ethylamine (0.77 mL, 5.58 mmol) in CH_2Cl_2 (10 mL) at ambient temperature. After 3 h the solvent was evaporated under vacuum, and the residue was dissolved in EtOAc (40 mL) and CH_3CN (10 mL). The solution was washed with ice-cold water (4 × 20 mL) and brine. The organic layer was dried ($MgSO_4$), and the solvent was removed to furnish 1.07 g of **3d**[27-29] (91% yield): mp 105 °C dec; TLC HI (300 nm) 99.4%. The material was recrystallized from CH_2Cl_2/*n*-hexane to obtain crystals for X-ray crystallography: mp 108 °C dec; TLC HI (300 nm) 99.8%; MS 236 [(M + H)$^+$].

1*H*-Benzotriazole-1-carboxylic Acid, Benzyl Ester, 3-Oxide (3e). Carbamate **3e** was prepared by the method described above for **3d** in 80% yield.[28] The product was recrystallized from CH_2Cl_2 and *n*-hexane to produce crystals suitable for X-ray determination: mp 139–140 °C (lit.[21] mp 130–131 °C); TLC[28,29] HI (300 nm) 99%; MS, 270 [(M + H)$^+$].

1*H*-Benzotriazole-1-carboxylic Acid, Cinnamyl Ester, 3-Oxide (3f). Compound **3f** was made by the method described in ref 23. The material was recrystallized from toluene: mp 127–129 °C (lit.[23] mp 125 °C); TLC[28,29] HI (260 nm) 99.7%; MS, 252 [(M + H)$^+$ - CO_2], 591 [(2M + 1)$^+$].

1-[(Methylsulfonyl)oxy]benzotriazole (2i). Sulfonate ester **2i** was prepared by the literature method.[9a] Crystals for X-ray analysis were obtained by recrystallization from CH_2Cl_2-*n*-hexane; mp 89–90 °C (lit.[9a] mp 92 °C); MS, 214 [(M + H)$^+$].

1-[(2-Amino-4-thiazolyl)(methoxyimino)acetyl]-1*H*-benzotriazole, 3-Oxide (3k). Preparation of **3k** in 75% yield was conducted by a modified (at ambient temperature instead of 0 °C) procedure described in ref 5: mp ~157 °C. The substance was recrystallized from acetone to produce crystals (mp 163–164 °C) for X-ray crystallography.

Acknowledgment. We gratefully acknowledge Dr. Christopher M. Cimarusti and Dr. R. H. Mueller for helpful discussions. We thank Jeannette Manello for literature searches and our colleagues in the analytical Chemistry Department for their help.

Supplementary Material Available: Tables of spectral data for compounds prepared, positional parameters, bond distances and angles, and temperature factors for **3d**, **3e**, **3f**, **2i**, and **3k** (36 pages). Ordering information is given on any current masthead page.

Another Rearrangement during the Photolysis of Lithium 3-[(*p*-Tolylsulfonyl)amino]-1,2,3-benzotriazin-4-(3*H*)-one

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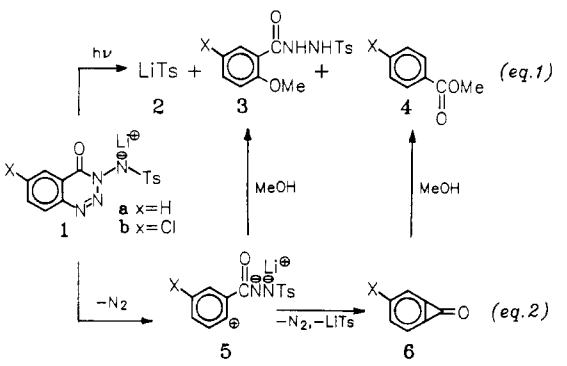
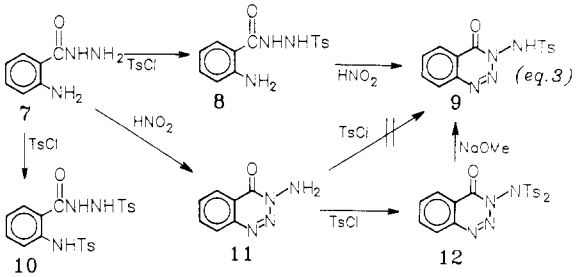
The title compound **1a** in methanol solution has been reported[1] to fragment (eq 1) under UV excitation into nitrogen, lithium *p*-toluenesulfonate [sic],[2] *o*-methoxybenzoic acid tosylhydrazide (**3a**), and methyl benzoate (**4a**). On the basis of the fact that a similar reaction with the 6-chloro derivative **1b** gave only methyl *p*-chlorobenzoate (**4b**) and none of the corresponding meta isomer, a mechanism (eq 2) was proposed involving a rearrangement via an intermediate with the symmetry of a benzocyclopropenone **6**, which underwent regiospecific ring opening with methanol. The unrearranged products **3** were suggested as arising by methanol trapping of the dipolar species **5**. As part of a larger study on the chemistry of aryl-fused cyclopropenones, the above reactions in the **a** series have been reexamined with the result that a revised structure for the compound claimed to be **3a** reveals the presence of another rearrangement during the photolysis of **1a** and casts doubt on the intervention of dipolar species such as **5** in the decompositions of benzo-1,2,3-triazin-4-(3*H*)-ones.



The precursor **9** of the starting material **1a** was prepared according to the cited[1,3] procedure (eq 3) with the two noted[4,5] minor exceptions. Conversion to the lithium salt



1a and irradiation as described[1,3] gave three products that were identified as lithium *p*-toluenesulfinate (**2**), methyl benzoate (**4a**), and a product whose infrared and ^{1}H NMR spectra were similar to those reported[3] for the *o*-methoxy tosylhydrazide **3a** and consistent with that structure.

The mass spectrum and, initially at least, the ^{13}C NMR spectrum of this material also seemed to support structure **3a**, but upon closer inspection, prompted by a melting point discrepancy of 18 °C with the literature,[1,3] the chemical shift of the methoxyl carbon (51.9 ppm) was noted to be more in the range of that of a methyl ester (51.2–52.1 ppm) than of an aryl methyl ether (54.7–57.3 ppm).[10] For these reasons, an authentic sample of **3a** was

(1) Ao, M. S.; Burgess, E. M.; Schauer, A.; Taylor, E. A. *J. Chem. Soc. D* **1969**, 220.

(2) This must be a misprint since the compound actually found[3] is the expected lithium *p*-toluenesulfinate (**2**).

(3) Ao, M. S. Dissertation, Georgia Institute of Technology, 1970; *Diss. Abstr. Int. B* **1971**, *31*, 6490B.

(4) Tosylation of anthranilic acid hydrazide **7** according to the literature procedure[6] may lead to ineffective mixing of the reagents and formation of the ditosyl derivative **10** whose mp and CH analysis (but not spectra, mmp, and acid/base solubility) are very similar to those of the desired monotosylhydrazide **8**. Effective preparations and characterization of **8** and **10** are given in the Experimental Section.

(5) Because the mp of our sample of **9** was 10–12 °C below the literature value,[1,3] an alternative preparation was attempted involving tosylation of the known[7] aminobenzotriazinone **11**. Under a variety of conditions only the disulfonimide[8] **12** was produced, which could, however, be cleaved to the desired sulfonamide **9** as described in the Experimental Section. Similar observations have been made with other *N*-aminotriazine derivatives.[9]

(6) Barlin, G. B. *J. Appl. Chem.* **1962**, *12*, 148.

(7) Adamson, J.; Forster, D. L.; Gilchrist, T. L.; Rees, C. W., *J. Chem. Soc. C* **1971**, 981.

(8) Regarding nomenclature of these species, see footnote 4 In DeChristopher, P. J.; Adamek, J. P.; Lyon, G. D.; Klein, S. A.; Baumgarten, R. J. *J. Org. Chem.* **1974**, *39*, 3525.

(9) Hoffmann, R. W.; Guhn, G.; Preiss, M.; Dittrich, B. *J. Chem. Soc. C* **1969**, 769.

(10) Johnson, L. F.; Jankowski, W. C. *Carbon-13 NMR Spectra*; Wiley: New York, 1972.

(11) Neunhoeffer, H.; Wiley, P. F. *Chemistry of 1,2,3-Triazines and 1,2,4,-Triazines, Tetrazines, and Pentazines*; Wiley: New York, 1978; p 55–60.

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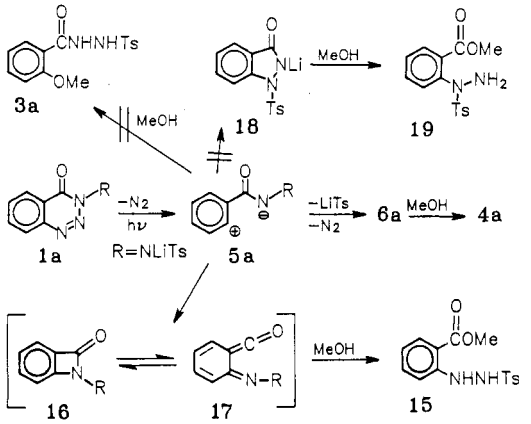
prepared by tosylation of the hydrazide **13** of *o*-methoxybenzoic acid and found to have the expected resonance of 56.2 ppm and other properties quite different from either those reported[1,3] or observed in this work for the photolyses products.

Mechanistic considerations suggested two alternative structures for this photoproduct, both of which are methyl esters in agreement with the above ^{13}C NMR observations. Instead of being trapped by methanol as proposed,[1,3] the dipolar species **5** could cyclize to either benzazetinone **16**, in equilibrium with the imino ketene **17**, or to indazolone **18**. Methanolysis of these intermediates would then lead



to the N-2 and N-1 tosyl derivatives of (*o*-carbomethoxyphenyl)hydrazine, **15** and **19**, respectively. There are ample precedents for the thermal and photo formation or intermediacy of species such as **16** ⇄ **17** from a variety of benzo-1,2,3-triazin-4(3*H*)-ones and of indazolone (**18**; Li, Ts = H) from the aminotriazinone **11** specifically.[13] Recent studies have shown, however, that, at least thermally, this latter reaction also proceeds with rearrangement via **16** ⇄ **17** and not by direct cyclization of the dipolar species **5**.[14] This suggests that **15** is a more likely structure than **19** for the photoproduct, which is also consistent with the presence of two different NH peaks in its ^1H NMR spectrum at 6.44 and 8.97 ppm. This hypothesis was verified by the synthesis of **15** from methyl anthranilate by diazotization, reduction with stannous chloride, and direct tosylation of the intermediate tin salt **14**. The resulting compound proved to be identical with the photoproduct from **1a**.

These results therefore indicate that the photolyses of the lithium salts **1** probably proceed through the same types of rearranged intermediates **16** ⇄ **17** as do other benzotriazinones[11-14] and that the major support for the intermediacy of 1,4-dipolar species such as **5** in this process has been removed. Although the same type of zwitterion has been invoked in the rationalization of the thermochemistry of a variety of benzo-1,2,3-triazin-4(3*H*)-ones,[14,15] a 1,4-diradical analogue of **5**, for which independent evidence in the form of hydrogen abstraction products is available,[16] can also explain the results.[15c]

Experimental Section[17]

Anthranilic Acid Tosylhydrazide (8). To a magnetically stirred solution of anthranilic acid hydrazide (**7**)[6] (15.1 g, 0.1 mol) in 50 mL of pyridine at 0 °C was slowly added a solution of *p*-toluenesulfonyl chloride (19.1 g, 0.1 mol) in 50 mL of pyridine. After addition was complete, the mixture was allowed to warm to room temperature for 2 h and poured into 500 mL of water; the precipitate was collected by filtration and recrystallized from 95% ethanol to give 22.4 g (73%) of the product **8**: mp 196–198 °C dec (lit.[6] mp 197.5–198.5 °C); IR 3420, 3300, 1620, 1560, 1510, 1370, 1310, 1230, 1135 cm^{-1}; ^1H NMR δ 2.35 (s, 3), 6.10 (br s, 2), 6.49 (t, 1, J = 8.0), 6.66 (d, 1, J = 7.6), 7.14 (t, 1, J = 7.0), 7.33 (d, 2, J = 8.2), 7.42 (d, 1, J = 6.8), 7.74 (d, 2, J = 8.2), 9.75 (s, 1), 10.37 (br s, 1); ^{13}C NMR δ 21.0, 112.0, 114.6, 116.1, 127.7, 128.3, 129.1, 132.4, 136.2, 143.0, 149.6, 167.6; MS, m/e 305 (2), 150 (4), 121 (7), 120 (100), 93 (3), 92 (21), 91 (9), 66 (2), 65 (26), 63 (2). Compound **8** dissolved in both concentrated HCl and 10% NaOH and could be regenerated on neutralization. A mixture melting point with **10** was 167–181 °C.

***o*-[(*p*-Tolylsulfonyl)amino]benzoic Acid Tosylhydrazide (10).** To a magnetically stirred solution of the hydrazide **7** (1.0 g, 6.6 mmol) in 15 mL of pyridine at room temperature was added a solution of 2.5 g (13.1 mmol) *p*-toluenesulfonyl chloride in 15 mL of pyridine. The solution was heated to 50 °C for 1.5 h, cooled to room temperature overnight, and poured into 500 mL of water, and the resulting precipitate was recrystallized from 95% ethanol to give 2.55 g (84%) of **10**: mp 197–198 °C (mmp with **8**, 167–181 °C); IR 3230, 3160, 1640, 1580, 1465, 1410, 1380, 1310, 1280, 1260, 1240, 1140, 1065 cm^{-1}; ^1H NMR δ 2.33 (s, 3), 2.39 (s, 3), 7.10 (t, 1, J = 7.6), 7.32–7.42 (m, 6), 7.57–7.61 (m, 3), 7.75 (d, 2, J = 8.2), 10.13 (d, 1, J = 3.4),[18] 10.45 (s, 1), 10.95 (d, 1, J = 3.4);[18] ^{13}C NMR δ 20.9, 21.0, 118.4, 118.8, 123.2, 126.7, 127.7, 128.6, 129.3, 129.8, 133.1, 135.6, 136.0, 138.0, 143.5, 143.9, 167.0; MS, m/e 459 (0.1), 275 (6), 274 (31), 210 (12), 209 (10), 139 (8), 120 (61), 119 (22), 92 (60), 91 (100), 65 (80), 64 (16), 63 (17), 51 (11). Anal. Calcd for $C_{21}H_{21}N_3O_5S_2$: C, 54.89; H, 4.61. Found: C, 54.89; H, 4.87. Compound **10** dissolved in 10% NaOH but not in concentrated HCl and could be recovered on neutralization.

3-[(*p*-Tolylsulfonyl)amino]-1,2,3-benzotriazin-4(3*H*)-one (9).[1,3] To a stirred suspension of 10.0 g (33 mmol) of the tosylhydrazide **8** in 200 mL of water and 15 mL of concentrated HCl at 0 °C was added a solution of 4.5 g $NaNO_2$ in 10 mL of water, and the resulting precipitate was collected after 15 min, washed with water, dried, and recrystallized from benzene to give 8.0 g (77%) of **9**: mp 194–194.5 °C dec (lit.[1,3] mp 204–206 °C); IR 3160, 1670, 1580, 1410, 1340, 1280, 1150, 1040 cm^{-1}; ^1H NMR δ 2.42 (s, 3), 7.43 (d, 2, J = 8.2), 7.74 (d, 2, J = 8.2), 7.97 (t, 1, J = 7.5), 8.14 (t, 1, J = 7.5), 8.23 (d, 1, J = 8.1), 8.26 (d, 1, J = 8.0), 12.12 (br s, 1); ^{13}C NMR δ 21.0, 120.5, 125.3, 127.6, 128.6, 129.6, 133.5, 136.0, 136.5, 142.4, 144.0, 152.9; MS, m/e 105 (15), 104 (13), 91 (32), 77 (100), 75 (51), 69 (17), 65 (39), 63 (17), 57 (14), 55 (16), 51 (41), 50 (62); DCI/MS,[19] m/e 317 (4) (MH^+), 291 (9), 289 (24), 225 (19),

(12) Kobylecki, R. J.; Mckillop, A. *Adv. Heterocycl. Chem.* **1976**, *19*, 215.
(13) Bashir, N.; and Gilchrist, T. L. *J. Chem. Soc., Perkin Trans. 1* **1973**, 868.
(14) Paterson, T. McC.; Smalley, R. K. *J. Chem. Res. Synop.* **1980**, 246.
(15) (a) Alkhader, M. H. and Smalley, R. K. *J. Chem. Res., Synop.* **1982**, 295. (b) Paterson, T. McC.; Smalley, R. K.; Suschitzky, H.; Barker, A. J. *J. Chem. Soc., Perkin Trans. 1* **1980**, 633. (c) Barker, A. J.; Paterson, T. McC.; Smalley, R. K., Suschitzky, H. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2203. (d) Paterson, T. McC.; Smalley, R. K.; Suschitzky, H. *Synthesis* **1975**, 187, 709. (e) Crabtree, H. E.; Smalley, R. K.; Suschitzky, H. *J. Chem. Soc. C* **1968**, 2730.
(16) Hey, D. H.; Rees, C. W.; Todd, A. R. *J. Chem. Soc. C* **1968**, 1028.

(17) Unless otherwise noted, the following instrumentation, procedures, and conventions were used. Mass spectra were obtained in EI mode on a Finnegan 1020 OWA instrument (70 eV) and are reported as m/e (relative intensity) for selected peaks above m/e 45 including all those with relative intensity > 10. GC analyses were performed on the same instrument with a DB-1 30 m × 0.25 mm capillary column. NMR spectra were taken in DMSO-d_6 on a Varian XL-300 instrument at 300 MHz (^1H) or 75 MHz (^{13}C). Chemical shifts are referred to TMS on the δ scale, and observed multiplicities are reported with apparent coupling constants to ±0.3 Hz. Infrared spectra were taken as KBr disks on a Perkin-Elmer Model 710B spectrophotometer and are reported as ±10 above and ±5 below 2000 cm^{-1}. A Perkin-Elmer 552A spectrophotometer was used to measure UV spectra in nanometers in methanol. Elemental analyses were carried out by M-H-W Laboratories of Phoenix, AZ, and uncorrected melting points were measured in open capillary tubes in a Mel-Temp apparatus. TLC was performed on precoated sheets of silica gel 60 without indicator (EM Catalogue No. 5506) and visualized with iodine vapor. Methanol and benzene were dried over 3A molecular sieves, and *p*-toluenesulfonyl chloride was recrystallized from low-boiling petroleum ether before use. Pyridine was dried over KOH.
(18) These signals collapsed to broad singlets if the DMSO-d_6 was even slightly wet.
(19) DCI mass spectra were obtained through the courtesy of Dr. Gunther Eigendorf of the University of British Columbia on a NERMAG R10-10-C instrument with methane as the reagent gas. Selected peaks above m/e 70 including all those with relative intensity > 10 are reported.

185 (14), 172 (24), 157 (100), 156 (13), 155 (66), 139 (85), 135 (53), 134 (38), 133 (25), 123 (12), 121 (11), 107 (12), 105 (76), 104 (12), 93 (27), 92 (48), 91 (61), 77 (30). Anal. Calcd for $C_{14}H_{12}N_4SO_3$: C, 53.14; H, 3.83; N, 17.72. Found: C; 53.11, H, 3.72; N, 17.86. Compound **9** dissolved in 10% NaOH or $NaHCO_3$ but could be recovered on neutralization only from the latter.

3-[*N*,*N*-Bis(*p*-tolylsulfonyl)amino]-1,2,3-benzotriazin-4-(3*H*)-one (12). A solution of 0.86 g (5.3 mmol) of the aminotriazinone **11**[7] and 2.03 g (10.6 mmol) of *p*-toluenesulfonyl chloride in 10 mL of pyridine was stirred for 3 h at 25 °C and added to 100 mL of H_2O, and the resulting 2.66 g (107%) of crude **12** (mp 218–221 °C dec) was collected. Recrystallization from toluene gave 1.70 g (68%) of an analytical sample: mp 236–237 °C dec; IR 3040 (w), 1715, 1580, 1380 (Ts_2N),[9] 1280, 1160, 1065, 975, 865, 635 cm^{-1}; ^1H NMR δ 2.48 (s, 6), 7.51 (d, 4, J = 8.3), 7.84 (d, 4, J = 8.4), 8.07 (t, 1, J = 8.6), 8.25 (t, 1, J = 8.2), 8.36 (d, 2, J= 8.4); ^{13}C NMR δ 21.4, 120.2, 125.9, 128.9, 129.4, 129.9, 134.2, 134.6, 137.1, 141.9, 146.5, 152.9; MS, m/e 470 (0.01), 315 (1), 155 (16), 140 (12), 139 (98), 105 (12), 104 (100), 92 (11), 91 (72), 77 (12), 76 (78), 65 (34), 50 (25); DCI/MS,[19] m/e 471 (17, MH^+), 351 (7), 275 (10), 259 (9), 157 (18), 155 (71), 140 (10), 139 (100), 133 (13), 93 (10). Anal. Calcd for $C_{21}H_{18}N_4S_2O_5$: C, 53.61; H, 3.86; N, 11.91. Found: C, 53.78; H, 3.91; N, 11.83.

Cleavage of 12 to 9. To a stirred suspension of 700 mg (1.49 mmol) of the disulfonimide **12** in 100 mL of dry benzene and 50 mL of dry methanol at 40 °C under nitrogen was added over a 1-h period from an addition funnel 50 mL of a dry methanol solution of sodium methoxide prepared from 34.2 mg (1.49 g-atom) of sodium. The resulting yellow solution was stirred for another 20 min, the solvent was removed on a Rotovap, and the residue was partially dissolved in 100 mL of water and stirred for 30 min. The remaining solid was removed by filtration, the cooled (0 °C) filtrate was acidified with 20% H_2SO_4, and the precipitate of the monotosyl derivative **9** was collected (290 mg, 62%) and recrystallized from benzene to give material whose mp (194–195 °C dec) and ^1H and ^{13}C NMR spectra were identical with the sample of **9** prepared as described above.

Photolysis of 3-Lithio[(*p*-tolylsulfonyl)amino]-1,2,3-benzotriazin-4(3*H*)-one (1a).[3] To a vigorously stirred suspension of 2.0 g (5.7 mmol) of the monotosylated aminotriazinone **9** in 250 mL of dry methanol under a nitrogen atmosphere was added 38 mg (5.7 mmol) of lithium hydride, and the resulting yellow solution [λ_{max} 320, log ϵ 4.48 (lit.[1,3] λ_{max} 320)] was irradiated with a 550-W[20] Hanovia high-pressure mercury vapor lamp[21] for 2 h with a Pyrex filter and a nitrogen sweep in an apparatus similar to that described in ref 3. Evaporation of the solvent on a Rotovap with no particular precautions to retain volatile products left a residue, which on TLC (10% ethanol in benzene) showed three spots with R_f 0.00, 0.23, and 0.56 (lit.[3] R_f 0.00, 0.26, and 0.55). Trituration of the residue with benzene, filtration, and then addition of hexane to the filtrate separated a total of 600 mg (59%) of the product with the lowest R_f, lithium *p*-toluenesulfinate (**2**): ^1H NMR δ 2.29 (s, 3), 7.15 (d, 2, J = 7.9), 7.43 (d, 2, J = 7.9); ^{13}C NMR δ 20.8, 124.4, 128.1, 136.9, 156.1.

Upon cooling of the above filtrate to 0 °C, 80 mg (4%) of the product with R_f 0.23 crystallized and was collected by filtration: mp 162–163 °C dec (lit.[3] mp 179–180 °C dec); IR 3270, 3210, 1660, 1600, 1570, 1490, 1430, 1325, 1250, 1150, 1080, 800, 740, 705 cm^{-1} [lit.[3] IR ($CHCl_3$) 3318, 1692, 1338, 1260, 1080 cm^{-1}]; ^1H NMR δ ($CDCl_3$), 2.42 (s, 3), 3.82 (s, 3), 6.44 (br s, 1), 6.78 (t, 1, J = 7.4), 7.32 (m, 4), 7.78 (d, 2, J = 8.4), 7.85 (d, 1 J = 7.8), 8.97 (br s, 1) [lit.[3] ^1H NMR ($CDCl_3$, 60 MHz), δ 2.42 (s, 3), 3.83 (s, 3), 6.12–7.00 (br, 2), 7.14–8.08 (m, 8)]; ^{13}C NMR ($CDCl_3$) δ 21.7, 51.9, 111.3, 113.8, 118.6, 128.2, 129.8, 130.9, 134.3, 134.6, 144.6, 150.2, 168.5; MS, m/e 320 (2), 166 (13), 165 (100), 135 (5), 134 (13), 133 (92), 105 (82), 104 (10), 92 (13), 91 (30), 78 (14), 77 (58), 76 (16), 65 (17), 51 (16) (lit.[3] MS, m/e 320).

The filtrate from this second filtration contained the component with R_f 0.56, which was identified as methyl benzoate (**4a**) by comparison of its GC retention time (2.36 min at 150 °C) and MS with those of an authentic sample: MS, m/e 137 (13), 136 (66), 135 (10), 106 (12), 105 (100), 92 (12), 91 (14), 78 (11), 77 (73), 76 (16), 74 (20), 51 (69), 50 (44). The yield of **4a** was calculated to be 15% by comparing the NMR integration of the methyl protons (3.70 ppm) with those of a known added quantity of *p*-nitrotoluene (2.15 ppm).

***o*-Methoxybenzoic Acid Tosylhydrazide (3a).** A solution of *p*-toluenesulfonyl chloride (860 mg, 4.5 mmol) in 5 mL of pyridine was slowly added to a stirred pyridine solution (10 mL) of 750 mg (4.5 mmol) of the known hydrazide **13**, mp 180–181 °C (lit.[22] mp 180–181 °C) prepared from methyl *o*-methoxybenzoate. The mixture was allowed to react at room temperature for 4 h and poured in 50 mL of water, and the precipitate was collected and recrystallized from 95% ethanol to give 820 mg (57%) of the product **3a**: mp 143–143.5 °C; IR 3330, 3120, 1645, 1600, 1480, 1410, 1340, 1300, 1230, 1160, 1110, 1010 cm^{-1}; ^1H NMR δ 2.37 (s, 3), 4.01 (s, 3), 7.00 (m, 2), 7.22 (d, 2, J = 9.0), 7.47 (t, 1 J = 7.4), 7.79 (m, 4), 9.61 (br s, 1); ^{13}C NMR δ 21.6, 56.2, 111.3, 118.1, 121.2, 128.3, 129.3, 131.9, 133.3, 133.8, 144.4, 157.2, 163.6; MS, m/e 320 (2), 136 (18), 135 (100), 105 (2), 92 (20), 91 (16), 78 (14), 77 (41), 76 (4), 65 (13), 51 (7). Anal. Calcd for $C_{15}H_{16}N_2O_4S$: C: 56.24; H, 5.03. Found: C, 56.25; H, 5.09.

1-(*o*-Carbomethoxyphenyl)-2-tosylhydrazine (15). To a solution of 2.00 g (13 mmol) of methyl anthranilate in 21 mL of concentrated HCl at 0 °C was added a cold solution of 970 mg (14.1 mmol) of $NaNO_2$ in 12 mL of water. The resulting solution of the diazonium salt at 0 °C was added in one portion to a solution of $SnCl_2 \cdot 2H_2O$ (10.00 g, 44.3 mmol) in 20 mL of concentrated HCl, and the resulting mixture was stirred at room temperature for 15 min. The white precipitate was collected and washed with cold concentrated HCl to give 5.3 g (69%) of the tin salt **14**: mp 163–165 °C dec; ^1H NMR δ 3.83 (s, 3), 6.84 (t, 1, J = 7.3), 7.22 (d, 1, J = 8.5), 7.54 (t, 1, J = 7.8), 7.85 (d, 1, J = 7.0), 8.68 (br s, 1), the NH_3^+ peak is probably part of the concentration dependent, broad, residual water peak between 3.6–4.2; ^{13}C NMR δ 51.9, 110.7, 112.8, 117.7, 130.8, 134.5, 149.9, 167.3; MS, m/e 166 (15), 134 (52), 105 (80), 78 (15), 77 (100), 52 (12), 51 (23), 50 (11), plus four tin isotope clusters whose most intense peaks are 260 (0.9) ($SnCl_4$), 225 (9) ($SnCl_3$), 155 (3) (SnCl), and 120 (4) (Sn).

A solution of 900 mg of *p*-toluenesulfonyl chloride in 10 mL of pyridine was added to a stirred solution of 1.00 g of the tin salt **14** in 10 mL of pyridine, and the mixture was allowed to stir at room temperature for 16 h. The precipitate that formed after the reaction was added to 80 mL of water was collected and recrystallized from benzene to give 400 mg (74%) of **15** whose melting point and spectral properties were identical with those of the photoproduct with R_f 0.23. Anal. Calcd for $C_{15}H_{16}N_2O_4S$: C, 56.24; H, 5.03. Found: C, 56.17; H, 4.98.

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(20) This coincides with ref 3 rather than with the 450-W lamp reported in ref 1.

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Direct α-Mesyloxylation of Ketones and β-Dicarbonyl Compounds with [Hydroxy(mesyloxy)iodo]benzene

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In view of the current interest in α-keto mesylates (**1**, R′ = Me) as progenitors of α-keto carbocations[1] and in the potential utility of α-(sulfonyloxy) ketones in organic

(1) Creary, X. *Acc. Chem. Res.* **1985**, *18*, 3 and references therein.

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