Photoinduced Electron Transfer Reaction of Cyclopropanone Acetals with Arylmethyl Methanesulfonate: Generation of β-Keto Radical Species and Application to C–C Bond Formation

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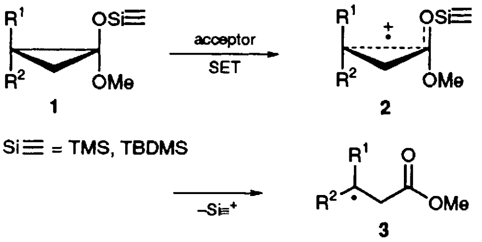
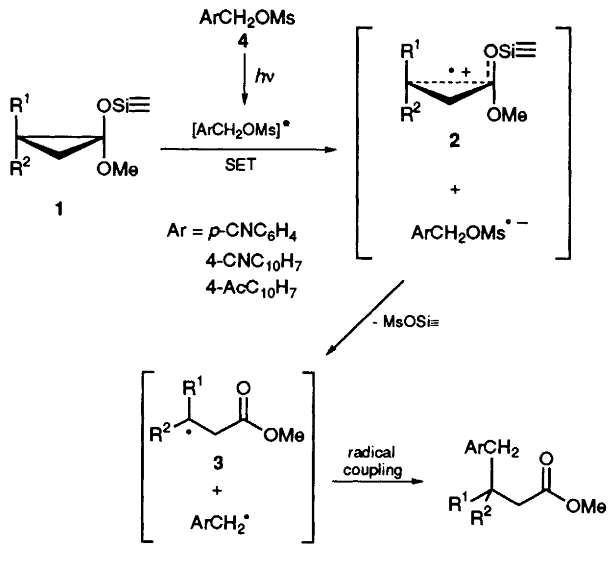
The photoinduced electron transfer reaction of the cyclopropanone acetals **1** with arylmethyl methanesulfonates **4** or **10** as electron acceptors was found to generate a transient pair of radicals, the β-keto radical **3** and the arylmethyl radical, which underwent a novel carbon–carbon bond formation reaction at the sterically hindered β-position of the esters.

Ring-opening reactions of cyclopropane derivatives accompanied by carbon–carbon bond formation reactions are synthetically useful for introducing a C_3 unit into an organic molecule in one step.[1] Oxidation of cyclopropanes with electron acceptors is one of the methods for cleaving the ring system.[2] Recently, we reported the high donor character of cyclopropanone acetals **1**, which was demonstrated in the non-irradiated reaction with quinones (DDQ and chloranil).[3] Based on these results obtained, we deduced that cyclopropanone acetals **1**, after single electron transfer to an appropriate acceptor, can be transformed into a β-keto radical species **3**[4] by loss of a silyl group. (Scheme 1).[5]

We report here a novel type of C–C bond-forming reaction which is designed to take advantage of the fact that in the photoinduced electron transfer reaction of the cyclopropanone acetals **1** with an arylmethyl methanesulfonate, a transient pair of radicals are formed resulting in the formation of a C–C bond at the sterically hindered β-position of the esters (Scheme 2). (By comparison the site selectivity of the ring-opening in the homoenolate type reaction of **1** is reversed.[6])



Scheme 1

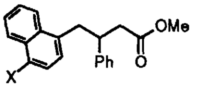
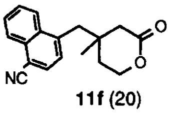


Scheme 2

p-Cyanobenzyl methanesulfonate **4** and the 4-substituted-1-naphthylmethyl methanesulfonate **10** were selected for study because of their high electron-accepting ability and synthetic versatility. Initially the reaction of 2-(*p*-methoxyphenyl) cyclopropanone acetal **1a** (2 equiv.)[7] with *p*-cyanobenzyl methanesulfonate **4**† in degassed MeCN was studied. Irradiation with a high-pressure mercury lamp using a quartz filter produced the desired coupling product **5a** (41%) together with radical dimers **7** (3%) and **8** (20%). The formation of **7** and **8** suggests the intervention of two different radicals, *i.e.* the *p*-cyanobenzyl radical[8] and the β-keto radical **3** (Table 1, reaction 1). When a solution of **1b** (2 equiv.) and **4** in MeCN was irradiated, the yield of **5b** increased to 67% (a 51% conversion of **4**) without giving the dimer of the β-keto radical (reaction 2). Acetal **1b**, however, was unstable in the reaction medium, therefore, **1c** was prepared in which a *tert*-butyldimethylsilyl (TBDMS) group was substituted for a trimethylsilyl (TMS) group of **1b** (reaction 3). As expected, **5b** was obtained in a higher yield and, furthermore, unreacted **1c** was recovered efficiently (reaction 3). Intervention of radical species **3** was verified by the trapping experiment performed under an oxygen atmosphere (reaction 5), in which the formation of **5b** was suppressed and, instead, β-ketoester **9** was obtained.

To extend the synthetic utility of the present C–C bond forming reaction, alkyl-substituted acetal **1d**, bicycloacetals **1e** and **f**, and spiroacetal **1g** were adopted as donors (reactions 6–10). Desired coupling products **5** and **6** were obtained in reasonable yields. When isobutyronitrile was used in place of

Table 1 Reaction of cyclopropanone acetals **1** with *p*-cyanobenzyl methanesulfonate **4**[a]

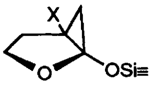
Reaction	Cyclopropanone acetal	Conversion (%)[b]	Products and yields (%)[c]	
1[b,c]		63	 **11a** (X = H) (53)	
2[d]	1c	78	**11b** (X = Ac) (72)	**12** (12)
3[e]	1c	60	**11c** (X = CN) (65)	**13** (26)
4[e]		100	 **11f** (20)	**13** (69)

[a] Acetonitrile was used as the solvent unless otherwise noted. Quartz filter was used for the irradiation. Reaction time varied from 0.5 to 1.5 h. [b] On the basis of consumed mesylate **4**. [c] Isolated yields based on the conversion of **4**. [d] The reaction was performed under an oxygen atmosphere. [e] Isobutyronitrile was used as the solvent.

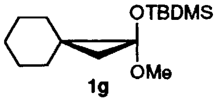
Table 2 Reaction of cyclopropanone acetals **1** with naphthylmethyl methanesulfonate **10**[a]

Reaction	Cyclopropanone acetal	Conversion (%)	Products and yields (%)[c]		
1	**1a**	50	**5a** (41)	**8** (20)	**7** (3)
2	**1b**	51	**5b** (67)		**7** (7)
3	**1c**	56	**5b** (81)		**7** (5)
4	**1c**	77	**5b** (71)		**7** (5)
5[d]	**1c**	27	**5b** (59)	**9** (22)	
6	**1d**	56	**5d** (31)	**6d** (13)	**7** (6)
7	**1e**	50	**5e** (36)	**6e** (13)	**7** (4)
8[e]	**1e**	76	**5e** (45)	**6e** (17)	**7** (3)
9[e]	**1f**	82	**5f** (53)	**6f** (8)	**7** (11)
10[e]	**1g**	80	**5g** (55)		**7** (6)

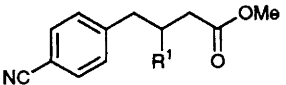
1a R^1 = p-MeOC$_6$H$_4$
b R^1 = Ph
c Si≡ = TBDMS; R^1 = Ph
d Si≡ = TBDMS; R^1 = C^{n}_{5}



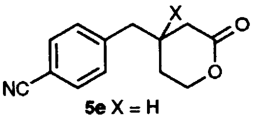
1e X = H; Si≡ = TBDMS
f X = Me; Si≡ = TBDMS



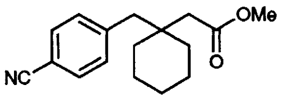
1g



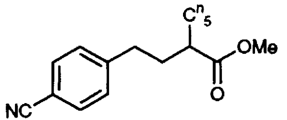
5a R^1 = p-MeOC$_6$H$_4$
b R^1 = Ph
d R^1 = C^{n}_{5}



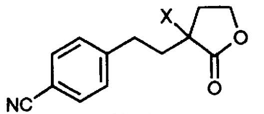
5e X = H
f X = Me



5g

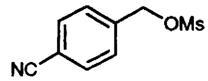


6d



6e X = H
f X = Me

[a] Acetonitrile was used as the solvent. Pyrex filter was used unless otherwise noted. [b] Quartz filter was used. [c] Isolated yields based on the conversion of **10**. X in **10**: [c] H; [d] Ac; [e] CN.



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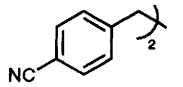

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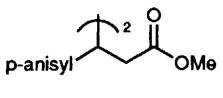

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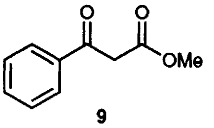

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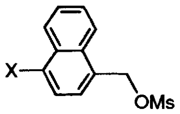

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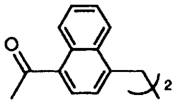

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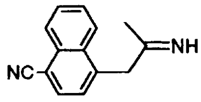

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acetonitrile as the solvent, both the conversion of **4** and yields of **5** and **6** were improved (compare reaction 8 with 7). Thus, the solvent seems to be participating in the elimination step of the silyl group in terms of nucleophilicity. In addition, as shown by the product ratios of **5** to **6** in reactions 6–10, regioselectivity in the ring-opening step apparently depends upon the stability of the radicals generated.

The structural modification of the acceptors was also investigated by using 4-substituted-1-naphthylmethyl methanesulfonates **10** which are presumed to be more efficient acceptors than **4** (Table 2). Expected coupling products **11** were obtained in good to moderate yields (reactions 1–4). When 4-cyanonaphthylmethyl methanesulfonates **10** (X = CN) was used, imine **13** was formed in addition to **11** (reactions 3 and 4). The imine was probably formed by the reaction of solvent (acetonitrile) with the 4-cyanonaphthylmethyl anion which derived from the 4-cyanonaphthylmethyl radical after the second electron transfer.

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Footnote

† When p-cyanobenzyl bromide or chloride was used, the yield of **5** decreased due to the unimolecular decomposition of the halide under photoirradiation.

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