

agreement with experimental values for the parent systems suggest that the AM1 method is quite accurate for calculating vibrational frequencies. Given the variation of the TS geometry with substituents, one might have anticipated a significant variation of activation entropies as well. The almost constant value of  $\Delta S^\ddagger$  may possibly be related to the near constant value of  $\bar{R}_{ts}$ , i.e. all TS's have approximately the same degree of "looseness". A possible explanation for the discrepancy could be that some or all of the reactions considered in this study in fact proceed via a "two-stage" mechanism, as discussed in the "Computational Methods" part.

Finally we would like to note that the above results are not significantly changed by inclusion of thermodynamical enthalpy corrections (most importantly zero point energies), which can easily be evaluated from vibrational frequencies. For reaction 1b the substituent effect including these effects are -13.8, -3.3, -3.7, and -3.2 kcal/mol for  $\text{NH}_2$ ,  $\text{NO}_2$ ,  $\text{CH}_3$ , and  $\text{CHO}$ , respectively, compared to values of -14.2, -3.5, -3.9, and -3.5 kcal/mol without these corrections, i.e. inclusion of these factors only give insignificant changes.

### Summary

The performance of the AM1 method using spin-restricted single-determinant wave functions has been tested

for the retro-Diels-Alder reaction of substituted bicyclo-[2.2.2]octa-2,5-diene and ethanoanthracene compounds for which experimental data are available. The calculated geometries of the TS's appear quite reasonable when compared to ab initio results. The degree of asynchronicity depends markedly on substituents, with electron donors on the diene component making the TS more, and electron acceptors less, asymmetrical relative to the unsubstituted system. The asymmetry as a function of substituents on the dienophile follow rather closely the calculated TS stabilization. The method, however, is unable to reproduce trends in activation entropies, although absolute values for the parent systems are close to experimental values. A direct comparison between relative activation enthalpies is difficult due to the error limits on the experimental data, but it appears that the method in general predicts a too large stabilization for most substituents. None of the substituents considered here is calculated to be destabilizing, in contrast to experimental data. Nevertheless, trends in reactivity are reproduced surprisingly well, although the qualitatively wrong prediction for some substituents make conclusions based on such calculations regarding reaction mechanisms very prone to errors.

**Registry No.** 1a ( $R_2 = \text{H}$ ), 500-23-2; 1b ( $R_2 = \text{H}$ ), 70209-62-0; 2a ( $R_2 = \text{H}$ ), 5675-64-9; 2b ( $R_2 = \text{H}$ ), 13294-86-5.

## Meta-Substituent Effects on Benzyl Free-Radical Stability

Thomas H. Fisher,\* Stephen M. Dershem, and M. Lynn Prewitt

Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762

Received May 8, 1989

A series of 5-substituted 3-cyanotoluenes was synthesized, and the relative rates of *N*-bromosuccinimide bromination were determined in benzene at 80 °C. The resulting  $\sigma_F^\ddagger$  values of meta Me, H, Br,  $\text{NO}_2$ , and CN were found to be 0.03, 0.00, -0.03, -0.04, and -0.10, respectively. Of these meta substituents, all but methyl were found to be destabilizing to the intermediate benzyl free radical. These meta substituent results are consistent with reported  $\sigma_\alpha^\ddagger$  and  $\alpha_c^\ddagger$  values and cast doubt upon reports that assume meta substituents have no influence on free-radical stability.

The influence of a substituent on the stability of a free-radical intermediate is, in general, less than the corresponding influence of the same substituent on a carbocation or carbanion intermediate. This diminished influence makes quantification more difficult.<sup>1</sup> In the past decade the development of free-radical substituent constants, usually called  $\sigma^\ddagger$ , has helped to clarify and quantify free radical substituent effects. A general consensus now exists that some substituents, e.g. para nitro, cyano, acetyl, and phenyl tend to be relatively good at stabilizing a free radical, whereas the stabilizing or destabilizing nature of others, such as para-fluoro and most meta substituents, is still in dispute.

Four new  $\sigma^\ddagger$  scales have appeared since our original  $\sigma^\ddagger$  scale<sup>2</sup> (here called  $\sigma_F^\ddagger$ ) was developed based on the *N*-bromosuccinimide (NBS) bromination of 4-substituted 3-cyanotoluenes (1). Jackson<sup>3</sup> defined a  $\sigma_J^\ddagger$  scale based on

the thermal decomposition of dibenzylmercurials; Arnold<sup>4</sup> used a nonkinetic approach to define the  $\sigma_\alpha^\ddagger$  scale based on esr benzylic  $\alpha$ -hydrogen hyperfine coupling constants; Creary<sup>5</sup> chose the thermal rearrangement of 3-aryl-2,2-dimethylmethylenecyclopropanes to 2-arylisopropylidenecyclopropanes to define the  $\sigma_c^\ddagger$  scale; and Jiang<sup>6</sup> developed a  $\sigma_T^\ddagger$  scale based on the cyclodimerization of  $\alpha,\beta,\beta$ -trifluorostyrenes.

Our quantitative understanding of aryl substituent effects in free-radical reactions has also been enhanced by numerous non-sigma-dot approaches including (a) the thermal decomposition rates of phenylazomethanes,<sup>7</sup>

(1) *Substituent Effects in Free Radical Chemistry*; Viehe, H. G., Janousek, Z., Merenji, R., Eds.; Reidel: Dordrecht, Holland, 1986.

(2) (a) Fisher, T. H.; Meierhoefer, A. W. *Tetrahedron* 1975, 31, 2019. (b) Fisher, T. H.; Meierhoefer, A. W. *J. Org. Chem.* 1978, 43, 220. (c) Fisher, T. H.; Meierhoefer, A. W. *J. Org. Chem.* 1978, 43, 224.

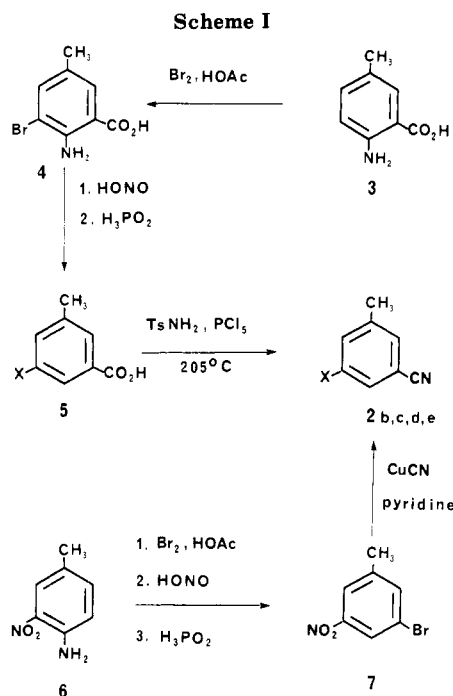
(3) (a) Dincturk, S.; Jackson, R. A.; Townson, M. *J. Chem. Soc., Chem. Commun.* 1979, 172. (b) Dincturk, S.; Jackson, R. A.; Townson, M.; Agirbas, H.; Billingham, N. C.; March, G. *J. Chem. Soc., Perkin Trans. 2* 1981, 1121. (c) Dincturk, S.; Jackson, R. A. *Ibid.* 1981, 1127. (d) Agirbas, H.; Jackson, R. A. *Ibid.* 1983, 739.

(4) (a) Dust, J. M.; Arnold, D. R. *J. Am. Chem. Soc.* 1983, 105, 1221, 6531. (b) Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* 1984, 62, 1164. (c) Arnold, D. R.; Nicholas, A. M.; Snow, M. S. *Ibid.* 1985, 63, 1150. (d) Wayner, D. D. M.; Arnold, D. R. *Ibid.* 1985, 63, 2378. (e) Nicholas, A. M.; Arnold, D. R. *Ibid.* 1986, 64, 270. (f) Arnold, D. R.; Nicholas, A. M.; Young, K. M. *Ibid.* 1986, 64, 769.

(5) (a) Creary, X. *J. Org. Chem.* 1980, 45, 280. (b) Creary, X.; Benage, B.; Mehrsheikh-Mohammadi, M. E.; Bays, J. P. *Tetrahedron Lett.* 1985, 26, 2383. (c) Creary, X.; Mehrsheikh-Mohammadi, M. E. *J. Org. Chem.* 1986, 51, 1110. (d) Creary, X.; Mehrsheikh-Mohammadi, M. E. *Ibid.* 1986, 51, 2664. (e) Creary, X.; Mehrsheikh-Mohammadi, M. E.; McDonald, S. *Ibid.* 1987, 52, 3254.

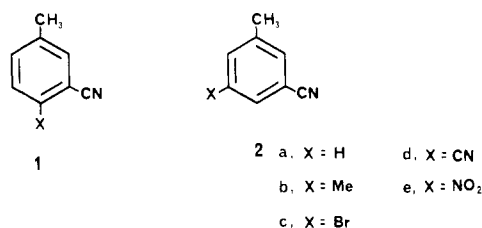
(6) (a) Jiang, X. K.; Ji, G. Z.; Yu, C. X. *Acta Chim. Sin. (Engl. Ed.)* 1984, 82. (b) Jiang, X. K.; Li, X. Y.; Zhao, C. X.; Ji, G. Z. *Rev. Chem. Intermed.* 1986, 7, 195.

(7) Bandlish, B. K.; Garner, A. W.; Hodges, M. L.; Timberlake, J. W. *J. Am. Chem. Soc.* 1975, 97, 5856.



phenylazoethanes,<sup>8</sup> and azocumenes;<sup>9</sup> and (b) acidity-oxidation-potential (AOP) values for fluorenes and phenylacetonitriles.<sup>10</sup> Proximate substituent effects—where the substituent and the unpaired electron are on the same carbon atom—also provide much useful information on factors affecting free-radical stabilities. Several relevant proximate studies include the thermolysis of 2-substituted azopropanes,<sup>7,9b,11</sup> the AOP values for 9-substituted fluorene,<sup>10</sup> and theoretical 4-31G studies of the radical stabilization energies of substituted methyl radicals.<sup>12</sup>

In this work a series of 5-substituted 3-cyanotoluenes (2) was brominated with NBS, and the  $\sigma_F^*$  values of the meta substituents were determined. The influence of meta substituents on free-radical stabilities is of interest because of conflicting claims that meta substituents have no effect on benzyl radical stabilities<sup>3c,d,6b</sup> and other claims that most meta substituents destabilize benzyl radicals.<sup>4a,d,5e</sup>



## Results and Discussion

**Synthesis.** The reactions used to synthesize 5-substituted 3-cyano-toluenes 2b-e are shown in Scheme I.

(8) (a) Shelton, J. R.; Liang, C. K. *J. Org. Chem.* **1973**, *38*, 2301. (b) Scheppele, S. E.; Miller, D. W.; Grizzle, P. L.; Mauerci, F. A. *J. Am. Chem. Soc.* **1971**, *93*, 2549.

(9) (a) Shelton, J. R.; Liang, C. K.; Kovacic, P. J. *J. Am. Chem. Soc.* **1968**, *90*, 354. (b) Kovacic, P.; Flynn, R. R.; Gormish, J. F.; Kappelman, A. H.; Shelton, J. R. *J. Org. Chem.* **1969**, *34*, 3312. (c) Timberlake, J. W.; Hodges, M. L. *Tetrahedron Lett.* **1970**, *48*, 4147.

(10) (a) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979. (b) Bordwell, F. G.; Bausch, M. J. *Ibid.* **1986**, *108*, 1985.

(11) (a) Timberlake, J. W.; Gardner, A. W.; Hodges, M. L. *Tetrahedron Lett.* **1973**, 309; (b) Dube, M. F.; Timberlake, J. W. *Tetrahedron* **1980**, *36*, 1753. (c) Luedtke, A. E.; Timberlake, J. W. *J. Org. Chem.* **1985**, *50*, 268.

(12) Pasto, D. J.; Krasnansky, R.; Zercher, C. J. *J. Org. Chem.* **1987**, *52*, 3062.

**Table I. Relative Rates of NBS Bromination of Toluenes 2 at 80 °C**

X	obsd <sup>a</sup> $k_X/k_H$	obsd <sup>b</sup> $k_X/k_H$
CH <sub>3</sub>	1.34 ± 0.02	1.36 ± 0.02
H	1.00	1.00
Br	0.26 ± 0.01	0.24 ± 0.02
CN	0.12 ± 0.01	—
NO <sub>2</sub>	0.082 ± 0.004	0.086 ± 0.007

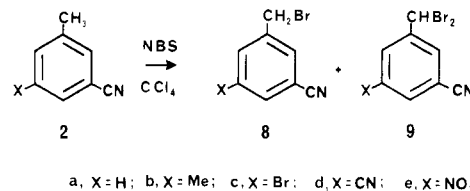
<sup>a</sup>Using GC method. <sup>b</sup>Using NMR method.

3,5-Dimethylbenzoic acid and uvitic acid were converted into 2b and 2d, respectively, by heating the acids with toluenesulfonamide and phosphorus pentachloride at 200–205 °C using the procedure of Miller.<sup>13</sup> To avoid complications, the final pot temperature should not exceed 205 °C.

The bromo compound 2c was synthesized by two independent procedures. *m*-Tolunitrile was converted into 4-nitro-3-cyanotoluene with  $\text{KNO}_3$  and  $\text{H}_2\text{SO}_4$ ;<sup>14</sup> reduction of the nitro compound with Sn and HCl resulted in 4-amino-3-cyanotoluene;<sup>14</sup> bromination with  $\text{Br}_2$  in HOAc gave 4-amino-5-bromo-3-cyanotoluene; and, finally, deamination by diazotization and heating in ethanol<sup>15</sup> gave 2c in 15% overall yield. Alternately, 2-amino-5-methylbenzoic acid (3) was brominated to give 4, followed by deamination to give 5, which was then converted into 2c, as shown in Scheme I, in 42% overall yield.

Toluene 2e was synthesized from 4-methyl-2-nitroaniline (6) by bromination, deamination, and a Rosenmund-von Braun reaction, in 44% overall yield, as also shown in Scheme I. This synthesis of 2e is a considerable improvement over the reported procedure starting with 1,3-dimethyl-5-nitrobenzene.<sup>16</sup>

The benzyl bromide products of 2a-e were each synthesized with 1 equiv of NBS in  $\text{CCl}_4$  and then purified in order to determine GC response factors. The benzyl bromides of 2a-c were obtained cleanly, but 2d,e (X = CN, NO<sub>2</sub>) gave mixtures of about equal amounts of unreacted 2, benzyl bromide 8, and benzal bromide 9. The pure benzyl and benzal bromides in these two cases were purified via column chromatography. To prevent this problem in the kinetic runs, the quantity of NBS used in each run was not greater than 5 mol % of total toluenes or 20 mol % of the most reactive toluene.



**Kinetics.** The results of the relative rate studies on 5-substituted 3-cyanotoluenes 2 are shown in Table I. The usual NMR method was not successful with 2d (X = CN) because the benzylic hydrogens of the two benzyl bromide products were not resolved. A GC method was developed to determine  $k_{\text{CN}}/k_{\text{H}}$  for 2d, and the GC method was also used to determine the other relative rates in order to check the precision of the two methods. As can be seen in Table I, the two methods give good agreement.

The  $\sigma_F^*$  values for these meta substituents are given in Table II, along with literature  $\sigma^*$  values. It should be noted

(13) Miller, C. S. *Organic Syntheses*; Wiley: New York, 1955; collect. Vol. III, pp 646–648.

(14) Findeklee V. *Chem. Ber.* **1905**, *38*, 3542.

(15) Wroblewsky, B. *Justus Liebigs Ann. Chem.* **1918**, *92*, 203.

(16) Gabriel, S.; Thieme, A. *Chem. Ber.* **1919**, *52*, 1091.

Table II. Values of  $\sigma^*$  for Meta Substituents

X	$\sigma_F^{*a}$	$\sigma_\alpha^{*b}$	$\sigma_C^{*c}$
Me	+0.03	+0.002	+0.03
H	0.00	0.000	0.00
Br	-0.03		
NO <sub>2</sub>	-0.04		-0.11
CN	-0.10	-0.026	-0.12

<sup>a</sup>This work. <sup>b</sup>Reference 4b. <sup>c</sup>Reference 5e.

that no steric problems exist in **2** since the substituents are not located on alternating positions on the benzene ring. The agreement between the three  $\sigma^*$  systems shown in Table II is excellent. All meta substituents of this series, except methyl, were found to be slightly destabilizing. This finding casts doubt on the validity of the model system used by Jackson, in which meta substituents were assumed to have no influence on benzyl free-radical stability.

Exner<sup>17</sup> suggested that the minimum set of substituents that must be included in a comprehensive study of an ionic reaction is 4-OMe, H, 4-Cl, 4-NO<sub>2</sub>, 3-Me, 3-Cl, and 3-NO<sub>2</sub>. When studying free-radical reactions, Arnold<sup>4a</sup> recommended that, in addition to the above lists, the following should also be included: 4-F, 4-Me, 4-*t*-Bu, 4-CN, and 3-CN. The five free-radical substituent studies  $\sigma_F^*$ ,  $\sigma_J^*$ ,  $\sigma_\alpha^*$ ,  $\sigma_C^*$ , and  $\sigma_T^*$  have reported 10, 6, 10, 11, and 4 of these 12 substituents, respectively. Three of the five systems are fairly comprehensive by Arnold's criteria. In terms of total  $\sigma^*$  values reported  $\sigma_F^*$ ,  $\sigma_\alpha^*$ , and  $\sigma_C^*$  have reported 16, 34, and 43, respectively. Thus, the Creary and Arnold systems are the most inclusive.

There is general agreement among these five  $\sigma^*$  systems that para electron-withdrawing groups, e.g. NO<sub>2</sub>, CN, Ac, and CO<sub>2</sub>Et provide substantial free-radical stabilization. All five of the systems also agree that 4-Cl is stabilizing, and four of the five find 4-F to be destabilizing to a benzyl radical (only  $\sigma_J^*$  finds 4-F to be stabilizing). All reported  $\sigma^*$  values of 4-Br and 4-I indicate slight stabilization. Another contrast of these five systems is that only Jackson finds all values of  $\sigma^*$  to be positive. The negative (destabilizing) values of  $\sigma_F^*$  reported<sup>2c</sup> for 4-OMe and 4-Me are suspect due to the dominant polar effect for these two very carbocation stabilizing substituents.

The origin of substituent effects in free-radical abstraction reactions has been controversial.<sup>1,2c,4a,5e,18</sup> The polar transition state interpretation has been the most durable explanation and, depending on the specific situation, such effects as BDE,<sup>18</sup> viscosity,<sup>19</sup> and entropy<sup>20</sup> should also be considered. The agreement of  $\sigma_F^*$ ,  $\sigma_\alpha^*$ , and  $\sigma_C^*$  for meta substituents shows that, even though the defining reactions for these three are very different, a similar underlying influence is being measured experimentally.

In conclusion, the  $\sigma^*$  systems of Jackson and Jiang are not very comprehensive, and both also make the questionable assumption that meta substituents have no effect on benzyl free-radical stabilities. The Arnold system is very comprehensive, but it has the limitation<sup>4a</sup> that the range of its  $\sigma_\alpha^*$  values is only +0.06 to -0.03 even after use of "improved conditions". The  $\sigma_\alpha^*$  values are also not normalized to other Hammett substituent constants. The  $\sigma_C^*$  system of Creary is the most comprehensive and, on

balance, it has the most positive features.

## Experimental Section

*m*-Tolunitrile (Aldrich), 2,2'-azobisisobutyronitrile (K&K), and benzene (Fisher AR) were used without purification. *N*-Bromosuccinimide (Aldrich) was recrystallized from hot (80 °C) water, and 2,4-dinitrochlorobenzene was recrystallized from aqueous ethanol.

Nuclear magnetic resonance spectra were obtained using a Varian CFT-20 spectrometer. Melting points are uncorrected. Elemental analyses were done by Galbraith Laboratories, Knoxville, TN.

**Kinetic Method.** The NMR relative rate procedure was reported earlier.<sup>2b</sup> Unfortunately, the methylene singlets for the substituted and unsubstituted benzyl bromides were not always sufficiently resolved to permit quantification. Complete resolution was obtained for **8e**, intermediate resolution for **8b** and **8c**, and no resolution for **8d**.

To avoid this problem, a gas chromatographic analytical method was devised to quantify the benzyl bromide products. Gas chromatography was performed using a Varian 3000 instrument equipped with a 15-m DB-225 megabore fused silica column configured for on-column injection. A temperature program was used that started at 80 °C for 1 min, ramped to 200 °C over 10 min, and then was maintained at 200 °C for 10 min. 2,4-Dinitrochlorobenzene was used as the internal standard. A minimum of three replicate injections were made for each sample, and several different samples were run for each kinetic pair. The quantities of the two benzyl bromides were then determined according to the equation:

$$X_{\text{mg}} = \frac{(S_{\text{mg}})(A_X)}{(R_{\text{fX/S}})(A_S)}$$

where  $X_{\text{mg}}$  and  $S_{\text{mg}}$  represent the milligrams of benzyl bromide and internal standard, respectively,  $A_X$  and  $A_S$  represent the corresponding GC integral areas, and  $R_{\text{fX/S}}$  the response factor for the benzyl bromide versus the internal standard.

**3,5-Dimethylbenzonitrile (2b).** 3,5-Dimethylbenzoic acid (Aldrich) was converted to the corresponding nitrile by the method of Miller<sup>13</sup> using *p*-toluenesulfonamide and phosphorus pentachloride at 200–205 °C (do not exceed 205 °C), in 57% yield, mp 41.5–43 °C (lit.<sup>21</sup> mp 42–43 °C).

**3-Bromo-5-cyanotoluene (2c).** Bromination of 2-amino-5-methylbenzoic acid in glacial acetic acid gave crude 2-amino-3-bromo-5-methylbenzoic acid, which was then deaminated by diazotization followed by reaction with hypophosphorus acid. 3-Bromo-5-methylbenzoic acid, obtained in 63% overall yield, mp 178–179.5 °C (lit.<sup>22</sup> mp 178 °C), was converted into 3-bromo-5-cyanotoluene in 67% yield by Miller's method: white solid; mp 67–68.5 °C (lit.<sup>23</sup> mp 62 °C).

**3,5-Dicyanotoluene (2d).** Uvitic acid, prepared from mesitylene by nitric acid oxidation<sup>18</sup> in 21% yield, was converted to the dinitrile in 35% yield.<sup>13</sup> After crystallization from ethanol, 3,5-dicyanotoluene was obtained as white crystals: mp 163–165 °C (lit.<sup>21</sup> mp 126.5–127, lit.<sup>24</sup> mp 163–165 °C); IR (KBr) 3065 (Ar CH str), 2236 (CN) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.50 (s, 3 H), 7.77 (s, 3 H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub> + acetone-*d*<sub>6</sub>)  $\delta$  20.2 (CH<sub>3</sub>), 113.5

(17) Exner, O. *Advances in Linear Free Energy Relationships*; Shorter, J., Ed.; Plenum Press: New York, 1972; p 50.

(18) Zavitsas, A. A.; Pinto, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 7390.

(19) Tanner, D. D.; Nam, N. H. *J. Org. Chem.* **1987**, *52*, 4686.

(20) Kim, S. S.; Choi, S. Y.; Kang, C. H. *J. Am. Chem. Soc.* **1985**, *107*, 4234.

(21) Gryszkiewica-Trachimowski, E.; Schmidt, W.; Gryszkiewicz-Trachimowski, O. *Bull. Soc. Chem. Fr.* **1948**, 593.

(22) Bures, E.; Mandel-Borgmannova, A. *Chem. Abstr.* **1928**, *22*, 4503.

(23) Jones, B. *J. Chem. Soc.* **1955**, 3850.

(24) Schenker, K.; Druey, J. *Helv. Chim. Acta* **1962**, *45*, 1344.

(C-3), 116.5 (CN), 132.3 (C-4), 136.4 (C-2), 141.2 (C-1) ppm.

**3-Cyano-5-nitrotoluene (2e).** 4-Methyl-2-nitroaniline was brominated in glacial acetic acid to give 2-bromo-4-methyl-6-nitroaniline in 85% yield, mp 62–63.5 °C (lit.<sup>15</sup> mp 64.5 °C), which was then deaminated as above to give 3-bromo-5-nitrotoluene in 90% yield, yellow crystals, mp 83–84 °C (lit.<sup>25</sup> mp 83 °C). A modified Rosenmund–von Braun reaction using cuprous cyanide in dry pyridine was then used to convert 3-bromo-5-nitrotoluene into 3-cyano-5-nitrotoluene in 58% yield, yellow needles, mp 104–105 °C (lit.<sup>16</sup> mp 104.5 °C).

**Benzylic Brominations.** Each of the 5-substituted 3-cyanotoluenes **2** was individually brominated by overnight reflux of a carbon tetrachloride solution of equimolar amounts of toluene and NBS with a catalytic amount of 2,2'-azobisisobutyronitrile. The resulting solution was filtered hot, the solvent was removed under vacuum, and the product benzyl bromides were purified by recrystallization or column chromatography. The following benzyl bromides were obtained.

**$\alpha$ -Bromo-3-cyanotoluene (8a):** mp 92–93 °C (lit.<sup>26</sup> mp 93 °C).

**3-(Bromomethyl)-5-methylbenzonitrile (8b):** mp 92–93 °C (lit.<sup>21</sup> mp 87–88 °C).

**$\alpha$ -Bromo-3-bromo-5-cyanotoluene (8c):** mp 112–113 °C, after repeated sublimation; IR (KBr) 3060 (ArH), 2237 (CH)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.45 (s, 2 H), 7.6–8.0 (m, 3 H) ppm; MS (70 eV) *m/e* (relative abundance) 277 (5), 275 (10), 273 (6), 196 (100), 194 (98), 115 (46).

Anal. Calcd for  $\text{C}_8\text{H}_5\text{Br}_2\text{N}$ : C, 34.93; H, 1.82; N, 5.09. Found: C, 35.20; H, 1.72; N, 4.92.

**$\alpha$ -Bromo-3,5-dicyanotoluene (8d):** mp 124–125 °C; separated by column chromatography on silica gel using hexane/toluene;

white crystals; IR (KBr) 3062 (ArH), 2243 (CN)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.50 (s, 2 H), 7.94 (s, 3 H) ppm; MS 222 (3), 220 (4), 141 (100), 114 (23).

Anal. Calcd for  $\text{C}_8\text{H}_5\text{BrN}_2$ : C, 48.49; H, 2.26; N, 12.68. Found: C, 49.10; H, 2.33; N, 12.57.

**$\alpha$ -Bromo-3-cyano-5-nitrotoluene (8e):** mp 102–103.5 °C; separated by column chromatography on silica gel using petroleum ether; IR (KBr) 3085 (ArH), 2243 (CN), 1543 and 1358 ( $\text{NO}_2$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.60 (s, 2 H), 8.03 (s, 1 H), 8.47 (s, 2 H) ppm; MS 244 (2), 240 (3), 161 (100), 115 (39).

Anal. Calcd for  $\text{C}_8\text{H}_5\text{BrN}_2\text{O}_2$ : C, 39.85; H, 2.08; N, 11.62. Found: C, 40.54; H, 2.34; N, 11.32.

**$\alpha,\alpha$ -Dibromo-3,5-dicyanotoluene (9d):** mp 118–120 °C; separated from **8d** by column chromatography on silica gel with hexane/toluene; IR (KBr) 3060 (ArH), 2245 (CN)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.73 (s, 1 H), 8.03 (s, 1 H), 8.23 (s, 2 H) ppm; MS 221 (97), 219 (100), 140 (27), 113 (14).

Anal. Calcd for  $\text{C}_8\text{H}_4\text{Br}_2\text{N}_2$ : C, 36.02; H, 1.33; N, 9.34. Found: C, 35.79; H, 1.19; N, 9.15.

**$\alpha,\alpha$ -Dibromo-3-cyano-5-nitrotoluene (9e):** mp 97–98.5 °C; separated from **8e** by column chromatography on silica gel with 2:1 cyclohexane–toluene; IR (KBr) 2238 (CN), 1555 and 1357 ( $\text{NO}_2$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.80 (s, 1 H), 8.30 (s, 1 H), 8.57 (s, 1 H), 8.77 (s, 1 H) ppm; MS 319 (1), 241 (95), 239 (100), 117 (74).

Anal. Calcd for  $\text{C}_8\text{H}_4\text{Br}_2\text{N}_2\text{O}_2$ : C, 30.02; H, 1.25; N, 8.76. Found: C, 29.84; H, 1.11; N, 8.48.

**Registry No.** **2a**, 104-85-8; **2b**, 22445-42-7; **2c**, 124289-21-0; **2d**, 39718-07-5; **2e**, 124289-22-1; **3**, 2941-78-8; **4**, 13091-43-5; **5** (X = Br), 58530-13-5; **5** (X = Me), 499-06-9; **6**, 89-62-3; **7**, 52488-28-5; **8a**, 28188-41-2; **8b**, 124289-23-2; **8c**, 124289-24-3; **8d**, 124289-25-4; **8e**, 124289-26-5; **9d**, 124289-27-6; **9e**, 124289-28-7; uvitic acid, 499-49-0; 2-bromo-4-methyl-6-nitroaniline, 827-24-7.

(25) Gibson, J. J. *Chem. Soc.* 1924, 1244.

(26) Braum, J.; Reich, H. *Justus Liebig's Ann. Chem.* 1925, 445, 237.

## Cumulene Photochemistry: Substituent Effects on the Mechanism of 1,2-Cyclononadiene Photochemistry

Thomas J. Stierman, William C. Shakespeare, and Richard P. Johnson\*

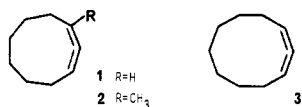
Departments of Chemistry, University of New Hampshire, Durham, New Hampshire 03824, and Iowa State University, Ames, Iowa 50011

Received July 26, 1989

The photoreactions of 1-methyl-1,2-cyclononadiene (**2**) are described and contrasted with those of 1,2-cyclononadiene (**1**). Direct irradiation yields as primary products seven isomers. The major singlet products are best accounted for by excited-state 1,2-hydrogen migration to 3-methylcyclonon-2-enylidene (**15**). Independent generation of this vinylcarbene and an isomeric carbene are reported. Minor products from **2** include 3-methylcyclononyne (**9**) and two isomeric tricyclo[4.3.0.0<sup>2,9</sup>]nonanes (**7** and **8**). An important conclusion is that in contrast to the apparently concerted reaction of **1**, methyl derivative **2** seems to favor vinylcarbene intermediates. Triplet-sensitized reactions of **2** are similar to **1**, affording isomeric tricyclononanes **7** (46%) and **8** (41%).

### Introduction

Previous investigations of the solution- and gas-phase photochemistry of 1,2-cyclononadiene (**1**)<sup>1,2</sup> and 1,2-cyclodecadiene (**3**)<sup>3</sup> have demonstrated the diversity of singlet and triplet excited-state reactions of the allene (1,2-propadiene) chromophore.<sup>4</sup> Simple  $\pi$  bond rotation, which interconverts enantiomers, is observed to be the most rapid reaction of optically active **1**<sup>2</sup> in the solution phase. The other dominant singlet reaction of **1** and **3**



is 1,2-hydrogen migration, which may be a concerted process. This is accompanied by less efficient 1,3-hydrogen migration and transannular insertion. Vapor-phase triplet reactions of **1** and **3** afford primarily tricyclic isomers, which result from intramolecular hydrogen abstraction.<sup>1-3</sup>

Comparison of the singlet excited state behavior of **1** with reactions of other allenes suggested a close relationship between concerted 1,2-hydrogen migration and rearrangement via vinylcarbene intermediates.<sup>5,6</sup> We describe here the photoreactions of 1-methyl-1,2-cyclo-

(1) Ward, H. R.; Karafiath, E. *J. Am. Chem. Soc.* 1969, 91, 522.

(2) Stierman, T. J.; Johnson, R. P. *J. Am. Chem. Soc.* 1985, 107, 3971.

(3) Price, J. D.; Johnson, R. P. *J. Am. Chem. Soc.* 1985, 107, 2187.

(4) Reviews: (a) Steinmetz, M. G.; Srinivasan, R.; Leigh, W. J. *Rev. Chem. Intermed.* 1984, 5, 57. (b) Johnson, R. P. *Org. Photochem.* 1985, 7, 75.

(5) Klett, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* 1985, 107, 3963.

(6) Steinmetz, M. G.; Mayes, R. T. *J. Am. Chem. Soc.* 1985, 107, 2111.

\* Address correspondence to this author at the University of New Hampshire.