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Rearrangements of the Isomeric Tolylmethylenes

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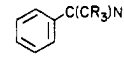
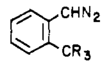
Abstract: We present evidence for a mechanism in which the isomeric tolylmethylenes interconvert via methylcycloheptatetraene intermediates. Photolysis (>470 nm) of diazo compounds **1–4**, matrix isolated in argon at 10 K, generates triplet tolylmethylenes **8–11**. Photolysis of carbenes **8–11** (>416 nm, T_0–T_1 excitation) leads to two distinct modes of reactivity. Carbenes **9b**, **10a**, **10b**, **11a**, and **11b** ring expand to produce substituted 1,2,4,6-cycloheptatetraene derivatives, while carbenes **8a**, **8b**, and **9a** undergo intramolecular hydrogen (deuterium) migrations to produce styrenes **5a** and **5b** and *o*-xylylene (**6a**), respectively. *o*-Xylylene (**6a**) photochemically cyclizes to benzocyclobutene (**7a**) upon shorter wavelength irradiation (>261 nm). Thus, benzocyclobutene formation from *o*-tolylmethylene occurs by a two-step migration–cyclization process, not by direct insertion of the carbene into the methyl group. Flash vacuum thermolysis of *o*-tolyldiazomethane (**2a**) yields styrene and benzocyclobutene in a ratio of **5a**:**7a** = 1:1.3. This ratio differs from the ratio (1.3:1) obtained from *m*- and *p*-tolyldiazomethane (**3a** and **4a**). This anomaly does not occur in the deuterio case, as all three diazo compounds (**2b**, **3b**, and **4b**) give the same ratio of **5b**:**7b** = 1.7:1. Hydrogen atom tunneling is a likely cause for this discrepancy. Flash vacuum thermolysis of diazo compounds **2b**, **3a**, **3b**, **4a**, and **4b**, followed by cocondensation of the pyrolyzate with argon at 26 K, produces styrene (**5a** or **5b**), benzocyclobutene (**7a** or **7b**), and small amounts of cycloheptatetraenes (**13a** and **14a**, or **13b** and **14b**), as observed by infrared spectroscopy. Our observation of cycloheptatetraene intermediates under both thermal and photochemical conditions strongly suggests that a single mechanism describes both thermal and photochemical rearrangement pathways.

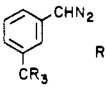
The isomeric tolylmethylenes present a fascinating array of carbene rearrangements.[1] They interconvert by a carbene-to-carbene rearrangement mechanism, and they react with the methyl substituent via hydrogen shifts to ultimately produce benzocyclobutene and styrene. The mechanism of the interconversions has continued to plague organic chemists ever since the report by Vander Stouw and Shechter in 1964 that thermolysis of *o*-tolyldiazomethane produces benzocyclobutene (**7a**) and styrene (**5a**) (Scheme I).[2] Baron, Jones, and Gaspar proposed a slightly different mechanism when they reported that thermolysis of *m*- and *p*-tolyldiazomethanes also produces benzocyclobutene (**7a**) and styrene (**5a**) (Scheme II).[3] Hedaya and Kent's pyrolysis study of ^{13}C-labeled *p*-tolyldiazomethane ruled out isomerization via a ring-flipping mechanism in a bicyclo[4.1.0]hexenyl biradical (Scheme III).[4] W. M. Jones established that gas-phase *photolysis* of the tolyldiazomethanes generates benzocyclobutene (**7a**) and styrene (**5a**).[5] In addition, he noted that thermolysis of 2-methyltropone and 4-methyltropone tosylhydrazone sodium salts produces styrene (**5a**) and styrene (**5a**) plus benzocyclobutene (**7a**), respectively.[5] Shortly thereafter, Wentrup presented a study of the thermolysis of the tolylmethylenes, as generated from numerous precursors.[6] Wentrup summarized the literature in his 1976 review.[1e]



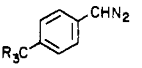
1a
b



2a
b

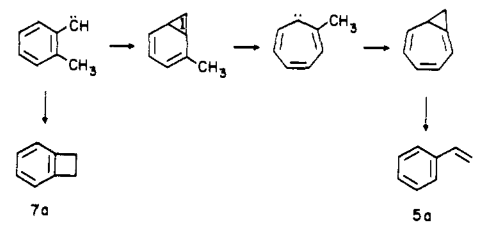


3a
b

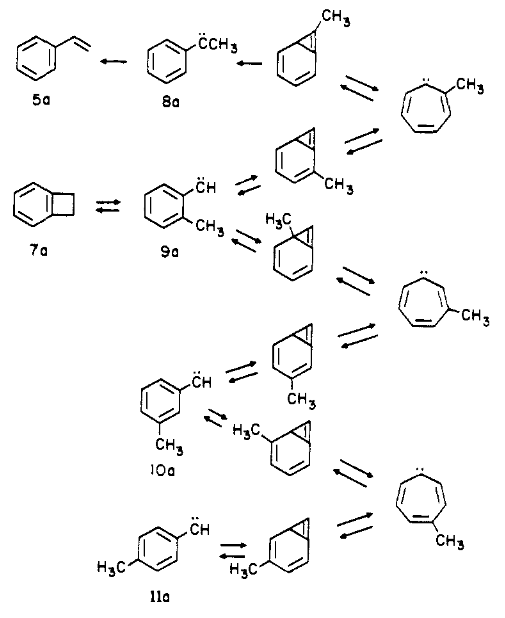


4a
b

Scheme I



Scheme II



The cycloheptatrienylidene mechanism for tolylmethylene interconversions (Scheme II) achieved wide acceptance during the 1970s.[1,7] Since that time, however, we failed to observe *either* bicyclo[4.1.0]hepta-2,4,6-triene intermediates or cycloheptatrienylidene intermediates upon photolysis or thermolysis of phenylmethylene.[8,9] Rather, we find that phenylmethylene

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[1] (a) Jones, W. M.; Brinker, U. H. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic: New York, 1977; Vol. 1, Chapter 3. (b) Jones M. W. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Academic: New York, 1980; Vol. 1, Chapter 3. (c) Wentrup, C. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1980; Vol. 1, Chapter 4. (d) Wentrup, C. *Reactive Molecules*; Wiley-Interscience: New York, 1984; Chapter 4. (e) Wentrup, C. *Top. Curr. Chem.* **1976**, *62*, 173–251.

[2] Vander Stouw, G. G. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 1964. Vander Stouw, G. G.; Kraska, A. R.; Shechter, H. *J. Am. Chem. Soc.* **1972**, *94*, 1655–1661.

[3] Baron, W. J.; Jones, M.; Gaspar, P. P. *J. Am. Chem. Soc.* **1970**, *92*, 4739–4740.

[4] Hedaya, E.; Kent, M. E. *J. Am. Chem. Soc.* **1971**, *93*, 3283–3285.

[5] Jones, W. M.; Joines, R. C.; Myers, J. A.; Mitsuhashi, T.; Krajca, K. E.; Waali, E. E.; Davis, T. L.; Turner, A. B. *J. Am. Chem. Soc.* **1973**, *95*, 826–835.

[6] Gleiter, R.; Rettig, W.; Wentrup, C. *Helv. Chim. Acta* **1974**, *57*, 2111–2124.

[7] Gaspar, P. P.; Hsu, J.-P.; Chari, S.; Jones, M. *Tetrahedron* **1985**, *41*, 1479–1507.

[8] West, P. R.; Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1982**, *104*, 1779–1782. McMahon, R. J.; Abelt, C. J.; Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J.-P.; Mooring, A. M.; West, P. R. *J. Am. Chem. Soc.* **1987**, *109*, 2456–2469.

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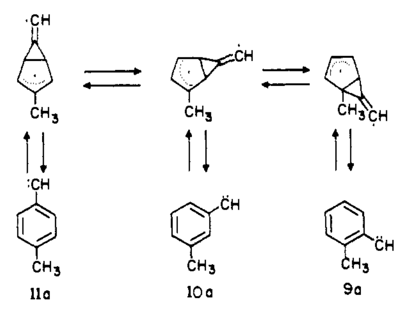
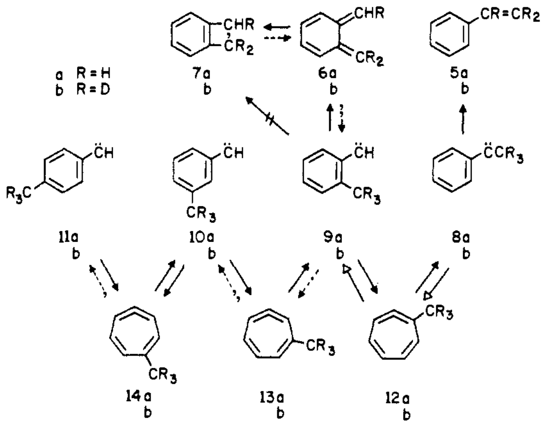
Scheme III



Scheme IV



ring expands to 1,2,4,6-cycloheptatetraene.[8] This contrasts sharply with the cycloheptatrienylidene mechanism (Scheme II). Our preliminary report described the interconversion of the isomeric tolylmethylenes (**8–11**) via methylcycloheptatetraenes (**12–14**) (Scheme IV).[10] Recent labeling studies of the isomerization of benzocyclobutene (**7a**) to styrene (**5a**) and of the high-temperature cracking of alkyl aromatics have been interpreted in terms of the cycloheptatetraene mechanism.[11,12]

Both the cycloheptatrienylidene mechanism (Scheme II) and the cycloheptatetraene mechanism (Scheme IV) apparently fail to accommodate one experimental observation: thermolysis of *o*-tolyldiazomethane produces a different benzocyclobutene to styrene ratio than the meta and para isomers. Baron et al.[3] and Gleiter et al.[6] proposed that conformational effects cause this anomaly. Recently, however, Gaspar et al. looked for alternatives to the "linear" rearrangement mechanisms of Schemes II and IV.[7]

Gaspar et al. considered three different pathways that circumvent the sequential arylcarbene-to-arylcarbene mechanisms. They ruled out processes involving loose "carbon atom–arene" complexes or norbornadienylidene intermediates. They proposed a minor pathway involving direct interconversion of cycloheptatetraenes via norcaradienylidene intermediates (Scheme V). This pathway can account for both 2,6-dimethylstyrene formation from (3,4,5-trimethylphenyl)methylene (Scheme V) and the anomalous product ratio from pyrolysis of *o*-tolyldiazomethane.

In this paper, we present our evidence for the tolylmethylene/methylcycloheptatetraene mechanism. We characterized each intermediate in Scheme IV utilizing argon matrix isolation techniques. We conclude that the mechanism in Scheme IV describes all major rearrangement pathways (both thermal and photochemical) of the isomeric tolylmethylenes. Of particular interest, we find that deuterium substitution produces a dramatic effect on both the thermal chemistry and photochemistry of *o*-tolylmethylene. These experiments suggest a new explanation for the anomalous product ratio obtained from pyrolysis of *o*-tolyldiazomethane.

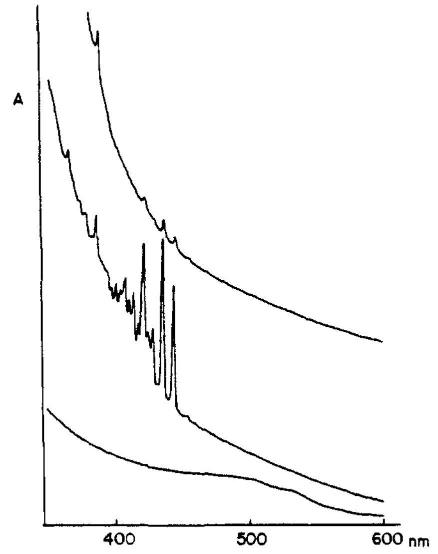
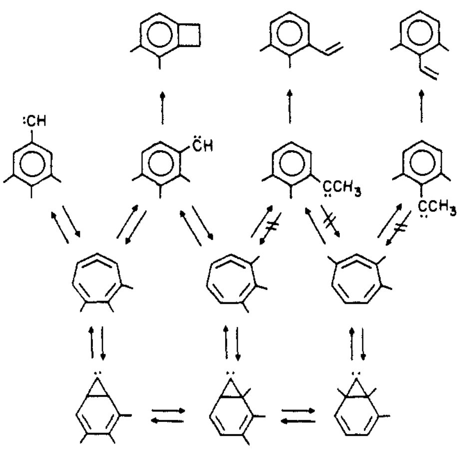


Figure 1. UV/visible absorption spectra obtained upon irradiation of *p*-tolyldiazomethane (**4a**) matrix isolated in argon at 15 K. Bottom: **4a** prior to irradiation. Middle: Formation of *p*-tolylmethylene (**11a**) (>470 nm, 3960 min). Top: Disappearance of **11a** (>416 nm; 285 min).

Scheme V



Results

Structural Assignments. The detailed arguments concerning the interpretation of spectroscopic data and the structural assignments of the tolylmethylenes and methylcycloheptatetraenes are presented in the Discussion section.

***p*-Tolyldiazomethane (4a).** Irradiation (>470 nm) of argon matrix-isolated *p*-tolyldiazomethane (**4a**) produces triplet *p*-tolylmethylene (**11a**): IR (Ar, 15 K) 3073 w, 3053 vw, 3021 vw, 2987 w, 2957 w, 2925 w, 2891 vw, 2871 w, 2847 vw, 2736 vw, 1881 vw, 1573 m, 1522 w, 1518 w, 1512 w, 1467 m, 1454 w, 1449 m, 1380 w, br, 1116 w, 1089 w, 1035 w, 1029 w, 1018 w, 1000 w, 992 w, 983 w, 953 w, 948 w, 798 s, 779 w, 494 w, 446 s, br cm^{-1}; UV (Ar, 15 K) λ_{max} 444, 436, 429, 426, 422, 418, 415, 411, 408, 405, 402, 398, 395 nm (Figure 1); ESR (Ar, 17 K) $|D/hc|$ = 0.516 cm^{-1}; $|E/hc|$ = 0.0240 cm^{-1}; Z_1 2191 G, X_2 4883 G, Y_2 5883 G, Z_2 8828 G, microwave frequency 9.248 GHz. Irradiation (>416 nm) results in the total disappearance of the IR and UV absorptions of **11a** (Figure 1), as well as a dramatic decrease in the ESR signal. 5-Methylcycloheptatetraene (**14a**) appears: IR (Ar, 15 K) 3042 m, 3020 m, 2998 vw, 2960 w, 2929 m, 2901 vw, 2896 vw, 2868 vw, 1819 w, 1811 w, 1581 w, 1519 w, 1512 w, 1454 m, 1448 w, 1416 m, 1386 w, 1379 m, 1367 m, 1350 vw, 1334 w,

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[12] Trahanovsky, W. S.; Scribner, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 7976–7978.

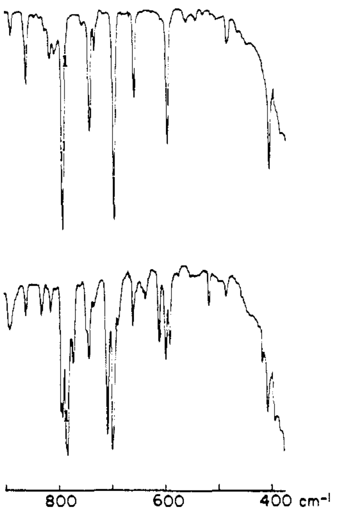

Figure 2. Top: Infrared spectrum (in transmittance) of 5-methylcycloheptatetraene (**14a**) obtained upon irradiation (>416 nm, 229 min) of *p*-tolylmethylene (**11a**) matrix isolated in argon at 15 K. Bottom: Infrared spectrum of a mixture of 4-methylcycloheptatetraene (**13a**) and 5-methylcycloheptatetraene (**14a**) obtained upon irradiation (>416 nm, 233 min) of *m*-tolylmethylene (**10a**) matrix isolated in argon at 15 K.

1276 w, 1210 w, 1180 vw, 1170 vw, 1111 vw, 1057 w, 1038 w, 960 w, 891 w, 862 m, 829 vw, 819 w, 809 w, 795 s, 744 m, 734 w, 698 s, 660 m, 598 m, 485 w, 407 m, 378 w, cm^{-1} (Figure 2). Short-wavelength photolysis (>279 nm) of this species produces a small amount of 4-methylcycloheptatetraene (**13a**): IR (Ar, 15 K) 3070 w, 3042 m, 3025 m, 3012 m, 2985 m, 2958 m, 2924 m, 1827 vw, 1816 w, 1491 m, 1458 w, 1445 w, 1436 m, 1427 w, 1401 w, 1374 m, 1342 w, 1280 w, 1269 w, 1153 m, 1095 w, 1072 w, 1033 w, 942 w, 893 w, 888 w, 831 w, 812 w, 781 s, 771 m, 748 w, 706 s, 686 w, 636 w, 610 m, 590 m, 518 w, 419 w, 397 w, 392 w, cm^{-1}. Under these irradiation conditions, ESR spectroscopy indicates that a small, steady-state concentration of triplet carbene remains.

Flash vacuum thermolysis (375 °C, 100% conversion) of **4a** followed by cocondensation of the pyrolyzate with argon produces styrene (**5a**) (IR, vide infra) and benzocyclobutene (**7a**) (IR, vide infra) in a ratio of ca. 1.3:1. The infrared spectrum also contains small amounts of both 4- and 5-methylcycloheptatetraenes (**13a**, **14a**) (IR, vide supra) (Figure 3). A third minor product [IR (Ar, 15 K) 857, 750, 537 cm^{-1}] remains unidentified.

[*p*-(Trideuteriomethyl)phenyl]diazomethane (4b). Irradiation (>470 nm) of argon matrix isolated [*p*-(trideuteriomethyl)-phenyl]diazomethane (**4b**) produces triplet [*p*-(trideuteriomethyl)phenyl]methylene (**11b**): IR (Ar, 15 K) 3070 w, 3050 w, 3030 w, 3020 w, 2240 w, 2210 w, 2135 w, 1573 s, 1470 m, 1455 w, 996 w, 942 w, 870 m, 776 s cm^{-1}. Irradiation (>416 nm) results in the total disappearance of the IR absorptions of **11b**. 5-(Trideuteriomethyl)cycloheptatetraene (**14b**) appears: IR (Ar, 15 K) 3040 w, 3018 w, 2975 w, 2120 w, 1820 w, 1810 w, 1412 m, 1366 m, 1329 m, 1020 w, 960 w, 891 w, 888 w, 790 s, 773 s, 728 m, 695 s, 680 w, 630 w, 581 m cm^{-1}. Short-wavelength photolysis (>279 nm) of this species produces a small amount of 4-(trideuteriomethyl)cycloheptatetraene (**13b**): IR (Ar, 15 K) 3018 m, 2120 w, 1819 w, 1442 w, 1438 w, 1402 w, 1281 w, 1095 w, 851 w, 794 s, 768 s, 750 m, 588 w, 573 s cm^{-1}.

Flash vacuum thermolysis (500 °C, 100% conversion) of **4b** followed by cocondensation of the pyrolyzate with argon produces α,β,β-trideuteriostyrene (**5b**) (IR, vide infra) and trideuteriobenzocyclobutene (**7b**) (IR vide infra) in a ratio of ca. 1.7:1.

***m*-Tolyldiazomethane (3a).** Irradiation (>470 nm) of argon matrix isolated *m*-tolyldiazomethane (**3a**) produces triplet *m*-tolylmethylene (**10a**): IR (Ar, 15 K) 3072 w, 3047 w, 3029 w, 2991 w, 2985 w, 2962 w, 2933 w, 2876 w, 1570 m, 1567 m, 1520 w, 1462 m, 1379 w, 927 w, 922 w, 873 w, 852 w, 786 m, 764 s, 761 s, 747 w, 697 m, 687 m, 669 s, 540 w, 471 w, 463 m, 457 m, 421 m, cm^{-1}; UV (Ar, 15K) λ_{max} 448, 439, 433, 430, 426, 424, 420, 415, 410, 403, 399, 394 nm; ESR (Ar, 16 K) $|D/hc| = 0.517$ cm^{-1}, $|E/hc| = 0.0246$ cm^{-1}, rotomers indistinguishable; Z_1 2206 G, X_2 4875 G, Y_2 5897 G, Z_2 8826 G, microwave frequency 9.248 GHz. Irradiation (>416 nm) results in the total disappearance of the IR and UV signals of **10a** and in the simultaneous appearance of both 4- and 5-methylcycloheptatetraenes (**13a** and **14a**) (IR, vide supra) (Figure 2). Short-wavelength photolysis (>279 nm) of the mixture of **13a** and **14a** produces no detectable change in the infrared spectrum.

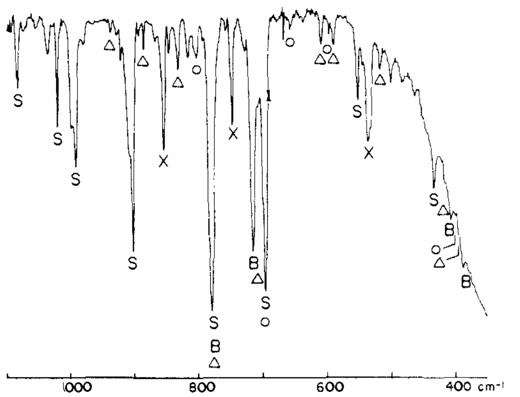

Figure 3. Infrared spectrum (in transmittance) of the product mixture formed upon flash vacuum thermolysis (375 °C) of *p*-tolyldiazomethane (**4a**) followed by cocondensation of the pyrolyzate with argon: S, styrene (**5a**); B, benzocyclobutene (**7a**); Δ, 4-methylcycloheptatetraene (**13a**); O, 5-methylcycloheptatetraene (**14a**); X, unidentified product.

Flash vacuum thermolysis (375 °C, 100% conversion) of **3a** followed by cocondensation of the pyrolyzate with argon produces styrene (**5a**) (IR, vide infra) and benzocyclobutene (**7a**) (IR, vide infra) in a ratio of ca. 1.3:1. The infrared spectrum contains small amounts of both 4- and 5-methylcycloheptatetraenes (**13a** and **14a**) (IR, vide supra). A trace amount of a third minor product [IR (Ar, 15 K) 857, 750, 537 cm^{-1}] remains unidentified.

[*m*-(Trideuteriomethyl)phenyl]diazomethane (3b). Irradiation (>470 nm) of argon matrix isolated [*m*-(trideuteriomethyl)-phenyl]diazomethane (**3b**) produces triplet [*m*-(trideuteriomethyl)phenyl]methylene (**10b**): IR (Ar, 15 K) 3000 w, 2238 w, 2133 w, 1555 m, 1456 w, 1153 m, 1118 w, 1040 w, 973 m, 836 w, 738 s, 688 m, 660 s, 533 m cm^{-1}. Irradiation (>416 nm) results in the total disappearance of the IR absorptions of **10b** and in the simultaneous appearance of both 4- and 5-(trideuteriomethyl)cycloheptatetraenes (**13b** and **14b**) (IR, vide supra). Short-wavelength photolysis (>279 nm) produces no detectable change in the infrared spectrum.

Flash vacuum thermolysis (480 °C, 100% conversion) of **3b** followed by cocondensation of the pyrolyzate with argon produces α,β,β-trideuteriostyrene (**5b**) (IR, vide infra) and trideuteriobenzocyclobutene (**7b**) (IR, vide infra) in a ratio of ca. 1.7:1.

***o*-Tolyldiazomethane (2a).** We examined the photochemistry of *o*-tolyldiazomethane (**2a**) under three different types of irradiation conditions.

(1) Long-wavelength irradiation (>470 nm) of argon matrix isolated **2a** produces triplet *o*-tolylmethylene (**9a**) and *o*-xylylene (**6a**). **9a**: UV (Ar, 15 K) λ_{max} 450, 440, 437, 435, 431, 427, 422, 419, 417, 413, 305, 292, 249, 244 nm; ESR (Ar, 20 K) major rotomer $|D/hc| = 0.503$ cm^{-1}, $|E/hc| = 0.0253$ cm^{-1}; Z_1 2055 G, X_2 4839 G, Y_2 5879 G, Z_2 8679 G; microwave frequency 9.263 GHz; minor rotomer $|D/hc| = 0.503$ cm^{-1}; $|E/hc| = 0.0244$ cm^{-1}; Z_1 2055 G; X_2 4900 G; Y_2 5826 G; Z_2 8679 G, microwave frequency 9.263 GHz. **6a**: UV (Ar, 15 K) λ_{max} 403, 395, 389, 384, 379, 376, 367, 362, 347, 342, 329, 326 nm; IR (Ar, 15 K) 1575 w, 1548 m, 1493 m, 1469 w, 869 s, 774 m, 754 m, 635 m, 436 w cm^{-1} (Figure 4). The structural assignment of *o*-xylylene (**6a**) is based on comparison with the IR and UV spectra reported in the literature.[13] We could not detect *o*-tolylmethylene (**9a**) by IR spectroscopy, due to its low steady-state concentration. In addition, 1-methylcycloheptatetraene (**12a**) was not observed under

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[13] Tseng, K. L.; Michl, J. *J. Am. Chem. Soc.* **1977**, *99*, 4840–4842.

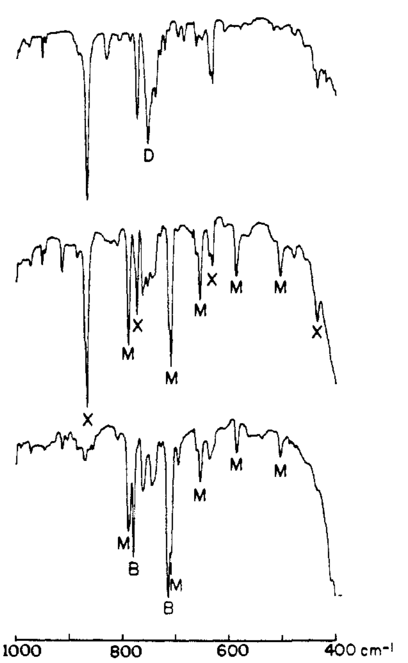

Figure 4. Top: Infrared spectrum (in transmittance) of *o*-xylylene (**6a**) obtained upon irradiation (>514 nm, 820 min; >470 nm, 4196 min) of *o*-tolyldiazomethane (**2a**) matrix isolated in argon at 15 K. D, residual diazo compound. Middle: Infrared spectrum of the product mixture obtained upon irradiation (>416 nm, 1301 min) of *o*-tolyldiazomethane (**2a**) matrix isolated in argon at 15 K. X, *o*-xylylene (**6a**); M, 1-methylcycloheptatetraene (**12a**). Bottom: Infrared spectrum showing the disappearance of *o*-xylxylene (**6a**) and appearance of benzocyclobutene (**7a**) upon irradiation (>267 nm, 1938 min) of the sample shown immediately above. B, benzocyclobutene (**7a**); M, 1-methylcycloheptatetraene (**12a**).

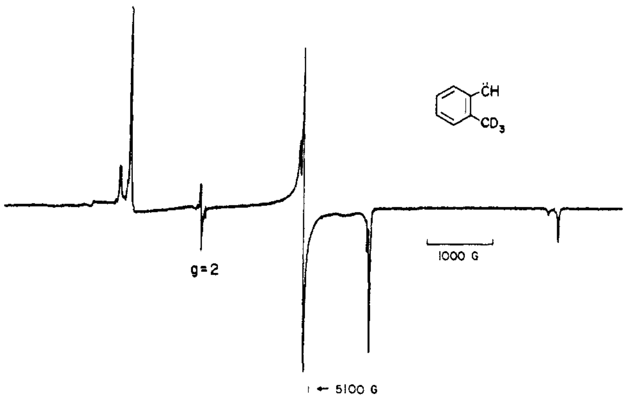

Figure 5. ESR spectrum of [*o*-(trideuteriomethyl)phenyl]methylene (**9b**) formed upon irradiation (>470 nm, 3912 min) of [*o*-(trideuteriomethyl)phenyl]diazomethane (**2b**) matrix isolated in argon at 19 K.

these irradiation conditions. The UV absorptions of carbene **9a** reach a maximum after ca. 25 h of irradiation. Continued photolysis (>470 nm) for up to 86 h results only in a *decrease* in the absorptions, even though the longest wavelength absorption maximum of **9a** lies at 450 nm. Irradiation (>416 nm) leads to the rapid and irreversible disappearance of the ESR and UV signals of carbene **9a**.

(2) Irradiation (>416 nm, 1300 min) of **2a**, matrix isolated in argon, produces *o*-xylylene (**6a**) (IR, vide supra) and 1-methylcycloheptatetraene (**12a**) [IR (Ar, 15 K) 1386 m, 790 s, 710 s, 655 m, 588 m, 503 w cm^{-1}] in a ca. 2:1 ratio, as observed by IR spectroscopy (Figure 4). Short-wavelength irradiation (>267 nm) destroys *o*-xylylene (**6a**) and produces benzocyclobutene (**7a**), as monitored by IR and UV spectroscopy.

(3) Flash irradiation (>200 nm, 1.0 min) of a thin argon matrix containing *o*-tolyldiazomethane (**2a**) gives high conversion to triplet *o*-tolylmethylene (**9a**). The high conversion afforded by the flash irradiation method enables us to observe **9a** by IR, as well as UV and ESR spectroscopy [IR (Ar, 10 K) 742 cm^{-1}; UV and ESR, vide supra]. IR and UV spectroscopy indicate that small amounts of *o*-xylylene (**6a**) and 1-methylcycloheptatetraene (**12a**) also form.

Flash vacuum thermolysis (370 °C, 100% conversion) of **2a** followed by cocondensation of the pyrolyzate with argon produces styrene (**5a**) (IR, vide infra) and benzocyclobutene (**7a**) (IR, vide infra) in a ratio of ca. 1:1.3. We discussed the details of the thermal conversion of triplet *o*-tolylmethylene (**9a**) to singlet *o*-xylylene (**6a**) at 4.6 K in argon in an earlier publication.[14]

[*o*-(Trideuteriomethyl)phenyl]diazomethane (2b). Irradiation (>470 nm) of argon matrix isolated **2b** produces triplet [*o*-(trideuteriomethyl)phenyl]methylene (**9b**): IR (Ar, 15 K) 3070 m, 2240 w, 1041 w, 747 m, 739 s, 669 m, 442 w cm^{-1}; UV (Ar, 15 K) λ_{max} 449, 440, 431, 417, 414, 299, 245, 241 nm; ESR (Ar, 19 K) major rotomer $|D/hc| = 0.521$ cm^{-1}, $|E/hc| = 0.0246$ cm^{-1}; Z_1 2256 G, X_2 4894 G, Y_2 5920 G, Z_2 8852 G, microwave frequency 9.266 GHz; minor rotomer $|D/hc| = 0.505$ cm^{-1}, $|E/hc| = 0.0246$ cm^{-1}; Z_1 2070 G, X_2 4856 G, Y_2 5873 G, Z_2 8687 G, microwave frequency 9.266 GHz (Figure 5). Irradiation (>420 nm) destroys the IR, UV, and ESR signals of [*o*-(trideuteriomethyl)phenyl]methylene (**9b**) and generates 1-(trideuteriomethyl)cycloheptatetraene (**12b**) [IR (Ar, 15 K) 2235 w, 1819 w, 1810 w, 1379 m, 840 w, 772 s, 679 s, 581 m, 442 w, 408 w cm^{-1}] and trideuterio-*o*-xylylene (**6b**) [IR (Ar, 15 K) 1387 w, 880 w, 808 w, 787 m, 759 m, 689 s, 631 w cm^{-1}]. The structural assignment of **12b** is based on the allene bands at 1819 and 1810 cm^{-1}, the characteristic 1379-cm^{-1} band exhibited by cycloheptatetraene,[15] and the similar intensity pattern, although slightly shifted position, of the C–H deformation modes (772, 679 cm^{-1}) relative to those assigned to 1-methylcycloheptatetraene (**12a**) (790, 710 cm^{-1}). The structural assignment of **6b** is based on analogy with the photochemistry of the protio compound and on weak UV absorptions observed at 382, 362, and 344 nm. Short-wavelength photolysis (>200 nm, 22 h) produces an extremely slow decrease in intensity of trideuterio-*o*-xylylene (**6b**).

Flash vacuum thermolysis (470 °C, 100% conversion) of **2b** followed by cocondensation of the pyrolyzate with argon produces α,β,β-trideuteriostyrene (**5b**) (IR, vide infra) and trideuteriobenzocyclobutene (**7b**) [IR (Ar, 15 K) 2955 w, 2920 w, 2850 w, 2235 m, 1378 m, 1292 m, 775 s, 681 s cm^{-1}] in a ratio of ca. 1.7:1. In order to confirm the structural assignments of **5b** and **7b**, we pyrolyzed a sample of diazocompound **2b** on a preparative scale. The product mixture was analyzed by ^{1}H NMR, ^{2}H NMR, and GC–FTIR spectroscopy. The GC retention times, as well as the proton and deuterium NMR data, confirm α,β,β-trideuteriostyrene (**5b**) and trideuteriobenzocyclobutene (**7b**) as the major pyrolysis products. The GC–FTIR experiment establishes that these products are the species observed in the flash vacuum pyrolysis/matrix isolation trapping experiments. The structural assignment of α,β,β-trideuteriostyrene (**5b**) is also based on comparison of the infrared spectrum with that of the material prepared by thermolysis or photolysis of 2,2,2-trideuterio-1-phenylethylidene (**8b**) (vide infra). The structural assignment of **7b** is supported by the distinctive benzocyclobutene-like aliphatic C–H stretching modes. In addition, the C–H deformation modes of trideuteriobenzocyclobutene (**7b**) (775, 681 cm^{-1}) and 1-(trideuteriomethyl)cycloheptatetraene (**12b**) (772, 679 cm^{-1}) are quite similar. This was also observed with benzocyclobutene (**7a**) (780, 708 cm^{-1}) and 1-methylcycloheptatetraene (**12a**) (790, 710 cm^{-1}).

1-Phenyldiazoethane (1a). Irradiation (>470 nm) of argon matrix-isolated 1-phenyldiazoethane (**1a**) produces triplet 1-phenylethylidene (**8a**): IR (Ar, 15 K) 3090 w, 3075 m, 3038 w, 2942 w, 2920 w, 2893 w, 2862 m, 2807 w, 2690 vw, 1468 m, 1018 m, 1007 w, 875 w, 740 s, 670 s, 480 m, cm^{-1}; UV (Ar, 15 K) λ_{max} 449, 446, 432, 428, 417, 412, 405, 399, 392, 388, 381, 302, 251, 244 nm; ESR (Ar, 15 K) $|D/hc| = 0.508$ cm^{-1}, $|E/hc| = 0.0279$

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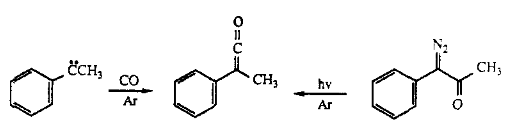
(14) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1987**, *109*, 683–692.

(15) This band is most prominent in cycloheptatetraene, 1-deuteriocycloheptatetraene, and 1-fluorocycloheptatetraene.[8]

Scheme VI



8a 15 16

cm^{-1}; Z_1 2100 G, X_2 4784 G, Y_2 5937 G, Z_2 8734 G, microwave frequency 9.313 GHz. A small amount of styrene (**5a**) [IR (Ar, 25 K) vide infra] is also produced. Neither prolonged irradiation (>470 nm), nor standing at 12 K (14 h), nor warming to 36 K results in a change in the infrared spectrum of the products.

Irradiation (>440 nm) leads to the disappearance of the IR, UV, and ESR signals of **8a** and to the appearance of styrene (**5a**): IR (Ar, 15 K) 3115 vw, 3095 m, 3070 m, 3035 m, 3000 vw, 1960 vw, 1942 vw, 1889 vw, 1872 vw, 1811 w, 1800 vw, 1746 vw, 1690 vw, 1637 m, 1603 w, 1581 w, 1499 m, 1456 m, 1431 w, 1415 w, 1338 w, 1320 w, 1295 w, 1262 vw, 1208 w, 1182 vw, 1103 vw, 1084 m, 1022 m, 994 m, 980 w, 905 s, 780 s, 698 s, 552 m, 433 m cm^{-1}; UV (Ar, 15 K) λ_{max} 288, 280, 278, 271, 255, 245, 237, 211 nm. Irradiation (>470 nm) of 1-phenyldiazoethane (**1a**) in a carbon monoxide doped argon matrix generates 1-phenylethylidene (**8a**) (IR, vide supra) and a trace of ketene **15** (2110 cm^{-1}). Warming the matrix to 49 K (30 min) results in the decrease in intensity of the IR bands of **8a** and CO (2139 cm^{-1}) and in the increase in intensity of the IR bands of the ketene **15**. The identity of ketene **15** was established by comparison of the IR spectrum with that of the material prepared by irradiation (>336 nm) of 1-diazo-1-phenyl-2-propanone (**16**) [IR (15 K) vide infra] (Scheme VI).

Flash vacuum thermolysis of **1a** (350 or 815 °C, 100% conversion) followed by cocondensation of the pyrolyzate with argon generates styrene (**5a**) cleanly. 1-Methylcycloheptatetraene (**12a**), benzocyclobutene (**7a**), or other isomeric C_8H_8 compounds were not observed by IR spectroscopy. We discussed the details of the thermal conversion of 1-phenylethylidene (**8a**) to styrene (**5a**) at 65 K in xenon in an earlier publication.[14]

2,2,2-Trideuterio-1-phenyldiazoethane (1b). Irradiation (>470 nm) of argon matrix-isolated 2,2,2-trideuterio-1-phenyldiazoethane (**1b**) produces triplet 2,2,2-trideuterio-1-phenylethylidene (**8b**): IR (Ar, 15 K) 2179 w, 2095 w, 2079 w, 1468 m, 1432 w, 1424 w, 1181 w, 1090 w, 1060 w, 1033 m, 1019 w, 947 m, 878 m, 862 w, 736 s, 670 s, 475 m cm^{-1} (Figure 6); UV (Ar, 15 K) λ_{max} 449 sh, 446, 432, 428, 420, 416, 411, 404, 400, 303, 251, 245, 203 nm; ESR (Ar, 15 K) $|D/hc| = 0.511\ cm^{-1}$, $|E/hc| = 0.0285\ cm^{-1}$; Z_1 2138 G, X_2 4775 G, Y_2 5960 G, Z_2 8763 G, microwave frequency 9.264 GHz. A small amount of α,β,β-trideuteriostyrene (**5b**) (IR, vide infra) was also produced. Irradiation (>416 nm) of 2,2,2-trideuterio-1-phenylethylidene (**8b**) rapidly produces α,β,β-trideuteriostyrene (**5b**): IR (Ar, 15 K) 3110 w, 3095 m, 3070 m, 3030 m, 2258 w, 2220 w, 1601 s, 1568 m, 1497 m, 1449 m, 1180 w, 1092 w, 1081 w, 1049 w, 1044 w, 1019 w, 1004 w, 911 w, 833 w, 790 m, 743 s, 710 s, 690 s, 582 w, 570 w, 562 w, 548 w, 508 m, 408 w, 397 w cm^{-1} (Figure 6); UV (Ar, 15 K) λ_{max} 290, 286, 281, 278, 275, 270, 256, 247, 239, 211 nm. The trideuteriostyrene (**5b**) assignment is based on comparison of the IR and UV spectra with those of styrene (**5a**). The UV spectra are virtually identical, and the IR spectra exhibit striking similarities. The ^1H NMR, ^2H NMR, and GC–FTIR experiments performed in conjunction with the preparative pyrolysis of **2b** further confirm the structural assignment of **5b**.

Flash vacuum thermolysis of **1b** (390 °C, 100% conversion) followed by cocondensation of the pyrolyzate with argon generates α,β,β-trideuteriostyrene (**5b**) cleanly (Figure 6). 1-(Trideuteriomethyl)cycloheptatetraene (**12b**) and trideuteriobenzocyclobutene (**7b**) were not observed by IR spectroscopy.

1-Diazo-1-phenyl-2-propanone (16). Irradiation (>336 nm) of argon matrix-isolated diazoketone **16** produces methylphenylketene (**15**): IR (Ar, 15 K) 2110 s, 1612 m, 1500 w, 1338 w, 1332 m, 1196 w, 1075 m, 1032 w, 751 m, 692 m, 492 w cm^{-1}.

[2.2]Paracyclophane (17). Flash vacuum thermolysis of **17** (655 °C, 100% conversion) followed by cocondensation of the pyrolyzate with argon produces *p*-xylylene (**18**): IR (Ar, 15 K) 3102 m, 3059 m, 3047 m, 3038 m, 3010 w, 1603 m, 1449 m, 1342 m, 1136 w, 966 w, 940 w, 868 s, 821 m, 780 m, 468 s cm^{-1}. The structural assignment is based on comparison with the IR spectrum of **18** reported in the literature.[16] Styrene (**5a**), benzocyclobutene (**7a**), or other isomeric C_8H_8 compounds were not observed. The origin of a medium-intensity band at 1733 cm^{-1} remains unclear. It may be an overtone of the very intense 868-cm^{-1} deformation mode, or it may be due to some type of oxygen incorporation product.

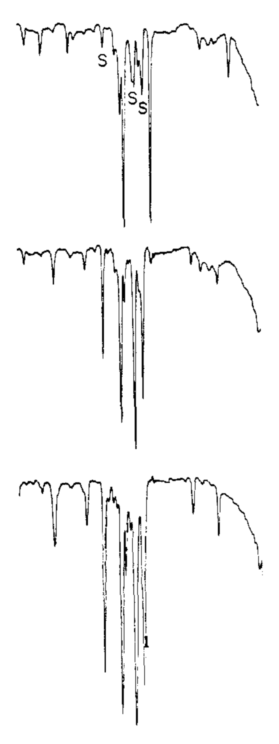
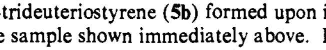


Figure 6. Top: Infrared spectrum (in transmittance) of 2,2,2-trideuterio-1-phenylethylidene (**8b**) formed upon irradiation (>470 nm, 1532 min) of 2,2,2-trideuterio-1-phenyldiazoethane (**1b**) matrix isolated in argon at 15 K. S, α,β,β-trideuteriostyrene (**5b**). Middle: Infrared spectrum of α,β,β-trideuteriostyrene (**5b**) formed upon irradiation (>420 nm, 20 min) of the sample shown immediately above. Bottom: Infrared spectrum of α,β,β-trideuteriostyrene (**5b**) formed upon flash vacuum thermolysis (390 °C) of 2,2,2-trideuterio-1-phenyldiazoethane (**1b**) followed by cocondensation of the pyrolyzate with argon.



17 18

Benzocyclobutene (7a). Flash vacuum thermolysis of benzocyclobutene (**7a**) followed by cocondensation of the pyrolyzate with argon does not result in trapping of *o*-xylylene (**6a**). Only benzocyclobutene was observed by infrared spectroscopy. At 845 °C, a small amount of styrene (**5a**) was detected. The IR spectrum reveals substantial conversion of benzocyclobutene (**7a**) to styrene (**5a**) at 910 °C.

Discussion

Carbene Characterization. Observation of triplet ESR signals for carbenes **8**–**11** at 15 K implies that the triplet state is the ground state, or lies within several calories/mole of the ground state,[17] as expected for arylcarbenes.[18] *p*-Tolylmethylene (**11a**) displays only one set of transitions (no rotational isomers), due

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to its symmetry. *m*-Tolylmethylene (**10a**) could, in principle, exhibit rotational isomerism.[19] However, the remote meta substituent does not significantly perturb either the electronic or the steric environment of the carbene center. Other than slight fine structure in the Z_1 and Z_2 transitions, the spectrum does not reveal rotational isomerism in **10a**. We attributed the rotational isomerism in *o*-tolylmethylenes **9a** and **9b** (Figure 5) to a steric effect.[14] We presented a detailed analysis of the ESR spectra of *o*-tolylmethylenes **9a** and **9b** and 1-phenylethylidenes **8a** and **8b** in an earlier publication.[14] A carbon monoxide trapping experiment provided chemical evidence for the triplet carbene structure of **8a**. Warming **8a** in a CO-doped argon matrix produces ketene **15** (Scheme VI). We find this type of trapping study to be diagnostic for the presence of triplet carbenes.[8,21]

The UV/visible spectra of **8–11** provide strong confirmation of the triplet arylcarbene structural assignment. Each carbene displays the weak, long-wavelength π–π^* transitions with extensive vibronic coupling (Figure 1) characteristic of triplet arylcarbenes[8,20,21] and the benzyl radical.[22] In addition, carbenes **8a**, **8b**, **9a**, and **9b** each exhibit a weak absorption at 300–305 nm and two strong, closely spaced absorptions at 240–250 nm. These bands have been observed previously in phenylmethylene.[8] The position of the absorptions is matrix dependent. Xenon red-shifts the absorptions 5–8 nm relative to argon.

The simplicity of the IR spectra of **8–11** indicates that these species contain intact aromatic rings. We observed only one infrared absorption for *o*-tolylmethylene (**9a**) due to our ability to generate it only in low concentration. As expected, the position of the absorption corresponds to the position of the most intense absorption for the trideuteriomethyl analogue (**9b**). The 1-phenylethylidenes (**8a** and **8b**) both display the ca. 740, 670, and 480 cm^{-1} bands characteristic of monosubstituted arylcarbenes (Figure 6). These bands have been observed previously in phenylmethylene and α-(deuteriophenyl)methylene.[8] In an earlier publication, we discussed the influence of the triplet carbene center on the IR vibrational modes of the methyl groups in **8a** and **8b**.[14]

Cycloheptatetraene Characterization. Our previous work demonstrated the role of 1,2,4,6-cycloheptatetraene in phenylmethylene rearrangements[8] and failed to provide evidence for bicyclo[3.2.0]hepta-1,3,6-triene,[8] bicyclo[4.1.0]hepta-2,4,6-triene,[8] and cycloheptatrienylidene[9] intermediates. In the present work we reach the same conclusions for the tolylmethylene/methylcycloheptatetraene system. Cycloheptatetraenes **12b**, **13a**, **13b**, **14a**, and **14b** each exhibit the characteristic, weak allene absorptions at ca. 1810 cm^{-1}. The concentration of **12a** was too low to observe the allene absorption. However, **12a** exhibits an absorption near 1380 cm^{-1}, which seems to be characteristic of cycloheptatetraenes.[15]

Tolylmethylene/Methylcycloheptatetraene Interconversions. Photochemistry. Each of the isomeric tolylmethylenes or [(trideuteriomethyl)phenyl]methylenes undergoes photochemical rearrangement upon T_0–T_1 excitation (ca. 450 nm; 58 kcal/mol). Irradiation (>416 nm) of *p*-tolylmethylene (**11a**) produces 5-methylcycloheptatetraene (**14a**) (Figure 2). Shorter wavelength photolysis (>261 nm) of **14a** results in equilibration with 4-methylcycloheptatetraene (**13a**). This presumably occurs via *m*-tolylmethylene (**10a**). ESR spectroscopy reveals a very small concentration of triplet carbene under these photolysis conditions, but the similar zero-field splitting parameters of **10a** and **11a** render them indistinguishable. The signal is likely due to a mixture of **10a** and **11a**.

Irradiation (>416 nm) of *m*-tolylmethylene (**10a**) produces a mixture of 4-methylcycloheptatetraene (**13a**) and 5-methylcycloheptatetraene (**14a**) (Figure 2). Surprisingly, short-wavelength irradiation (>261 nm) did not generate any change in the mixture of **13a** and **14a** detectable by IR spectroscopy. Specifically, products derived from equilibration of 4-methylcycloheptatetraene (**13a**) with *o*-tolylmethylene (**9a**), namely *o*-xylylene (**6a**), benzocyclobutene (**7a**), or 1-methylcycloheptatetraene (**12a**), were not observed. We note that the reverse reaction, photochemical ring expansion of *o*-tolylmethylene (**9a**) to 4-methylcycloheptatetraene (**13a**), was not observed either (vide infra).

The study of the *photochemistry* of *o*-tolylmethylene (**9a**) is complicated by the facile *thermal* chemistry of **9a**. The [1,4] hydrogen shift in triplet **9a** to form singlet *o*-xylylene (**6a**) occurs thermally at temperatures as low as 4.6 K.[14] The most straightforward behavior is observed by generating *o*-tolylmethylene (**9a**) from *o*-tolyldiazomethane (**2a**) with a flash of short-wavelength light (>200 nm, 1.0 min). This produces **9a** rapidly and efficiently. Overirradiation (>200 nm, 2.0 min) generates the photoproducts of **9a**, namely *o*-xylylene (**6a**) and 1-methylcycloheptatetraene (**12a**). 4-Methylcycloheptatetraene (**13a**) is not observed. Thermal rearrangement of **9a** to **6a** is negligible under these short irradiation times. Thus, the [1,4] hydrogen shift in **9a** to form **6a** occurs photochemically, as well as thermally. The same photoproducts are obtained in the same ratio upon >416-nm irradiation of **2a**. Again, **9a** is the primary photoproduct of **2a**. In this instance, however, the photochemical conversion of **9a** to products is much more efficient than the photochemical conversion of **2a** to **9a**. Consequently, **9a** cannot be spectroscopically observed under these conditions. While irradiating **2a** under conditions where **9a** does not absorb light (>470 nm), our attempt to observe **9a** is confounded not by photochemical rearrangement of **9a** but by thermal rearrangement. We observe only a small steady-state concentration of *o*-tolylmethylene (**9a**) by UV/visible and ESR spectroscopy. We cannot detect the small amount of **9a** in the IR spectrum, due to overlap with the bands of starting material and product. The major species observed by infrared spectroscopy is the thermal rearrangement product *o*-xylylene (**6a**) (Figure 4).

The chemistry of the deuteriated carbene **9b** shows a striking contrast to that of the protio analogue **9a**. The large deuterium isotope effect (at 10 K) totally suppresses thermal [1,4] hydrogen (deuterium) shift. As a result, >470-nm irradiation of diazo compound **2b** produces carbene **9b** exclusively. Irradiation (>416 nm) of **9b** produces trideuterio-*o*-xylylene (**6b**, minor product) and 1-(trideuteriomethyl)cycloheptatetraene (**12b**, major product), but no 4-(trideuteriomethyl)cycloheptatetraene (**13b**). This product ratio differs dramatically form the ratio obtained in the protio case. Simple deuterium substitution reverses the preference for [1,4] migration over ring expansion. The failure of carbenes **9a** and **9b** to ring expand to 4-substituted cycloheptatetraenes is precedented. Other 2-substituted arylcarbenes [[2-methyl-5-(trideuteriomethyl)phenyl]methylene,[12] (2-fluorophenyl)methylene,[8,23] and 2-pyridylmethylene[24]] ring expand exclusively to 1-substituted cycloheptatetraenes.[34]

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(23) Chapman, O. L.; Johnson, J. W.; McMahon, R. J.; Mooring, A. M., unpublished results.

(24) Chapman, O. L.; Sheridan, R. S.; LeRoux, J.-P. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 334–337 and references cited therein.

(25) The deuterium isotope does not alter the partitioning of **8b** between [1,2] migration and ring expansion, relative to **8a** (vide infra).

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Short-wavelength irradiation (>261 nm) drives *o*-xylylene (**6a**) to benzocyclobutene (**7a**) (Figure 4). Benzocyclobutene (**7a**) formation therefore occurs not by direct insertion of the carbene into the C–H bond of the methyl group but by hydrogen migration followed by closure of *o*-xylylene (**6a**). Irradiation (>261 nm) of 1-methylcycloheptatetraene (**12a**) may produce styrene (**5a**), but the conversion is so slight that a firm assignment cannot be made.

Irradiation (>416 nm) of 1-phenylethylidene (**8a**) produces styrene (**5a**). Ring expansion to 1-methylcycloheptatetraene (**12a**) was not observed. We observe the same results with the deuteriated analogue. In contrast to the situation observed for the *o*-tolylmethylenes (**9a** and **9b**), deuterium substitution does not slow the rate of photochemical [1,2] hydrogen migration enough to allow ring expansion to 1-(trideuteriomethyl)cycloheptatetraene (**12b**) to compete.

Thermal Chemistry. Flash vacuum thermolysis (370 °C, 100% conversion) of *o*-tolyldiazomethane (**2a**), followed by cocondensation with argon, produces styrene (**5a**) and benzocyclobutene (**7a**). No cycloheptatetraenes were detected by infrared spectroscopy. As reported by others previously, the ratio of **5a** to **7a** (ca. 1:1.3) is not the same as the ratio obtained from the meta and para isomers (ca. 1.3:1).[1e] This is not true in the deuterio case. Flash vacuum thermolysis of all three [(trideuteriomethyl)phenyl]diazomethane isomers (**2b**, **3b**, and **4b**) gives the same ratio (ca. 1.7:1) of α,β,β-trideuteriostyrene (**5b**): trideuteriobenzocyclobutene (**7b**). The **5b**:**7b** ratio differs slightly from the **5a**:**7a** ratio (from meta and para). Presumably, the deuterium isotope effect alters the partitioning of **9b** between [1,4] migration and ring expansion, relative to **9a**.[25]

Of the six tolyldiazomethanes studied (**2**–**4**), only the protio diazo compound **2a** produces an anomalous product ratio. This suggests the involvement of some special effect in the hydrogen (protium) transfer. Hydrogen atom tunneling must be considered. The precise explanation for this effect is still open to speculation. The decomposition pathway of **2a** undoubtedly involves a delicate balance among several factors: facile conformational processes, the timing of N_2 loss and [1,4] migration, intramolecular [1,4] migration by either classical (over the barrier) or nonclassical (tunneling through the barrier) pathways, and the critical distance dependence of tunneling reactions. Neither of the previous explanations of the anomalous product ratio from *o*-tolyldiazomethane (**2a**) is directly contradicted by our new experimental observations.[6,7] However, the modifications necessary to incorporate this curious isotope effect as an integral part of the mechanism make the previous explanations very complex.

Gaspar et al. proposed the norcaradienylidene intermediate as a means of circumventing *o*-tolylmethylene (**9a**) as a common intermediate in the rearrangement mechanism[7] (Scheme V). This provides an explanation for the unusual product ratio obtained from *o*-tolyldiazomethane (**2a**). Our results show that no such anomaly exists in the deuteriated series (**2b**, **3b**, **4b**). Hence, there is no reason to invoke a norcaradienylidene intermediate. Furthermore, there is no direct experimental evidence to support a norcaradienylidene intermediate in any major rearrangement pathway of arylcarbenes. The Gaspar mechanism can be made compatible with our observations by invoking a kinetic isotope effect, which alters the partitioning of carbene **9b** between [1,4] migration and ring expansion. However, the magnitude of the isotope effect would have to be precisely correct to balance a complex series of rates such that **9b** fortuitously gives the same product ratio as **10b** and **11b**. We feel this scenario is highly unlikely.

Gleiter et al. proposed a dynamic conformational effect as the basis for the anomalous product ratio from *o*-tolyldiazomethane (**2a**).[6] Gleiter suggested that the relative motion of the methyl group and the carbene center in **9** differs, depending on whether **9** is formed by N_2 loss from **2** or by ring contraction from **13**. Hence, the reactivity of **9** will depend on the precursor. The Gleiter proposal does not, therefore, explain our observation that diazo compound **2b** gives the same product ratio as diazo compounds **3b** and **4b**. The explanation can be salvaged by invoking an unusual isotope effect in **9**, as generated from **2**. This explanation falls into the gray area regarding reactive conformations, etc., which cannot be adequately sorted out at this time.

The simplest explanation is that hydrogen atom transfer (tunneling?) occurs in diazo compound **2a** prior to nitrogen loss.[35] As a result of this facile shift, the diazo compound can "leak away" to benzocyclobutene (**7a**) without passing through carbene **9a**. This gives rise to the preponderance of benzocyclobutene over styrene. Substitution of hydrogen by deuterium changes the partitioning of diazo compound between [1,4] migration and nitrogen loss by virtue of a kinetic isotope effect. (The isotope effect could be large in the case of a tunneling process.) As a result, diazo compound **2b** decomposes exclusively to carbene **9b** (no [1,4] migration). In each case (protio or deuterio), carbene **9** is a common intermediate in the carbene-to-carbene rearrangement mechanism, and hence gives the same ratio of **5** to **7** observed from the isomeric carbenes (**10** and **11**).

Flash vacuum thermolysis of diazo compounds **2b**, **3a**, **3b**, **4a**, and **4b**, followed by cocondensation of the pyrolyzate with argon at 26 K, produces small amounts of cycloheptatetraenes (**13a** and **14a**, or **13b**, or **14b**), in addition to styrene (**5a** or **5b**) and benzocyclobutene (**7a** or **7b**) (Figure 3). *p*-Tolyldiazomethane (**4a**) produces an unidentified minor product, which is also present in trace amount in the pyrolysis mixture of *m*-tolyldiazomethane (**3a**). We considered *p*-xylylene (**18**) as a likely structure for the minor product. Infrared spectroscopy, however, rules out *p*-xylylene (**18**) and *p*-tolualdehyde (a potential oxygen-scavenging product) as possible structures. Flash vacuum thermolysis (350 °C, 100% conversion) of 1-phenyldiazoethane (**1a**) produces styrene (**5a**) cleanly. Neither benzocyclobutene (**7a**) nor the cycloheptatetraenes **12a**, **13a**, or **14a** were observed by infrared spectroscopy. Deuterium substitution does not slow the rate of the thermal [1,2] migration enough to allow ring expansion to compete. Thus, flash vacuum thermolysis (390 °C, 100% conversion) of diazo compound **1b** gives α,β,β-trideuteriostyrene (**5b**) cleanly (Figure 6). Again, neither trideuteriobenzocyclobutene (**7b**) nor 1-(trideuteriomethyl)cycloheptatetraene (**12b**) were observed by infrared spectroscopy.

Summary. Matrix isolation studies provided insight into the mechanism of both the thermal and photochemical rearrangements of the isomeric tolylmethylenes. The carbenes interconvert via methylcycloheptatetraene intermediates, as shown in Scheme IV. Each intermediate in this mechanism has been observed spectroscopically. The present work establishes the reactions indicated with solid arrows in Scheme IV. In addition, Tsou's labeling experiments require the steps shown with broken arrows.[11] We do not have direct evidence for the steps shown with open arrowheads, but the corresponding rearrangements are known in the fluoro,[23,26] chloro,[23,26] and trimethylsilyl[27] series. The relative reaction rates of these steps will vary, depending on whether thermal or photochemical conditions are employed. The thermolysis experiments provide several important results. They provide important new information concerning *o*-tolyldiazomethane pyrolysis, a long-standing problem in arylcarbene rearrangement chemistry. We attribute the anomalous product ratio obtained upon *o*-tolydiazomethane pyrolysis to an unusually facile hydrogen migration on the diazo compound. As a result of this explanation, we eliminate the need to invoke a norcaradienylidene intermediate in the arylcarbene rearrangement mechanism.[7] The observation of cycloheptatetraene intermediates upon thermolysis of diazo compounds **2b**, **3**, and **4** strongly suggests that our mechanism (Scheme IV) describes both thermal and photochemical rearrangement pathways of the tolylmethylenes.[1,10–12] In addition, the mechanism provides a basis for understanding

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[34] In addition, several 2-substituted arylnitrenes ring expand in only one direction: Sundberg, R. J.; Suter, S. R.; Brenner, M. *J. Am. Chem. Soc.* **1972**, *94*, 513–520.

[35] This explanation has been invoked on other occasions: Tomioka, H.; Kitagawa, H.; Izawa, Y. *J. Org. Chem.* **1979**, *44*, 3072–3075. Platz, M. S.; Carrol, G.; Pierrat, F.; Zayas, J.; Auster, S. *Tetrahedron* **1982**, *38*, 777–785.

the isomerization of benzocyclobutene (**7a**) to styrene (**5a**).[11,12,28]

Experimental Section

^{1}H NMR spectra were recorded on a Varian T-60 instrument. Chemical shifts (δ) are reported downfield from internal $SiMe_4$. Melting points were determined on a Thomas-Hoover Unimelt apparatus in open capillaries and are uncorrected. Elemental analyses were performed by Spang Microanalytical Laboratory (Eagle-Harbor, MI). Mass spectra were obtained on an AEI MS-9 or MS-902 spectrometer. Infrared spectroscopy was performed with a Perkin-Elmer 580B with Model 3600 data station or with a Nicolet 60SX FTIR. Ultraviolet/visible spectroscopy was performed with a Perkin-Elmer 330 with Model 3600 data station. ESR spectra were obtained with an X-band spectrometer constructed from a variety of commerical components. The magnetic field was calibrated with an NMR gaussmeter, and the microwave frequency was determined by the use of a DPPH reference. The best fit of the observed ESR spectra with the spin Hamiltonian[29] (assuming $g_x = g_y = g_z = g_e$) provided the zero-field splitting parameters.

Matrix Isolation Spectroscopy. The apparatus and experimental technique used for the study of reactive species matrix isolated in argon at 10 K have been described elsewhere.[21b]

Flash Vacuum Pyrolysis. Our flash vacuum pyrolysis/matrix isolation trapping technique has been described previously.[8] For preparative scale pyrolyses, we employed the apparatus described by Tsou et al.[11] Pyrolysis products were characterized by ^{1}H NMR, ^{2}H NMR, and GC–FTIR spectroscopy.

Sample Preparation. General procedures for syntheses of the tosylhydrazones, tosylhydrazone sodium salts, and diazo compounds used in this study are described elsewhere.[8]

General Procedure for the Preparation of (Trideuteriomethyl)benzaldehydes. Morpholine (0.43 g, 4.86 mmol, 1.2 equiv; Baker) was dissolved in 10 mL of dry THF, and the resultant mixture was cooled to −41 °C and treated with 2.4 M *n*-BuLi/hexane (2 mL, 4.86 mmol).[30] After the resultant mixture was stirred for 5 min, 0.75 g of the appropriate bromobenzaldehyde (4.05 mmol, 1.0 equiv) in 10 mL of dry THF was added dropwise via syringe over 2 min. The reaction was stirred 15 min and then cooled to −78 °C. After the protected aldehyde was treated with 2.4 M *n*-BuLi/hexane (2.7 mL, 6.48 mmol, 1.6 equiv) dropwise over 7 min, 5 g of CD_3I (34.5 mmol, 8.5 equiv.; Aldrich) was added and the mixture stirred at −78 °C for 1 h. The solution was warmed to room temperature, poured into 50 mL of 6 N HCl to deprotect the aldehyde, and extracted with Et_2O (4 × 25 mL). The organic layers were washed with saturated aqueous $NaHCO_3$ (1 × 25 mL) and saturated aqueous NaCl (1 × 25 mL), dried over $MgSO_4$, and filtered. Removal of the solvent at reduced pressure afforded a dark brown liquid. Purification by column chromatography (SiO_2, Et_2O) yielded the (trideuteriomethyl)benzaldehyde as a light yellow liquid.

_p_-Tolualdehyde tosylhydrazone: prepared from *p*-tolualdehyde (Aldrich) in 84% yield; mp 142–144 °C (lit.[5] 149–151.5 °C) ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3 H), 2.33 (s, 3 H), 7.07 (AB, 2 H, $J = 8.5$ Hz), 7.24 (AB, 2 H, $J = 8$ Hz), 7.43 (AB, 2 H, $J = 8.5$ Hz), 7.73 (s, 1 H), 7.87 (AB, 2 H, $J = 8$ Hz), 8.45 (br s, 1 H); Anal. ($C_{15}H_{16}N_2O_2S$) C, H, N.

_p_-Tolyldiazomethane (4a): IR (Ar, 15 K) 3210 w, 3185 w, 3095 w, 3060 w, 3040 w, 2990 w, 2960 w, 2935 w, 2905 w, 2870 w, 2065 w, 1882 w, 1720 w, 1625 m, 1611 m, 1577 w, 1526 m, 1518 m, 1460 w, 1427 w, 1379 m, 1319 w, 1209 w, 1188 m, 1122 w, 1040 w, 810 s, 762 w, 602 m, 452 s, 282 w cm^{-1}; UV (Ar, 15 K) λ_{max} 500 br sh nm. The deep red diazo compound was sublimed at −23 °C (10^{-6} Torr) and codeposited with argon to form a matrix.

_p_-(Trideuteriomethyl)benzaldehyde: prepared from *p*-bromobenzaldehyde (Aldrich) in 80% yield; ^{1}H NMR ($CDCl_3$) δ 7.3–7.9 (m, 4 H), 10.1 (s, 1 H); IR (neat) 2732 m (aldehyde ν_{C-H}), 2231 w, 2127 w, 2055 w (trideuteriomethyl ν_{C-D}), 1702 s $\nu_{C=O}$ cm^{-1}.

_p_-(Trideuteriomethyl)benzaldehyde tosylhydrazone: prepared from *p*-(trideuteriomethyl)benzaldehyde in 40% yield; mp 145–148 °C; ^{1}H NMR ($CDCl_3/Me_2SO$-d_6) δ 2.39 (s 3 H), 7.1–7.9 (m, 8 H), 8.0 (s, 1 H), 9.55 (br s, 1 H); mass spectrum (70 eV) *m/z* (relative intensity) 291 (M$^+$, 27), 136 (76), 135 (17), 118 (10), 109 (17), 108 (11), 107 (100), 92 (17), 91 (32); high-resolution mass spectrum calcd for $C_{15}H_{13}D_3N_2O_2S$ 291.1121, found 291.1131.

[_p_-(Trideuteriomethyl)phenyl]diazomethane (4b): IR (Ar, 15 K) 3200 w, 3180 w, 3138 w, 3090 m, 3060 w, 3030 m, 3020 w, 2260 w, 2240 w, 2230 w, 2218 w, 2065 s, 1618 s, 1602 m, 1599 m, 1569 w, 1519 s, 1499 w, 1425 m, 1378 s, 1373 s, 1312 w, 1289 w, 1238 w, 1201 m, 1183 m, 1113 m, 1050 w, 878 m, 841 w, 782 s, 749 w, 738 m, 690 w, 680 w, 642 w, 588 s, 445 s, cm^{-1}. The deep red diazo compound was sublimed at −29 °C (10^{-6} Torr) and codeposited with argon to form a matrix.

_m_-Tolualdehyde tosylhydrazone: prepared from *m*-tolualdehyde (Aldrich) in 79% yield; mp 119–121 °C (lit.[5] 119–119.5 °C); ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3 H), 2.37 (s, 3 H), 7.10–7.43 (m, 6 H), 7.78 (s, 1 H), 7.90 (AB, 2 H, $J = 8$ Hz), 8.42 (s, 1 H); Anal. ($C_{15}H_{16}N_2O_2S$) C, H, N.

_m_-Tolyldiazomethane (3a): IR (Ar, 15 K) 3240 w, 3200 w, 3110 w, 3070 w, 3050 w, 2980 w, 2960 w, 2875 w, 2070 s, 1610 s, 1588 m, 1497 s, 1470 m, 1400 w, 1393 m, 1380 w, 1370 m, 1269 m, 1181 m, 1170 m, 1089 w, 1040 w, 881 w, 862 w, 775 s, 749 s, 710 w, 690 s, 655 m, 642 m, 565 m, 521 w, 469 m, 426 m cm^{-1}; UV (Ar, 15 K) λ_{max} 530 br sh nm. The deep red diazo compound was sublimed at −29 °C (10^{-6} Torr) and codeposited with argon to form a matrix.

_m_-(Trideuteriomethyl)benzaldehyde: prepared from *m*-bromobenzaldehyde in 75% yield; ^{1}H NMR ($CDCl_3$) δ 7.4–7.8 (m, 4 H), 10.2 (s, 1 H); IR (neat) 2738 m (aldehyde ν_{C-H}), 2230 w, 2139 w, 2070 w (trideuteriomethyl ν_{C-D}), 1699 s $\nu_{C=O}$ cm^{-1}; mass spectrum (16 eV) *m/z* (relative intensity) 123 (M$^+$, 100), 122 (94), 106 (78), 94 (35).

_m_-(Trideuteriomethyl)benzaldehyde tosylhydrazone: prepared from *m*-(trideuteriomethyl)benzaldehyde in 65% yield; mp 96–99 °C; ^{1}H NMR ($CDCl_3/Me_2SO$-d_6) δ 2.40 (s, 3 H), 7.0–8.0 (m 9 H), 8.1 (s, 1 H), (N–H not observed, sample slightly wet); mass spectrum (70 eV) *m/z* (relative intensity) 291 (M$^+$, 24), 136 (54), 135 (29), 107 (100), 92 (44), 91 (73); high-resolution mass spectrum calcd for $C_{15}H_{13}D_3N_2O_2S$ 291.1121, found 291.1112.

[_m_-(Trideuteriomethyl)phenyl]diazomethane (3b): IR (Ar, 15 K) 3100 w, 3080 w, 3075 w, 3060 w, 3043 w, 3030 w, 2235 w, 2215 w, 2065 s, 1604 s, 1580 w, 1440 s, 1450 m, 1390 m, 1377 w, 1363 w, 1180 w, 1167 w, 1080 w, 1049 w, 908 w, 878 w, 753 m, 726 w, 682 w, 650 w, 640 w, 420 w cm^{-1}. The deep red diazo compound was sublimed at −41 °C and codeposited with argon to form a matrix.

_o_-Tolualdehyde tosylhydrazone: prepared from *o*-tolualdehyde (Aldrich) in 81% yield; mp 139–141 °C (lit.[31] 143–144 °C); ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3 H), 2.34 (s, 3 H), 7.05–7.75 (m, 6 H), 7.88 (AB, 2 H, $J = 8$ Hz), 8.06 (s, 1 H), 8.59 (br s, 1 H); Anal. ($C_{15}H_{16}N_2O_2S$) C, H, N.

_o_-Tolyldiazomethane (2a): IR (Ar, 15 K) 3220 w,3160 w, 3110 w, 3080 w, 3060 w, 3035 w, 2980 w, 2960 w, 1814 w, 2870 w, 2070 s, 1608 m, 1603 m, 1579 m, 1497 s, 1472 m, 1445 w, 1379 s, 1302 w, 1289 w, 1230 m, 1099 w, 1054 w, 1038 w, 790 w, 750 s, 715 w, 632 m, 546 w, 460 w, 425 m cm^{-1}; UV (Ar, 10 K) λ_{max} 500 br sh, 307, 294, 280, 275, 225, 219, 215 sh nm. The deep red diazo compound was sublimed at −29 °C (10^{-6} Torr) and codeposited with argon to form a matrix.

_o_-(Trideuteriomethyl)benzaldehyde: prepared from *o*-bromobenzaldehyde (Aldrich) in 60% yield; ^{1}H NMR ($CDCl_3$) δ 7.0–8.0 (m, 4 H), 10.0 (s, 1 H); IR (neat) 2735 m (aldehyde ν_{C-H}), 2220 w, 2125 w, 2055 w (trideuteriomethyl ν_{C-D}), 1695 s $\nu_{C=O}$ cm^{-1}; mass spectrum (16 eV) *m/z* (relative intensity) 123 (M$^+$, 41), 122 (22), 94 (18).

_o_-(Trideuteriomethyl)benzaldehyde tosylhydrazone: prepared from *o*-(trideuteriomethyl)benzaldehyde in 51% yield; mp 139–142 °C; ^{1}H NMR ($CDCl_3/Me_2SO$-d_6) δ 2.37 (s, 3 H), 7.0–8.0 (m, 8 H), 8.12 (s, 1 H), (N–H not observed, sample slightly wet); mass spectrum (70 eV) *m/z* (relative intensity) 291 (M$^+$, 22), 136 (42), 135 (38), 124 (33), 107 (76), 92 (52), 91 (100); high-resolution mass spectrum calcd for $C_{15}H_{13}D_3N_2O_2S$ 291.1121, found 291.1119; Anal ($C_{15}H_{13}D_3N_2O_2S$) C, N, S.

[_o_-(Trideuteriomethyl)phenyl]diazomethane (2b): IR (Ar, 15 K) 3115 w, 3080 w, 3035 w, 2235 w, 2070 s, 1603 s, 1495 s, 1453 m, 1388 m, 1382 m, 1296 w, 1238 w, 1055 w, 749 s, 691 w, 646 w, 632 m, 450 w, 440 vw, 423 w cm^{-1}; UV (Ar, 15 K) λ_{max} 480 br sh, 307, 301 sh, 299, 294, 278, 217 nm. The deep red diazo compound was sublimed at −29 °C (10^{-6} Torr) and codeposited with argon to form a matrix.

Acetophenone Tosylhydrazone: prepared from acetophenone (Eastman) in 80% yield; mp 133–135 °C; ^{1}H NMR ($CDCl_3/Me_2SO$-d_6) δ 2.22 (s, 3 H), 2.42 (s, 3 H), 7.2–8.2 (m, 9 H), 10.4 (s, 1 H); mass spectrum (16 eV) *m/z* (relative intensity) 288 (M$^+$, 16), 133 (100), 132 (28), 105 (10), 104 (96), 92 (30), 91 (12); Anal. ($C_{15}H_{16}N_2O_2S$) C, H, N, S.

1-Phenyldiazoethane (1a): IR (Ar, 15 K) 3115 w, 3095 w, 3068 w, 3035 w, 3005 w, 2980 w, 2950 w, 2925 w, 2900 w, 2865 w, 2050 s, 1603 s, 1580 m, 1505 s, 1487 m, 1470 m, 1452 m, 1440 m, 1387 m, 1348 s, 1338 m, 1317 w, 1272 w, 1268 w, 1190 m, 1080 s, 1031 m, 999 w, 948 w, 888 w, 750 s, 718 w, 691 s, 635 m, 512 w, 482 m cm^{-1}; UV (Ar, 15 K) λ_{max} tail out to 580, 315, 301 sh, 299 sh, 280, 243, 232, 224, 220 nm. The deep red diazo compound was sublimed at −23 °C (10^{-6} Torr) and codeposited with argon to form a matrix.

α,α,α-Trideuterioacetophenone tosylhydrazone: prepared from α,α,α-trideuterioacetophenone (Merck) in 95% yield; mp 141–143 °C dec; ^{1}H NMR ($CDCl_3/Me_2SO$-d_6) δ 2.40 (s, 3 H), 7.2–8.0 (m, 9 H), 10.24 (s, 1 H); mass spectrum (16 eV) *m/z* (relative intensity) 291 (M$^+$, 21), 140 (12), 137 (14), 136 (72), 135 (72), 134 (14), 107 (100), 106 (24); high-resolution mass spectrum calcd for $C_{15}H_{13}D_3N_2O_2S$ 291.1121, found 291.1111; Anal. ($C_{15}H_{13}D_3N_2O_2S$) C, N, S.

2,2,2-Trideuterio-1-phenyldiazoethane (1b): IR (Ar, 15 K) 3110 w, 3088 w, 3063 w, 3035 w, 2210 w, 2138 w, 2128 w, 2050 s, 1601 s, 1575 w, 1503 s, 1380 w, 1455 m, 1351 m, 1341 m, 1332 m, 1268 w, 1189 w, 1098 m, 1080 w, 1059 m, 993 w, 984 w, 889 w, 788 w, 747 s, 701 m, 690 m, 608 m, 508 w, 481 m, cm^{-1}; UV (Ar, 15 K) λ_{max} 312, 302, 298 sh, 280, 245, 235, 228 222 nm. The deep red diazo compound was sublimed at −23 °C (10^{-6} Torr) and codeposited with argon to form a matrix.

1-Diazo-1-phenyl-2-propanone (16): prepared by the method of Regitz;[32] IR (Ar, 15 K) 2098 m, 2070 vs, 1679 s, 1660 w, 1611 w, 1503 m, 1369 s, 1331 m, 1290 m, 1245 s, 1148 w, 1036 m, 1008 w, 908 m, 752 s, 691 m, 618 m, 494 w cm^{-1}. The sample was sublimed at 8 °C (10^{-6} Torr) and codeposited with argon to form a matrix.

[2.2]Paracyclophane (17). [2.2]Paracyclophane (**17**; Aldrich) was purified by sublimation (120 °C, 0.1 Torr) prior to use: IR (Ar, 15 K) 3115 w, 3082 m, 3045 m, 3025 m, 3000 w, 2960 s, 2943 s, 2902 m, 2862 s, 1885 w, 1602 m, 1507 m, 1488 w, 1457 w, 1438 m, 1417 m, 1412 m, 1247 m, 1183 w, 1090 w, 932 m, 892 s, 815 m, 809 s, 765 m, 721 s, 629 s, 509 s cm^{-1}. The sample was sublimed at 95 °C (10^{-6} Torr) and codeposited with argon to form a matrix.

Benzocyclobutene (7a): prepared by thermolysis of *o*-(chloromethyl)toluene.[33] We thank Dr. U. E. Tsou for providing a sample: IR (Ar, 15 K) 3083 m, 3078 m, 3065 w, 3048 w, 3032 w, 3018 w, 2978 m, 2950 s, 2943 s, 2870 w, 2840 w, 1897 w, 1790 w, 1463 s, 1460 s, 1449 w, 1440 m, 1425 m, 1346 w, 1278 m, 1207 m, 1193 m, 1181 w, 1150 w, 1131 w, 1075 w, 1002 m, 929 w, 894 w, 847 w, 780 s, 716 s, 540 w, 410 w, 390 w cm^{-1}; UV (Ar, 15 K) λ_{max} 270, 264, 258 nm. The sample was sublimed at −56 °C (10^{-6} Torr) and codeposited with argon to form a matrix.

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Photochromism of Salicylideneanilines Incorporated in a Langmuir–Blodgett Multilayer

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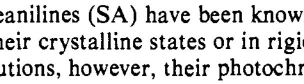
Abstract: The photochromic behavior of an amphiphilic salicylideneaniline derivative, *N*-(4-dodecoxysalicylidene)-4-carboxyaniline (DSA), incorporated in a Langmuir–Blodgett film was studied. DSA formed a stable and condensed monolayer at an air–water interface, and the monolayer was transferred on quartz substrates. The built-up multilayer was found to possess a highly ordered and densely packed structure. Reversible photochromism of a salicylideneaniline group was observed in built-up DSA films on repeating irradiation with UV light. The rate of thermal decoloration was proved to be suppressed by the ordered molecular environment in the multilayer.

N-Salicylideneanilines (SA) have been known to exhibit photochromism in their crystalline states or in rigid solid solutions. In their fluid solutions, however, their photochromic behavior is not observable owing to a fast thermal back-reaction.[2-4] The rates of thermal back-reaction of the photocolored SA species are markedly dependent on the regularity and rigidity of their environment. Therefore, one expects that incorporation of the photochromic SA group in highly ordered and densely packed structures will cause the suppression of its thermal back-reaction.

In the present paper, we propose the use of the Langmuir–Blodgett (LB) technique for the control of the molecular environment of the photochromic SA group. An amphiphile that possesses the SA group in its hydrophobic portion, *N*-(4-dodecoxysalicylidene)-4-carboxyaniline (DSA), was adopted. At first,



DSA

we describe the preparation and characterization of the LB multilayer from the amphiphile and show that the LB films thus obtained possess a well-defined layered structure. Then, the photocoloration and thermal decoloration (reversible photochromism) of the SA group in the multilayer is demonstrated.

Experimental Section

Materials. An amphiphile DSA was prepared by the condensation of 4-dodecoxysalicylaldehyde and 4-carboxyaniline:[5] mp 204 °C. Anal. Calcd from $C_{26}H_{35}N_1O_4$: C, 73.38; H, 8.29; N, 3.29. Found: C, 73.41; H, 8.20; N, 3.23. Arachidic acid was used as received from Aldrich Chemical Co.

Preparation of LB Films. A conventionally available Langmuir trough with a Wilhelmy-type film balance (Kyowa Kaimenkagaku Co., HBM-AP) was used for both surface pressure–area isotherm measurements and LB film preparations. The subphase was pure water from a Milli-Q system (Millipore Ltd.) containing 10^{-3} M $BaCl_2$. Monolayers on the subphases were deposited on quartz substrates at the surface pressure of 20 mN m^{-1} at 15 °C by the usual vertical dipping method.

Optical Absorption and X-ray Diffraction Measurements. The optical absorption spectra of the multilayers were obtained by use of a conventional spectrophotometer (Hitachi 330). Small-angle X-ray diffraction patterns were obtained on the multilayers deposited on polyester films by use of a focused monochromatic beam X-ray diffractometer (Stoe & Cie Co., STADI/P) using Cu Kα radiation at the Center of Advanced Instrumental Analysis, Kyushu University.

Observation of Photochromism. For the photocoloration of the multilayers, 308-nm UV pulses from a XeCl excimer laser (Lambda Physik, EMG-50E) with the intensity of about 2 mJ cm^{-2}/pulse were used. For the detection of the colored species, the time trace of the absorbance at 480 nm was monitored by use of the monochromatized 480-nm light from a halogen lamp and a photomultiplier.

Results and Discussion

DSA formed a stable well-behaved condensed phase at an air–water interface. Figure 1 shows the surface pressure–area

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(1) On leave from Japan Synthetic Rubber Co. Ltd.

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(5) We thank M. Honma (Ajinomoto Co., Inc.) for his helpful advice on the preparation of 4-dodecoxysalicylaldehyde.

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