cold window and quartz outer windows were used in the UV-vis experiments. A nickel-plated, polished copper block was used to deposit matrices for obtaining luminescence spectra. The temperature of the matrix was controlled by an Air Products APD-E controller (gold vs Chromel thermocouple) or by an Lake Shore DRC 81C controller (silicon diode sensor) interfaced to a HP86 microcomputer.

Argon (Messer Griesheim, 99.9995%), oxygen (Messer Griesheim, 99.998%), [$^{18}O_2$]oxygen (Ventron, 99.8% isotopic purity), and very volatile organic compounds (**12**, **15**) were mixed in a gas handling system by standard manometric techniques. The ratio argon/oxygen/compound in typical experiments was 1000/10/1. Less volatile compounds were directly sublimed on the cold window and simultaneously a large excess of argon/oxygen was deposited. The degree of matrix-isolation was monitored by observing the line width of the IR bands as a function of the argon/compound ratio. Matrices were generally deposited at 28-30 K (ca. 15 mmol/h) to obtain optically clear matrices. Deposition at lower temperatures gave more highly scattering matrices but otherwise the same results.

Irradiations were carried out by using the same lamps as described for obtaining luminescence spectra or by an Osram HBO 500 W/2 mercury high pressure arc lamp. To avoid unnecessary heat load of the matrix, IR irradiation was absorbed by a 10-cm path length of water and by a Schott KG 1 filter (if only $\lambda > 300$ nm was required). For broad-band irradiation Schott cut-off filters were used (50% transmittance at the wavelengths specified); for narrow-band irradiation interference filters (Schott or Oriel) were used to isolate mercury lines.

Chemiluminescence Spectroscopy. Details of obtaining chemiluminescence spectra with an optical multichannel analyzer (OMA) and simultaneously glow curves (total luminescence as a function of the matrix temperature) are given elsewhere.[2b] The warm-up experiments were performed by either switching off the displex system at 10 K (free warm-up, giving a temperature rise of approximately 1 K/min in a highly reproducible manner) or by digitally controlling the temperature rise (0.5-2 K/min). In the free warm-up experiments the first and second stage of the expander module warm up simultaneously, and the first stage is always warmer than the second stage. This prevents the argon from subliming rapidly from the cold window to the first stage at temperatures where its vapor pressure is appreciable ($T > 35$ K). The matrix evaporated rapidly at $T > 55$ K. If only the second stage (cold window) is warmed by a heater, the argon sublimes rapidly to the cold first stage at $T > 43$ K and thus the usable temperature range is reduced. Otherwise, the results up to 43 K were identical with those in the free warm-up experiments.

Chemiluminescence spectra and glow curves were generally taken from matrices deposited on CsI windows. This allowed us to take IR spectra both prior to and after warming the matrix. Control experiments with matrices deposited on the surface of a nickel-plated copper block (high thermal conductivity to avoid small temperature differences between the center and outer portions of the matrix) did not show a dependence of the shape of the glow curves from the matrix support.

Materials. Sodium trifluoroacetophenone tosylhydrazide was prepared by treating the tosylhydrazone, dissolved in dry CH_2Cl_2, with 1.1 equiv of NaH (50% suspension in mineral oil). After removing the CH_2Cl_2 in vacuo, the residue was washed three times with pentane. The yellow salt was stored at -40 °C in an N_2 atmosphere and was stable at room temperature for several days. 1-Phenyl-2,2,2-trifluorodiazoethane (**4**)[27] was generated by gently heating the salt to 32-35 °C and directly sublimed on the cold window. IR (Ar, 10 K): 3074 (w), 2098 (s), 2090 (vs), 1605 (m), 1506 (s), 1368 (m), 1362 (m), 1353 (s), 1328 (s), 1275 (m), 1175 (s), 1150 (s), 1131 (s), 959 (s), 747 (m), 670 (m) cm^{-1}.

Bis(trifluoromethyl)diazomethane (**12**)[28] and hexafluoroacetone[29] were synthesized according to literature procedures. Phenyl trifluoroacetate was obtained from the reaction of phenol and trifluoroacetic acid anhydride[30] and was distilled prior to use. Trifluoroacetophenone (Aldrich) and trifluoroacetic acid anhydride (Aldrich) were reagent grade substances.

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Registry No. 1, 111351-10-1; 2, 111351-11-2; 3, 81123-05-9; 6, 434-45-7; 8, 111351-13-4; 11, 3142-79-8; 15, 684-16-2; 18, 111351-12-3.

Supplementary Material Available: IR, UV, and luminescence spectra of compounds prepared (3 pages). Ordering information is given on any current masthead page.

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Methyl Substituent Effects on Electrophilic Additions to Some Benzobicyclooctadienes

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Methyl hypoiodite (prepared from iodine plus iodic acid in methanol) has been added to 2-methyl-5,8-dimethoxy-1,4-dihydro-1,4-ethanonaphthalene. Four products were isolated and their structures established by 2-D NMR techniques. The stereochemistry of the epoxidation of the above olefin (and its 5,8-diacetoxy analogue) was studied in ether and in methylene chloride by using a series of substituted peroxybenzoic acids. The mechanistic implications of this work are considered in comparison with earlier work on the unsubstituted double bond analogues.

In recent years, a number of examples of electrophilic additions to benzobicyclooctadienes have been reported.[1-3] Paquette and co-workers[2] studied the stereochemistry of the addition of a number of electrophiles (*m*-chloroperbenzoic acid, oxymercuration, methylene addition, singlet oxygen) to 2-methyl-5,8-dimethoxy-1,4-dihydro-1,4-

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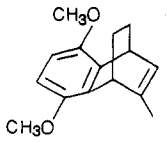
ethanonaphthalene (1) and related olefins. They con-



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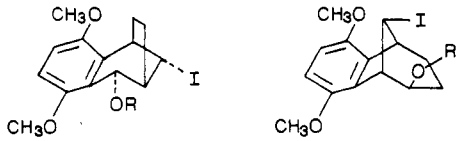
cluded that addition was dominated by steric considerations and a through-bond $\sigma-\pi$ electron coupling causing a π bond disrotation. Homoconjugative stabilization of the transition states for these additions appeared not to be important in explaining the predominate syn additions found experimentally. Nor was any justification for such an interaction found in the MINDO/3 calculations carried out on their molecules. The computational problems caused by the increased parameterization due to the methyl group were avoided by ommitting it from their calculations. They also avoided potential complications possible through phenyl group participation by choosing only reagents which would not introduce molecular rearrangements.

Concurrently, a study of the epoxidation of **2** (**1** without the olefin methyl group) and its 5,8-diacetoxy analogue was being concluded.[3] It was found that the rate of reaction and the ratio of anti/syn oxygen delivery was markedly affected by the solvent in which the reaction was being conducted; the peroxy acids derived from substituted benzoic acids becoming increasingly weaker electrophiles as the solvent was changed to those permitting hydrogen bonding. Oxygen delivery to the face of the double bond anti (sterically less favored) to the aromatic ring was increased markedly by the less reactive, more selective electrophiles. This was attributed to an increasing importance of a stabilizing homoconjugative interaction between the developing positive center and the π electrons of the aromatic ring.

Subsequently,[3c] a study was carried out on the addition of acetyl hypoiodite, hypoiodous acid, and methyl hypoiodite to **2**. Rearranged products **3** and **4** were formed with increasing amounts of the latter for the weaker electrophiles. This result is also consistent with an increase in



3 4

R= Ac, H, CH_3

homoconjugative stabilization of the transition state as the strength of the electrophile decreases.

Intuitively, the enhanced carbocation stabilization offered by the presence of the methyl group on the double bond (**1** vs **2**) should reduce the importance of homoconjugation as a factor in the stereochemistry of the addition of electrophiles to **1**. This work was carried out to test this hypothesis.

Experimental Section

Elemental analyses were by Galbraith Laboratories, Knoxville, TN. High-resolution mass spectra were provided by Dr. David Russell, Texas A&M University.

Both 1-D and 2-D NMR spectra were obtained in chloroform solutions on a Varian XL-300 instrument using techniques and parameters described elsewhere.[4] All chemical shifts are available as supplementary material (see below).

2-Methyl-5,8-dimethoxy-1,4-dihydro-1,4-ethanonaphthalene (1). The adduct of 2-methyl-1,3-cyclohexadiene and *p*-benzoquinone[2] was converted to **1** by the addition of freshly powdered potassium hydroxide to a solution of the adduct in DMSO containing methyl iodide.[3a] The NMR agreed with the reported[2] chemical shifts.

The Addition of Iodine in Methanol to 1. A solution of **1** (0.46 g, 2 mmol) in methanol (25 mL) was treated with iodic acid (0.30 g) and iodine (0.51 g) under a nitrogen blanket. The reaction mixture was stirred at room temperature for 1 h in the dark. The mixture was poured into 50 mL of 6% sodium thiosulfate solution and extracted with two 50-mL portions of 1:1 petrolem ether–benzene. The solvent was removed by rotary evaporation, yielding a light yellow oil (0.75 g). Analytical TLC on silica gel was conducted with two developments (1:1 hexane–benzene followed by 99:1 benzene–acetone) and seven spots were visualized. Preparative-scale TLC (PTLC) was carried out on commercially available 2-mm silica gel plates (E. Merck) using the same development program. The seven components were isolated from these plates and examined individually by NMR.

The top band corresponded to a small amount of hydrocarbon grease persistently found on these commercial plates. Band **2** was a viscous oil (35 mg from 0.375 g of reaction product), which was assigned structure **5** on the basis of the NMR data. Anal. Found: 356.0271. Calcd for $C_{15}H_{17}O_2I$: 356.0269.

Band three was isolated also as a viscous oil (21 mg) which appeared pure by proton and ^{13}C NMR. The compound proved to be very unstable as two attempts to obtain a satisfactory high-resolution mass spectrum failed. On the basis of the COSY and HETCOR results structure **6** was assigned to this molecule.

Band **4** (41 mg) was also a viscous oil assigned as structure **7** on the basis of the NMR analysis and the chemical results presented below. Anal. Found: 388.0528. Calcd for $C_{16}H_{21}O_3I$: 388.0530.

The fifth band (23 mg) proved to be a intractable mixture of at least three components. The sixth band was the major product (126 mg), which formed a white crystalline solid on extraction from the plate. Recrystallization from hexane produced material with mp 141.5–142.5 °C. Anal. Found: C, 49.44; H, 5.46. Calcd for $C_{16}H_{21}O_3I$: C, 49.50; H, 5.46. On the basis of the NMR evidence this material was assigned as structure **8**. The seventh band (38 mg) was found to consist of two inseparable components.

Quantitation of the products from the reaction was accomplished by weighing the fractions from the PTLC and by the integration of the methyl group proton signals. The following is a summary of these results.

	band number					
	2	3	4	5	6	7
% composition (NMR)	16	5	14		46	18
by weight	12	7	14	8	43	13

The agreement between the two methods was considered satisfactory for the purpose of this study.

Reduction of 7 with Sodium/Methanol. A solution of 97 mg of **7** in 1 mL of THF was stirred at room temperature with 15 mg of sodium chips. Methanol (1 mL) was added dropwise. After 15 min, when the sodium had completely dissolved, the reaction mixture was poured into water and extracted with three 10-mL portions of ether. Rotary evaporation of the solvent gave 52 mg of yellow oil, which was identified by NMR as the olefin **1**.

Reduction of 7 by Tributyltin Hydride. A solution of 51 mg of **7** and 40 mg of tributyltin hydride in 0.5 mL toluene was refluxed overnight under nitrogen. The toluene was then removed by rotary evaporation and the resultant brown oil triturated with hexane, forming a tan precipitate. Removed by filtration, this precipitate contained only aliphatic protons in the NMR. The hexane filtrate was evaporated under vacuum, leaving a brown oil. The NMR of this residue indicated that it was *anti*-2-methoxy-*syn*-2-methyl-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (**9**). An authentic sample of this material was prepared and characterized as describe below.

2-Keto-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalene. A solution of 1.60 g (9.5 mmol) of 2-(trimethyl-

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siloxy)-1,3-cyclohexadiene[5] and 1.54 g (14.3 mmol) of benzoquinone in 15 mL of benzene was stirred in the dark for 1 day at room temperature. The solvent was removed by rotary evaporation, yielding a dark solid residue (3.13 g). Crystallization from ethanol gave the adduct; mp 90–90 °C.

A solution of the adduct (1.38 g, 5 mmol) in 20 mL of dry THF was reacted with methyl iodide (1.56 g, 11 mmol) and sodium hydride (0.27 g 11.3 mmol) by being stirred at room temperature overnight under a nitrogen atmosphere. The mixture was poured into water and extracted with three portions of ether (25 mL each). After drying over anhydrous magnesium sulfate, the filtered solution was concentrated under vacuum, yielding a viscous oil (1.20 g). This oil was crystallized from ethanol, giving the title compound (0.88 g, 75%) as pale yellow crystals; mp 84–86 °C (lit.[6] mp 84.5–86 °C).

***anti*-2-Methoxy-*syn*-2-methyl-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (9).** The ketone above treated with methylmagnesium bromide as described previously,[7] and the isomeric alcohols were separated by PTLC with toluene–ethyl acetate (4:1).

anti-2-Hydroxy-*syn*-2-methyl-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (107 mg, 0.4 mmol) was dissolved in 4 mL of dry dimethoxyethane (DME) and reacted with 20 mg of sodium hydride plus 0.5 mL of methyl iodide at room temperature under nitrogen. After the cessation of hydrogen evolution, the mixture was refluxed overnight. An additional 0.5 mL of methyl iodide was added and refluxing was continued for a total of 48 h. Four additional 0.5-mL portions of methyl iodide were added over the course of this time as convenient. After cooling, the mixture was poured into water and extracted with three 15-mL portions of ether. Rotary evaporation of the solvent gave 85 mg of yellow oil, which was purified by PTLC using toluene–ethyl acetate (9:1). Anal. Found: 262.1570. Calcd for $C_{16}H_{22}O_3$: 262.1569.

Epoxidation Studies: 5,8-Dimethoxy-1,4-dihydro-1,4-ethanonaphthalene (**2**) and 5,8-diacetoxy-1,4-dihydroethanonaphthalene (**11**) were prepared as previously described.[3a] *p*-Nitroperbenzoic acid (*p*-NPBA) and *p*-methoxyperbenzoic acid (*p*-MPBA) were prepared by the method of Vilkas.[8] Perbenzoic acid (PBA) was prepared by the method of Ogata and Sawaki.[9] Purity was established by conventional iodometric titration.

2-Methyl-5,8-diacetoxy-1,4-dihydro-1,4-ethanonaphthalene (10). The adduct of 2-methyl-1,3-cyclohexadiene and benzoquinone (2.32 g, 11.5 mmol) in 0.5 mL of dry benzene was treated with 2 mL of acetic anhydride and 2 mL of triethylamine overnight at room temperature. The crude mixture was washed with dilute hydrochloric acid and the solvent removed by rotary evaporation. The resultant brown oil (2.89 g) was crystallized from 95% methanol, yielding buff crystals (2.26 g, 69%). The analytical sample was obtained by further crystallization from methanol; mp 112–113 °C. Anal. Found: C, 71.2; H, 6.6. Calcd for $C_{17}H_{18}O_4$: C, 71.3; H, 6.6.

Standard Epoxidation Procedure. All epoxidations were carried out under standard conditions as follows. To 20 mL of solvent were added 1 mmol of olefin and 1.1 mmol of the appropriate peracid. This mixture was capped and stirred at room temperature (21–23 °C) for 40 h. The reaction mixture was then poured into 5% sodium thiosulfate, and the solvent layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation and the residue examined by TLC (4:1 toluene–ethyl acetate). NMR characterization of the epoxides from **1**, **2**, and **11** have been detailed elsewhere.[2,3a] Analysis of the reaction products was by proton integration.

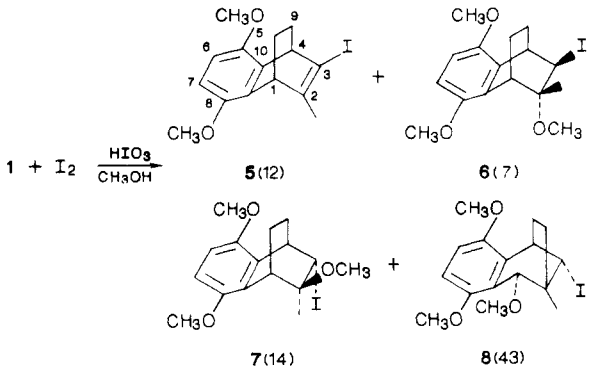
The epoxides from **10** had not been prepared previously. The anti epoxide **12** was best prepared from **10** and *p*-MPBA in diethyl ether by the procedure above. Separation was by PTLC (4:1, toluene–ethyl acetate). The anti epoxide was the less polar of the two and was isolated in 45% yield. Crystallization was from methanol, mp 149.5–151 °C. Anal. Found: C, 67.4; H, 5.8. Calcd for $C_{17}H_{18}O_5$: C, 67.5; H, 6.0.

The syn epoxide **13** from **10** was isolated from the above mixture in 24% yield but was better prepared from **10** by the reaction of *p*-NPBA in methylene chloride. Isolation was by flash column chromatography (4:1 toluene–ethyl acetate) in 45% yield. Crystallization from methanol gave white crystals, mp 154–155 °C. Anal. Found: C, 67.2; H, 6.3. Calcd for $C_{17}H_{18}O_5$: C, 67.5; H, 6.0.

The Decomposition of Perbenzoic Acids in Diethyl Ether. An aliquot (25 mL) of standard PBA (0.42 M) in chloroform was dried by rotary evaporation at room temperature. The residue was taken up in diethyl ether to a volume of 25 mL, and the titer was determined as 0.41 M. This sample plus a similar chloroform aliquot were allowed to stand at room temperature for 14 h and titrated again. The solution in chloroform decreased to 0.40 M, while the ether solution had decreased to 0.02 M.

A similar study was carried out with *p*-MPBA and *p*-NPBA. After 40 h the ether solutions for these had decreased by 8% and 9%, respectively, from the initial titers.

Scheme I[a]



[a] % yields are given in parentheses.

Results and Discussion

The reaction of **1** with iodine–iodic acid in methanol leads to a considerably more complex reaction mixture than does the reaction of **2**. The latter gave only the rearranged products **3** and **4** from the addition of methyl hypoiodite.[3c] The products from **1** are shown in Scheme I. These were separated by PTLC, and their structures were established by NMR with techniques described before.[4] The utility of the double quantum filtered, phase-sensitive COSY sequence of Marion and Wüthrich[9] in providing higher resolution of multiplet structures is to be noted. This sequence was of particular value in assigning stereochemistry by utilization of the long-range four-bond coupling between syn protons on the ethano bridge and syn protons on C-2 and C-3 related via the *W*-letter rule in compounds such as **6**, **7**, and **8**.

The structure of **7** was confirmed by conversion to starting material upon treatment sodium in methanol. Reduction of **7** with tributyltin hydride gave the anti methoxide **9** characterized by independent synthesis. A difference NOE spectrum on **7** was carried out with irradiation of the C-2 methyl. Enhancements were found for the C-2 methoxy methyl and for H-1, confirming their assignments. A very detailed NMR examination was carried out on molecules **6** and **7** as they are the first examples of the addition of two part (or biparticulate) electrophiles in these systems found to proceed without molecular rearrangement.

Some 76% of the reaction products from methyl hypoiodite and **1** are accounted for in Scheme I; the balance being inseparable reaction/or degradation products.

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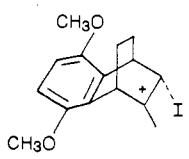
Table II. Anti/Syn Ratios (% Conversions) for 40-h Epoxidations

olefin	peracid	CH_2Cl_2	ether
1	p-MPBA	0.66 (100)	2.3 (80)
	PBA	0.20 (100)	1.4 (100)
	p-NPBA	0.11 (100)	1.1 (100)
2	p-MPBA	0.78 (54)	2.9 (26)
	PBA	0.61 (77)	2.4 (23)[a]
	p-NPBA	0.55 (88)	1.1 (64)
10	p-MPBA		1.8 (70)
	p-NPBA	0.72 (100)	
11	p-MPBA	1.3 (57)	3.1 (38)
	PBA	0.88 (80)	2.6 (20)[a]
	p-NPBA	0.78 (100)	2.4 (56)

[a] Due to the peculiarly unique decomposition of PBA in ether these percents reflect only that the decomposition of the PBA is fast compared to the rate of epoxidation. For additional information on this decomposition, see: Tokumaru, K.; Osamaru, O. Bull. Chem. Soc. Jpn. 1962, 35, 1955.

Reasonably, these products are best accounted for by the intermediacy of carbocations 14 and 15 or possibly the



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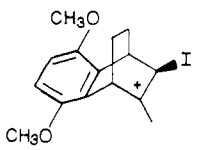

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corresponding iodonium ions. Proton elimination from one or both of these would form 5, while attack by solvent would give 6 and 7, respectively. Rearrangement by migration of the ethano bridge in 14 followed by solvent attack accounts for the major product 8. No evidence of aryl migration or participation was found among the products. The olefinic methyl group stabilizes conventional carbocation formation from 1 removing the need for significant homoconjugative stabilization in the hypoiodite reaction; a result in marked contrast to those previously obtained with 2.[3c]

The results from the epoxidation of 1 and 2 with perbenzoic acid (PBA) and its p-methoxy (p-MPBA) and p-nitro (p-NPBA) analogues are given in Table II. Compounds 10 and 11 are the 5,8-diacetoxy analogues of 1 and 2 with and without the olefin methyl group, respectively.

It has been known for some years that the order of epoxidation reactivity toward a given olefin is p-MPBA < PBA < p-NPBA.[11] The results in Table II are consistent with this order both with regard to the qualitative rates of conversion and the anti/syn ratio of epoxides. As previously observed,[3a] the weaker the electrophilic character of the epoxidizing agent, the greater is the amount of the anti epoxide in the product. The strength of the peracids as electrophiles may be controlled by substituents on the aryl ring or by the degree in which the solvent hydrogen bonds to the peracid proton. The methyl group on the double bond enhances bond reactivity while reducing the amount of anti attack by the reagent.

Acknowledgment. Grateful acknowledgement is hereby extended to the Robert A. Welch Foundation for their support of this work.

Supplementary Material Available: Table I containing the NMR parameters for 1, 5, 6, 7, and 8 and the NMR parameters for other new molecules (3 pages). Ordering information is given on any current masthead page.

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Electrophilic Substitution at Azomethine Carbon Atoms. Reaction of Aromatic Aldehyde Hydrazones with Trifluoroacetic Anhydride

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Reaction of dimethylhydrazones of aromatic aldehydes with trifluoroacetic anhydride at room temperature affords high yields of products bearing trifluoroacetyl groups. These electrophilic substitution reactions generally occur on the azomethine carbon, although competitive N-acylation is observed in highly electron-rich systems. Use of diisopropylhydrazones suppressed this N-acylation completely, leading to high yields of C-acylated products. The trifluoroacetyl hydrazones can be cyclized thermally to imidazole and oxadiazine derivatives and can be converted into 1-trifluoromethyl 1,2-diketones by acid hydrolysis.

Introduction

In our investigation of electrophilic substitution at olefinic carbon atoms we became interested in the reaction of the analogous azomethine carbon atoms of aldehyde hydrazones. The structure of hydrazone 1 is similar to those of vinyl ethers, vinyl sulfides, N-vinylcarboxamides, and N-vinylsulfonamides (2), in which release of the n-electrons to the olefinic β carbon is a key factor in electrophilic substitution at the olefinic carbon atoms.[1-5] In the hydrazone system 1 the N=C double bond is analogous to the C=C double bond of 2, and the conjugation shown in eq 1 should favor electrophilic substitution at the azomethine carbon. Hydrazone is a nitrogen analogue of enamines, and some hydrazones are known to behave as 1,3-dipolar compounds[6] in which the azomethine carbon

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