as 0.43 g of a pale yellow solid; recrystallization from chloroform gave white crystalline material, mp 125.5–126.5 °C. Further elution gave 1.26 g of diketone **2**, also pale yellow, also purified to a white crystalline solid by chloroform recrystallization, mp 137–138 °C. The structure of the latter was also confirmed by X-ray diffraction.[11]

For **1**: NMR ($CDCl_3$, 360 MHz) δ 1.48 (dd, J = 4.2, 11.3 Hz, 1 H), 1.60 (br d, J = 11.3 Hz, 1 H), 1.90 (dd, J = 4.2, 17.8 Hz, 1 H), 2.20 (dd, J = 4.5, 17.8 Hz, 1 H), 2.62 (d, J = 5.2 Hz, 1 H), 2.65 (br s, 1 H), 2.90 (d, J = 4.5 Hz, 1 H), 3.10 (dd, J = 3.0, 5.2 Hz, 1 H), 7.38 (m, 3 H), 7.60 (d, J = 3.0 Hz 1 H), 7.72 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 30.3 (t), 37.5 (d), 41.7 (d), 42.8 (t), 51.3 (d), 53.0 (d), 126.9 (d, 2 C), 128.3 (d, 2 C), 128.8 (d), 130.5 (s), 146.9 (s), 156.0 (d), 206.1 (s), 214.6 (s); IR ($CHCl_3$) 1700, 1740 cm^{-1}.

For **2**: NMR ($CDCl_3$, 360 MHz) δ 1.55 (br s, 2 H), 2.02 (br d, J = 17.8 Hz, 1 H), 2.25 (dd, J = 4.5, 17.8 Hz, 1 H), 2.66 (d, J = 5.3 Hz, 1 H), 2.72 (d, J = 4.5 Hz, 1 H), 2.89 (br s, 1 H), 3.05 (dd, J = 3.0, 5.3 Hz, 1 H), 7.40 (m, 3 H), 7.72 (m, 2 H), 7.75 (d, J = 3.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 30.2 (t), 37.1 (d), 43.4 (t), 46.3 (d), 47.7 (d), 51.5 (d), 126.9 (d, 2C), 128.3 (d, 2C), 128.8 (d), 130.5 (s), 147.3 (s), 158.6 (d), 205.0 (s), 213.3 (s); IR ($CHCl_3$) 1700, 1740 cm^{-1}; high-resolution mass spectrum, calcd for $C_{16}H_{14}O_2$ 238.0944, found 238.0972. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.58; H, 5.93.

X-ray Crystal-Structure Determination for 1. Crystals **1** were grown from chloroform. Data were collected at 85 K on a Syntex $P2_1$ diffractometer equipped with a locally built low-temperature apparatus. No loss in intensity of two standard reflections was observed. Computer programs were those of SHELXTL, version 3. Scattering factors were from common sources.[12] Absorption corrections were not applied. Crystal data: rectangular parallelpiped, dimensions 0.25 × 0.25 × 0.25 mm, orthorhombic, space group $P2_12_12_1$ determined by a series of axial photographs and preliminary fast scans showing the conditions $00l$, $l = 2n$, $0k0$, $k = 2n$, $h00$, $h = 2n$. M_r = 238.29, a = 9.373 (3), b = 10.243 (3), and c = 12.418 (4) Å, cell vol = 1192.2 (7) Å^3, Z = 4, d_{calc} (85 K) = 1.33 g cm^{-3}, abs coeff μ = 0.81 cm^{-1}, Mo Kα radiation (λ 0.71069 Å), graphite monochromator. Intensity data were colleted to $2\theta_{max}$ of 55° in the quadrant $+h,+k,+l$ by using an ω scan of 0.9° width at 60° min^{-1} [13] and an 0.6° offset for background counts. A total of 1588 unique reflections were collected of which 171 were suppressed as unobserved ($I < 2\sigma(I)$), leaving 1417 for solution and refinement of the structure. The structure was solved by direct methods. No difficulty was encountered in the location of all the atoms, including hydrogen atoms. In the final cycles of refinement hydrogen atoms were tied to bonded carbons. Isotropic thermal parameters were assigned to all atoms. The final difference map showed no significant features. A weighting scheme of $w = 1/(\sigma^2(F) + 0.05F^2)$ was used. Final agreement factors were R = 0.076 and R_w = 0.092 (73 parameters). The final structure is illustrated in the supplementary materials.

Pauson–Khand Cycloaddition of 1-Methyl-5-norbornen-2-ol with Propyne. Preparation of Keto Alcohols 9 and 10 and Oxidation to Diketones 7 and 8. Dicobalt octacarbonyl (0.58 g, 1.70 mmol) was stirred in 40 mL of dry 2,2,4-trimethylpentane under 1 atm of propyne gas for 3 h. A solution of 0.74 g (5.97 mmol) of 1-methyl-5-norbornen-2-ol in 3 mL of 2,2,4-trimethylpentane was added, and the mixture was stirred at 70 °C under an atmosphere consisting of comparable amounts of CO and propyne for 48 h. After cooling, the mixture was precoated onto silica gel and subjected to column chromatography. Hexane elution removed unreacted cobalt complexes and alkyne trimerization products. Elution with ether afforded a 59:41 mixture of crude keto alcohols (by ^1H NMR), which, after further purification by MPLC (ether), provided 0.76 g (59% yield) of a 59:41 mixture of keto alcohols as a colorless oil. From a portion of this mixture it proved to be possible to separate small quantities of the pure minor isomer (later identified as **10**) by MPLC, allowing complete spectroscopic characterization of both **9** and **10** (see supplementary materials).

Identification of the major and minor keto alcohols from the above reaction as **9** and **10**, respectively, was achieved as follows. Pyridinium chlorochromate (0.10 g, 0.48 mmol) and sodium acetate (0.10 g) were added to a solution of keto alcohol mixture (0.046 g, 0.24 mmol) in 25 mL of dichloromethane. After being stirred under N_2 for 7 h, the mixture was diluted with ether and filtered through a short silica gel column. Concentration yielded 0.044 g (96% yield) of a 59:41 mixture of diketones **7** and **8**, identical spectroscopically with the previously isolated and identified products of reaction 4 (see Table I and the supplementary materials).

Acknowledgment. We are greatful to Mark Knudsen for recording some of the NMR spectra. We thank the National Institutes of Health (Grant GM26294) for financial support of this research.

Registry No. **1**, 111616-22-9; **2**, 111616-23-0; **3**, 111616-24-1; **4**, 111616-25-2; **5**, 111616-26-3; **6**, 111616-27-4; **7**, 111616-28-5; **8**, 111616-29-6; **9**, 111616-30-9; **10**, 111616-31-0; PhC≡CH, 536-74-3; MeC≡CH, 74-99-7; 5-norbornen-2-one, 694-98-4; *endo*-5-norbornen-2-ol, 694-97-3; 1-methyl-5-norbornen-2-one, 19740-13-7; *endo*-1-methyl-5-norbornen-2-ol, 29750-14-9.

Supplementary Material Available: Spectroscopic and analytical data for compounds **3–10**, tables of atomic coordinates, thermal parameters, bond lengths, and bond angles for **1**, and a figure illustrating computer-generated representation of **1** (6 pages). Ordering information is given on any current masthead page.

(11) Procedures similar to those used for **1**. Space group $P2_1/c$; a = 10.227 (5), b = 11.092 (10), and c = 10.676 (5) Å, β = 106.41 (3), cell vol = 1161.64 Å^3, Z = 4. A total of 2804 unique reflections were collected of which 537 were suppressed as unobserved, leaving 2267 for solution and refinement of the structure. Final agreement factor was R = 0.070.

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The Structures of Alkoxycarbonyl, Acyl, and Sulfonate Derivatives of 1-Hydroxybenzotriazole: N- vs O-Substitution

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1-Hydroxybenzotriazole (**1**) is widely used as an activating group for construction of an amide bond during the synthesis of peptides[1-3] and β-lactam antibiotics.[4-7] Active esters of **1** also have been employed in the formation of a C–C bond during the preparation of the antibiotic malonomicin.[8] There has been intensive investigation of

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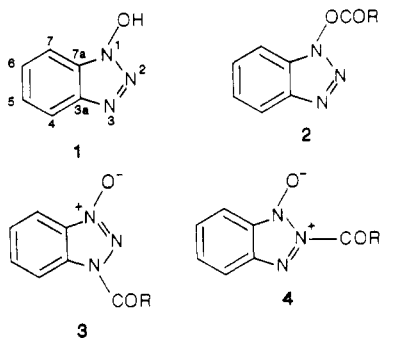
0022-3263/88/1953-0205$01.50/0

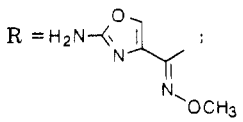
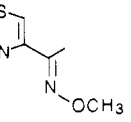
Table I. X-ray Data

	3d	3e	3f	2i	3k
a, Å	8.322 (4)	15.030 (1)	10.377 (3)	20.394 (4)	10.833 (2)
b, Å	6.846 (2)	15.154 (6)	5.857 (1)	5.733 (1)	15.716 (3)
c, Å	10.548 (4)	5.553 (3)	23.669 (5)	16.087 (5)	8.144 (1)
α, deg	90	90	90	90	90
β, deg	103.64 (3)	90	93.12 (2)	99.01 (3)	91.78 (1)
γ, deg	90	90	90	90	90
V, Å^3	584 (1)	1265 (1)	1436 (1)	1858 (1)	1385.9 (7)
space group	$P2_1/m$	$P2_12_12_1$	$P2_1/c$	$C2/c$	$P2_1/n$
D_{obsd}			1.35		1.51
D_{calcd}	1.34	1.41	1.37	1.525	1.525
Z	2	4	4	8	4
(2θ)max	140	140	140	140	115
NREF[a]	1182	1401	2677	1676	1270
NOBS[b]	682	991	1985	1321	991
NVAR[c]	95	182	200	128	200
R	0.047	0.056	0.052	0.043	0.040
R_w	0.058	0.068	0.064	0.054	0.044

[a] Total number of symmetry independent measured reflections. [b] Total number of "observed" reflections with $I > 3\sigma(I)$ used in refinements. [c] Number of variables in least-squares refinements.

Chart I[a]



[a] **a**, R = $CH_3CH{=}CHCH{=}CH$; **b**, R = $(CH_3SCH_2)(Ph_3CNH)CH$; **c**, R = Ph; **d**, R = $(CH_3)_3CO$; **e**, R = $PhCH_2O$; **f**, R = $PhCH{=}CHCH_2O$; **g**, R = CH_3O; **h**, R = PhO; **i**, RCO = CH_3SO_2; **j**, R =  ; **k**, R = 

the structure and reactivity of the derivatives of 1[9-18] (Chart I).

Rinehart[14] reported the rearrangement of the unsaturated acyl benzotriazole **2a** to **3a**. The structure of **3a** was confirmed by X-ray crystallography. Davies[15] has recently proposed the intermediacy of analogues of **4** to explain enhanced racemization rates of certain amino acid esters of **1** relative to the esters derived from *N*-hydroxysuccinimide. The structure of 3-(N^{α}-tritylmethionyl)benzotriazole 1-oxide (**3b**) has been confirmed by X-ray crystallography.[16] 1-(Benzoyloxy)benzotriazole (**2c**) was prepared by McCarthy and its structure was proven by X-ray determination.[18] The isomeric N(3)-acylated compound **3c** is so far unknown.

Recently there has been increased interest in the reactive derivatives of **1** for use in the preparation of protected amine[19] or hydroxyl functions[10] and for the synthesis of active amides **3j**.[6] This report is concerned with the structures of alkoxycarbonyl, acyl, and sulfonate derivatives of **1**.

The *tert*-butoxycarbonyl (Boc), benzyloxycarbonyl (Z), and cinnamyloxycarbonyl (Coc) groups are generally employed for the temporary protection of the amine function of amino acids.[1-3,22] The corresponding derivatives of **1** have been developed as efficient protecting group transfer reagents. These compounds are stable, crystalline solids and have been assigned the carbonate structures **2d**,[19,20] **2e**,[19,21] and **2f**[23] respectively. However, on the basis of ^{13}C NMR studies, the related methoxycarbonyl- and phenoxycarbonyl-substituted benzotriazoles have been formulated as the corresponding carbamates **3g** and **3h**.[18,24] During work on the synthesis of β-lactam antibiotics, we encountered what appeared to be either **2d** or **3d** as a minor byproduct of an amidation reaction. In view of the uncertainity about these structures, we have carried out single-crystal X-ray analysis of **3d-f,k** and **2i**.

Compound **3d** was prepared for this purpose by reaction of di-*tert*-butyl dicarbonate with **1** in the presence of Et_3N in CH_2Cl_2. The IR and ^1H NMR spectra of this substance were identical with the spectra of a sample prepared by the literature method.[25] The homogeneity index (HI) of

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3d at 300 nm was 99.4%.[26-29] The UV spectrum displayed bands at wavelengths >300 nm [λ_{max} 334 (ϵ 9500), 321 (11 625), and 310 nm (8000)], which suggested the *N*-oxide structure for the molecule.[14] The ^{13}C NMR spectrum showed the carbonyl carbon at 145.7 ppm. This value is compatible with the assigned structure **3d** by analogy with the data reported for related compounds.[24] The carbonyl stretching in the IR spectrum was phase dependent; ν_{max} (in KBr) 1749 and (in $CHCl_3$) 1759 cm^{-1}. The structure of carbamate **3d** was firmly established by a single-crystal X-ray determination (Table I).

The benzyloxycarbonyl derivative **3e** was made by a modified literature procedure,[20] and cinnamyloxycarbonyl derivative **3f** was prepared by the reported method.[23] IR, UV, and ^{13}C NMR spectra of **3e** and **3f** were closely related to the corresponding spectra of **3d**. It proved possible to prepare crystals of **3e** and **3f** suitable for X-ray analyses (Table I).

Wheeler[6] has recently described the use of 1-[(methylsulfonyl)oxy]benzotriazole **2i** for the preparation of active amide **3j**. Compound **2i** was prepared by the literature method.[9a] The UV spectrum of **2i** was transparent in the longer wavelength region (~320 nm), where *N*-oxide structures exhibit characteristic absorption. In the ^{13}C NMR the signal for C(3a) at 143.1 ppm is also consistent with O-substitution.[24] The structure of **2i** has been confirmed by single-crystal X-ray analysis (Table I).

During our work on β-lactam antibiotics we had prepared the related active amide **3k** by the reaction of **1** with α-(methoxyimino)aminothiazoleacetic acid in the presence of DCC in DMF at ambient temperature.[7] When this reaction was performed following a patent procedure[5] (DCC–DMF, at 0 °C), the isomeric active ester **2k** was the predominant product. The IR spectra of **2k** (KBr, carbonyl at ~1810 cm^{-1}) and **3k** (KBr, carbonyl at 1735 cm^{-1}) clearly indicate the active ester and amide linkages, respectively.

Although the sterically crowded structure **3k** is more favorable than **4k** for electronic reasons,[11] a distinction between these two possibilities could not be made on spectral grounds. X-ray analysis revealed **3k** to be the correct formulation for this substance (Table I).[26]

The geometry of the $^{-}O^{+}N_1{=}N_2N_3C{=}O$ group in the carbamates **3d–f** and the acyl derivative **3k** (an iminalogous carbamate) is the same as previously reported for the acyl derivatives **3a**[14] and **3b**.[16] The torsional angle N_2-$N_3C{=}O$ deviates no more than 8° from 180° in any of these crystal structures. The geometry of **2i** is consistent with that reported for **2c**.[18] Torsional angles N–O–S–C and N–N–O–S in **2i** are −83° and 92°, respectively.

In conclusion, the previously proposed carbonate structures of Boc,[19,20] Z,[19,21] and Coc[23] derivatives of 1-hydroxybenzotriazole (**1**) should be revised to the carbamate structures **3d**, **3e**, and **3f**, respectively.[27,29] It should be noted that the (9-fluorenylmethyl)oxycarbonyl[30] and 2-(trimethylsilyl)ethoxycarbonyl derivatives[31] of **1** and the alkoxycarbonyl derivatives of 6-(trifluoromethyl)benzotriazole,[32] have been reported to be carbonates. However, these structural assignments have not been proven by X-ray analyses, and these compounds could well posess the carbamate structures.

The structure of 1-[(methylsulfonyl)oxy]benzotriazole (**2i**) was confirmed. Formulation **3k** for the active amide derived from α-(methoxyimino)aminothiazoleacetic acid and **1** was unambiguously established.[29-33]

Experimental Section

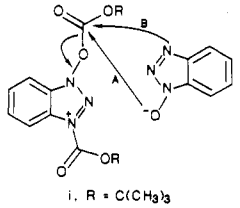
Infrared spectra were recorded on a Mattson Sirius 100 FT spectrometer. ^{13}C NMR spectra (67 MHz) were measured on a JEOL FX-270 spectrometer. UV spectra were measured on Shimadzu 260 spectrophotometer. Mass spectra (CI) were recorded on a Finnigan TSQ-4600 spectrometer. For homogeneity index (HI)[29] values the developed TLC plates were evaluated spectrodensitometrically by using a Shimadzu CS-920 densitometer.

X-ray Determinations. Crystal data and some details of the structure refinements are given in Table I. The unit cell parameters were obtained through a least-squares analysis of the experimental diffractometer settings of 15 high angle reflections. Crystal densities were measured by flotation in carbon tetrachloride/hexane mixtures. Intensities were measured diffractometrically by using Cu Kα radiation (λ = 1.5418 Å) at 23 °C with the θ–2θ variable scan technique and were corrected only for Lorentz polarization factors. Background counts were collected at the extremes of the scan for half of the time of the scan. Two standard reflections were measured every 50 reflections with no decrease of intensity during the course of the measurements.

Structures were solved by direct methods and refined on the basis of "observed" reflections with $I \geq 3\sigma$. All calculations utilized the SDP program[33] package with minor local modifications. The least-squares weights $w = \sigma^{-2}(F_o)$ were calculated with the assumption that $\sigma^{-2}(I) = \epsilon^2 + (pI)^2$, where ϵ is the statistical counting error and p = 0.02–0.04. The function minimized in the least-squares refinements is $\sum w(|F_o| - |F_c|)^2$. R is defined as $\sum||F_o| - |F_c||/\sum F_o$, while R_w is defined as $[\sum w(F_o - |F_c|)^2/\sum wF_o^2]^{1/2}$. Most hydrogen positions were observed on difference maps during the latter stages of refinement. The scattering of all the hydrogens was taken into account in the terminal stages of refinement. Final difference maps contained no significant features. Tables of atomic coordinates, thermal parameters, bond distances and bond angles are included as supplementary material.

1*H*-Benzotriazole-1-carboxylic Acid, 1,1-Dimethylethyl Ester, 3-Oxide (3d). A solution of di-*tert*-butyl dicarbonate (1.09 g, 5 mmol) in CH_2Cl_2 (5 mL) was added to a solution of 1-hydroxybenzotriazole (**1**, HOBt) (0.675 g, 5 mmol) and tri-

(26) The predominant formation of O-acylation product **2k** at low temperature (below 0 °C) suggests this to be the kinetic product. Rearrangement of **2k** (in DMF solution) to the thermodynamic product **3k** occurs at ambient temperature. It is possible that carbonates **2d–f** also are formed as kinetic products, but are too reactive toward rearrangement to the corresponding carbamates **3d–f**. The exact mechanism of this rearrangement is not certain. It is possible that the ion pair i (e.g., in case of *tert*-butoxycarbonyl substitution) is involved in the isomerization. Collapse of i via path A would generate a 1:1 mixture of **2d** and **3d**, whereas the alternate route B would create two molecules of **3d**.



i, R = $C(CH_3)_3$

(27) TLC:[28] silica gel, acetone/dichloromethane (1:9); the chromatogram was visualized by UV light and Rydon's spray. R_fs: **2d** (presumed), 0.75; **3d**, 0.47; HOBt (**1**) 0.0.

(28) TLC of the reaction mixture before work up indicated the presence of a product of higher R_f (0.75 in ref 27). This material is most likely the isomer **2d**, which undergoes decomposition and/or isomerization during workup. Presumed **2d** was detected in a trace amount (HI, 300 nm, 0.3%)[29] in the isolated solid **3d**. Similar phenomena have been observed during the preparation of **3e** and **3f**.

(29) Homogeneity index (HI) expresses the relative percentage of the compound under investigation as compared to other components. In the present case HI values were determined by densitometric scanning of TLC chromatograms at the specified wavelengths and are not corrected for differences in extinction coefficients. Due to the instability of the derivatives of **1** on silica gel plates, the homogeneity indices were determined by TLC on EM HP-TLC plates CN-254.

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(32) Takeda, K.; Tsuboyama, K.; Hoshino, M.; Kishino, M.; Ogura, H. *Synthesis* **1987**, 557–560.

(33) "SDP, Structure Determination Package"; A. Frenz & Associates, College Station, TX 77840.

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.

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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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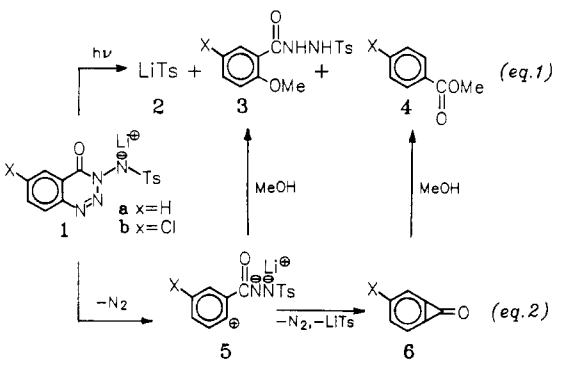
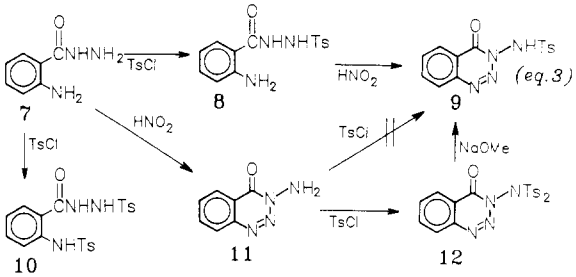
The title compound **1a** in methanol solution has been reported[1] to fragment (eq 1) under UV excitation into nitrogen, lithium *p*-toluenesulfonate [sic],[2] *o*-methoxybenzoic acid tosylhydrazide (**3a**), and methyl benzoate (**4a**). On the basis of the fact that a similar reaction with the 6-chloro 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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