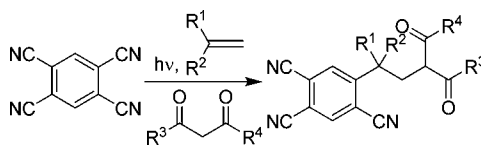# Photoinduced Three-Component Reactions of Tetracyanobenzene with Alkenes in the Presence of 1,3-Dicarbonyl Compounds as Nucleophiles

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Photoinduced three-component reactions between tetracyanobenzene (TCNB), an aromatic olefin, and a β-dicarbonyl compound afford products composed of the three components via formal elimination of hydrogen cyanide, leading to the vicinal dialkylation of the olefin and the α-alkylation of the β-dicarbonyl compounds. It is shown that these reactions are initiated by photoinduced electron transfer (PET) from the olefin to the singlet excited TCNB and proceed by a nucleophile−olefin combination, aromatic substitution (NOCAS) reaction sequence with the enolized β-dicarbonyl compound as a nucleophile. Therefore, aromatic olefins are suitable substrates in photo-NOCAS reactions when TCNB is used as the electron acceptor. In addition, these results show that the enol of β-dicarbonyl compound serves as a carbon nucleophile to trap the alkene cation radical in PET reactions to lead to C−C bond formation.

Introduction

The photoinduced nucleophile−olefin combination, aromatic substitution (photo-NOCAS) reaction[1] is a class of novel three-component reactions between a cyanoarene (as electron acceptor), an olefin (as electron donor), and a nucleophile initiated by photoinduced electron transfer (PET) between the cyanoarene (usually *p*-dicyanobenzene (DCNB) or 1,2,4,5-tetracyanobenzene (TCNB)) and the olefin. The olefin cation radical formed is captured by the nucleophile to give nucleophile−olefin addition radical (nucleophile−olefin combination), which takes part in radical pair combination with the cyanoarene anion radical followed by extrusion of a cyanide anion (aromatic substitution) to give the products. While mechanistic issues of these reactions have been under active research, the reaction scope in regard to the olefin substrate and the nucleophile has so far been rather limited. The olefins investigated are mainly aliphatic ones because it is believed that for aromatic olefins, once the olefin cation radical is trapped by the nucleophile, the subsequent reaction pathway is back electron transfer (BET) from the cyanoarene anion radical to the nucleophile−olefin addition radical (which in the case of aromatic olefin is a better electron acceptor than that derived from aliphatic olefin) followed by protonation of the formed anion to give an anti-Markovnikov addition product of the nucleophile to the olefin, with the cyanoarene only playing the role of a sensitizer.[2] On the other hand, in the absence of a nucleophile, the neutral aromatic olefin itself (which is more nucleophilic than aliphatic olefin) would capture its cation radical to give a dimeric cation radical, which upon BET from the cyanoarene anion radical furnishes tetralin and cyclobutane products.[3–5] The nucleophiles studied up to now are mainly limited to alcohol,[6] cyanide[7] and fluoride[8] anion, and amines.[9] Therefore, a further extension of the type of reactants would not only serve

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(1) For a review, see: Mangion, D.; Arnold, D. R. *Acc. Chem. Res.* **2002**, *35*, 297–304.

(2) (a) Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080–4081. (b) Arnold, D. R.; Snow, M. S. *Can. J. Chem.* **1988**, *66*, 3012–3026. (c) Arnold, D. R.; Du, X. *J. Am. Chem. Soc.* **1989**, *111*, 7666–7667.
(3) (a) Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 5806–5808. (b) Ansanuma, T.; Gotoh, T.; Tsuchida, A.; Yamamoto, M.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1977**, 485–486.
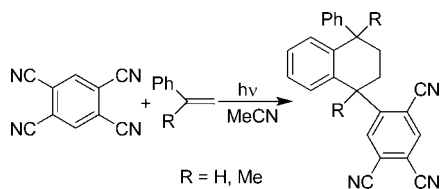(4) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1986**, *108*, 7356–7361.
(5) (a) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133–139. (b) Bauld, N. L. *Tetrahedron* **1989**, *45*, 5307–5363. (c) Lewis, F. D.; Kojima, M. *J. Am. Chem. Soc.* **1988**, *110*, 8664–8670. (d) Jungwirth, P.; Bally, T. *J. Am. Chem. Soc.* **1993**, *115*, 5783–5789. (e) Schepp, N. P.; Johnston, L. J. *J. Am. Chem. Soc.* **1994**, *116*, 6895–6903. (f) Schepp, N. P.; Johnston, L. J. *J. Am. Chem. Soc.* **1996**, *118*, 2872–2881. (g) Johnston, L. J.; Schepp, N. P. *Pure Appl. Chem.* **1995**, *67*, 71–78.

SCHEME 1

to expand the scope of these reactions to increase their synthetic value, but also shed new light on mechanistic details for these photo-multicomponent reactions.

In our previous work on photoreactions of TCNB with a series of aromatic olefins, we have shown that BET between the alkene dimer cation radical and TCNB anion radical could not take place because the latter is a too weak electron donor, and the reaction takes a pathway of radical pair combination between the alkene dimer radical and the TCNB anion radical to give a product of (olefin dimerization–aromatic substitution) (Scheme 1).[10] This result implies that aromatic alkenes would be even better olefin substrates in the photo-NOCAS reactions than aliphatic olefins whose reactions are often complicated by the allylic deprotonation side reaction. As a part of our effort in diversifying the reactant types in PET reactions to explore new photo-multicomponent reactions, we report here photoreactions of TCNB with aromatic alkenes in the presence of β-dicarbonyl compound as added nucleophile.

Results and Discussion

Photoinduced reactions of TCNB with the alkenes and the β-dicarbonyl compounds listed in Chart 1 were investigated.

I. Photoreactions of TCNB with α-Methylstyrene in the Presence of β-Dicarbonyl Compounds. Irradiation of TCNB (0.025 M) with α-methylstyrene (0.05 M) in the presence of acetylacetone (0.2 M) in MeCN with light of $\lambda > 300$ nm gave products **1** (78%), **2** (5%), and **3** (5%) (Chart 2 and Table 1). Products **2** and **3** are a pair of diastereomers derived from the olefin dimerization–aromatic substitution reaction.[10] Product **1** is a three-component reaction product and is proposed to be formed by a reaction sequence as shown in Scheme 2.

β-Diketones have high enol contents in solutions of common organic solvents.[11] For acetylacetone, the enol content in

CHART 1
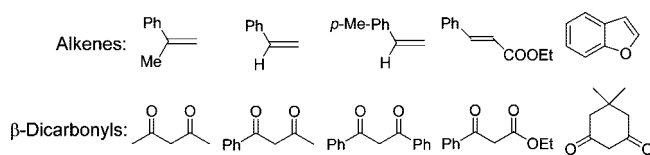
acetonitrile is determined to be in the range of 54.5–68.7%, depending on the analytical methods (NMR,[12] HPLC,[13] or UV–visible spectroscopy[14]). The alkene cation radical formed in single electron transfer (SET) with the singlet excited TCNB (^{1}TCNB*)[15] is trapped by the strongly nucleophilic acetylacetone enol to give the addition radical **A**, which on radical pair combination with the TCNB anion radical (TCNB⁻•) and extrusion of a cyanide anion gives product **1**. An alternative mechanism for the formation of **1** as shown in Scheme 3 can also be envisaged. SET between the enol and ^{1}TCNB* leads to the enol cation radical, which gives the carbon centered radical **B** by deprotonation. Radical addition of **B** to the alkene affords the addition radical **A**, which combines with TCNB⁻• to give **1** after extrusion of a cyanide anion. In Scheme 3, the mechanism for the formation of radical **A** is similar to that proposed in thermal addition reactions of β-diketones to alkenes mediated by the ground state one-electron oxidant ceric ammonium nitrate (CAN).[16,17] The formation of the carbon radical as **B** by CAN induced oxidation of the diketone enol followed by deprotonation of the enol cation radical to the solvent[18] was proven by ESR measurement,[19] and these radicals tend to dimerize to give the diketone dimers in the absence of added alkene.[20] In the presence of an alkene, the carbon radical (as **B**) adds to the alkene to give an addition radical as **A** (Schemes 2 and 3). Further SET from this radical to Ce(IV) leads to a carbocation that on intramolecular cyclization gives dihydrofuran product.[16,17] To examine the two possible mechanisms, we carried out a control experiment, which showed that irradiation of TCNB with acetylacetone in MeCN in the absence of an alkene resulted in no net reactions and the two reactants are not consumed. However, when the photolysis of TCNB with acetylacetone was carried out with added biphenyl (BP) as a cosensitizer,[21,22] both TCNB and acetylacetone were found to be consumed steadily to gave a complicated product mixture. These results suggest that, although SET between ^{1}TCNB* and the diketone enol

(6) (a) Borg, R. M.; Arnold, D. R.; Cameron, T. S. *Can. J. Chem.* **1984**, *62*, 1785–1802. (b) McManus, K. A.; Arnold, D. R. *Can. J. Chem.* **1994**, *72*, 2291–2304. (c) Maroulis, A. J.; Shigemitsu, Y.; Arnold, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 535–541. (d) Arnold, D. R.; Snow, M. S. *Can. J. Chem.* **1988**, *66*, 3012–3026. (e) McManus, K. A.; Arnold, D. R. *Can. J. Chem.* **1995**, *73*, 2158–2169. (f) Arnold, D. R.; Du, X.; de Lijser, H. J. P. *Can. J. Chem.* **1995**, *73*, 522–530. (g) Connor, D. A.; Arnold, D. R.; Bakshi, P. K.; Cameron, T. S. *Can. J. Chem.* **1995**, *73*, 762–771. (h) Arnold, D. R.; Connor, D. A.; McManus, K. A.; Bakshi, P. K.; Cameron, T. S. *Can. J. Chem.* **1996**, *74*, 602–612. (i) Arnold, D. R.; Chan, M. S. W.; McManus, K. A. *Can. J. Chem.* **1996**, *74*, 2143–2166. (j) Arnold, D. R.; Wong, P. C.; Maroulis, A. J.; Cameron, T. S. *Pure Appl. Chem.* **1980**, *52*, 2609–2619.
(7) Arnold, D. R.; McManus, K. A.; Chan, M. S. W. *Can. J. Chem.* **1997**, *75*, 1055–1075.
(8) Chan, M. S. W.; Arnold, D. R. *Can. J. Chem.* **1997**, *75*, 1810–1819.
(9) Yamashita, T.; Itagawa, J.; Sakamoto, D.; Nakagawa, Y.; Matsumoto, J.; Shiragami, T.; Yasuda, M. *Tetrahedron* **2007**, *63*, 374–380.
(10) Zhang, M.; Lu, Z.-F.; Liu, Y.; Grampp, G.; Hu, H.-W.; Xu, J.-H. *Tetrahedron* **2006**, *62*, 5663–5674.
(11) (a) Forsen, S.; Nilsson, M. In *The Chemistry of Carbonyl Group*; Zabicky, J., Ed.; Interscience Publishers: London, UK, 1970; pp 157–240. (b) Hart, H. *Chem. Rev.* **1979**, *79*, 515–528. (c) Toullec, J. *Adv. Phys. Org. Chem.* **1982**, *18*, 1–77. (d) Rappoport, Z.; Biali, S. E. *Acc. Chem. Res.* **1988**, *21*, 442–449. (e) Toullec, J. Keto-enol Equilibrium Constants. In *The Chemistry of Enols*; Rappoport, Z., Ed.; J. Wiley & Sons: Chichester, England, 1990; pp 323−398. (f) Emsley, J. *Struct. Bonding (Berlin)* **1984**, *57*, 147. (g) Iglesias, E. *Curr. Org. Chem.* **2004**, *8*, 1–24.

(12) Mills, S. B.; Beak, P. *J. Org. Chem.* **1985**, *50*, 1216–1212.
(13) Moriyasu, M.; Kato, A.; Hashimoto, Y. *J. Chem. Soc., Perkin Trans. 2* **1986**, 515–520.
(14) Murthy, A. S. N.; Balasubramanian, A.; Rao, C. N. R.; Kasturi, T. R. *Can. J. Chem.* **1962**, *40*, 2267–2271.
(15) (a) Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80–86. (b) Gould, I. R.; Noukakis, D.; Gomes-Jahn, L.; Young, R. H.; Goodman, J. L.; Farid, S. *Chem. Phys.* **1993**, *176*, 439–456. (c) Dresner, J.; Prochorow, J.; Ode, W. *J. Phys. Chem.* **1989**, *93*, 671–677. (d) Zhou, J.; Zhong, C.; Francis, T. M.; Braun, C. L. *J. Phys. Chem. A* **2003**, *107*, 8319–8326. (e) Mella, M.; Fasani, E.; Albini, A. *J. Org. Chem.* **1992**, *57*, 3051–3057.
(16) For reviews, see: (a) Nair, V.; Deepsi, A. *Chem. Rev.* **2007**, *127*, 1862–1891. (b) Nair, V.; Matthew, J.; Prabkakaran, J. *Chem. Soc. Rev.* **1997**, 127–132. (c) Molander, G. A. *Chem. Rev.* **1992**, *92*, 29–68.
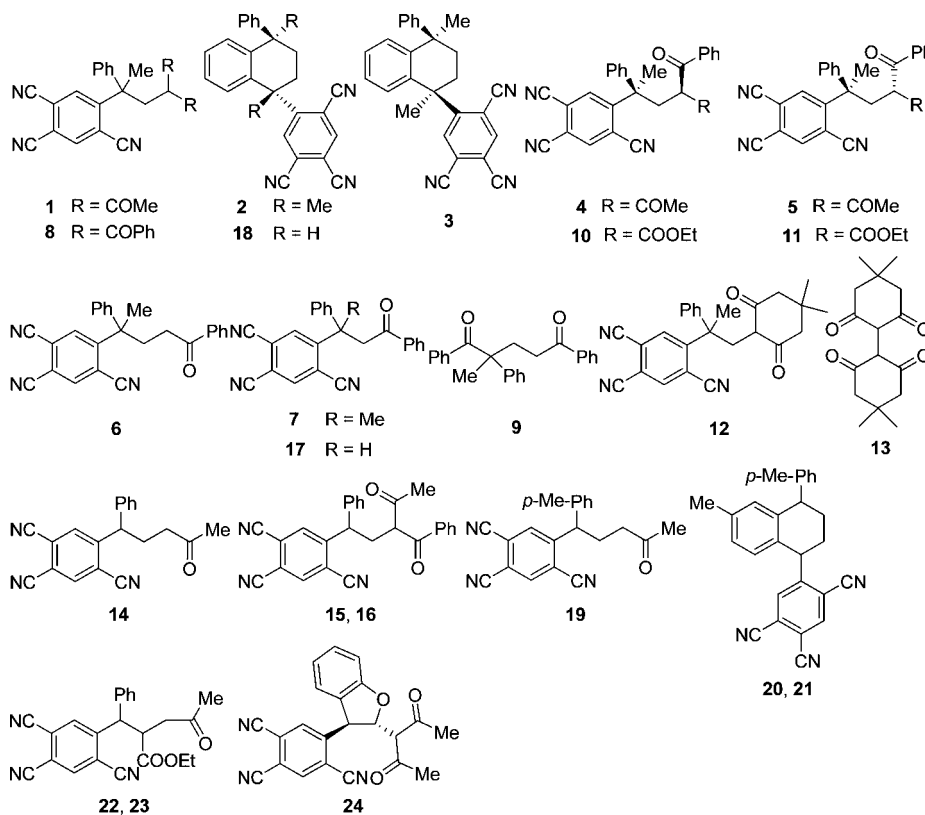(17) (a) Baciocchi, E.; Ruzziconi, R. *J. Org. Chem.* **1991**, *56*, 4772–4778. (b) Nair, V.; Mathew, J. *J. Chem. Soc., Perkin Trans. 1* **1995**, 187–188. (c) Roy, S. C.; Mandol, P. K. *Tetrahedron* **1996**, *52*, 2193–2198.
(18) The mechanism of the oxidation of β-dicarbonyls by CAN has been investigated: (a) Jiao, J.; Zhang, Y.; Devery, J. J., III; Xu, L.; Deng, J.; Flowers, R. A., II *J. Org. Chem.* **2007**, *72*, 5486–5492. (b) Zhang, Y.; Flowers, R. A., II *J. Org. Chem.* **2003**, *68*, 4560–4562. The enol cation radical of mono-ketone is moderately acidic. As an example, 4-methoxylphenylacetone enol cation radical has a $pK_a \approx 3.2$. See: (c) Schepp, N. P. *J. Org. Chem.* **2004**, *69*, 4931–4935.
(19) Russell, G. A.; Lokensgard, J. *J. Am. Chem. Soc.* **1967**, *89*, 5059–5060.
(20) Cho, L. Y.; Romero, J. R. *Tetrahedron Lett.* **1995**, *36*, 8757–8760.
(21) Tamai, T.; Ichinose, N.; Tanaka, T.; Sasuga, T.; Hashida, I.; Mizuno, K. *J. Org. Chem.* **1998**, *63*, 3204–3212.

CHART 2

1 R = COMe
8 R = COPh

2 R = Me
18 R = H

3

4 R = COMe
10 R = COOEt

5 R = COMe
11 R = COOEt

6

7 R = Me
17 R = H

9

12

13

14

15, 16

19

20, 21

22, 23

24

(which is a stronger electron donor than α-methylstyrene) is thermodynamically feasible, the reactivity of the singlet ion radical pair [TCNB⁻• enol⁺•] seems to be quite different from that of the free enol cation radical formed in the thermal SET reaction with the Ce⁴⁺ ions. For the singlet [TCNB⁻• enol⁺•] pair, BET predominates to suppress any further reactions. This is not a surprising fact taking into account the highly exothermic nature of the PET process of the ¹TCNB* with enol[23a] and the relevant small energy gap for the BET process in the [TCNB⁻• enol⁺•] pair.[23e] This means that the BET process would have very high rate constant to result in inefficient ion radical pair dissociation.[23f,g] Only with the use of the cosensitizer to mediate the SET process to avert the formation of the geminal ion radical pair could the fast BET be inhibited to allow ion radical pair dissociation and the ensuing chemical reactions to take place. Furthermore, singlet excited TCNB is a much stronger electron acceptor ($E_{1/2}^{red}$ = 3.17 V, SCE)[15] than the ground state CAN ($E_{1/2}^{red}$ = 1.28 V, SCE). Since most alkenes without strong electron-donating substituents have oxidation potential higher than 1.28 V, in CAN-mediated addition reactions of β-diketones with alkenes, CAN can only oxidize the diketone enol but not the alkene. In contrast with this, in photoreactions of TCNB with alkene in the presence of a β-diketone, electron transfer from the alkenes to ¹TCNB* is exothermic and therefore thermodynamically favorable (see oxidation potentials of the alkenes in Table 1). All these facts are in support of the mechanism shown in Scheme 2 for the formation of product 1.

Significant cosensitizer effect[21,22] and special salt effect[24] in accelerating the reaction were noticed in the photoreactions. Therefore, while irradiation of TCNB (0.025 M), α-methylstyrene (0.05 M), and acetylacetone (0.2 M) in MeCN for 7 h led to a 27% conversion of TCNB to give 1 (75%), 2 (3%), and 3 (4%), photolysis of the same reaction mixture with added BP

(0.025 M) as a cosensitizer for 7 h resulted in a 68% TCNB conversion to give 1 (80%), 2 (5%), and 3 (5%). Similarly, adding anhydrous magnesium perchlorate (0.0125 M) to the reaction mixture of TCNB, α-methylstyrene, and acetylacetone raised the TCNB conversion to 79% and afforded 1 (79%), 2 (4%), and 3 (5%). Since BP has a similar oxidation potential (1.90 V, SCE) as the alkene, the rate enhancement primarily takes advantage of BP's role as a relay in the electron transfer between ¹TCNB* and the alkene to circumvent the formation of the singlet geminate ion radical pair [TCNB⁻• alkene⁺•], leading to a suppression of the energy wasting BET process. The longer lifetime of the BP cation radical than ¹TCNB* also helps to enhance the SET efficiency.[21] These cosensitizer and special salt effects lend further support to the mechanism involving electron transfer between ¹TCNB* and the styrene as shown in Scheme 2.

Photoreaction of TCNB with α-methylstyrene in the presence of benzoylacetone under the same conditions afforded products

(22) (a) Schaap, A. P.; Siddiqui, S.; Prasad, G.; Palomino, E.; Lopez, L. *J. Photochem.* **1984**, *25*, 167–181. (b) Schaap, A. P.; Siddiqui, S.; Gagnon, S. D.; Lopez, L. *J. Am. Chem. Soc.* **1983**, *105*, 5149–5150. (c) Majima, J.; Pac, C.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499–4508.

(23) (a) ΔG$_{ET}$ for SET between ¹TCNB* and the enol is estimated to be <−2.17 eV by the Weller equation,[23b] assuming the oxidation potential of the enols to be <1 V (SCE).[18,23c,d] (b) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259–271. (c) Rock, M.; Schmittel, M. *J. Chem. Soc., Chem. Commun.* **1993**, 1739–1741. (d) Lal, M.; Langels, A.; Deiseroth, H. J.; Schlirf, J.; Schmittel, M. *J. Phys. Org. Chem.* **2003**, *16*, 373–379. (e) The BET process in the singlet ion radical pair [TCNB⁻• enol⁺•] has a free energy change ΔG$_{BET}$ = $E_{1/2}^{red}$(TCNB)− $E_{1/2}^{ox}$(enol) ≈−0.65−1 =−1.65 eV. This small energy gap for the BET process implies that BET has a high rate constant. See:(f) Lewis, F. D.; Bedell, A. M.; Dykstra, R. E.; Elbert, J. E.; Gould, I. R.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 8055–8064. (g) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290–4301.

(24) (a) Gollnick, K.; Wellnhofer, G. *J. Photochem. Photobiol. A: Chem.* **1993**, *74*, 137–145. (b) Mizuno, K.; Ichinose, N.; Otsuji, Y. *Chem. Lett.* **1985**, *14*, 455–458.

TABLE 1. Photoreactions of TCNB with Alkenes in the Presence of β-Dicarbonyl Compounds[a]

| entry	Alkene	$E_{1/2}^{ox\ b}$ (V)	β-Dicarbonyls	Products and yield (%)[c]
1	Ph / Me	1.86	(acetylacetone)	1 (78), 2 (5), 3 (5)
2			(benzoylacetone, Ph)	4 (26), 5 (21), 6 (5), 7 (6), 2 (2), 3 (2)
3			(dibenzoylmethane, Ph...Ph)	8 (82), 9, 2 (2), 3 (2)
4			(ethyl benzoylacetate, Ph...OEt)	10 (21), 11 (17), 2 (15), 3 (10)
5			(dimedone)	12 (62), 13, 2 (5), 3 (6)
6	Ph / H	1.93	(acetylacetone)	14 (85)
7			(benzoylacetone, Ph)	15 (49), 16 (25), 17 (7), 18 (10)
8	p-Me-Ph / H	1.74	(acetylacetone)	19 (52), 20 (8), 21 (9)
9	Ph / COOEt	2.16	(acetylacetone)	22 (24), 23 (58)
10	(benzofuran)		(acetylacetone)	24 (86)

[a] All the reactions were carried out in MeCN solution. [TCNB] = 0.025 M, [alkene] = 0.05 M, [β-dicarbonyl compound] = 0.2 M. [b] Oxidation potential vs SCE in MeCN. [c] Yield of isolated products.

SCHEME 2

SCHEME 3
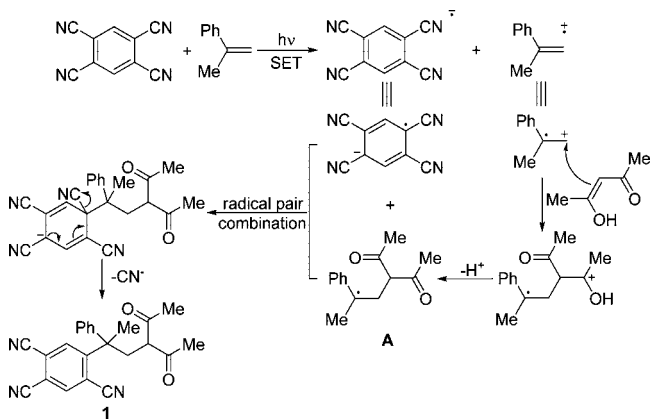
4 (26%), 5 (21%), 6 (5%), and 7 (6%) and the untrapped products 2 (2%) and 3 (2%) (Chart 2 and Table 1). The steric configurations of products 4 and 5 can be assigned by comparison of their ^{1}H NMR spectra with that of products 10 and 11 whose steric structures are based on an X-ray crystallographic analysis of product 10 (vide infra). Products 4 and 5 are diastereomers. TLC monitoring of the reaction course showed that compound 6 is not a primary product formed in the photoreactions, but was formed during the silica gel chromatographic separation of the reaction mixture. Indeed, a
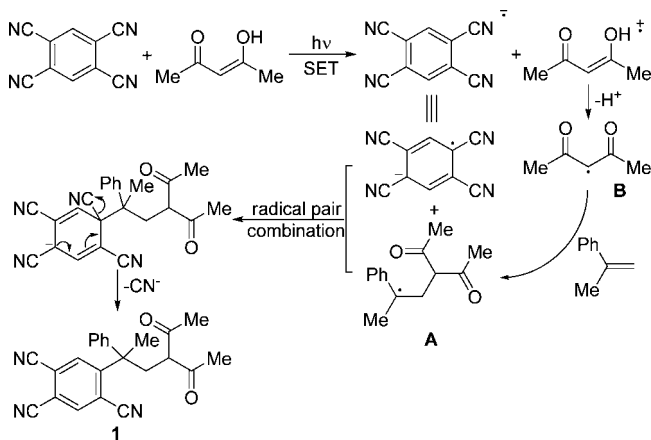
control experiment showed that when 4 was heated on silica gel, it underwent decarbonylation to give 6 in 55% yield. Product 6 is proposed to be formed by an acid-catalyzed decomposition mechanism shown in Scheme 4.

When dibenzoylmethane was used as nucleophile, products 8 (82%), 2 (2%), and 3 (2%) were formed. Also obtained is a 1,5-diketone product 9 derived from de Mayo reaction[25] of triplet excited dibenzoylmethane with the alkene. Dibenzoylmethane has rather strong absorption (λ_{max} = 339 nm, ϵ =
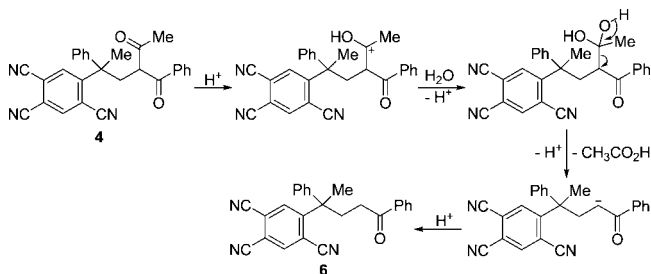
SCHEME 4

SCHEME 5
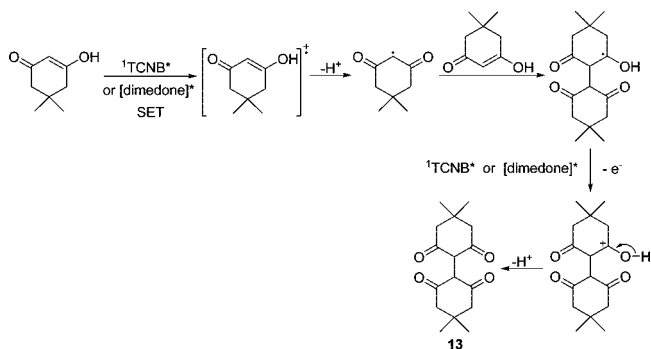
26 900, in methanol) in the wavelength region used for the photolysis and is excited in competition with TCNB.

With ethyl benzoylacetate as a nucleophile, the photoreaction gave products **10** (21%) and **11** (17%) as diastereomers, together with a significantly higher yield of **2** (15%) and **3** (10%) than in the above-mentioned reactions with diketones as nucleophile. The steric structure of **10** is established by an X-ray crystallographic analysis (see the Supporting Information).

In this case, the much higher yield of the untrapped products **2** and **3** can be attributed to the lower enol concentration derived from the benzoylacetate in the reaction mixture. It is known that β-ketoesters have much lower enol contents than structurally similar β-diketones. Therefore, while in pure liquid, acetylacetone has an enol content of 81%, only 22% of ethyl benzoylacetate is in the enol form.[1,26] This low concentration of the enol in the reaction mixture enables the neutral α-methylstyrene to compete more favorably with the enol to trap the alkene cation radical to give products **2** and **3**.

Photolysis of TCNB with α-methylstyrene in the presence of dimedone (5,5-dimethylcyclohexa-1,3-dione) furnished products **12** (62%), **2** (5%), and **3** (6%), together with a dimeric dimedone product **13**. A control experiment showed that **13** can be formed by either irradiation of dimedone alone or dimedone in the presence of TCNB. We therefore propose that product **13** may derive from PET reaction of dimedone enol (as electron donor) with its excited keto-form or singlet excited TCNB (as electron acceptor) as shown in Scheme 5.

II. Photoreactions of TCNB with the Other Alkenes in the Presence of 1,3-Diketone. Photoreactions of TCNB with styrene in the presence of acetylacetone afforded product **14** (85%) as the sole product. Similar irradiation of TCNB with styrene and benzoylacetone gave products **15** (49%), **16** (25%), **17** (7%), and **18** (10%). Product **14** is formed from the primary

products (similar to **15** and **16**) by acid-catalyzed decomposition during the chromatographic separation by a mechanism shown in Scheme 4.

In the photoreaction of TCNB with *p*-methylstyrene in the presence of acetylacetone, product **19** (52%) was formed together with **20** (8%) and **21** (19%). Considering the stronger electron donor ability of *p*-methylstyrene as reflected by its lower oxidation potential, the higher yields of **20** and **21** are the result of the higher nucleophilicity of the neutral alkene.

For ethyl cinnamate, similar reactions with TCNB and acetylacetone gave the three-component products **22** (24%) and **23** (58%) as diastereomers without the formation of the olefin dimerization–aromatic substitution products. This result is consistent with the high electrophilic reactivity of the cinnamate cation radical and the low nucleophilicity of the neutral cinnamates.

Photoreactions of TCNB, benzofuran, and acetylacetone led to the formation of product **24** as the sole product in 86% yield. The steric structure of **24** is also established by an X-ray crystallographic analysis (see the Supporting Information).

It is seen that these three-component reactions with the enolized 1,3-dicarbonyl compound as carbon nucleophiles result in sequential formation of two C−C bonds at both carbon atoms of the alkene, therefore contributing a new photochemical scenario to the synthetically important strategy of tandem vicinal dialkylation (dicarbocondensation) of alkenes.[27–29] They also provide a new method for selective α-alkylation of the β-diketones[30] without the complication of *O*-alkylation and α,α-dialkylation in the conventional base-induced α-alkylation reactions. Furthermore, these reactions lead to the addition of 1,3-dicarbonyls to a styrene derivative, which is an area of much interest.[31–33]

Conclusions

In summary, photoinduced three-component reactions of TCNB with alkene and β-dicarbonyl compound have been reported, which provide new photochemical strategies for the tandem

(25) (a) de Mayo, P. *Acc. Chem. Res.* **1970**, *4*, 41–47. (b) Baldwin, S. W. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, p 123. (c) Crimmins, M. T. *Chem. Rev.* **1988**, *88*, 1453–1473.

(26) Burdett, J. L.; Rogers, M. T. *J. Am. Chem. Soc.* **1964**, *86*, 2105–2109.

(27) For reviews, see: (a) Hulce, M.; Chapdelaine, M. J. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Semmelhack, M. F., Eds.; Pergamon Press: New York, 1991; Vol. 4, pp 237−268. (b) Chapdelaine, M. J.; Hulce, M. *Org. React. (N. Y.)* **1990**, *38*, 225–653.

(28) (a) Taylor, R. J. K. *Synthesis* **1985**, 364–392. (b) Noyori, R.; Sazuki, M. *Chemtracts Org. Chem.* **1990**, *3*, 173–197. (c) Normant, J. F.; Alexankis, A. *Synthesis* **1981**, 841–870.

(29) (a) Murai, A.; Tanimoto, N.; Sakamoto, N.; Masamune, T. *J. Am. Chem. Soc.* **1988**, *110*, 1985–1986. (b) Norinder, U.; Wennerström, O. *Tetrahedron Lett.* **1984**, *25*, 4787–4790. (c) Suzuki, M.; Kawagishi, T.; Suzuki, T.; Noyori, R. *Tetrahedron Lett.* **1982**, *23*, 4057–4060. (d) Asao, N.; Uyehara, T.; Yamamoto, Y. *Tetrahedron* **1988**, *44*, 4173–4180. (e) Funk, R. L.; Vollhardt, K. P. C. *Chem. Soc. Rev.* **1980**, *9*, 41–61.

(30) For reviews, see: (a) Kel'in, A. V.; Maioli, A. *Curr. Org. Chem.* **2003**, *7*, 1855–1886. (b) Moreno-Manas, M.; Marquet, J.; Vallribera, A. *Tetrahedron* **1996**, *52*, 3377–3401.

(31) (a) Nakamura, M.; Endo, K.; Nakamura, E. *J. Am. Chem. Soc.* **2003**, *125*, 13002–13003. (b) Kennedy-Smith, J. J.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 4526–4527, and references cited therein.

(32) (a) Pei, T.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2001**, *123*, 11290–11291. (b) Pei, T.; Widenhoefer, R. A. *Chem. Commun.* **2002**, 650–651. (c) Qian, H.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2003**, *125*, 2056–2057. (d) Pei, T.; Wang, X.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2003**, *125*, 648–649. (e) Wang, X.; Pei, T.; Han, X. Q.; Widenhoefer, R. A. *Org. Lett.* **2003**, *5*, 2699–2701. (f) Yang, D.; Li, J. H.; Gao, Q.; Yan, Y. L. *Org. Lett.* **2003**, *5*, 2869–2871. (g) Trost, B. M.; Jaekel, C.; Plietker, B. *J. Am. Chem. Soc.* **2003**, *125*, 4438–4439. (h) Leitner, A.; Larsen, J.; Steffens, C.; Hartwig, J. F. *J. Org. Chem.* **2004**, *69*, 7552–7557. (i) Yao, X. Q.; Li, C.-J. *J. Am. Chem. Soc.* **2004**, *126*, 6884–6885. (j) Nguyen, R.-V.; Yao, X. Q.; Bohle, D. S.; Li, C.-J. *Org. Lett.* **2005**, *7*, 673–675. (k) Yao, X. Q.; Li, C.-J. *J. Org. Chem.* **2005**, *70*, 5752–5755. (l) Wang, X.; Widenhoefer, R. A. *Chem. Commun.* **2004**, 660–661. (m) Liu, P. N.; Zhou, Z. Y.; Lau, C. P. *Chem. Eur. J.* **2007**, *13*, 8610–8619. (n) Rueping, M.; Nachtsheim, B. J.; Kuenkel, A. *Synlett* **2007**, 1391–1394.

vicinal dialkylation of the alkene and for α-alkylation of the β-dicarbonyl compounds. The reaction mechanisms have been clarified. It is shown that these reactions proceed by a photo-nucleophile−olefin combination, aromatic substitution (photo-NOCAS) mechanism with the β-dicarbonyl compounds serving as nucleophiles. We have shown that, aromatic alkenes such as styrene derivatives are good alkene substrates in photo-NOCAS reactions when TCNB is used as electron acceptor. The anti-Markovnikov addition of the nucleophile to the alkene and the alkene dimerization (leading to tetralin and cyclobutane products) are not competing with the three-component reactions because back electron transfer from TCNB$^{-\bullet}$ to the nucleophile−alkene addition radical or the alkene dimeric radical is thermodynamically unfavorable. The main side reactions to the three-component reactions when using aromatic alkenes are the olefin dimerization, aromatic substitution reactions (leading to products **2** and **3**). We have also shown that there is a close correlation between the nucleophilic reactivity of the diketones (in trapping the alkene cation radicals) and the diketone enol content. With an increase in the enol content of the diketone, the yield of the three-component reactions is raised at the cost of products **2** and **3**. To our knowledge, this is the first report on using β-dicarbonyl compounds as nucleophilic trapping agent for alkene cation radicals in photoinduced electron transfer reactions. Since carbon nucleophiles have been rarely investigated in PET reactions except for the cyanide anion,[34] the introduction of enolized β-dicarbonyl compounds as nucleophiles may serve to expand the reaction scope of PET reactions and increase their synthetic utility by enabling them for C−C bond formation.

Experimental Section

General Procedures for the Preparative Photolysis of TCNB with an Alkene in the Presence of a β-Dicarbonyl Compound. The light source was a medium-pressure mercury lamp (500 W) in a glass cooling water jacket to cut off light of wavelength shorter than 300 nm. The solution of tetracyanobenzene (TCNB), alkene, and β-dicarbonyl compound in MeCN was purged with N_2 for 30 min and then irradiated under continuous N_2 purging. The reaction course was monitored by TLC. At the end of the reaction, the solvent was removed under reduced pressure and the residue was separated by flash chromatography on a silica gel or neutral alumina column with petroleum ether/ethyl acetate as eluents (gradient elution).

Representative Procedure for the Preparative Photolysis of TCNB with Alkenes in the Presence of β-Dicarbonyl Compounds. A solution of TCNB (534 mg, 3 mmol), α-methylstyrene (709 mg, 6 mmol), and acetylacetone (2.40 g, 24 mmol) in MeCN (120 mL) was photolyzed for 14 h to reach a 85% conversion of TCNB. The solvent was removed under reduced pressure and the residue was separated by flash chromatography on a neutral alumina column with petroleum ether/ethyl acetate as eluents to give **1** (735 mg, 78%), **2** (48 mg, 5%), and **3** (51 mg, 5%).

5-(4-Acetyl-5-oxo-2-phenylhexan-2-yl)benzene-1,2,4-tricarbonitrile (1): colorless crystals from petroleum ether−acetone, mp 214−215 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.19 (s, 1H), 7.96 (s, 1H), 7.37−7.34 (m, 3H), 7.08−7.05 (m, 2H), 3.53 (t, J = 4.9 Hz, 1H), 2.92 (dd, J = 13.6, 4.7 Hz, 1H), 2.81 (dd, J = 13.6, 5.2 Hz, 1H), 2.14 (s, 3H), 1.74 (s, 6H) ppm; ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 202.5, 202.0, 158.1, 142.4, 139.4, 131.9, 131.0, 128.4, 128.2, 119.3, 118.4, 115.0, 114.4, 114.2, 113.4, 64.6, 47.3, 38.1, 29.1, 28.8, 25.5 ppm; IR (KBr) 3117, 2986, 2241, 2230, 1735, 1711, 1387, 1364, 1250, 1148, 914, 766, 699, 520 cm^{-1}; MS (EI) m/z (%) 351 (4), 326 (18), 284 (21), 268 (5), 257 (18), 256 (100), 242 (10), 229 (2), 215 (4), 178 (2), 113 (8), 77 (2), 71 (32), 43 (49). Anal. Calcd for C$_{23}$H$_{19}$N$_3$O$_2$: C, 74.78; H, 5.18; N, 11.37. Found: C, 74.61; H, 5.37; N, 11.22.

Supporting Information Available: Detailed experimental section, ^{1}H NMR and ^{13}C NMR spectra of all new compounds, and crystallographic information files of compounds **10** and **24**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) (a) Duan, Z.; Xuan, X.; Wu, Y. *Tetrahedron Lett.* **2007**, *48*, 5157–5159. (b) Nedelec, J.-Y.; Lachaise, I.; Nohair, K.; Paugam, J. P.; Hakiki, M. *Bull. Soc. Chim. Fr.* **1995**, *132*, 843–849. (c) Vinogradov, M. G.; Dolinko, V. N.; Nikishin, G. I. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1984**, 375–383.

(34) At the completion of the manuscript, a report by K. Mizuno and his co-workers to use malononitrile as a carbon nucleophile to trap the alkene cation radical had just been published. See: Ohashi, M.; Nakatani, K.; Maeda, H.; Mizuno, K. *Org. Lett.* **2008**, *10*, 2741–2743.