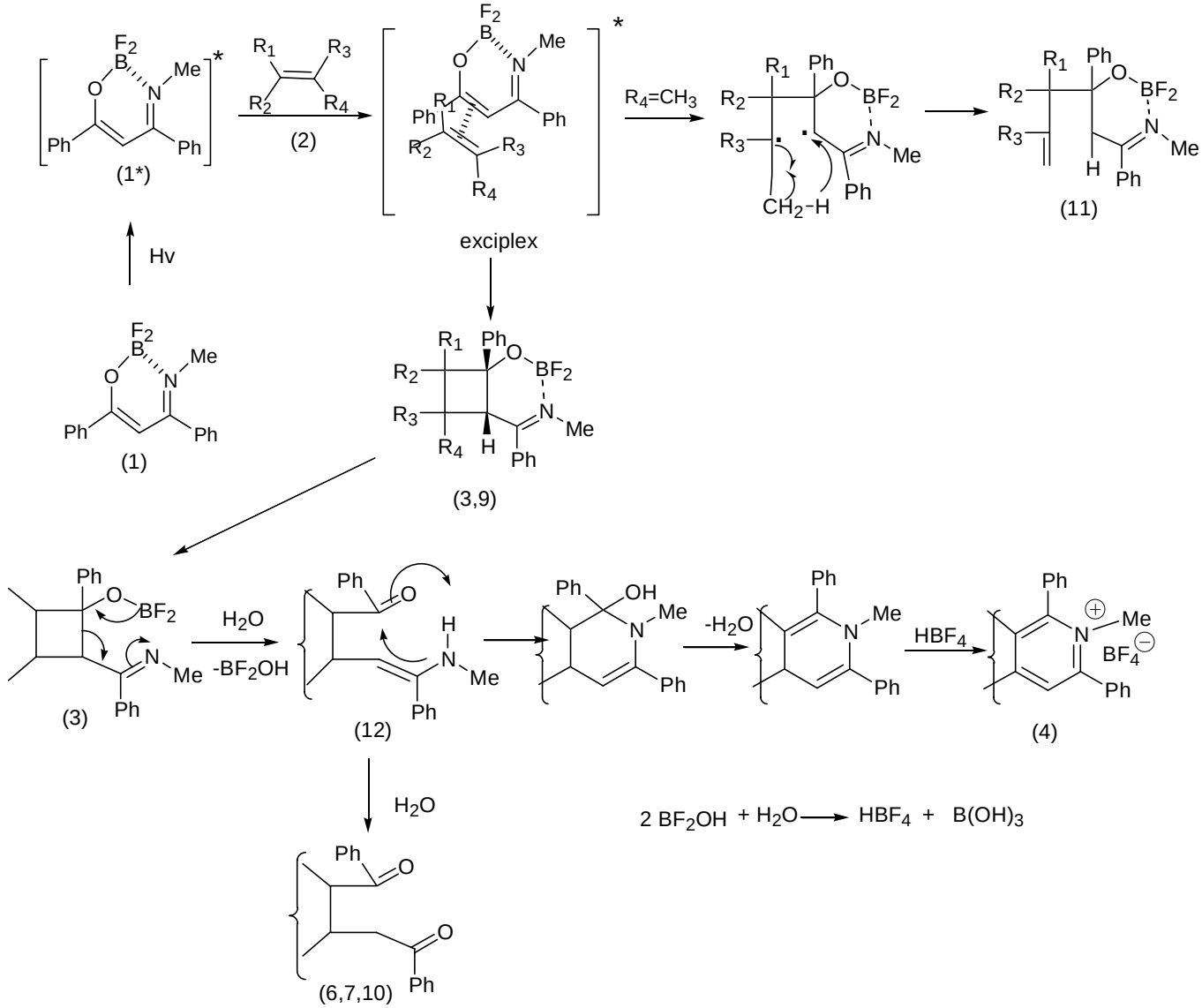
In the reaction of 2,3-dimethyl-2-butene (**2f**), both the cyclobutane (**9f**) and the dimer (**5**) were obtained. The derivative (**11**) from the [2+2] photoadduct (**9f**) was also among the products. The MS spectra showed that the highest mass number peak (330) arose from the loss of F atom from the photoadduct (**9f**). Its ^{1}H-NMR spectra displayed signals due to two olefinic protons (4.75, 4.96 ppm) and four other methyl groups. Also, the ^{13}C-NMR spectra showed signals due to the two olefinic carbons (113.7, 152.1 ppm). Furthermore, the above relation was confirmed by the COLOC spectra. The imine group was observed at 183.3 ppm and at 1674 cm^{-1}, but the carbonyl group was not noticed. The stretching bands of B-O and B-F in the IR spectrum were observed at 1142 and 1060 cm^{-1}. From these spectral data, the structure was assigned as (N-B)-3-difluoroboryloxy-1,3-diphenyl-1-methylimino-4,4,5-trimethyl-5-hexene (**11**).

The scheme of formation of some major photoproducts (3, 4, 6, 7, 9, 10, 11)

As the exciplex is assumed to be the immediate precursor of the cycloaddition, the results described above must, in spite of steric hindrance, originate from and be controlled by the properties governing the orientation (*cis-syn-cis*) and the efficiency of the cycloaddition[13]. In other words, all photoproducts except of dimer (**5**) and enaminoketone (**8**) are produced *via* the exciplex[14] generated by the interaction between the excited state BF_2-complex (**1***) and the ground state of the olefin (**2**) **(**Scheme 3). The cyclobutanes (**3**, **9**) are formed, after spin inversion, directly by the usual ring closure from the exciplex. The rearrangement compound (**11**) arises *via* 1,5-hydrogen shift from the exciplex. Thus, the radical produced from the exciplex is a moderately stable tertiary radical, which might undergo rearrangement leading to the compound (**11**) together with a hydrogen shift before the ring closure.

On the other hand, the cyclobutane (**3, 9**) undergo hydrolysis to deborondifluoride, which assists the cyclobutane ring opening by means of retro-aldol type cleavage, giving the 1-carbonyl-5-amine derivative (**12**). The compound (**10**) undergoes hydrolysis to give the diketones (**6, 7, 10**).[15] In an experiment to confirm the scheme of the pyridinium salt (**4**) formation, the irradiation of the BF_2-complex (**1**) in cyclopentene (**2a**) in the presence of an acid catalyst (5% phosphoric acid) gave an increased yield of the pyridinium salt (21% → 33% yield) together with a decreased

yield of the cyclobutane (**3a**) (21% → 11%) (Table 1). This result suggests that the formation of the pyridinium salt occurs *via* the cyclobutane, namely, the derivative (**12**). This is followed by the attack on the carbonyl carbon by the lone pair electrons of the nitrogen atom. At the end of the reaction, dehydration and aromatization occur to yield the pyridinium salt (**4**) (Scheme 3). The ligand, however, is not the difluoroboroxy anion but rather the tetrafluoroborate anion. The tetrafluoroborate is produced from the resulting hydroxyldifluoroborate and water.[16] Meyers and Singh[17]



Scheme 3

reported that, on addition of acid, enamino alcohols are converted smoothly to their corresponding dihydropyridinium salt in good yield. These undergo facile air oxidation to produce pyridinium salt (**4**). In the intermediate (**12**), the restricted

carbonyl carbon atom and the nitrogen atom linking with cycloalkane are located at neighboring positions. However, acyclic olefins not possessing the same restriction as cyclic olefins can easily convert to the rearrangement compound, and hence do not produce pyridinium salt. Additionally, the electron density at the nitrogen atom is increased by the neighboring phenyl group. Therefore, the cyclization is accelerated and preferred to the hydrolysis. Similar products (dihydropyrans) result in the photoreaction of 1,3-diketones. Chow *et al*.[18] reported that the dihydropyrans were obtained in the photoreaction of the mixture of 1,3-diketone substituted by restricting cyclohexyl groups linking benzene ring. Also, Tada *et al*.[13] obtained the dihydropyrans from the photoreaction of 3-cyano-2,4-pentenedione in the presence of cyclohexene.

CONCLUSION

The behavior of the BF_2-complex (**1**) in photoaddition to olefins is discussed.

1) The acyclic olefins show a lesser tendency to undergo photoreaction than the cyclic olefins. 2) In some [2+2] photoadducts, rearrangement occurs under the reaction conditions.

The lesser photocycloaddition of the acyclic olefin as compared with the cyclic olefin suggests that exciplex formation is influenced by the extent to which cyclobutane bond formation can be suppressed. The exciplex of the cyclic olefin shows a probable interaction between the lone pair electrons of the nitrogen and oxygen atoms of the BF_2-complex (**1**) and those hydrogen atoms in the cyclic olefin not suffering steric hindrance. However, in the acyclic olefins (**2e**, **2f**), the steric factor produced by the dimethyl group should prevent or reduce exciplex formation.

The most interesting characteristic of the photocycloaddition is as an easy route to cyclobutane derivative *via* the [2+2] photoadduct. This is in sharp contrast to the case of 1,3-diketones[1] (known as *de Mayo reaction)* and their BF_2-complexes[6] which yield no cyclobutane. This result seems to stem from the strength of coordination between the nitrogen and boron atoms and the mild strain energy of the cyclobutane formed.

The photoreaction of both cyclic and acyclic olefins yields the dimers (**5**). Reactive electron-rich olefins (e.g. 2-methyl-2-butene, 2,3-dimethyl-2-butene) produce a good deal of the cyclobutane (**9**), and a small amount of the dimer (**5**). In contrast, an

unreactive olefin, such as 1-hexene, yields a small amount of the cyclobutane (**9**), and a good deal of the dimers (**5**). Thus, the dimerization and the cyclization are seen to be competition reactions.[12] Also, the 1,3-diketones are reported to produce the dimer.[19]

EXPERIMENTAL

The IR spectrum was recorded with KBr tablets on Hitachi I-2000 spectrophotometer. The ^{1}H and ^{13}C-NMR spectra were recorded in deuterochloroform on JEOL FX-90Q and Bruker AC-250 spectrometers. Tetramethylsilane was used as the internal reference for the proton spectra. The MS spectra were recorded on an ESCO EMD-05A and HRMS was taken on a JMS-D300 spectrometer. Melting points were determined on a Yanaco micro hot-plate apparatus and are uncorrected.

The 1,3-diphenyl-3-methylimino-1-propenone and its BF_2-complex (**1**) were prepared as described in the previous publication.[8,12,20]

Photocycloaddition; the general procedure

A solution of the BF_2-complex (**1**) (285 mg, 1 mmol) in cyclic olefin (**2**) (100 mL) was gassed out with nitrogen and irradiated at 0°C for 10 h. After irradiation, the precipitate produced was separated, dissolved in ethylene dichloride, and the insoluble solid separated. The combined filtrate was concentrated under reduced pressure to give a solid. The solids were chromatographed on silica gel with hexane-ethyl acetate (9:1 → 3:1) as eluent to give the products.

Photoaddition of the BF_2-complex (1) with Cyclopentene (2a): (N-B)-c-6-Difluoroboryloxy-c-7-methyliminobenzyl-t-6-phenylbicyclo[3.2.0]-heptane (3a):

mp 136.0 ~ 138.0 °C (ethyl acetate-n-hexane). MS: m/z, 353(M^+), 352, 285, 284, 258, 220. IR: 2956, 1658, 1152, 1072, 888, 702 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ=1.42 ~ 1.67 (2H, m), 1.93 ~ 2.03 (2H, m), 2.35 ~ 2.42 (2H, m), 2.85 ~ 3.02 (2H, m), 3.31(3H, s), 4.09 (1H, d, *J*=9.1 Hz), 7.26 ~ 7.41 (5H, m), 7.56 ~ 7.67 (5H, m). ^{13}C-NMR ($CDCl_3$): δ=25.6, 27.8, 29.1, 37.6, 40.0, 48.1, 52.8, 74.7, 124.8, 124.9, 126.7, 127.1, 128.1, 129.5, 134.5, 148.2, 181.4 ppm. Anal. Calcd for $C_{21}H_{22}NOBF_2$: C, 71.41, H, 6.28, N, 3.97. Found: C, 71.29, H, 6.15, N, 4.13.

1,3-Diphenylcyclopenta[2,3-*c*]-2-methylpyridinum tetrafluoroborate (4a):

mp 199.5 ~ 201.5 °C (CH_2Cl_2-n-hexane). MS: m/z, 305, 285, 270. IR: 1626, 1472, 1052, 702 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ=2.22 (2H, q, *J*=7.6 Hz), 2.83 (2H, t, *J*=7.6 Hz), 3.27 (2H, t, *J*=7.6 Hz), 3.71 (3H, s), 7.55 (1H, s), 7.25 ~ 7.68 (11H, m) ppm; ^{13}C-NMR ($CDCl_3$): δ=24.7, 32.3, 34.5, 44.5, 124.5, 128.4, 129.1, 129.4, 129.8, 130.9, 131.7, 133.4, 144.7, 151.6, 155.0, 164.6 ppm. Anal. Calcd for $C_{21}H_{20}NBF_4$: C, 67.58, H, 5.40, N, 3.75. Found: C, 67.61, H, 5.48, N, 3.75.

The Dimer (5) of the BF_2-complex:

mp 126.0 ~ 127.0 °C (CH_2Cl_2-n-hexane). MS: m/z, 285 (M^+/2), 284, 149, 118, 105, 77, 56. IR: 1660, 1532, 1144 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ=3.12 (6H, s), 4.80 (2H, s), 6.55 (4H, d, *J*=7.4 Hz), 7.18 ~ 7.71 (16H, m) ppm; ^{13}C-NMR ($CDCl_3$): δ=37.4, 62.6, 127.3, 127.5, 127.7, 128.1, 128.6, 128.7, 129.2, 131.5, 141.8, 178.9 ppm. Anal. Calcd for $C_{32}H_{28}N_2O_2B_2F_4$: C, 67.41, H, 4.95, N, 4.91. Found: C, 67.49, H, 5.09, N, 4.99.

***trans*-1-Benzoyl-2-benzoylmethylcyclopentane (6a):**

Oil. MS: m/z, 292 (M^+), 224, 173, 105. IR: 2960, 1682, 1598, 1450, 1220, 690 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ=1.61 ~ 2.13 (7H, m), 2.95 (1H, d, *J*=13.1 Hz), 2.98 (1H, q, *J*= 13.8 Hz), 4.00 ~ 4.11 (1H, m), 7.18 ~ 7.50 (6H, m), 7.74 ~ 7.97 (4H, m) ppm. ^{13}C-NMR ($CDCl_3$): δ=23.8, 29.1, 39.3, 39.8, 48.6, 52.7, 128.0, 128.4, 128.5, 128.7, 132.9, 133.0, 137.1, 137.8, 199.8, 203.3 ppm. HRMS m/z (M^+): Calcd for $C_{20}H_{20}O_2$: 292.3812, Found: 2923.3742.

***cis* -1-Benzoyl-2-benzoylmethylcyclopentane (7a):**

Oil. MS: m/z, 292 (M^+), 224, 173, 105. IR: 2956, 1682, 1598, 1450, 1220, 690 cm^{-1}. ^{1}H-NMR($CDCl_3$): δ =1.35 ~ 1.50 (2H, m), 1.70 ~ 1.80 (2H, m), 2.01 ~ 2.20 (2H, m), 2.87 (1H, dd, *J*=8.3 Hz, 14.5 Hz), 2.93 ~ 3.07 (1H, m), 3.19 (1H, dd, *J*=5.2 Hz, 14.5 Hz), 3.52 (1H, q, *J*=8.0 Hz), 7.40 ~ 7.56 (6H, m), 7.93 ~ 7.98 (4H, m) ppm. ^{13}C-NMR ($CDCl_3$): δ=24.8, 31.4, 32.5, 38.9, 43.8, 52.7, 128.3, 128.5, 128.6, 132.9, 133.0, 137.0, 137.3, 199.8, 202.3 ppm. HRMS m/z (M^+): Calcd for $C_{20}H_{20}O_2$: 292.3812, Found: 292.3742.

Photoaddition of the BF_2-complex (1) with Cyclohexene (2b):

(N-B)-c-7-Difluoroboryloxy-c-8-methyliminobenzyl-t-7-phenylbicyclo[4.2.0]-

octane (3b):

mp 145.0 ~ 146.0 °C (ethyl acetate-n-hexane). MS: m/z, 366 (M^+), 301, 286, 285, 272, 258. IR: 2928, 1650, 1448, 1150, 1084, 905, 702 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ=1.04 ~ 2.10 (6H, m), 2.44 ~ 2.51 (1H, m), 2.66 ~ 2.77 (1H, m), 3.30 (3H, s), 4.09 (1H, d, *J*=8.8 Hz), 7.22 ~ 7.40 (5H, m), 7.56 ~ 7.69 (5H, m). ^{13}C-NMR ($CDCl_3$): δ=20.3, 22.3, 22.6, 24.4, 35.7, 37.2, 43.4, 48.1, 79.0, 125.1, 126.5, 126.9, 128.1, 129.4, 131.6, 133.3, 146.3, 181.1 ppm. Anal. Calcd for $C_{22}H_{24}NOBF_2$: C, 71.95, H, 6.59, N, 3.81. Found: C, 71.49, H, 6.28, N, 4.03.

1,3-Diphenylcyclohexa[2,3-*c*]-2-methylpyridinum tetrafluoroborate (4b):

mp 204.6 ~ 206.0 °C (CH_2Cl_2-n-hexane). MS: m/z, 355, 299, 284, 270. IR: 2936, 1620, 1470, 1082, 750, 706 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ=1.82 ~ 1.86 (4H, m), 2.44 (2H, t, *J*=6.2 Hz), 3.07 (2H, t, *J*=6.1 Hz), 3.66 (3H, s), 7.50 (1H, s), 7.54 ~ 7.67 (10H, m) ppm; ^{13}C-NMR ($CDCl_3$): δ =20.7, 21.6, 27.7, 30.2, 44.6, 128.1, 129.1, 129.2, 129.3, 130.1, 130.7, 130.8, 131.0, 132.9, 137.2, 152.4, 155.1, 158.0 ppm. Anal. Calcd for $C_{22}H_{22}NBF_4$: C, 68.24, H, 5.73, N, 3.62. Found: C, 68.55, H, 6.00, N, 3.81.

***trans* -1-Benzoyl-2-benzoylmethylcyclopentane (6b):**

Oil. MS: m/z, 306 (M^+), 228, 224, 187. IR: 2936, 1686, 1450, 1256, 792 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ=1.25 ~ 1.93 (8H, m), 2.70 ~ 2.78 (1H, m), 2.94 (1H, dd, *J*=5.1, 6.9 Hz), 3.09 (1H, dd, *J*=8.5, 16.9 Hz), 3.68 ~ 3.73 (1H, m), 7.32 ~ 7.54 (6H, m), 7.79 ~ 7.92 (4H, m) ppm. ^{13}C-NMR ($CDCl_3$): δ=23.1, 23.7, 26.1, 29.4, 32.5, 33.9, 39.2, 46.5, 128.1, 128.3, 128.5, 128.7, 132.8, 132.9, 137.3, 137.5, 199.8, 203.5 ppm. HRMS m/z (M^+): Calcd for $C_{21}H_{22}O_2$: 306.4083, Found: 306.4089.

***cis* -1-Benzoyl-2-benzoylmethylcyclopentane (7b):**

Oil. MS: m/z, 306 (M^+), 288, 224, 187. IR: 2932, 1682, 1450, 1214, 690 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ =1.25 ~ 2.00 (8H, m), 2.46 ~ 2.72 (2H, m), 3.00 ~ 3.46 (2H, m), 7.37 ~ 7.55 (6H, m), 7.93 ~ 8.06 (4H, m) ppm. ^{13}C-NMR ($CDCl_3$): δ=25.7, 26.1, 31.5, 36.1, 44.3, 50.9, 128.4, 128.5, 128.6, 128.8, 132.9, 133.1, 137.3, 199.8, 203.9 ppm. HRMS m/z (M^+): Calcd for $C_{21}H_{22}O_2$: 306.4083, Found: 306.4031.

Photoaddition of the BF_2-complex (1) with Cyclooctene (2c):

(N-B)-c-9-Difluoroboryloxy-c-10-methyliminobenzyl-t-9-phenylbicyclo[6.2.0]-decane (3c):

mp 144.5 ~ 145.8 °C (ethyl acetate-n-hexane). MS: m/z, 330, 329, 315, 301, 286, 253. IR: 2908, 1652, 1176, 1150, 888, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ=0.90 ~ 2.38 (12H, m), 2.41 (1H, m), 2.79 (1H, m), 3.30 (3H, s), 4.16 (1H, d, *J*=9.51 Hz), 7.22 ~ 7.40 (5H, m), 7.53 ~ 7.62 (5H, m). ^{13}C-NMR ($CDCl_3$): δ=18.6, 25.5, 25.7, 27.0, 27.6, 31.3, 37.2, 44.1, 48.5, 50.7, 77.2, 125.3, 126.9, 128.0, 129.5, 131.8, 145.2, 180.4 ppm. Anal. Calcd for $C_{24}H_{28}NOBF_2$: C, 72.92, H, 7.14, N, 3.54. Found: C, 73.03, H, 7.26, N, 3.68.

1,3-Diphenylcycloocta[2,3-c]-2-methylpyridinum tetrafluoroborate (4c):

mp 96.0 ~ 98.0 °C (CH_2Cl_2-n-hexane). MS: m/z, 346, 345, 270. IR: 2932, 1620, 1446, 1056, 758, 706 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ=1.30 ~ 2.00 (8H, m), 2.55 ~ 2.70 (2H, m), 2.92 ~ 3.11 (2H, m), 3.66 (3H, s), 7.55 ~ 7.65 (11H, m) ppm; ^{13}C-NMR ($CDCl_3$): δ=25.1, 26.7, 28.2, 29.7, 29.9, 31.3, 33.5, 44.8, 128.2, 128.3, 129.0, 129.1, 129.4, 130.4, 130.5, 131.9, 132.8, 140.0, 153.7, 154.3, 161.8 ppm. Anal. Calcd for $C_{24}H_{26}NBF_4$: C, 69.41, H, 6.31, N, 3.37. Found: C, 69.55, H, 6.41, N, 3.54.

***trans* -1-Benzoyl-2-benzoylmethylcyclooctane (6c):**

Oil. MS: m/z, 334 (M^+), 316, 215, 173, 105, 77. IR: 2928, 1682, 1598, 1448, 692 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ =1.25 ~ 1.89 (12H, m), 2.77 ~ 3.06 (3H, m), 3.91 ~ 3.99 (1H, m), 7.26 ~ 7.58 (6H, m), 7.77 ~ 7.95 (4H, m) ppm. ^{13}C-NMR ($CDCl_3$): δ=25.7, 26.5, 27.1, 29.0, 31.6, 34.9, 41.5, 45.8, 128.0, 128.2, 128.4, 128.7, 132.8, 137.2, 199.9, 204.6 ppm. HRMS m/z (M^+): Calcd for $C_{23}H_{26}O_2$: 334.4625, Found: 334.4631.

Photoaddition of the BF_2-complex (1) with 1-Hexene (2d):

3-Butyl-1,5-diphenyl-1,5-pentanedione (10d):

Oil. MS: m/z, 308 (M^+), 257, 224, 203, 189. IR: 2932, 2860, 1680, 1600, 1450, 1224, 690 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ=0.82 ~ 0.87(3H, m), 1.27 ~ 1.31(4H, m), 1.49 ~ 1.57 (1H, m), 1.77 ~ 1.85 (1H, m), 2.01 ~ 2.09 (1H, m), 2.14 ~ 2.26(1H, m), 2.78 ~ 2.91(1H, m), 3.00 ~ 3.10(1H, m), 3.55 ~ 3.66(1H, m), 7.26 ~ 7.58(6H, m), 7.88 ~ 7.99 (4H, m) ppm. ^{13}C-NMR ($CDCl_3$): δ=13.9, 22.9, 26.4, 29.6, 32.3, 36.0, 45.3, 128.1, 128.3, 128.6, 128.8, 133.0, 137.1, 137.6, 199.9, 204.0 ppm. HRMS m/z (M^+): Calcd for $C_{21}H_{24}O_2$: 308.4242, Found: 308.4615.

Photoaddition of the BF_2-complex (1) with 2-Methyl-2-butene (2e):

(N-B)-1-Difluoroboryloxy-2-methyliminobenzyl-1-phenyl-c-3,4,4-trimethyl-cyclobutane (9e):

mp 147 ~ 148.5 °C (ether-n-hexane). MS: m/z, 336, 285, 284, 264, 220, 208. IR: 2960, 1658, 1448, 1380, 1152, 1088, 886, 724 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ=0.71 (3H, s), 1.18 (3H, s), 1.26 (3H, d, *J*=7.6 Hz), 2.27 (1H, dq, *J*=7.6, 9.3 Hz), 3.28 (3H, s), 4.29 (1H, d, *J*=9.3 Hz), 7.26 ~ 7.65 (10H, m) ppm. ^{13}C-NMR ($CDCl_3$): δ=13.2, 15.9, 27.2, 37.2, 42.7, 42.8, 43.8, 79.2, 125.7, 126.9, 127.9, 129.5, 131.8, 133.5, 142.7, 181.0 ppm. Anal. Calcd for $C_{21}H_{24}NOBF_2$: C, 71.00, H, 6.81, N, 3.94. Found: C, 70.97, H, 6.96, N, 3.91.

1,5-Diphenyl-2,2,3-trimethyl-1,5-pentanedione (10e):

Oil. MS: m/z, 294 (M^+), 224, 189, 148. IR: 2960, 1680, 1448, 1254, 968 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ=0.95 (3H, d, *J*=6.8 Hz), 1.31 (3H, s), 1.34 (3H, s), 2.75 ~ 2.96 (2H, m), 3.02~3.09 (1H, m), 7.40 ~ 7.55 (6H, m), 7.88 (2H, dd, *J*=1.2, 8.1 Hz), 7.76(2H, dd, *J*=1.4, 7.9 Hz) ppm. ^{13}C-NMR ($CDCl_3$): δ=15.2, 22.1, 23.3, 35.5, 41.5, 51.0, 127.9, 128.1, 128.2, 128.6, 130.9, 132.9, 137.3, 139.0, 199.0, 208.7 ppm. Anal. Calcd for $C_{20}H_{22}O$: C, 81.60, H, 7.53. Found: C, 81.97, H, 6.96.

Photoaddition of the BF_2-complex (1) with 2,3-Dimethyl-2-butene (2f):

(N-B)-3-Difluoroboryloxy-c-2-methyliminobenzyl-1-phenyl-c-3,3,4,4-tetra-methylcyclobutane (9f):

mp 171.5 ~ 172.5 °C (ether-n-hexane). MS: m/z, 350, 285, 284, 266, 224. IR: 2964, 1653, 1374, 1146, 1076, 884 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ=0.62 (3H, s), 0.70(3H, s), 1.18 (3H, s), 1.36 (3H, s), 3.27 (3H, s), 3.95 (1H, s), 7.27 ~ 7.66 (10H, m) ppm. ^{13}C-NMR ($CDCl_3$): δ=16.3, 21.9, 23.5, 24.3, 37.2, 44.6, 46.5, 50.1, 78.0, 126.9, 127.0, 127.8, 129.4, 125.7, 131.9, 133.7, 142.7, 180.8 ppm. Anal. Calcd for $C_{22}H_{26}NOBF_2$: C, 71.56, H, 7.29, N, 3.81. Found: C, 71.53, H, 7.10, N, 3.90.

(N-B)-3-Difluoroboryloxy-1,3-diphenyl-1-methylimino-4,4,5-trimethyl-5-hexane (11f):

mp 119 ~ 119.5 °C (ether-n-hexane). MS: m/z, 350, 286, 285, 266, 225. IR: 2960, 1674, 1448, 1362, 1142, 1060, 896, 770 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ=0.62 (3H, s), 0.70 (3H, s), 1.88 (3H, s), 3.03 (3H, s), 3.52 (3H, s), 4.75 (1H, d, *J*=1.0 Hz), 4.96 (1H, d, *J*=1.0 Hz), 6.93 ~ 7.53 (10H, m) ppm. ^{13}C-NMR ($CDCl_3$): δ=23.2, 23.3, 24.3, 37.1,

41.8, 47.0, 80.5, 113.7, 125.7, 127.0, 129.2, 128.6, 131.2, 135.0, 142.9, 152.1, 183.3 ppm. Anal. Calcd for $C_{22}H_{26}NOBF_2$: C, 71.56, H, 7.29, N, 3.81. Found: C, 71.27: H, 6.96, N, 3.91.

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