

# Photochemical Addition of 2,2,2-Trifluoroethanol to Benzonitrile and *p*-, *m*-, and *o*-Methylbenzonitrile

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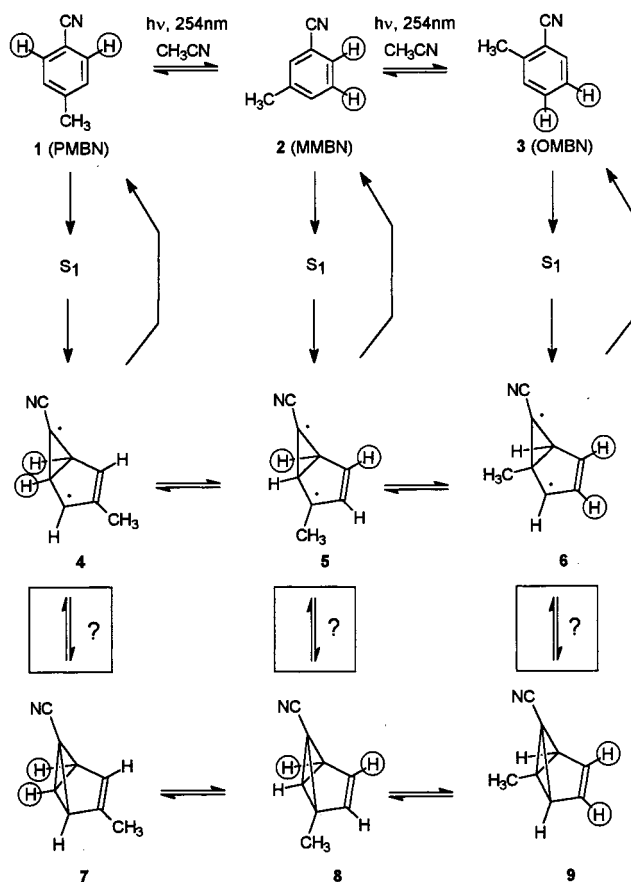
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**Abstract:** Irradiation of benzonitrile in 2,2,2-trifluoroethanol (TFE) with 254-nm light from low-pressure mercury lamps results in the formation of four addition products, the stereoisomers of 6-cyano-2-(2,2,2-trifluoroethoxy)bicyclo[3.1.0]hex-3-ene, **22–25**. The proposed mechanism begins by formation of the 6-cyanobicyclo[3.1.0]hex-3-en-2,6-diyl biradical/zwitterion from  $S_1$  followed by both endo and exo protonation by TFE at C6. Deuterium labeling demonstrated that the resulting 6-cyanobicyclo[3.1.0]hex-3-en-2-yl cation underwent a rapid degenerate 1,4-sigmatropic rearrangement with inversion of configuration at the migrating carbon before being trapped by the nucleophilic solvent. Irradiation of *p*- and *m*-methylbenzonitrile in the same way gave six major addition products. Three of them, **32**, **33**, and **35** were 6-cyano-2-(2,2,2-trifluoroethoxy)-4-methylbicyclo[3.1.0]hex-3-enes and the other three, **32**, **33**, and **35**, were 6-cyano-2-(2,2,2-trifluoroethoxy)-2-methylbicyclo[3.1.0]hex-3-enes. The proposed mechanism is again by TFE endo and exo protonation of the first formed biradical/zwitterion followed by trapping of the cations by the solvent. The 1,4-sigmatropic rearrangement of the cations now stops at the most stable structures, the *endo*- and *exo*-6-cyano-2-methylbicyclo[3.1.0]hex-3-en-2-yl cations, and all of the products are derived from them.

## Introduction

Recently, we reported that phototransposition reactions occur for *p*-, *m*- and *o*-methylbenzonitriles (**1** (PMBN), **2** (MMBN), and **3** (OMBN)).<sup>1</sup> Any one of three is converted, in the excited singlet state, to the other two by both 1,2- and 1,3-transpositions in a primary photochemical step. However, the reactivities are very different with relative efficiencies of conversion to the other isomers for para:meta:ortho = 32:4:1 (i.e., PMBN is the most reactive). Moreover, deuterium labeling (circled hydrogens) demonstrated that only the cyano-substituted carbon migrates. These observations were rationalized by the mechanism shown in Scheme 1. Excitation to  $S_1$  for each creates a spectroscopic minimum; distinct fluorescence is observed for all three isomers. An activation barrier separates the excited states from the corresponding singlet bicyclo[3.1.0]hex-3-en-2,6-diyl biradicals/zwitterions **4**, **5**, and **6** that are formed by the meta bonding that puts the cyano group at C6. The barrier height is dependent on which isomer is excited, being lowest for PMBN and highest for OMBN. These biradicals then equilibrate before collapsing back to one or the other of the benzonitriles. In principle, substituted benzvalenes, **7**, **8**, and **9**, could also be formed as intermediates in these conversions, but we had no evidence for that. Moreover, the observation of both 1,2- and 1,3-transpositions as primary photochemical events seemed to exclude the possibility that benzvalenes were the only intermediates. A better understanding of the structure and reactivity of the intermediates in phototransposition reactions would be obtained if they could be trapped; on the basis of literature precedents, we have chosen 2,2,2-trifluoroethanol (TFE) as the trap.

**Scheme 1.** Mechanistic Scheme for the Photochemical Transposition Reactions of the Methylbenzonitriles **1–3**

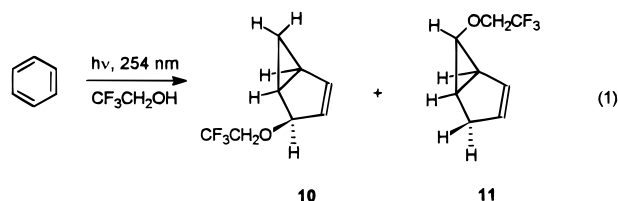


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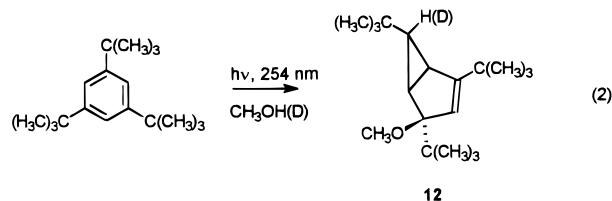
(1) MacLeod, P. J.; Pincock, A. L.; Pincock, J. A.; Thompson, K. A. *J. Am. Chem. Soc.* 1998, 120, 6443–6450.

The photochemical addition of alcohols to benzene and alkylbenzenes was first reported by Kaplan et al. in 1966.<sup>2</sup> Thus,

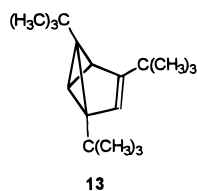
irradiation at 254 nm of benzene (0.02 M) in TFE gave two major products, **10** and **11**, eq 1, in a ratio of 2:1. Similar



irradiation of 1,3,5-tri-*tert*-butylbenzene in methanol gave, as the only detectable product, the methyl ether, **12**, eq 2.

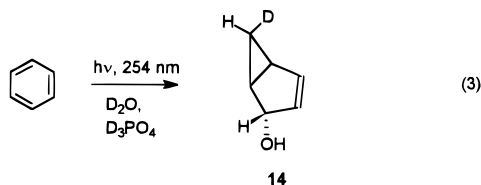


Moreover, the positional isomerization of this substrate was suppressed in favor of the addition reaction. The stereochemistry of the hydrogen (deuterium) at C6 in **12** was established by <sup>1</sup>H NMR coupling constants to the two other cyclopropyl hydrogens. The mechanistic conclusion reached was that these products result from ground-state addition of the alcohol to the expected benzvalene primary photoproduct. Therefore, **13** was



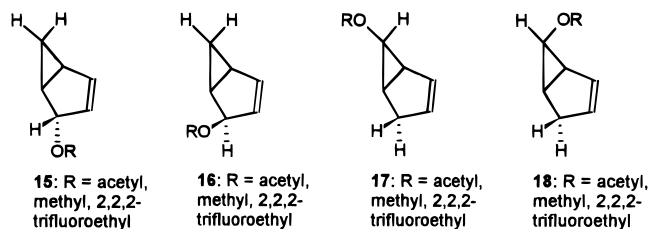
the proposed precursor for **12**. Similar additions of acetic acid and water (0.1 M in phosphoric acid) to benzene were observed in the same year.<sup>3</sup>

These conclusions were further supported by Berson and Hasty from the photolysis of benzene at 254 nm in D<sub>2</sub>O (0.1 N D<sub>3</sub>PO<sub>4</sub>), eq 3.<sup>4</sup> Analysis of the <sup>1</sup>H NMR of the isolated alcohol,

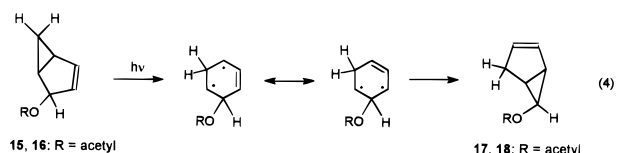


**14**, indicated that the deuterium at C6 was exclusively endo. The stereochemistry of the hydroxy group at C2 was exo, but any of the endo alcohol formed would have rapidly epimerized to the exo alcohol in the acidic solution. As well, irradiation of benzene in acetic acid gave all four possible regio- and

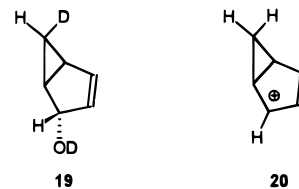
stereoisomers of the bicyclo[3.1.0]hex-3-en-2-yl<sup>5</sup> addition products, **15**–**18**, R = acetyl, but the composition varied with percent



conversion. In the earliest sample analyzed (after a 2-h irradiation), the ratio was approximately 40:41:4:16 (estimated from a plot in ref 4). Assuming rapid endo to exo ground-state conversion of the products, i.e., **16** R = acetyl to **15** R = acetyl, the major primary photoproduct is the endo adduct. Therefore, both the protonation and nucleophilic attack were predominantly endo, as expected for an addition to benzvalene on the basis of previously observed additions to one other bicyclobutane derivative.<sup>6</sup> After 48 h of irradiation the product ratio was 23:13:15:48. The photoequilibration of the products was proposed to occur by a vinylcyclopropane rearrangement as in eq 4, involving cleavage of the C1–C5 bond.



The intervention of benzvalene as an intermediate in these photoaddition reactions received even stronger support after it became available in “bounteous quantities” as a result of a nonphotochemical synthesis, developed by Katz and co-workers.<sup>7</sup> Reaction of benzvalene in ether with D<sub>2</sub>O/D<sub>3</sub>PO<sub>4</sub> for 30 min gave a quantitative yield of **19**.



Finally, Kaplan and co-workers,<sup>8</sup> using benzene-1,3,5-*d*<sub>3</sub> and benzene-*d*<sub>6</sub> as substrates, proved that (1) the photoaddition products **15**–**18** did come from protonation of benzvalene; (2) **15** and **16**, the primary photoproducts, were formed by nucleophilic trapping of the cation **20**; (3) both **17** and **18** were formed from **15** and **16** by benzene-sensitized secondary photolysis involving C1–C5 bond cleavage as in eq 4; and (4) **17** and **18** were equilibrated photochemically both by C1–C5 bond cleavage and C1–C6 cleavage, this latter pathway being dominant.

(5) The numbering for nomenclature of these compounds can be confusing. For the unsubstituted compound, bicyclo[3.1.0]hex-2-ene, the double bond takes priority whereas, for the addition products, the alcohol functional group takes priority.

(6) Wilberg, K. B.; Szeimies, G. *J. Am. Chem. Soc.* **1970**, *92*, 571.

(7) Katz, T. J.; Wang, E. J.; Acton, N. *J. Am. Chem. Soc.* **1971**, *93*, 3782–3783.

(8) Kaplan, L.; Rausch, D. J.; Wilzbach, K. E. *J. Am. Chem. Soc.* **1972**, *94*, 8638–8640.

(2) Kaplan, L.; Ritscher, J. S.; Wilzbach, K. E. *J. Am. Chem. Soc.* **1966**, *88*, 2881–2882.

(3) Farenhorst, E.; Bickel, A. F. *Tetrahedron Lett.* **1966**, *47*, 5911–5913.

(4) Berson, J. A.; Hasty, N. M. *J. Am. Chem. Soc.* **1971**, *93*, 1551–1552.

**Table 1.** <sup>1</sup>H and <sup>13</sup>C NMR Chemical Shifts ( $\delta$ ) for Compounds **22–25** and **30–35**

compd	H <sub>1</sub> /C <sub>1</sub>	H <sub>2</sub> /C <sub>2</sub>	H <sub>3</sub> /C <sub>3</sub>	H <sub>4</sub> /C <sub>4</sub>	H <sub>5</sub> /C <sub>5</sub>	H <sub>6</sub> /C <sub>6</sub>	CH <sub>2</sub>	CN	CH <sub>3</sub>
<b>22</b>	2.34	5.12	5.48	6.07	2.58	1.48	3.94, 3.97		
	23.8	85.8	130.6	134.7	31.8	13.0	67.8	119.3	
<b>23</b>	2.47	4.58	5.69	6.33	2.68	0.84	3.88		
	30.2	84.4	129.5	137.8	30.9	16.1	65.1	118.4	
<b>24</b>	2.30	4.60	5.97	6.25	2.62	2.01	3.91		
	28.1	84.3	131.5	135.1	29.3	16.5	65.7	nd <sup>a</sup>	
<b>25</b>	2.13	5.21	5.83	6.06	2.48	1.76	3.98		
	<i>b</i>								
<b>30</b>	2.09		5.46	5.96	2.58	1.48	3.87		1.52
	29.1	89.1	135.2	133.8	31.5	14.0	63.1	118.6 <sup>c</sup>	23.8
<b>31</b>	2.29		5.37	6.26	2.63	0.99	3.69, 3.64		1.49
	32.6	88.1	133.8	136.4	31.1	16.2	61.1	118.5 <sup>d</sup>	23.1
<b>32</b>	2.32	5.00	5.08		2.38	0.88	3.89		1.84
	24.8	85.5	123.7	145.6	34.6	15.8	67.6	119.5 <sup>d</sup>	15.8
<b>33</b>	2.51	4.52	5.28		2.44	0.88	3.87		1.96
	33.8	84.7	122.8	149.3	30.8	15.2	64.8	119.1 <sup>c</sup>	16.0
<b>34</b>	2.04		5.65	6.26	2.60	1.92	3.68		1.66
	29.9	87.5	135.2	134.6	29.0	16.0	60.5	nd <sup>a</sup>	20.3
<b>35</b>	2.25	4.54	5.55		2.43	1.96	3.84		1.97
	28.4	84.3	124.4	145.6	32.0	15.3	65.2	116.7	16.2

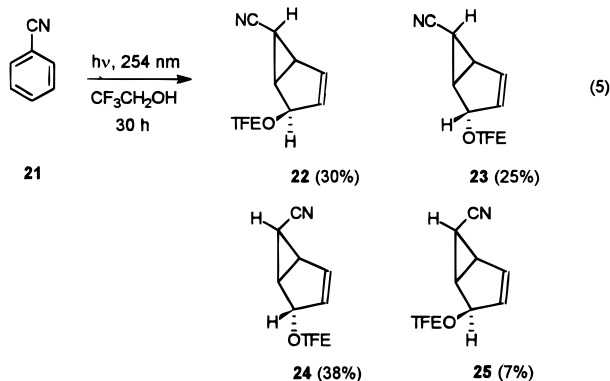
<sup>a</sup> Not detected. <sup>b</sup> Not enough material isolated for reliable spectra. <sup>c</sup> Assignment may be reversed. <sup>d</sup> Assignment may be reversed.

We now report on the photochemical reactivity and the structure of the addition products obtained from PMBN, MMBN, and OMBN in TFE. For comparison, benzonitrile (BN) itself was also examined.

## Results and Discussion

### Irradiation of Benzonitrile (21) in 2,2,2-Trifluoroethanol.

Irradiation of BN (1.87 mmol) in nitrogen-purged TFE (100 mL) at 25 °C using low-pressure Hg lamps (254 nm) in a Rayonet reactor for 30 h led to 50% conversion of the starting material. GC analysis as a function of time indicated four products, later shown to be the stereoisomers of 6-cyano-2-(2,2,2-trifluoroethoxy)bicyclo[3.1.0]hex-3-ene, **22–25**, in a final ratio of 44:24:22:10 and a mass balance (GC) of 82%, eq 5. These



isomers were stable in the dark in TFE. Extrapolation to very low conversions (<1%) gave a primary photochemical ratio of 30:25:38:7, indicating that the major secondary photoreaction occurring is conversion of **24** to **22**. Because both C2 and C6 epimerize simultaneously in this conversion, the mechanism involves C1–C5 bond rupture to a planar biradical that recloses by C1–C5 bond formation, as in eq 4, for the acetates **15** and **16**.

Preliminary information on the structures of **22–25** was obtained by GC/MS of the crude reaction mixture, which revealed essentially identical spectra for all four with M<sup>+</sup> at the expected (BN + TFE) *m/z* = 203. Dry flash chromatography

**Table 2.** HH Coupling Constants (Hz) for Compounds **22–25** and **30–35**

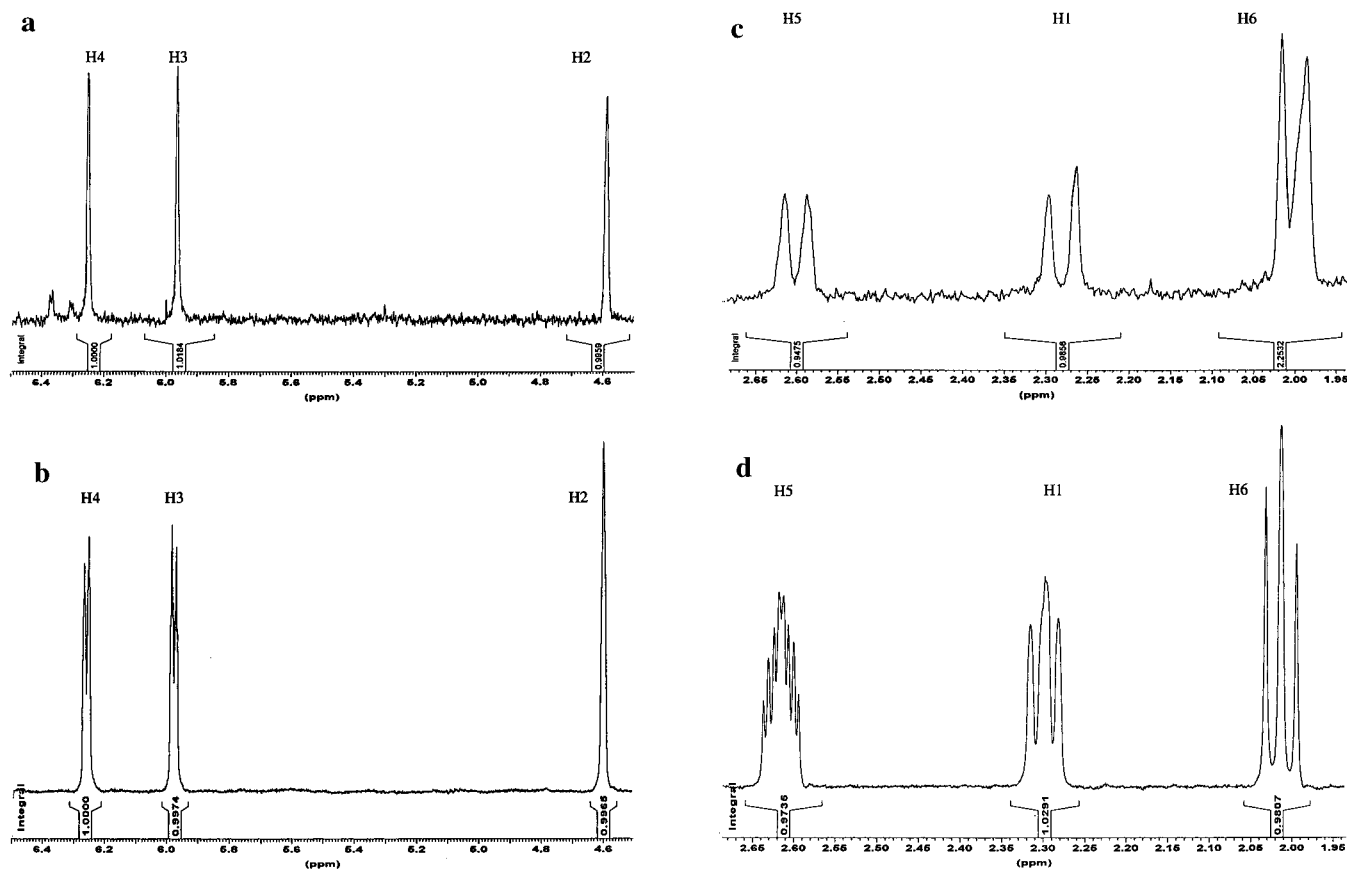
compd	<i>J</i> (1,2)	<i>J</i> (1,5)	<i>J</i> (1,6)	<i>J</i> (3,4)	<i>J</i> (5,6)	<i>J</i> (3,CH <sub>3</sub> ) = <i>J</i> (2,CH <sub>3</sub> )	<i>J</i> <sub>HF</sub>
<b>22</b>	5.9	5.8	3.3	5.2	3.3		8.6
<b>23</b>	<1	4.7	3.7	5.6	2.9		8.6
<b>24</b>	<1	6	7.3	5.6	7.4		8.6
<b>25</b>	6.1	7	7.5	5.5	7.5		8.5
<b>30</b>		6.3	3.5	5.6	3.4		8.5
<b>31</b>		5.8	2.7	5.5	3.7		8.5
<b>32</b>	5.7	6.6	3.1		3.4	1.8	8.6
<b>33</b>		5.6	2.8		3.6	1.3	8.6
<b>34</b>		7	7	5.5	7		8.6
<b>35</b>		7	7	5.5	6.7	1.2	8.6

on silica gel with ethyl acetate and hexane as eluant provided pure samples of **24** and **25** but **22** and **23** were not completely separated. However, fractions of different composition allowed assignment of <sup>1</sup>H NMR signals to each; complete <sup>1</sup>H and <sup>13</sup>C NMR data are given in Tables 1 and 2. Because the spectral arguments for assignments of the structures of these four isomers will be important for the more complicated products obtained from the methylbenzonitriles, a short discussion will be given here.

First, the substitution at C6 is obvious from the lack of the geminal cyclopropyl CH<sub>2</sub>; in the parent compound, bicyclo[3.1.0]hex-2-ene,<sup>5</sup> these Hs are at  $\delta$  0.75 (exo) and  $-0.20$  (endo), respectively.<sup>9</sup> Next, the substituent at C6 must be the cyano, not the 2,2,2-trifluoroethoxy, group; the chemical shift of H2 for the four isomers ( $\delta$  4.58–5.21) is only compatible with oxygen substitution at C2. Moreover, the range of chemical shifts observed for H6 (exo),  $\delta$  2.01 and 1.76 in **24** and **25**, respectively, and H6 (endo)  $\delta$  1.48 and 0.84 in **22** and **23**, respectively, are in good agreement with expectations on the basis of <sup>1</sup>H NMR spectra for *endo*-6-cyanobicyclo[3.1.0]hex-2-ene, H6 exo at  $\delta$  1.70, and *exo*-6-cyanobicyclo[3.1.0]hex-2-ene, H6 endo at  $\delta$  0.70.<sup>10</sup> The stereochemical assignments are made on the basis of coupling constants. When the cyano group is exo at C6 (**22** and **23**), H6 appears as a “triplet” with *J*<sub>16</sub> and *J*<sub>56</sub> in the range of 3–3.7 Hz, values consistent with a trans relationship to the hydrogens at C1 and C5; for *endo* cyano at

(9) Hoberg, J. O.; Jennings, P. W. *Organometallics* **1992**, *11*, 3452–3456.

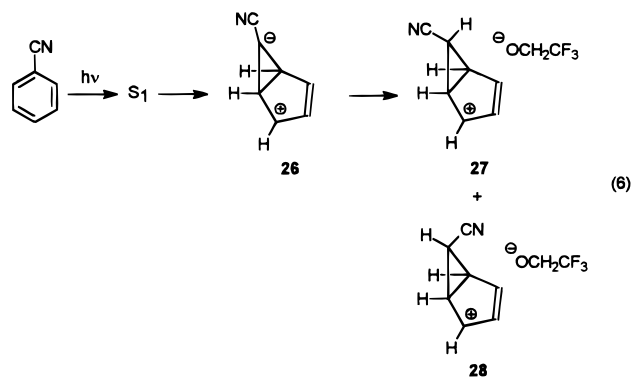
(10) Lubbe, F.; Sustmann, R. *Chem. Ber.* **1979**, *112*, 57–70.



**Figure 1.**  $^1\text{H}$  NMR (250 MHz) of product **24** from the photolysis of benzonitrile and 2,4,6-trideuteriobenzonitrile in TFE: (a) H2, H3, and H4 for **24- $d_3$** ; (b) H2, H3, and H4 for **24**; (c) H1, H5, and H6 for **24- $d_3$** ; (d) H1, H5, and H6 for **24**.

C6 (**24** and **25**), H6 still appears as a triplet but with  $J_{16}$  and  $J_{56} \sim 7.5$  Hz, consistent with a cis relationship to H1 and H5.<sup>2,11</sup> Finally, when the TFE group is endo (**22** and **25**),  $J_{12}$  is  $\sim 6$  Hz but when it is exo,  $J_{12}$  approaches zero.<sup>4,12,13</sup>

The products obtained from the photolysis of BN in TFE, eq 5, are consistent with the previously proposed mechanism for positional isomerization in *p*-, *m*- and *o*-methylbenzonitriles, Scheme 1. In the absence of the methyl group, only one intermediate singlet biradical/zwitterion with the cyano group at C6 is expected to be formed from  $S_1$ , eq 6. This intermediate,



**26**, is shown as the zwitterion with the negative charge on the cyano substituted carbon. Endo protonation of **26** would give

(11) Vogel, P.; Saunders, M.; Hasty, N. M., Jr.; Berson, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 1549–1552.

(12) Bentley, T. W.; Norman, S. J.; Gerstner, E.; Kemmer, R.; Christl, M. *Chem. Ber.* **1993**, *126*, 1749–1757.

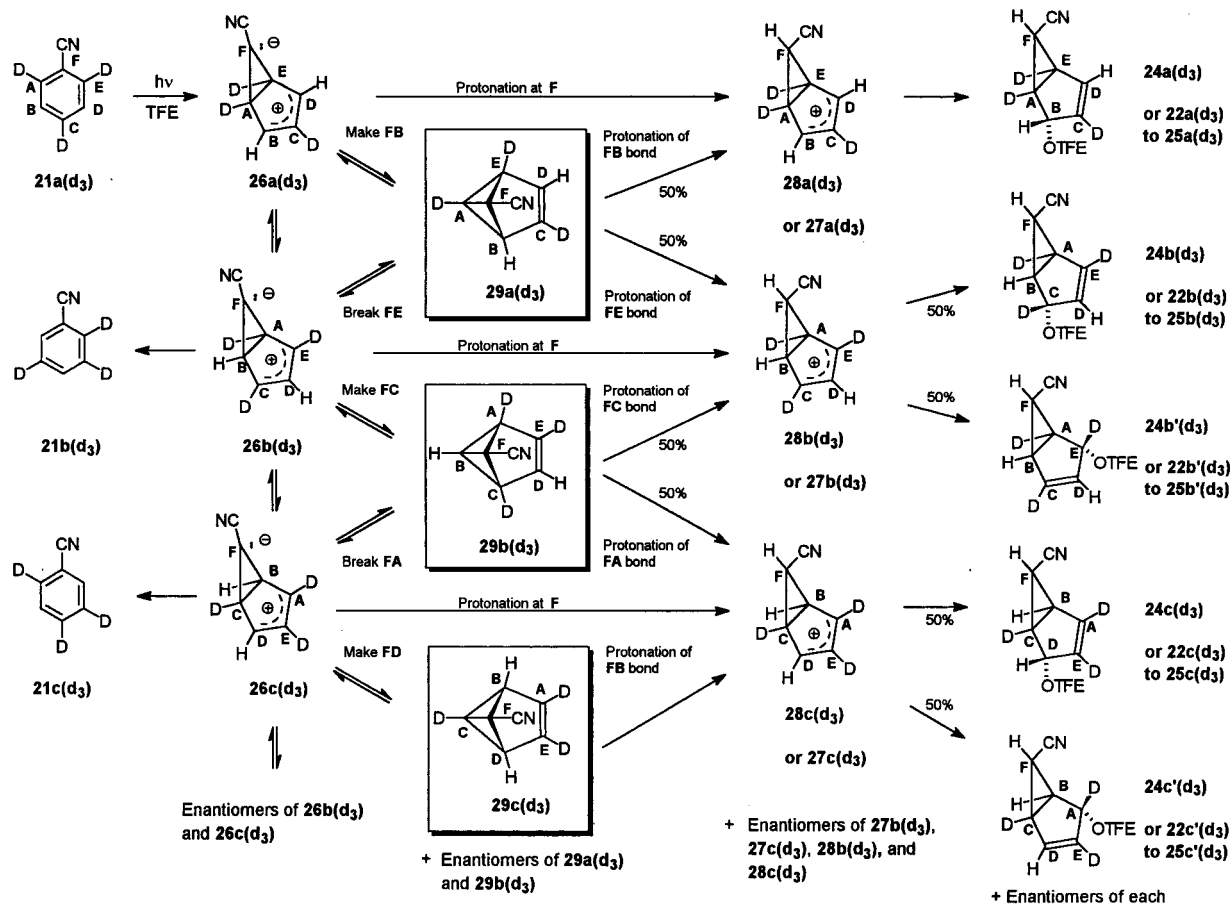
(13) Schneider, M. P.; Crawford, R. J. *Can. J. Chem.* **1970**, *48*, 628–632.

the allylic cation **27** and exo protonation would give **28**, both shown as ion pairs. The product distribution, at low conversions, indicates a slight preference (55%) for endo protonation. As discussed in the Introduction, this selectivity is very different from that previously observed for the addition of alcohols to benzvalene where protonation is exclusively endo. Trapping of the cations by the nucleophilic solvent or the solvent-derived anion would then give the four products, **22–25**, shown in eq 5. However, irradiation of a deuterated benzonitrile conclusively showed that this mechanism is overly simplified.

**Preparation and Irradiation of 2,4,6-Trideuteriobenzonitrile (BN- $d_3$ ) in TFE.** As has been discussed in the Introduction, selectively deuterated substrates can be very useful probes for both phototransposition and addition reactions. Therefore, BN- $d_3$  was synthesized by the same procedure used previously for 2,6-dideuterio-4-methylbenzonitrile;<sup>1</sup> anilinium hydrochloride was converted to 2,4,6-trideuteriobenzonitrile (**21- $d_3$** ) by exchange with  $\text{D}_2\text{O}$  followed by diazotization and Sandmeyer reaction with CuCN. The hydrogen-substituted carbons in benzonitrile appear at previously assigned<sup>14</sup> chemical shifts in the  $^1\text{H}$  decoupled  $^{13}\text{C}$  NMR (250 MHz) spectrum:  $\delta$  132.2 (C2, C6); 129.3 (C3, C5) and 132.9 (C6). In **21- $d_3$** , only the signal at  $\delta$  129.3 remains as a strong singlet, the other two having considerably lower intensity because of the decreased NOE resulting from deuterium substitution. Moreover, in the  $^1\text{H}$  NMR (250 MHz) spectrum, the hydrogens at C3 now appear as a broadened singlet at  $\delta$  7.48 in contrast to their appearance in the nondeuterated compound which was as expected (a pseudotriplet with additional couplings) for the  $\text{CC}'$  protons of an AA'BBCC' system. Integration of the  $^1\text{H}$  NMR in **21- $d_3$**

(14) Haupt, E. T. K.; Leibfritz, D. *Spectrochim. Acta* **1989**, *45A*, 119–121.



**Scheme 2.** Mechanistic Scheme for the Photochemical Addition of TFE to 2,4,6-Trideuteriobenzonitrile

indicated that the deuterium content at C2, C4, and C6 was greater than 95%.

Irradiation of **21-d<sub>3</sub>** in TFE as described above for BN gave the expected four addition products, **22–25**, but now deuterated. Separation of the mixture by silica gel chromatography gave samples of the isomers that allowed the determination of the deuterium distribution by <sup>1</sup>H NMR. An example is shown in Figure 1 for **24-d<sub>3</sub>**.

In panels a and b of Figure 1, the deshielded region for H2, H3, and H4 is shown for the deuterated and undeuterated compounds, respectively. In the deuterated compound, all the signals are singlets because the major coupling between the two alkene hydrogens,  $J_{34} = 5.6$  Hz, is missing. Moreover, the ratio of the signals is essentially 1:1:1 (observed 1.00:1.02:1.00). Panels c and d of Figure 1 show the cyclopropyl hydrogens H1, H5, and H6 for deuterated and undeuterated **24-d<sub>3</sub>**, respectively. In the deuterated compound, the ratio of H1:H5:H6 is 0.42:0.44:1.00.

The possible mechanisms for the addition of TFE to benzonitrile are shown in Scheme 2. Although this scheme looks complicated, its analysis can be simplified by the observation that the vertical columns of structures are regioisomers as a result of deuterium substitution. For instance, for **26-d<sub>3</sub>** there are five bridging positions that C6 = C<sub>F</sub> can occupy (To trace the carbons, letters, rather than numbers, are used to avoid the confusion with nomenclature numbering.): (1) between C<sub>A</sub> and C<sub>E</sub> gives **26a-d<sub>3</sub>** which has a plane of symmetry; (2) and (3) between C<sub>A</sub> and C<sub>B</sub> or C<sub>E</sub> and C<sub>D</sub> gives **26b-d<sub>3</sub>** or its enantiomer (not shown); and (4) and (5) between C<sub>B</sub> and C<sub>C</sub> or C<sub>C</sub> and C<sub>D</sub> gives **26c-d<sub>3</sub>** or its enantiomer (not shown).

As shown in Scheme 2 (horizontally across the top), the above observations of the deuterium distribution in **24-d<sub>3</sub>** are incom-

**Table 3.** Predicted Hydrogen Content at H1 to H5 (normalized to H6 = 1.0) for Mechanism A (One Intermediate Biradical/Zwitterion, **26a-d<sub>3</sub>**), Mechanism B (One Benzvalene, **29a-d<sub>3</sub>**), and Mechanism C (Complete Equilibration) and Observed Distribution for the Photoproducts **22-d<sub>3</sub>–25-d<sub>3</sub>** for the Photolysis of **21a-d<sub>3</sub>** in TFE

	cyclopropyl hydrogens			allylic hydrogens		
	H <sub>1</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>
mechanism A	0	0	1.0	1.0	0	1.0
mechanism B	0.25	0.25	1.0	0.50	0.50	0.50
mechanism C	0.40	0.40	1.0	0.40	0.40	0.40
<b>22-d<sub>3</sub></b>	0.45	0.45	1.0	0.44	0.43	0.42
<b>23-d<sub>3</sub></b>	0.38	0.39	1.0	0.41	0.42	0.47
<b>24-d<sub>3</sub></b>	0.42	0.44	1.0	0.39	0.40	0.39
<b>25-d<sub>3</sub></b>	<i>a</i>	<i>a</i>	1.0	0.4	0.3	0.4

<sup>a</sup> Samples of sufficient purity to obtain reliable integration of these signals were not obtained.

patible with mechanism A outlined in eq 6. This pathway predicts that **21a-d<sub>3</sub>**, after excitation to S<sub>1</sub>, would give the single zwitterion, **26a-d<sub>3</sub>**. Protonation by TFE would give **28a-d<sub>3</sub>**, and finally, nucleophilic trapping at either end of the allylic cation would give a 50:50 mixture of **24a-d<sub>3</sub>** and its enantiomer (not shown). However, **24a-d<sub>3</sub>** would then have a hydrogen ratio of H1:H2:H3:H4:H5:H6 = 0:1:0:1:0:1; the observed ratio is 0.42:0.39:0.40:0.39:0.44:1.0, normalized to 1.0 for H6, Table 3. This ratio can be explained as follows.

There are 10 possible deuterated regioisomers of **24-d<sub>3</sub>** (five pairs of enantiomers); one of each pair is shown as **24a-d<sub>3</sub>**, **24b-d<sub>3</sub>**, **24b'-d<sub>3</sub>**, **24c-d<sub>3</sub>**, and **24c'-d<sub>3</sub>** in Scheme 2 (The primed and unprimed letters indicate two different deuterium distributions in the two products obtained from the same precursor.) Each of these will be formed as a racemic mixture. If the five are

formed in equal amounts, then the two hydrogens on the five-membered ring will be statistically scrambled over H1 to H5, i.e., 0.4 of a hydrogen on each. The experimental hydrogen distribution for each of the photoproducts, **22-d<sub>3</sub>**–**25-d<sub>3</sub>** is given in Table 3. Clearly, all four isomers have the hydrogens, within experimental error, statistically equilibrated although not enough of **25-d<sub>3</sub>** was obtained to give reliable integration of H1 and H5. Another feature of the <sup>1</sup>H NMR of **24-d<sub>3</sub>** is the appearance of the “doublet” for H6, Figure 1(c). H6 will be a doublet in 80% of the molecules because it will be coupled to H1 ( $J = 7.3$  Hz) 40% of the time and to H5 ( $J = 7.4$  Hz) 40% of the time with essentially the same coupling constant. However, 20% of the time, i.e., in **24a-d<sub>3</sub>**, H6 will be coupled to deuterium atoms at both C1 and C5 ( $J \sim 1$  Hz) and will be a triplet, appearing as a broad singlet. This “singlet”, which could not be resolved from the H6 doublet even at 400 MHz, can be observed as a broadening of the low-frequency line in the doublet, presumably because there is a slight shift in frequency away from the center as a result of an isotope effect.

These observations also rule out another pathway, mechanism B, that seemed likely on the basis of the additions to benzene discussed in the Introduction. In this mechanism, the first formed zwitterion, **26a-d<sub>3</sub>**, proceeds to a single benzvalene, **29a-d<sub>3</sub>**, followed by rapid protonation by TFE to form the two allylic cations, **28a-d<sub>3</sub>** and **28b-d<sub>3</sub>**, which are then trapped by the nucleophile (before equilibration). A 2:1:1 mixture of **24a-d<sub>3</sub>**:**24b-d<sub>3</sub>**:**24b'-d<sub>3</sub>** would have been formed. The observed hydrogen distribution, Table 3, is inconsistent with this possibility. Moreover, products resulting from endo protonation would then be expected to dominate and this is not the case.

There are two places in Scheme 2 where the equilibration of the hydrogens and deuteriums can be observed: (1) in the starting materials, **21-d<sub>3</sub>**, or (2) in the photoproducts, **22-d<sub>3</sub>**–**25-d<sub>3</sub>**. There are four places in the mechanism where this equilibration can occur: (1) via the zwitterions, **26-d<sub>3</sub>**; (2) via the benzvalenes, **29-d<sub>3</sub>**; (3) via the allylic cations, **27-d<sub>3</sub>** and **28-d<sub>3</sub>**; or, finally, (4) in the photoproducts themselves, by secondary photochemistry.

Equilibration in the starting material was ruled out by analysis of <sup>1</sup>H NMR spectra of samples as a function of time. For instance, at only 3.3% conversion of benzonitrile, **21-d<sub>3</sub>**, to the TFE adducts, the hydrogen distribution in the photoproducts indicated complete equilibration. In the same sample, the growth of signals for the ortho and para hydrogens was apparent; i.e., **21a-d<sub>3</sub>** was being converted to **21b-d<sub>3</sub>** and **21c-d<sub>3</sub>**, Scheme 2. Integration of these signals gave a ratio of ortho:meta:para hydrogens = 4:94:2 as expected for a mixture consisting of a ratio of **21a-d<sub>3</sub>**:**21b-d<sub>3</sub>**:**21c-d<sub>3</sub>** = 92:4:4. In other words, the starting deuterated isomer was still absorbing 92% of the light and yet the hydrogens in the products were already completely equilibrated. Even at 24% conversion of **21-d<sub>3</sub>** to photoproducts, the ortho:meta:para ratio was only 12:81:7; the completely equilibrated ratio would be 40:40:20. In contrast, irradiation in acetonitrile, instead of TFE, for the same length of time did lead to complete equilibration of **21-d<sub>3</sub>**. These observations would seem to rule out equilibration mechanisms 1 and 2, either of which should lead to hydrogen scrambling in the starting material. Our current preference for the equilibration mechanism is case 3, in the allyl cations, **27-d<sub>3</sub>** and **28-d<sub>3</sub>**. For reasons that will be described below in the photoaddition of TFE to the methylbenzonitriles, we do not believe that the products are equilibrating rapidly under the photolysis conditions. This is reasonable because the starting material, with a molar absorptivity ( $\epsilon$ ) of  $\sim 400$  M<sup>-1</sup> cm<sup>-1</sup> at 254 nm, will be absorbing much

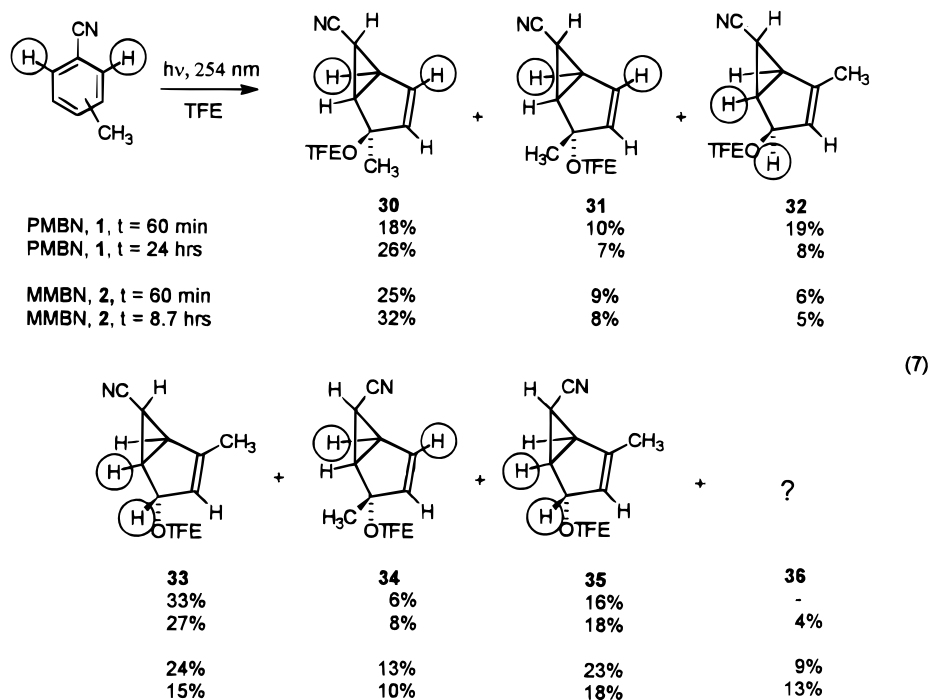
more strongly than the photoproducts, which have very low  $\epsilon$  values at the same wavelength, particularly at low conversions where the equilibration has already occurred.

Our proposed mechanism for the photoaddition of TFE to benzonitrile is essentially as outlined in eq 6, except with the addition of rapid equilibration of the first formed cations **27a-d<sub>3</sub>** and **28a-d<sub>3</sub>** with their deuterated isomers **27b-d<sub>3</sub>**/**28b-d<sub>3</sub>** and **27c-d<sub>3</sub>**/**28c-d<sub>3</sub>** (and their enantiomers) followed by trapping with the nucleophile (TFE or its anion). The equilibration of the cations is proposed to occur by an allowed 1,4-sigmatropic shift with inversion of configuration at the migrating carbon C6. Rapid equilibration of bicyclo[3.1.0]hex-3-en-2-yl cations has been observed previously. For instance, the heptamethyl compound has a free energy of activation for rearrangement<sup>11</sup> of only 9 kcal/mol at  $-89$  °C and even the barrier for the unsubstituted cation is quite small, 19.8 kcal/mol at  $-20$  °C.<sup>4</sup>

**Photolysis of *p*-, *m*-, and *o*-Methylbenzonitrile in TFE.** Irradiation in TFE of **1** (PMBN), **2** (MMBN), and **3** (OMBN) in the same way as described above for benzonitrile also resulted in 1:1 addition products. Gas chromatography analysis for PMBN demonstrated that there were seven major plus two minor photoproducts (<2% of the mixture). GC/MS analysis of the reaction mixture indicated that the products were 1:1 addition products, M<sup>+</sup> of  $m/z = 217$ . Moreover, a comparison of results for the photolysis of PMBN in acetonitrile for the same time again showed that the photoaddition reaction had prevented the phototransposition from occurring to any significant extent. Surprisingly, MMBN reacted to give the same products, although with somewhat different distribution. In contrast, OMBN behaved very differently. After 24 h of irradiation, the percentage conversion of starting material was only  $\sim 5\%$  and the only product observed (less than 2% yield) had the same GC retention time as **33**.

Dry flash chromatography again resulted in some separation of the photoproducts and gave fractions of varying composition so that the <sup>1</sup>H and <sup>13</sup>C NMR signals could be assigned, Tables 1 and 2. The product structures and their yields (normalized to 100%) are given in eq 7. The structure of **36** could not be determined because samples that were pure enough to allow unambiguous assignment were not obtained. The percentage conversions were 3% at 60 min and 58% at 24 h for PMBN and 6% at 60 min and 41% at 8.7 h for MMBN. Despite the fact that the reaction mixture obtained in these photolyses is complex, the process is actually rather selective. For instance, there are 336 possible trisubstituted bicyclo[3.1.0]hexenes but only seven major ones are observed in the photolysis reaction. Four of the potential products are the stereoisomers of 6-cyano-4-methyl-2-(trifluoroethoxy)bicyclo[3.1.0]hex-3-ene derivatives; three were observed, the missing one being that with both the cyano and TFE groups endo. There are also four possible 6-cyano-2-methyl-2-trifluoroethoxy stereoisomers; three were obtained; again the missing one is the endo, endo isomer. Compound **36** is probably one of these two missing compounds because it has the expected alkene doublet of doublets ( $\delta$  5.81 and 5.98,  $J = 5.8$  Hz) in the <sup>1</sup>H NMR. However, the lower field signal has a second coupling,  $J = 2$  Hz, which is not typical of the rest of the compounds (see below). As indicated in eq 7, the photoproduct composition changes very little, as a function of percentage conversion.

The assignments of the structures of **30**–**35**, eq 7, was made on the basis of NMR in the same way as the simpler adducts for benzonitrile. The cyano substitution on the cyclopropyl ring and its stereochemistry was easily established by chemical shifts and coupling constants. Those compounds with the methyl group



at C2 (**30**, **31**, **34**) gave sharp singlets whereas those with methyl group at C4 (**32**, **33**, **35**) appeared as narrow "triplets" ( $J \sim 1.5\text{--}2$  Hz) because of similar coupling constants to the two nonequivalent protons at C2 and C3. Moreover, correlated  $^1\text{H}$  to  $^{13}\text{C}$  NMR spectra showed that **32**, **33**, and **35** had a proton on C2 whereas **30**, **31**, and **34** did not. The assignment of C2, as an oxygen-substituted carbon, was made on the basis of the  $^{13}\text{C}$  chemical shift ( $\delta$  84.3–89.1). The assignment of stereochemistry for those compounds with a hydrogen at C2 (**32**, **33**, **35**) was made on the basis of the coupling constant between H1 and H2 ( $\sim 6$  Hz when the hydrogen is exo and unobservable when the hydrogen is endo). The difference in stereochemistry at C2 for **30**, **31**, and **34** was made on the basis of NOE difference spectra. Irradiation of the endo methyl group in **31** gave strong enhancements for endo H6 and for H3. In contrast, irradiation of the exo methyl group in **30** gave no enhancement for H6 but did for both H1 and H3. Finally, irradiation of the endo methyl group in **29** only gave an enhancement for H3.

The assignment of the photoproduct structures was convincingly confirmed by the irradiation of selectively labeled PMBN, **1-*d***<sub>2</sub>, with deuterium at the two positions ortho to the cyano group (circled in eq 7). Each of the dideuterated photoproducts was now missing one hydrogen from the shielded region of the cyclopropyl ring (H1 or H5) and one hydrogen from the deshielded region of the alkene and oxygen-substituted carbons (H2 or H4). These are also circled in eq 7. The removal of two hydrogens from the compounds greatly simplified their  $^1\text{H}$  NMR spectra and, therefore, helped in the assignment of protons and the evaluation of coupling constants. For instance, **30-*d***<sub>2</sub> now has a simple doublet of doublets ( $J_{16} = 3.5$  Hz) for H1 and H6, and H3 is a singlet.

The proposed mechanism for the formation of photoproducts is given in Scheme 3. For MMBN, the critical intermediates are the allylic cations **37** and **38** which are formed by endo (55%) and exo (36%) protonation at C6 of the singlet biradical/zwitterion **5**, (shown as the zwitterion) formed from the  $S_1$  excited state. These same cations, **37** and **38**, are formed from  $S_1$  of PMBN by the allowed 1,4-sigmatropic rearrangement of the initially formed less stable cations, **39** (74%) and **40** (22%). In this case, the rearrangement does not lead to complete

equilibration of the possible cations but rather stops at the most stable one with the methyl group at the terminal end of the allylic cation. Reaction of these allylic cations occurs at either end with nearly equal endo (**30**, **32**) and exo (**31**, **33**) products formed from **37** but highly favored exo products (**34**, **35**) from **38**. As described in the Introduction, Scheme 1, irradiation of any of PMBN, MMBN, and OMBN in acetonitrile results in equilibration of the three isomers, although very inefficiently for OMBN. Therefore, in the absence of a trapping reagent, the intermediates **4**, **5**, and **6** are long enough lived to equilibrate. As was observed for the phototransposition reaction, OMBN is quite unreactive to photoaddition of TFE. Both of these observations indicate a larger barrier on the  $S_1$  surface, relative to the other two isomers, for conversion to the biradical, **6**, by meta bonding.

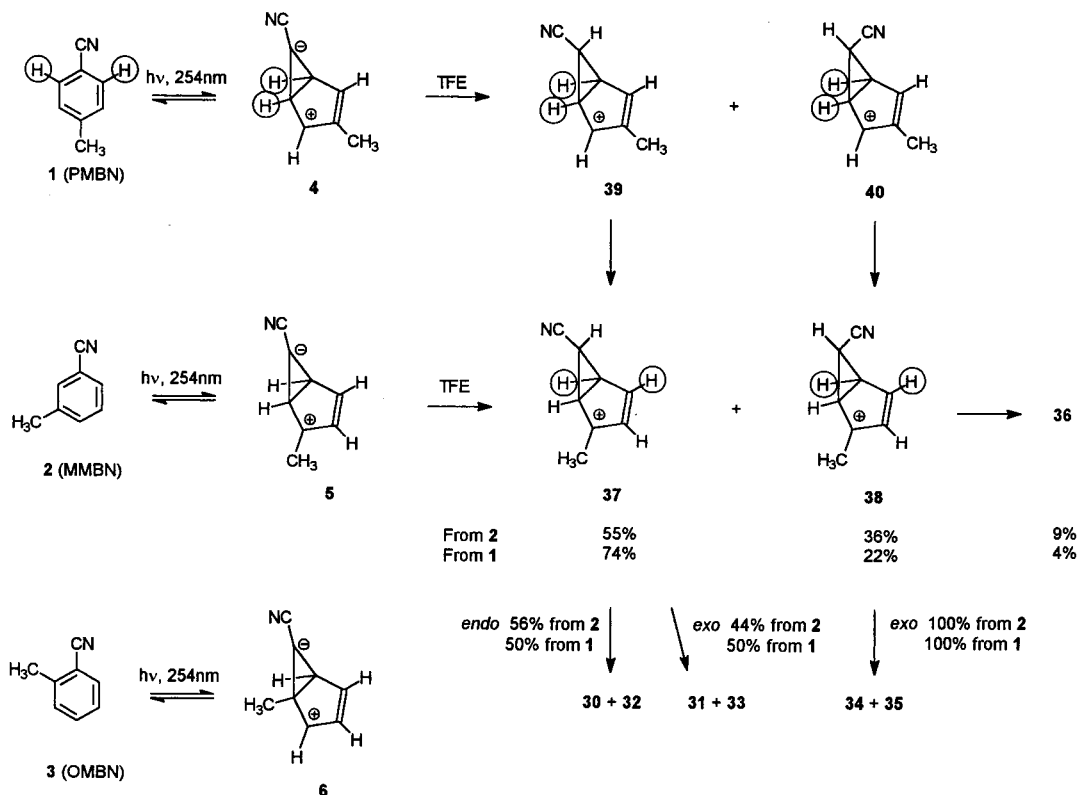
A reviewer has suggested that an alternate possibility for the mechanism of these addition reactions could be protonation by TFE of  $S_1$  of the aromatic at C1 followed by cyclization of the pentadienyl cation to the bicyclic one. This suggestion has merit because we have previously shown that the fluorescence of these compounds is quenched in acidic media.<sup>15</sup> However, the onset of fluorescence quenching in aqueous perchloric acid for **21**, **1**, **2**, and **3** occurs at approximately 2.4, 1.4, 0.9, and 0.4 M acid, respectively, i.e., considerably more acidic than TFE. In agreement with this expectation, the fluorescence of these aromatic nitriles was not quenched by TFE. For instance, the quantum yield of fluorescence for **1** actually increased slightly in TFE ( $\Phi_F = 0.20$ ) compared to acetonitrile ( $\Phi_F = 0.16$ ).

The reactions described above provide fundamental information about the changes in charge distribution and geometry that occur upon excitation of substituted benzenes to  $S_1$ . For instance, neither photoadditions nor phototranspositions were observed for anisole or the methylanisoles. Details on these examples (and others) will be reported soon.

## Experimental Section

**Chemicals.** *p*-, *m*-, and *o*-methylbenzonitrile and 2,6-dideuterio-4-methylbenzonitrile were purified as described previously.<sup>1</sup> Benzonitrile (Aldrich) was purified by bulb-to-bulb distillation and 2,4,6-trideute-

(15) Pincock, J. A.; Redden, P. R. *Can. J. Chem.* **1989**, *67*, 710–719.

**Scheme 3.** Mechanistic Scheme for the Photochemical Addition of TFE to Methylbenzonitriles **1–3** and to 2,6-Dideuterio-4-methylbenzonitrile

riobenzonitrile was prepared by the same method as for 2,6-dideuterio-4-methylbenzonitrile. TFE (Aldrich, 99+%) was used without further purification.

**Photolysis.** In a typical reaction, 273 mg of *p*-methylbenzonitrile in 100 mL of TFE was irradiated in a Rayonet reactor with 254-nm low-pressure mercury lamps while being purged with nitrogen. The reaction was thermostated at 25 °C with an immersion circulating water tube. Progress of the reaction was monitored by GC using a 30 m by 0.25 mm J&W DB-200 column using helium as carrier gas (split) and temperature programming (60 °C/3 min, 15 °C/min to 180 °C, 180 °C/5 min). Retention times (min) for the seven major products were **30** (11.22), **31** (11.29), **32** (11.56), **33** (11.92), **34** (11.34), **35** (11.51), and **36** (12.51). The separation of each of the peaks from the others was to the baseline, a reflection of the ability of this particular column to separate isomers, particularly aromatic ones. The reaction was stopped after 24 h at 58% conversion of starting material.

**Separation of Photoproducts.** The reaction mixture was separated by dry flash column chromatography on Macherey-Nagel TLC grade silica gel (funnel size, 5 cm high by 5 cm in diameter) using 7.5% ethyl acetate in hexanes as eluant (fraction volume, 25 mL). Fractions 25–32 contained compounds **30–33** in varying amounts depending on the fraction. Rechromatography using 2% ethyl acetate separated **30** and **31** from **32** and **33**. Fractions 60–75 contained mixtures of **34**

and **35**. Improved separation of these compounds was not achieved using a Chromatotron. Compound **36** eluted last in fractions 100–120 and was only obtained in milligram quantities and not pure enough for NMR proof of structure. <sup>1</sup>H and <sup>13</sup>C NMR spectral data for the bicyclo[3.1.0]hex-3-en-2-ol derivatives **22–25** and **30–35** are given in Tables 1 and 2.

**GC/MS of **22**:** *m/z* (relative intensity) 203 (42), 163 (29), 120 (22), 113 (67), 104 (82), 103 (15), 92 (66), 83 (15), 78 (13), 77 (44), 76 (16), 66 (17), 65 (100), 64 (14), 63 (12). The isomers **22–25** all gave essentially the same spectra.

**GC/MS of **30**:** *m/z* (relative intensity) 217 (36), 216 (14), 202 (67), 177 (12), 134 (44), 127 (15), 118 (100), 117 (45), 116 (100), 107 (19), 106 (59), 92 (19), 91 (75), 90 (65), 89 (35), 83 (18), 80 (18), 79 (74), 78 (25), 77 (62), 76 (14), 66 (15), 65 (43), 64 (25), 63 (30). The isomers **30–35** all gave essentially the same spectra.

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