Reaction of Chromium (Fischer) Carbenes and Sulfilimines[1]

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The photochemical reactions of alkoxychromium (Fischer) carbenes and sulfilimines lead to imidates in fair to excellent yields. Aromatic, heteroaromatic, and alkylsulfilimines, the latter bearing functional groups such as cyano, sulfone, ether, ester, and dioxolane groups, gave the corresponding imidates in good to excellent yield. However, acyl- and sulfonyl-substituted sulfilimines did not react with chromium carbenes, except for sulfilimines bearing ethoxycarbonyl and phtalimidylamino groups. A variety of differently substituted chromium carbene complexes bearing alkyl, cycloalkyl, styryl, allyl, and alkynyl groups attached either at the carbene carbon or at the oxygen also gave imidates in good yields. For α,β-unsaturated carbenes, the exclusive 1,2-addition of the sulfilimine nitrogen was observed at room temperature, in contrast to the behavior of other nitrogen nucleophiles which are reported to add in 1,4-fashion under these reaction conditions. In turn, optically active imidates of the type ArN=C(OR*)Me [R* = chiral substituent derived from (*R*)-(+)-1-phenyl-1-butanol, *l*-(−)-menthol, (1*S*)-*endo*-(−)-borneol, and (1*R*)-(−)-myrtenol] can be prepared efficiently by utilizing the corresponding chiral alkoxy group on the carbene moiety. The reactions above also occur in the dark but reaction times are considerably longer. *N*-Halosulfilimines reacted with alkoxychromium carbenes to yield *N*-acylsulfilimines instead of the expected *N*-haloimidates. Based upon a set of thermal and photochemical reactions between *N*-haloimidates and diphenyl sulfide in the absence of chromium complexes, the complex $(CO)_5CrNCMe$ is proposed to be responsible for this novel reaction of *N*-haloimidates and diphenyl sulfide.

Introduction

Synthetic methodology based on chromium carbene complexes has become a major tool in the building of complex organic molecules.[2] Both thermal and photochemical reactivity has been utilized. The thermal reactivity is exemplified by cocyclization with alkynes to give aromatic or heteroaromatic compounds (Dötz's reaction).[2] Additionally, the photochemical generation of ketenes from chromium carbene complexes[3] has opened new routes to a wide variety of interesting compounds such as β-lactams,[4] cyclobutanones,[5] α-amino acids,[3,6] and aromatic compounds.[7] Among other interesting properties, the activated ester-like behavior of group VI metal carbenes is specially attractive. Among others, α-deprotonation,[8] aminolysis, and in general, nucleophilic substitution on the carbene carbon[2c] show the similar chemistry of both types of compounds. However, in general the carbene complexes are more reactive. For example, reactions such as Diels–Alder cycloadditions occur faster and with higher selectivities when α,β-unsaturated carbene complexes are used instead of α,β-unsaturated esters, the differences being similar to those observed for Lewis acid catalyzed diene–olefin cycloaddition.[9] This intrinsic activation makes group VI carbenes a kind of "superesters" and makes possible some reactions not ordinarily found with organic esters.

One such reaction is that of alkoxychromium and tungsten carbenes with ylides. To date, these reactions have only been demonstrated with simple ylides. Thus, Casey reported on the reaction of pentacarbonyl(methoxyphenylcarbene)tungsten(0) and simple phosphorus ylides[10] to yield vinyl ethers. 1,1-Diphenylethylene has also been prepared from pentacarbonyl(diphenylcarbene)tungsten-(0) and methylenetriphenylphosphorane.[11] The reaction of simple diazoalkanes and tungsten carbenes to form vinyl ethers has also been reported by Casey.[12] This reaction with diazoalkanes circumvents the competitive abstraction of the α-proton from the carbon attached to the carbene carbon which takes place when alkyltungsten carbenes are reacted with phosphorous ylides. Recently, Hegedus has combined the photochemical generation of ketenes from alkoxychromium carbenes with the reactivity of these

(1) For a previous communication of a part of this work see: Alcaide, B.; Domínguez, G.; Plumet, J.; Sierra, M. A. *Organometallics* **1991**, *10*, 11.

(2) For reviews, see: (a) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1990; Vol. 5. (b) Wulff, W. D. In *Advances in Metal–Organic Chemistry*; Liebenskind, L. S., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol. 1. (c) *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluver Academic Publishers: Hingham, MA, 1989. (d) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

(3) Hegedus, L. S.; de Weck, G.; D'Andrea, S. *J. Am. Chem. Soc.* **1988**, *110*, 2122.

(4) For recent papers see: (a) Betschart, C.; Hegedus, L. S. *J. Am. Chem. Soc.* **1992**, *114*, 5010. (b) Narukawa, Y.; Juneau, K. N., Snustad, D.; Miller, D. B.; Hegedus, L. S. J. *Org. Chem.* **1992**, *57*, 5453. (c) Thompson, D. K.; Suzuki, N.; Hegedus, L. S.; Satoh, Y. *J. Org. Chem.* **1992**, *57*, 1461. (d) Alcaide, B.; Domínguez, G.; Plumet, J.; Sierra, M. A. *J. Org. Chem.* **1992**, *57*, 447.

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(6) (a) Hegedus, L. S.; Schwindt, M. A.; De Lombaert, S.; Imwinkelried, R. *J. Am. Chem. Soc.* **1990**, *112*, 2264. (b) Hegedus, L. S.; Lastra, E.; Narukawa, Y.; Snustad, D. C. *J. Am. Chem. Soc.* **1992**, *114*, 2991.

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(8) (a) Lattuada, L.; Licandro, E.; Maiorana, S.; Papagni, A. *J. Chem. Soc., Chem. Commun.* **1991**, 437. (b) Wulff, W. D.; Anderson, B. A.; Toole, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 5485 and references cited therein.

(9) Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642 and pertinent references cited therein.

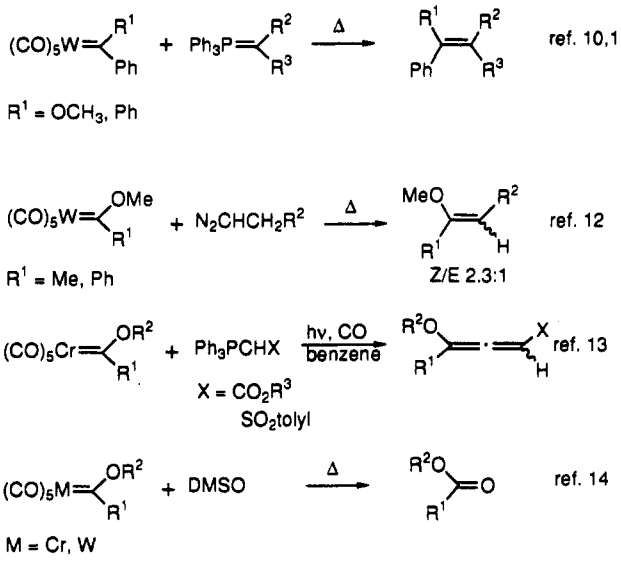
(10) Casey, C. P.; Burkhardt, T. *J. Am. Chem. Soc.* **1972**, *94*, 6543.

(11) Casey, C. P.; Burkhardt, T.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127.

(12) Casey, C. P.; Bertz, S. H.; Burkhardt, T. *Tetrahedron Lett.* **1973**, 1421.

0022-3263/93/1958-3886$04.00/0

Scheme I



ketenes toward phosphorus ylides to obtain captodative allenes in a very efficient process.[13] Finally, dimethyl sulfoxide oxidation is standard to replace the metal–carbene bond with a carbon–oxygen double bond (Scheme I).[11,14]

The reactions reviewed above show the feasibility of using group VI carbenes as the carbonyl moiety in Wittig-like processes that are unachievable in conventional carbonyl–ylide methodology[15] and suggest other Wittig-like processes of synthetic utility based on metal (Fischer) carbenes. Thus, we recently reported[16] the thermal and photochemical reactions of sulfur ylides and alkoxychromium carbenes to give functionalized vinyl ethers with good yields and selectivities. These reactions overcome the limitations found with phosphorus ylides since alkylcarbenes are not α-deprotonated by the sulfur ylides.

In turn, imidates have been obtained in several reactions of group VI carbenes with different functional groups. Thus, vinyl imidates were isolated by reacting chromium or tungsten alkoxycarbenes with azirines.[17] *N*-(Phenylmethoxy)benzylideneamine was formed by reacting pentacarbonyl(methoxymethylcarbene)chromium(0) or its tungsten analog with azobenzene.[18] The reaction of *O*-acetylphenylchromium complexes and imines has been reported to give acyl imidates.[19] Finally, imidates have been isolated in the reaction of pentacarbonyl(methoxymethylcarbene)chromium(0) or its tungsten analog with nitrosobenzene.[20] However, no general methodology to obtain the imidate functionality starting from chromium carbenes has been reported to date.

Scheme II

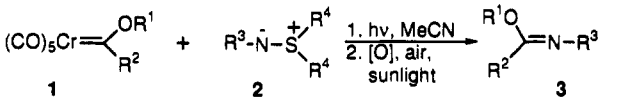
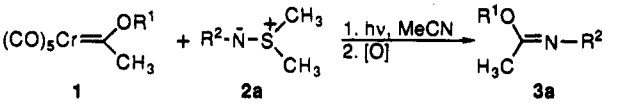


Table I



R1 [a]		R2		reactn time (h)	yield (%)	
1a	Me	2aa	2-pyridyl	4.0	3aa	80
1b	Et	2ab	2-thiazolyl	3.5	3ab	65
		2ac	2-pyrimidinyl	4.5	3ac	45
		2ad	2-pyrazinyl	6.0	3ad	62
		2ae	*p*-$NO_2C_6H_4$	4.5	3ae	52
		2af	C_6H_5	2.5	3af	70
		2ag	*p*-$MeOC_6H_4$	3.0	3ag	90

[a] In all cases R^1 = Me except for **3ab** where R^1 = Et.

Herein the scope and limitations of the photochemical reactions of alkoxychromium carbenes and sulfilimines to yield functionalized imidates are reported.[1] A novel rearrangement of *N*-haloimidates to give acylsulfilimines under photochemical conditions will also be discussed.

Results and Discussion

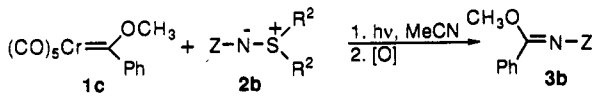
Alkoxychromium carbene complexes **1** react smoothly with sulfilimines **2** under irradiation with visible light to afford, after air–sunlight oxidation to eliminate the organometallic residue, imidates **3** as the sole organic reaction products (Scheme II). To determine the scope of this reaction four different types of sulfilimines were selected, covering a broad range of basicity of the ylide nitrogen, as well as diverse types of functionality.

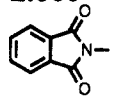
Firstly, aryl- and heteroaryl-substituted sulfilimines **2aa–2ag** were irradiated (450-W Hg lamp, Pyrex well) with pentacarbonyl(methoxymethylcarbene)- and pentacarbonyl(ethoxymethylcarbene)chromium(0) complexes, **1a–1b**, in acetonitrile as the solvent (Table I). Imidates **3a** were obtained in good to excellent yields. In all cases the crude reaction products were extremely clean, and analytically pure imidates were easily obtained by short-path silica gel flash chromatography. Imidates **3** are volatile compounds, and in some cases considerable loss of material is produced during evaporative solvent removal. As expected, a direct relationship between nitrogen ylide basicity[21] and reactivity toward the carbene was observed. Thus, the less basic *p*-nitrophenyl-substituted sulfilimine **2ae** requires longer irradiation time (4.5 h) than *p*-methoxy-substituted sulfilimine **2ag** (3 h).

Once the feasibility of imidate synthesis was established, the less basic *N*-acyl- and *N*-sulfonylsulfilimines **2ba–2be** were tested (Table II). Except for sulfilimine **2be**, which bears the ethoxycarbonyl moiety at the nitrogen, none of the remaining *N*-acyl- or *N*-sulfonylsulfilimines tested gave the corresponding imidates. Imidate **3be** was obtained in

(13) Sestrick, M. R.; Miller, M.; Hegedus, L. S. *J. Am. Chem. Soc.* **1992**, *114*, 4079.
(14) See, for example: (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726. (b) Chan, K. S.; Wulff, W. D. *J. Am. Chem. Soc.* **1986**, *108*, 5229. (c) Wulff, W. D.; Anderson, B. A.; Toole, A. *J. Am. Chem. Soc.* **1989**, *111*, 5485.
(15) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863.
(16) Alcaide, B.; Domínguez, G.; Rodríguez-López, J.; Sierra, M. A. *Organometallics* **1992**, *11*, 1979.
(17) (a) Hegedus, L. S.; Kramer, A.; Yijun, C. *Organometallics* **1985**, *4*, 1747. (b) Curtis, M. D.; Hay, M. S.; Butler, W. M.; Kampt, J. *Organometallics* **1992**, *11*, 2884.
(18) (a) Arndtsen, B. A.; Sleiman, H. F.; Chang, A. K.; McElwee-White, L. *J. Am. Chem. Soc.* **1991**, *113*, 4871. (b) Sleiman, H. F.; Mercer, S.; McElwee-White, L. *J. Am. Chem. Soc.* **1989**, *111*, 8007. (c) Hegedus, L. S.; Lundmark, B. *J. Am. Chem. Soc.* **1989**, *111*, 9194. (d) Hegedus, L. S.; Kramer, A. *Organometallics* **1984**, *3*, 1263. (e) Sleiman, H. F.; McElwee-White, L. *J. Am. Chem. Soc.* **1988**, *110*, 8700. (f) Maxey, C. T.; Sleiman, H. F.; Massey, S. T.; McElwee-White, L. *J. Am. Chem. Soc.* **1992**, *114*, 5153.
(19) Murray, C. K.; Warner, B. P.; Dragisich, V.; Wulff, W. D. *Organometallics* **1990**, *9*, 3142.
(20) (a) Herndon, J. W.; McMullen, L. A. *J. Organomet. Chem.* **1989**, *368*, 83. (b) Pilato, R. S.; Williams, S. D.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 3665.
(21) (a) Kapovits, I.; Ruff, F.; Kucsman, A. *Tetrahedron* **1972**, *28*, 4413. (b) Young, P. R.; McMahou, P. E. *J. Am. Chem. Soc.* **1985**, *107*, 7572.

Table II



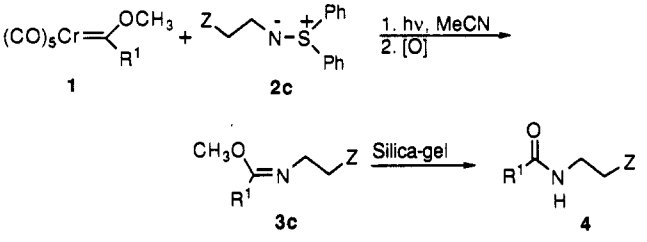
	R^2	Z	reactn time (h)	yield (%)
2ba	CH_3	CH_3CO		
2bb	Ph	*p*-$MeOC_6H_4CO$		
2bc	CH_3	*p*-$MeC_6H_4SO_2$		
2bd	CH_3	*p*-$MeC_6H_4CH_2SO_2$		
2be	Ph	EtOCO	26	**3be** 25
2bf	CH_3		14	**3bf** 60

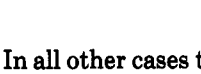
low yield (25%) as a pale yellow oil. In all other cases the starting ylide was recovered quantitatively even after long irradiation times. Those results show that conjugation with a carbonyl or a sulfonyl group renders the sulfilimine nitrogen less basic and unable to react with the electrophilic carbene carbon. Sulfilimine **2be** may be in the reactivity borderline needing 26 h of irradiation to give the corresponding imidate in the low yield reported. In this case electron delocalization onto the carbonyl group should be partially inhibited by the ethoxy group resulting in a more basic, more nucleophilic nitrogen. This is supported by the reaction of the related *N*-phthalimidylsulfilimine **2bf** and carbene complex **1c** to give imidate **3bf** in better yield and shorter reaction time.

In the third place, alkyl-substituted sulfilimines **2ca–2cf** were tested. We chose a wide variety of β-substituted alkylsulfilimines in order to determine whether imidate formation is compatible with different functional groups attached to the ylide moiety. Sulfilimines **2ca–2cf** can be prepared using standard methodology, starting from free sulfilimine Ph_2SNH, namely through Michael addition to an α,β-unsaturated system bearing the adequate functionality or nucleophilic displacement on an α,β-bromo derivative. However, although both routes seem to be very simple, we encountered several experimental problems when we used previously reported procedures for related compounds. After considerable effort, we found that simply by working in chloroform as the solvent instead of the previously described neat conditions,[22] compounds **2cc,2ce–2cf** derived from α,β-unsaturated reagents were readily obtained (see Experimental Section). Benzene was the solvent of choice for the synthesis of compounds **2ca**, **2cb**, and **2cd** from functionalized alkyl halides.

Alkylsulfilimines **2c** react nicely with alkoxychromium carbenes to yield the expected imidates **3c**, together with diphenyl sulfide which is the reaction byproduct (Table III). Except for sulfilimines **2ce–2cf** which reacted almost instantaneously, the remaining aliphatic ylides required irradiation to react. The reaction tolerates a variety of functional groups including cyano, sulfone, ether, ester, and acetal functionalities. Compounds **3ca–3cg** are extremely unstable toward hydrolysis to the corresponding amides **4**. Attempts to separate diphenyl sulfide from the imidate by column chromatography using different stationary phases and conditions, including silica gel (normal or deactivated by HCO_3Na washing), alumina, Florisil, cellulose, etc., result, in general, in extensive or total

Table III



	R^1		Z^b	reactn time (h)	yield (%)			
1a	Me	**2ca**	EtO	17	**3ca**	not isolated[a]	**4a**	50
1c	Ph	**2cb**	MeCOO	17	**3cb**	not isolated[a]	**4b**	50
		2cc	EtOCO	17	**3cc**	not isolated[a]	**4c**	55
		2cd		17	**3cd**	not isolated[a]	**4d**	98
		2ce	$PhSO_2$	*c*	**3ce**	80	**4e**	96
		2ce	$PhSO_2$	*c*	**3cf**	75	**4f**	70
		2cf	NC^-	*c*	**3cg**	62	**4g**	80

[a] See text. [b] In all cases R^1 = Ph except for **3cf** where R^1 = Me. [c] No irradiation was required.

hydrolysis to the corresponding amides. Moreover, distillation of the crude mixtures results in extensive decomposition of imidate to complex mixtures of unknown compounds as well as the corresponding amide. Thus, compounds **3ca–3cg** were isolated and analytically characterized as the corresponding amides, **4**, which are easily obtained by allowing the crude reaction mixture to stand at room temperature or by silica gel flash chromatography. Imidates **3ce–3cg** were the sole *N*-alkylimidates isolated in good yields by Florisil chromatography and then only using solvents and Florisil from which all traces of acid had been removed.[23]

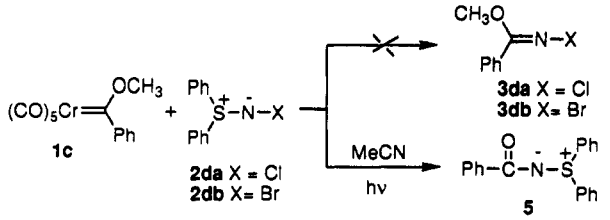
N-Halosulfilimines were the sole ylides tested which yielded products different from imidates. To our surprise, when *N*-halosulfilimines **2da–2db** were reacted with chromium carbene **1c**, instead of the expected *N*-haloimidates **3da–3db**, *N*-benzoylsulfilimine **5** was the reaction product as indicated by its spectroscopic and analytical data and by comparison with an authentic sample prepared by reaction of free sulfilimine Ph_2SNH and benzoyl chloride. *N*-Benzoylsulfilimine **5** may arise from the reaction of the initially formed, highly reactive *N*-haloimidates **3da–3db** and diphenyl sulfide, the reaction byproduct. However, although *N*-haloimidates are known to react with aliphatic sulfides yielding acylsulfilimines, it has been reported that aromatic sulfides are unreactive toward those imidates. Thus, only very low yields of *N*-benzoyl-*N'*-phenylurea were obtained upon heating *N*-chloroimidate **3da** and diphenyl sulfide at 193 °C.[24] In our hands, both the thermal (room temperature) and photochemical reactions (in analogous conditions to those used in this work) of *N*-chloroimidate **3da** and diphenyl sulfide gave benzamide, resulting from hydrolysis of starting imidate, as the major product, together with variable amounts of diphenyl sulfoxide. Therefore, an organometallic species may be involved in the photochemical production of benzoylsulfilimine from *N*-haloimidates and chromium carbene **1c**. Assuming that the reaction pathway previously proposed[24] for the reaction of *N*-haloimidates and aliphatic sulfides (Scheme IV) is

(22) (a) Furukawa, N.; Yoshimura, T.; Oae, S. *Tetrahedron Lett.* **1973**, *25*, 2113. (b) Yoshimura, T.; Furukawa, N.; Oae, S. *Synth. Commun.* **1976**, 30.

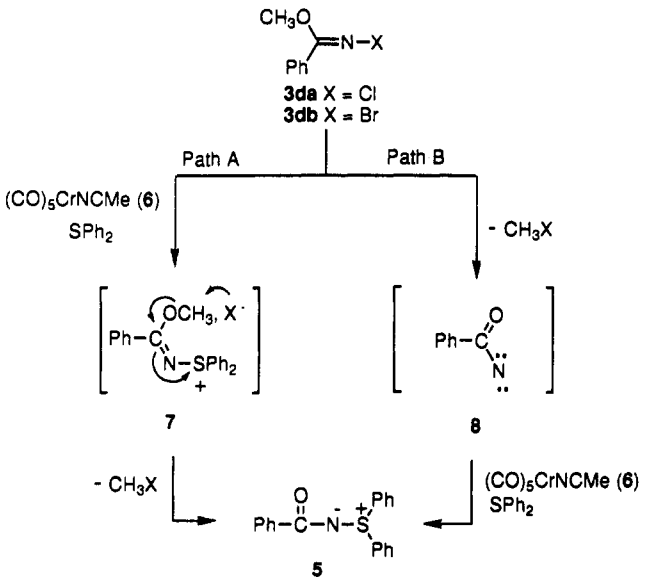
(23) Yields in Table III for compounds **3ce-3cg** are from the best of many experiments. Extensive hydrolysis was observed in most cases.

(24) Papa, A. J. *J. Org. Chem.* **1970**, *35*, 2837.

Scheme III



Scheme IV

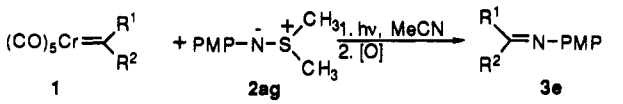


operative in our case, we propose that the complex $(CO)_5CrNCMe$, **6**, formed together with *N*-haloimidates **3da–3db** during the photochemical reaction[25] is an activating agent either in the nucleophilic attack of the diphenyl sulfide on the imidate (path A) to form the salt **7** or in the capture of the intermediate nitrene **8** (path B). A detailed study of the mechanism and synthetic applications of this novel reaction is underway in our laboratories.

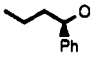
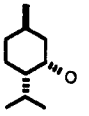
The reaction of chromium carbenes and sulfilimines was not restricted to the parent complexes **1a–1c**, but rather tolerated a variety of alkyl, vinyl, and alkynyl groups attached to the carbene carbon, as demonstrated by the reactions of complexes **1a–1m** and sulfilimine **2ag** (Table IV). Yields were usually high, allowing for the preparation a variety of differently C- and O-substituted imidates **3e**, including chiral O-substituted imidates derived from optically active alcohols attached to the chromium moiety. It is remarkable that the α,β-unsaturated carbene complexes **1h** and **1i** form imidates without any products derived from competitive 1,4-addition. As depicted in Scheme V, 1,2- and 1,4-addition of sulfilimine **2ag** to carbene complex **1h** would lead to intermediate zwitterions **9** and **10**, respectively (see below for a more detailed mechanistic discussion). Reaction of **9** yields the observed imidate **3ef** while decomposition of intermediate **10** would

(25) Complex **6** was isolated as a very unstable deep yellow oil by flash chromatography of crude reaction mixtures prior to oxidation, in the reaction of various carbene complexes and different sulfilimines. Nevertheless, compound **6** may not be the primary organometallic reaction product, as shown by the isolation of $(CO)_5CrSMe_2$ from crude reaction mixtures of reactions carried out in ether as solvent (see Experimental Section). Ligand interchange may account for the isolation of $(CO)_5CrNCMe$, **6**, as the final organometallic product when working in acetonitrile.

Table IV

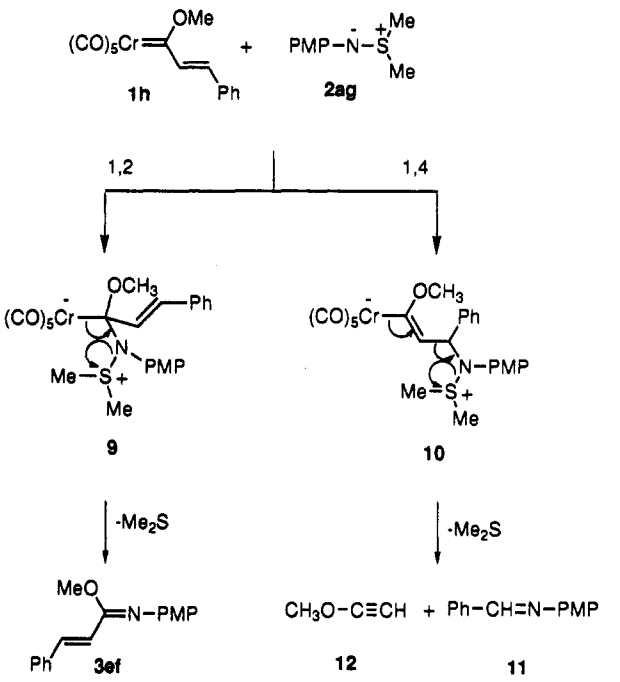


PMP = *p*-$MeOC_6H_4$

	R^1	R^2	reactn time (h)	yield (%)	
1a	MeO	Me	3	**3ag**	90
1c	MeO	Ph	15	**3ea**	71
1d	$PhCH_2O$	Me	16	**3eb**	85
1e	$CH_2{=}CHCH_2O$	Me	15	**3ec**	54
1f	$\equiv{-}CH_2CH_2O$	Me	15	**3ed**	50
1g	MeO	cyclopropyl	16	**3ee**	63
1h	MeO	CH=CHPh	20	**3ef**	85
1i	MeO	$\equiv$TMS	*a*	**3eg**	59
1j		Me	9	**3eh**	70
1k		Me	9	**3ei**	98
1l		Me	15	**3ej**	40
1m		Me	15	**3ek**	66

[a] No irradiation was required.

Scheme V



PMP = *p*-$MeOC_6H_4$

form imine **11** together with methoxyacetylene **12**. This result is in contrast with the addition of other nitrogen nucleophiles to α,β-unsaturated carbene complexes. Thus, amines add to α,β-unsaturated complexes related to **1h** in a conjugated fashion at room temperature while 1,2-addition has been reported to occur at lower temperatures.[2c]

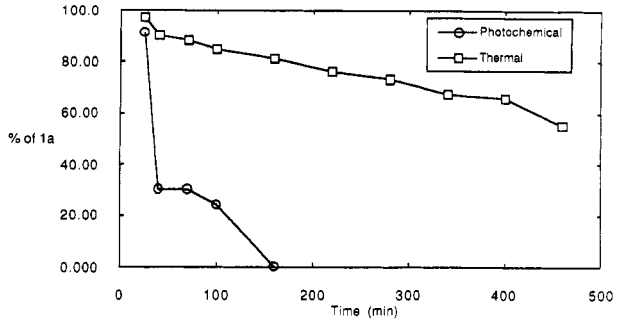
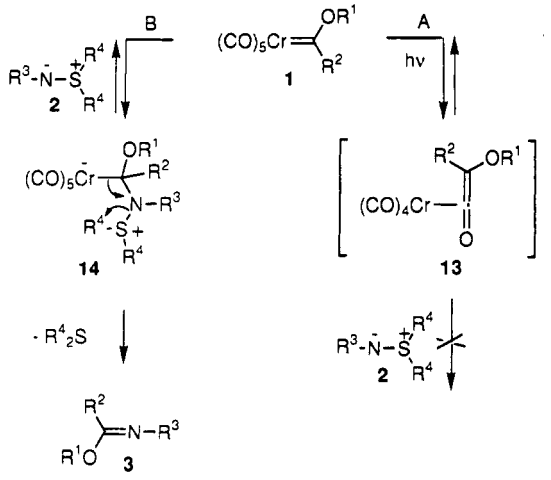


Figure 1. Evolution (monitored by ^{1}H NMR) of the reaction of complex **1a** (0.3 mmol) and sulfilimine **2aa** (0.3 mmol) in CD_3CN (1 mL) under photochemical (25 °C, standard procedure) and thermal (24 °C, dark) conditions.

Finally, the issue of the reaction pathway was addressed. Before proposing a mechanism for the reaction of chromium carbenes and sulfilimines the following facts should be pointed out. First, there are striking differences between the thermal and photochemical reactions. Both reaction conditions yield imidates as the sole reaction products, but considerably longer reaction times are needed under thermal conditions. For example, when the progress of the reaction between complex **1a** and sulfilimine **2aa** was monitored by ^{1}H NMR, it was found that under irradiation the starting metal carbene was consumed after 1.5 h, while 50% of the complex remains unaltered after 7 h in the dark at room temperature (Figure 1).[26] In a separate set of experiments the more basic aliphatic sulfilimine **2ca** was reacted with carbene complex **1c**, and the reaction progress was monitorized by TLC. While the starting carbene was fully consumed within 12 h of irradiation, in the thermal reaction unreacted complex remained after 4 days at room temperature even when an excess of sulfilimine was present. The same reactivity pattern was observed in other reactions, except for sulfilimines **2c** bearing remote cyano or sulfone substituents which reacted instantaneously at room temperature in the dark. Moreover, in general, irradiation produces cleaner crude product. In addition, imidate formation also occurs in solvents such as ether, benzene, THF, or Cl_2CH_2 without differences in reaction times and in the nature of reaction products.[27] Finally, in acetonitrile the organometallic reaction product was isolated and characterized as $(CO)_5CrNCMe$, **6**.[25] Some additional facts have been pointed out throughout the text. Acyl- and sulfonylsulfilimines **2b** (Table II) were unreactive even after long irradiation times. Moreover, for aryl-substituted sulfilimines, electron-withdrawing substituents on the aromatic ring resulted in longer reaction times than those required for sulfilimines bearing electron-donating substituents. Therefore, there is a direct relationship between sulfilimine basicity and nucleophilicity toward the carbene carbon.

Scheme VI



From these observations, the literature concerning the photochemical behavior of chromium carbenes,[3,13] and the known reactivity of ylides with these complexes,[10-12,14,16] the reaction pathway in Scheme VI is proposed for the reaction between sulfilimines and alkoxychromium carbenes. Path A involves the reversible photochemical CO insertion into the chromium carbene bound leading to chromium-bonded ketenes, **13**,[3] which may react with sulfilimines to yield ketene-derived products. Although it is well-known that sulfilimines react with ketenes to form different products,[28] ketene-derived reaction products were never found in our reactions. This is in contrast with the recently reported photochemical reaction of alkoxychromium carbenes and stabilized phosphorus ylides to form ketene-derived captodative allenes.[13] Two reasons may be responsible for this differential behavior: either the conditions used are not energetic enough to promote the reaction between the chromium-bound ketene and the sulfilimine or addition of the sulfilimine to the carbene carbon competes favorably with CO insertion, making path A nonproductive. Path B (Scheme VI) involves the nucleophilic addition of ylide nitrogen to the carbene carbon to generate the key zwitterionic intermediate **14**. Straightforward decomposition of intermediate **14** would form imidates **3** and the corresponding sulfide. However, relative reactivities we observed are not explained by this simple mechanism. For example, the rate-determining step should be the nucleophilic addition to the metal carbene carbon, and therefore all of the more basic aliphatic sulfilimines should react in the absence of light.[29] It is not easy, either, to explain the role of light, even assuming that it does catalyze decomposition of the intermediate **14**.[30]

In conclusion, the scope and limitations of the novel reaction between alkoxychromium carbenes and sulfilimines to yield functionalized imidates has been studied.

(26) Both experiments were carried out in NMR tubes at room temperature, using degassed CD_3CN as solvent and equimolar amounts of both reagents. Reaction progress of the starting complex was monitored by checking the signal at 4.60 (broad singlet) corresponding to the complex MeO group.

(27) Sulfilimine **2ag** and chromium carbene **1a** were reacted under standard photochemical conditions (see Experimental Section) in the solvents stated above. After oxidation to eliminate the organometallic residue, ^{1}H NMR analysis of the crude reaction mixture showed exclusive formation of imidate **3ag**, crude yields being analogous to those obtained in MeCN.

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(29) Differences in reaction rate may also been attributed to the effect of the Ph_2S group on alkylsulfilimines. To rule out this possibility, aromatic sulfilimine *p*-$NO_2C_6H_4N{=}SPh_2$ was prepared and its reactivity compared with that found for analogous sulfilimine **2ae**. Imidate **3ae** was produced together with Ph_2S only after irradiation.

(30) ^{1}H NMR analysis of the reaction between complex **1a** and sulfilimine **2aa** suggests formation of at least two intermediates related to some intermediates reported by Hegedus (see ref 18c). Attempts to elucidate the mechanism of the reaction between chromium carbenes and sulfilimines are underway in our laboratories.

The methodology described above is complementary to known methods of imidate synthesis,[31] works smoothly under neutral conditions, and allows the preparation of imidates not easily available through conventional procedures. Furthermore, a novel reaction of *N*-haloimidates and aromatic sulfides is reported.

Experimental Section

General Procedure. General experimental data and procedures have been previously reported.[4d] Specific rotation, $[\alpha]_D$, was reported in deg per dm at the specified temperature and the concentration (*c*) given in g per 100 mL in Cl_3CH. Irradiations were performed by a 400-W medium-pressure mercury lamp, Pyrex filter, and Pyrex well.

The following chemicals were prepared according to literature procedures: *S,S*-diphenyl-*N*-(*p*-toluenesulfonyl)sulfilimine,[32] *S,S*-diphenylsulfilimine,[33] *S,S*-diphenyl-*N*-(ethoxycarbonyl)sulfilimine,[33] *S,S*-diphenyl-*N*-(*p*-methoxybenzoyl)sulfilimine,[33] *S,S*-diphenyl-*N*-(2-cyanoethyl)sulfilimine,[22b] *S,S*-diphenyl-*N*-(2-(phenylsulfonyl)ethyl)sulfilimine,[22b] *S,S*-diphenyl-*N*-acetylsulfilimine,[34] *S,S*-dimethyl-*N*-(*p*-toluenesulfonyl)sulfilimine,[35] *S,S*-dimethyl-*N*-(α-toluenesulfonyl)sulfilimine,[35] *S,S*-diphenyl-*N*-chlorosulfilimine,[22a] *S,S*-diphenyl-*N*-bromosulfilimine,[22a] *S,S*-dimethyl-*N*-phthalimidylsulfilimine,[36] *S,S*-dimethyl-*N*-(2-pyrazyl)-sulfilimine,[37] *S,S*-dimethyl-*N*-(2-pyridyl)sulfilimine,[37] *S,S*-dimethyl-*N*-(2-thiazolyl)sulfilimine,[37] *S,S*-dimethyl-*N*-(2-pyrimidinyl)sulfilimine,[37] *S,S*-dimethyl-*N*-(*p*-nitrophenyl)-sulfilimine,[35] *S,S*-dimethyl-*N*-phenylsulfilimine,[35] *S,S*-dimethyl-*N*-(*p*-anisyl)sulfilimine,[35] *S,S*-dimethyl-*N*-benzoylsulfilimine,[35] pentacarbonyl(methoxymethylcarbene)chromium(0),[38] pentacarbonylmethoxyphenylcarbene)chromium(0),[38] pentacarbonyl-((benzyloxy)methylcarbene)chromium(0),[39] pentacarbonyl(cyclopropyl)methoxycarbene)chromium(0),[40] pentacarbonyl-(methoxystyrylcarbene)chromium(0),[41] pentacarbonyl(methoxy-(trimethylsilylacetylene)carbene)chromium(0),[42] pentacarbonyl-(methyl((tetramethylammonio)oxy)carbene)chromium(0),[43] pentacarbonyl((allyloxy)methylcarbene)chromium(0),[5c] pentacarbonyl((3-butyn-1-oxy)methylcarbene)chromium(0),[5c] pentacarbonyl(*l*-(−)-(menthyloxy)methylcarbene)chromium(0),[5c] methyl *N*-chlorobenzimidate.[24]

General Procedure for Synthesis of Sulfilimines 2c. Method A. A solution of Ph_2SNH (1 mmol) and the corresponding Michael acceptor (1.5 mmol) in chloroform (15 mL) was heated under reflux overnight. The solvent was then removed under vacuo, and the crude residue was purified by flash chromatography on silica gel using 20:1 Cl_3CH/CH_3OH mixtures to yield analytically pure sulfilimines **2c**.

Method B. A solution of Ph_2SNH (1 mmol) and the appropriate alkyl bromide (1.5 mmol) in benzene (15 mL) was heated under reflux overnight. The solvent was then removed under vacuo, and the residue was purified as in method A.

***S,S*-Diphenyl-*N*-(2-ethoxyethyl)sulfilimine, 2ca.** Following method B, from 500 mg (2.28 mmol) of Ph_2SNH and 524 mg (3.42 mmol) of 2-bromoethyl ethyl ether was obtained 460 mg (74%) of pure sulfilimine as a pale yellow oil: ^1H NMR δ 0.87 (t, 3H, J = 7.2 Hz, CH_3), 3.16 (q, 2H, J = 7.2 Hz, CH_2CH_3), 3.58 (t, 2H, J = 6.6 Hz, CH_2), 3.60 (t, 2H, J = 6.6 Hz, CH_2), 7.59–8.04 (m, 10H, arom); ^{13}C NMR δ 133.3, 132.9, 130.2, 128.1 (arom), 69.7 (CH_2O), 66.0 (CH_2O), 48.1 (CH_2N), 14.4 (CH_3); IR (Cl_3CH) ν 1485, 1450, 1125, 1090 cm^{-1}. Anal. Calcd for $C_{16}H_{19}SNO$: C, 70.30; H, 7.01; N, 5.13; S, 11.71. Found: C, 70.54; H, 7.23; N, 4.89; S, 12.07.

***S,S*-Diphenyl-*N*-(2-acetoxyethyl)sulfilimine, 2cb.** Following method B, from 0.50 g (2.28 mmol) of Ph_2SNH and 0.57 g (3.42 mmol) of 2-bromoethyl acetate was obtained 0.23 g (35%) of pure sulfilimine as a colorless oil: ^1H NMR δ 1.88 (s, 3H, CH_3), 3.57 (t, 2H, J = 5.2 Hz, CH_2N), 4.31 (t, 2H, J = 5.2 Hz, CH_2O), 7.61–7.69 (m, 7H, arom), 8.02–8.06 (m, 3H, arom); ^{13}C NMR δ 170.0 (CO), 144.8, 133.7, 130.5, 128.7 (arom), 62.9 (OCH_2), 46.0 (CH_2N), 20.4 (CH_3); IR (Cl_3CH) ν 1745 (C=O), 1480, 1450, 1410, 1375 cm^{-1}. Anal. Calcd for $C_{16}H_{17}SNO_2$: C, 66.88; H, 5.97; N, 4.88; S, 11.1. Found: C, 67.04; H, 6.11; N, 4.78; S, 10.81.

***S,S*-Diphenyl-*N*-(2-(ethoxycarbonyl)ethyl)sulfilimine, 2cc.** Following method A, from 0.33 g (1.5 mmol) of Ph_2SNH and 0.22 g (2.25 mmol) of ethyl acrylate was obtained 0.43 g (95%) of pure sulfilimine as a pale yellow oil: ^1H NMR δ 1.22 (t, 3H, J = 7.2 Hz, CH_3), 2.55 (t, 2H, J = 6.6 Hz, CH_2CO), 3.19 (t, 2H, J = 6.6 Hz, CH_2N), 4.07 (q, 2H, J = 7.2 Hz, CH_2CH_3), 7.26–7.59 (m, 10H, arom); ^{13}C NMR δ 172.7 (CO), 130.8, 129.1, 128.4, 126.8 (arom), 60.0 (OCH_2), 43.7 (CH_2N), 37.1 (CH_2CO), 13.9 (CH_3); IR (Cl_3CH) ν 1725 (C=O), 1470, 1440, 1370 cm^{-1}. Anal. Calcd for $C_{17}H_{19}SNO_2$: C, 67.75; H, 6.36; N, 4.65; S, 10.62. Found: C, 67.89; H, 6.10; N, 4.78; S, 10.88.

***S,S*-Diphenyl-*N*-(2-(1,3-dioxolan-2-yl)ethyl)sulfilimine, 2cd.** Following method B, from 0.33 g (1.5 mmol) of Ph_2SNH and 0.41 g (2.25 mmol) of 2-(bromoethyl)-1,3-dioxolane was obtained 0.31 g (69%) of pure sulfilimine as a colorless oil: ^1H NMR δ 2.13 (td, 2H, J = 6.9 Hz, J = 4.5 Hz, CH_2CH), 3.31 (t, 2H, J = 6.9 Hz, CH_2N), 3.76–3.93 (m, 4H, 2 × CH_2O), 4.94 (t, 1H, J = 4.5 Hz, CH), 7.56–7.97 (m, 10H, arom); ^{13}C NMR δ 145.0, 133.9, 130.7, 129.4 (arom), 101.8 (CH), 64.8 (2 × CH_2O), 41.9 (CH_2N), 33.5 (CH_2CH); IR (Cl_3CH) ν 1440, 1255, 1030 cm^{-1}. Anal. Calcd for $C_{17}H_{19}SNO_2$: C, 67.75; H, 6.36; N, 4.65; S, 10.62. Found: C, 67.54; H, 6.13; N, 4.83; S, 10.89.

General Procedure for the Preparation of Chromium Carbenes 1j–1m. In an oven-dried 250-mL airless flask equipped with a stir bar, 3.23 mmol of pentacarbonyl(methyl((tetramethylammonio)oxy)carbene)chromium(0) was dissolved in 50 mL of degassed methylene chloride. The solution was put under an argon atmosphere and cooled to −40 °C with an acetone/dry ice bath. To the faint yellow solution was added 3.23 mmol of either pivaloyl chloride or acetyl bromide dissolved in 5 mL of methylene chloride by syringe. The resulting deep brown solution was stirred at −40 °C for 30 min followed by addition of the corresponding alcohol (3.23 mmol) dissolved in 5 mL of methylene chloride. After 6 h at −40 °C, the reaction mixture was allowed to slowly reach room temperature overnight. To the resulting yellow solution was added 4 g of silica gel, and the solvent was removed on a rotatory evaporator. The residue was transferred to the top of a column filled with silica gel and separated by flash chromatography using pentane as eluent. The products were stored in a freezer (−30 °C) before use to minimize decomposition–oxidation. These complexes decompose within minutes at room temperature, and acceptable elemental analyses could not be obtained.

Pentacarbonyl(methyl-(*R*)-(+)-((1-phenylbutyl)oxy)carbene)chromium(0), 1j. From 1.0 g (3.23 mmol) of pentacarbonyl(methyl((tetramethylammonio)oxy)carbene)chromium(0), 0.39 g (3.23 mmol) of pivaloyl chloride, and 0.49 g (3.23 mmol) of (*R*)-(+)-1-phenylbutanol was obtained 0.61 g (2.24 mmol, 70%) of **1j** as an orange oil. ^1H NMR δ 0.96 (t, 3H, CH_3CH_2), 1.20 (m, 4H, 2 × CH_2), 2.03–2.15 (m, 1H, CH), 2.94 (s, 3H, CH_3), 7.20–7.40 (m, 5H, arom); ^{13}C NMR δ 354.0 (Cr=C), 218.4 (*trans*-CO), 216.4 (*cis*-CO), 138.9, 128.8, 128.6, 126.1 (arom), 60.3 (CHO), 40.1 (CH_3CCr), 27.1 (CH_2), 18.6 (CH_2), 14.1 (CH_3); IR (Cl_3CH) ν 2080 (*trans*-CO), 1940 (*cis*-CO), 1485, 1450 cm^{-1}.

Pentacarbonyl(methyl((1*R*)-(−)-myrtenyloxy)carbene)-chromium(0), 1l. From 1 g (3.23 mmol) of pentacarbonyl-(methyl((tetramethylammonio)oxy)carbene)chromium(0), 0.40 g (3.23 mmol) of acetyl bromide, and 0.5 g (3.23 mmol) of (1*R*)-(−)-myrtenol was obtained 0.48 g (1.3 mmol, 40%) of **1l** as an orange oil: ^1H NMR δ (broad signals) 0.89 (s, 3H, CH_3), 1.25–1.33

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(m, 4H, CH_3, CH), 2.03–2.47 (m, 5H, 2 × CH_2, CH), 2.94 (s, 3H, Cr=CCH_3), 5.21 (s, 2H, CH_2O), 5.76 (s, 1H, CH=), ^{13}C NMR δ 357.2 (Cr=C), 218.5 (*trans*-CO), 216.5 (*cis*-CO), 141.8 (C=), 124.5 (CH=), 98.5 (CH_2O), 43.6 (CH_3CCr), 40.5, 38.2, 31.4, 25.9, 21.0; IR ν 2300 (*trans*-CO), 1925 (*cis*-CO), 1540, 1470 cm^{-1}.

Pentacarbonyl(((1*S*)-*endo*-(−)-bornyloxy)methylcarbene)-chromium(0), 1m. Following the general procedure, from 1.0 g (3.23 mmol) of pentacarbonyl(methyl((tetramethylammonio)-oxy)carbene)chromium(0), 0.40 g (3.23 mmol) of acetyl bromide, and 0.50 g (3.23 mmol) of (1*S*)-*endo*-(−)-borneol was obtained 0.32 g (0.8 mmol, 25%) of **1m** as an orange oil: ^1H NMR (broad signals) δ 0.96 (9H), 1.20–1.60 (m, 3H), 1.80 (2H), 2.05 (1H), 2.60 (1H), 2.95 (3H), 5.65 (1H); ^{13}C NMR δ 354.3 (Cr=C), 218.5 (*trans*-CO), 216.5 (*cis*-CO), 98.6 (OCH), 50.3 (CH_3CCr), 45.1, 44.9, 37.1, 28.0, 19.5, 18.7, 12.8; IR (Cl_3CH) ν 2030 (*trans*-CO), 1980, 1930 (*cis*-CO), 1480, 1455, 1395, 1380, 1310, 1270 cm^{-1}.

General Procedure for the Synthesis of Imidates 3 and Amides 4. The carbene (1.0 mmol) was dissolved in 15 mL of degassed acetonitrile and placed in a Pyrex test tube which was sealed with a rubber septum, evacuated, and purged with argon (three times). A solution of 1.0 mmol of sulfilimine in 15 mL of degassed acetonitrile was added, and the resulting mixture was irradiated until total disappearance of the starting complex (TLC). The solvent was removed under vacuo. The resulting brown solid residue was dissolved in methyl acetate, filtered through Celite, diluted with one volume of pentane, and air oxidized in an open flask under direct sunlight (usually 10–12 h was required) or in a light box (9 × 20 fluorescent bulbs). Filtration through Celite of the brown precipitate and solvent removal gave crude imidate. Analytically pure imidates were obtained by chromatography. For unstable imidates **3ca–3cg** the corresponding amides were obtained by air oxidation or by flash chromatography as analytically pure compounds.

(1-Methoxyethylidene)-*N*-(2-pyridyl)amine, 3aa. Following the general procedure, 0.30 g (1.2 mmol) of complex **1a** and 0.18 g (1.2 mmol) of sulfilimine **2aa** were irradiated for 4 h. After oxidation the crude imidate was purified by silica gel flash chromatography (hexane/ethyl acetate (1:1)): pale yellow oil; yield 0.12 g (80%); ^1H NMR δ 1.90 (s, 3H, CH_3), 6.77 (dd, 1H), 6.94–6.99 (m, 1H), 7.58–7.64 (td, 1H), 8.37 (dd, 1H); ^{13}C NMR δ 163.6 (C=N), 161.3, 148.5, 137.5, 118.3, 116.2 (arom), 53.3 (OCH_3), 16.4 (CH_3); IR (Cl_3CH) ν 1680 (C=N) cm^{-1}; mass spectrum *m/z* 150 ($M^{\bullet+}$, parent), 134, 118, 117, 107, 78, 77. Anal. Calcd for $C_8H_{10}N_2O$: C, 64.00; H, 6.66; N, 18.66. Found: C, 64.32; H, 6.54; N, 18.35.

(1-Ethoxyethylidene)-*N*-(2-thiazolyl)amine, 3ab. Following the general procedure, 0.27 g (1 mmol) of complex **1b** and 0.16 g (1 mmol) of sulfilimine **2ab** were irradiated for 3.5 h. After oxidation the crude imidate was purified by silica gel flash chromatography (hexane/ethyl acetate (2:1)): pale yellow oil; yield 0.11 g (65%); ^1H NMR δ 1.30 (t, 3H, J = 7.20 Hz, CH_2CH_3), 2.11 (s, 3H, CH_3), 4.25 (q, J = 7.20 Hz, 2H, CH_2), 6.95 (d, 1H), 7.41 (d, 1H); ^{13}C NMR δ 170.3, 166.9 (C=N), 139.9, 115.3, 62.8 (OCH_2), 17.3 (CH_3), 14.0 (CH_2CH_3); IR (Cl_3CD) ν 1660 (C=N) cm^{-1}; mass spectrum *m/z* 170 ($M^{\bullet+}$), 129 (parent), 128, 127, 99. Anal. Calcd for $C_7H_{10}N_2SO$: C, 49.41; H, 5.88 N, 16.47; S, 18.82. Found: C, 49.63; H, 6.02; N, 16.59; S, 18.88.

(1-Methoxyethylidene)-*N*-(2-pyrimidinyl)amine, 3ac. Following the general procedure, 0.25 g (1 mmol) of complex **1a** and 0.16 g (1 mmol) of sulfilimine **2ac** were irradiated for 4.5 h. After oxidation the crude imidate was purified by silica gel flash chromatography (EtOAc): colorless oil; yield 0.02 g (45%); ^1H NMR δ 1.98 (s, 3H, CH_3), 3.86 (s, 3H, OCH_3), 6.98 (t, 1H), 8.62 (d, 2H); ^{13}C NMR δ 166.1 (C=N), 158.9, 158.5, 116.0, 54.1 (OCH_3), 17.2 (CH_3); IR (net) 1685 (C=N) cm^{-1}; mass spectrum *m/z* 151 ($M^{\bullet+}$), 137, 121, 109, 93 (parent). Anal. Calcd for $C_7H_9N_3O$: C, 55.63; H, 5.96; N, 27.81. Found: C, 55.89; H, 5.62; N, 27.89.

(1-Methoxyethylidene)-*N*-(2-pyrazinyl)amine, 3ad. Following the general procedure, 0.25 g (1.0 mmol) of complex **1a** and 0.15 g (1.0 mmol) of sulfilimine **2ad** were irradiated for 6 h. After oxidation the crude imidate was purified by silica gel flash chromatography (hexane/ethyl acetate (20:1)): yellow oil; yield 0.09 g (62%); ^1H NMR δ 1.96 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 8.19 (d, 1H, J = 1.5 Hz, H3), 8.23 (d, 1H, J = 2.7 Hz, H6), 8.31 (dd, 1H, J_1 = 1.5 Hz, J_2 = 2.7 Hz, H5); ^{13}C NMR δ 165.5 (C=N), 157.0, 142.6, 139.8, 139.0 (arom), 53.9 (OCH_3), 17.0 (CH_3); IR (Cl_3CH) ν 1665 (C=N) cm^{-1}. Anal. Calcd for $C_7H_9N_3O$: C, 55.63; H, 5.96; N, 27.81. Found: C, 55.32; H, 6.26; N, 28.00.

(1-Methoxyethylidene)-*N*-(*p*-nitrophenyl)amine, 3ae. Following the general procedure, 0.25 g (1 mmol) of complex **1a** and 0.20 g (1 mmol) of sulfilimine **2ae** were irradiated for 4.5 h. After oxidation the crude imidate was purified by silica gel flash chromatography (hexane/ethyl acetate (10:1)): yellow oil; yield 0.10 g (52%); ^1H NMR δ 1.85 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 6.85 (d, 2H), 8.18 (d, 2H); ^{13}C NMR δ 161.9 (C=N), 155.5, 125.0, 121.4, 53.8, (OCH_3), 16.2 (CH_3); IR (Cl_3CH) 1685 (C=N) cm^{-1}; mass spectrum *m/z* 194 ($M^{\bullet+}$, parent), 163, 152, 149, 138. Anal. Calcd for $C_9H_{10}N_2O_3$: C, 55.67; H, 5.15; N, 14.43. Found: C, 55.85; H, 5.22; N, 14.27.

(1-Methoxyethylidene)-*N*-phenylalanine, 3af. Following the general procedure, 0.25 g (1 mmol) of complex **1a** and 0.16 g (1 mmol) of sulfilimine **2af** were irradiated for 2.5 h. After oxidation the crude imidate was purified by silica gel flash chromatography (hexane/ethyl acetate (10:1)): colorless oil; yield 0.10 g (70%); ^1H NMR δ 1.80 (s, 3H, CH_3), 3.77 (s, 3H, OCH_3) 6.74 (d, 2H), 7.00 (t, 1H), 7.26 (t, 2H); ^{13}C NMR δ 161.5 (C=N), 148.9, 128.7, 122.7, 120.9, 53.0, (OCH_3), 15.75 (CH_3); IR (Cl_3CH) ν 1685 (C=N) cm^{-1}; mass spectrum: *m/z* 149 ($M^{\bullet+}$, parent), 119, 107, 77. Anal. Calcd for $C_9H_{11}NO$: C, 72.48; H, 7.38; N, 9.39. Found: C, 75.52; H, 7.47; N, 9.62.

(1-Methoxyethylidene)-*N*-(*p*-anisyl)amine, 3ag. Following the general procedure, 0.25 g (1 mmol) of complex **1a** and 0.18 g (1 mmol) of sulfilimine **2ag** were irradiated for 3 h. After oxidation of crude imidate was purified by silica gel flash chromatography (hexane/ethyl acetate (10:1)): pale yellow oil; yield 0.16 g (90%); ^1H NMR δ 1.82 (s, 3H, CH_3), 3.77 (s, 6H, 2 × OCH_3), 6.69 (d, 2H), 6.82 (s, 2H); ^{13}C NMR δ 161.4 (C=N), 155.3, 141.9, 121.8, 114.0, 55.2, ($ArOCH_3$), 52.9 (OCH_3), 15.6 (CH_3); IR (Cl_3CD) ν 1680 (C=N) cm^{-1}; mass spectrum *m/z* 179 ($M^{\bullet+}$, parent), 164, 148. Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.04; H, 7.26; N, 7.82. Found: C, 67.27; H, 7.53; N, 8.03.

***N*-(Ethoxycarbonyl)methoxybenzylideneamine, 3be.** Following the general procedure, 0.18 g (0.58 mmol) of complex **1c** and 0.16 g (0.58 mmol) of sulfilimine **2be** were irradiated for 26 h. After oxidation the crude imidate was purified by silica gel flash chromatography (hexane/ethyl acetate (15:1)): yellow oil; yield 0.03 g (25%); ^1H NMR δ 1.20 (t, 3 H, J = 6.9 Hz, CH_3CH_2O), 3.92 (s, 3H, OCH_3), 4.16 (q, 2H, J = 6.9 Hz, CH_2), 7.36–7.76 (m, 5H, arom); ^{13}C NMR δ 163.3 (C=N), 160.9 (C=O), 145.1, 131.7, 128.5, 127.9 (arom), 62.4 (OCH_2), 55.0 (CH_3O), 14.1 (CH_3CH_2); IR (Cl_3CH) ν 1710 (C=O), 1665 (C=N) cm^{-1}. Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.74; H, 6.33; N, 6.76. Found: C, 63.43; H, 6.50; N, 6.47.

***N*-Phthalimidylmethoxybenzylideneamine, 3bf.** Following the general procedure, 0.31 g (1 mmol) of complex **1c** and 0.22 g (1 mmol) of sulfilimine **2bf** were irradiated for 14 h. After oxidation the crude imidate was purified by silica gel flash chromatography (hexane/ethyl acetate (10:1)): yellow crystalline solid; mp 108–110 °C (hexane/Cl_3CH); yield 0.17 g (60%); ^1H NMR δ 4.12 (s, 3H, OCH_3), 7.20–7.67 (m, 9H, arom); ^{13}C NMR δ 174.4 (C=O), 164.4 (C=N), 133.8, 130.8, 130.7, 130.4, 128.3, 127.1, 123.1 (arom), 56.2 (OCH_3); IR (Cl_3CH) ν 1790 (C=O), 1720 (C=O), 1630 (C=N) cm^{-1}. Anal. Calcd for $C_{16}H_{12}N_2O_3$: C, 68.55; H, 4.32; N, 10.00. Found: C, 68.49; H, 4.09; N, 10.28.

***N*-(2-(Phenylsulfonyl)ethyl)methoxybenzylideneamine, 3ce.** Following the general procedure, 0.31 g (1 mmol) of complex **1c** and 0.37 g (1 mmol) of sulfilimine **2ce** gave (no irradiation was required) after oxidation of the crude imidate and Florisil chromatography (hexane/ethyl acetate (1:1)) 0.24 g (80%) of imidate **3ce** as a pale yellow oil: ^1H NMR δ 3.40 (t, 2H, J = 6.6 Hz, CH_2SO_2), 3.46 (s, 3H, OCH_3), 3.71 (t, 2H, J = 6.6 Hz, CH_2N), 7.20–7.85 (m, 10H, arom); ^{13}C NMR δ 161.8 (C=N), 139.6, 133.0, 129.4, 128.7, 127.6, 127.3 (arom), 57.5 (CH_2SO_2), 52.6 (OCH_3), 43.7 (CH_2N); IR (Cl_3CH) ν 1665 (C=N) cm^{-1}. Anal. Calcd for $C_{16}H_{17}SNO_3$: C, 63.35; H, 5.65; N, 4.62; S, 10.55. Found: C, 63.41; H, 5.50; N, 4.47.

***N*-(2-(Phenylsulfonyl)ethyl)methoxyethylideneamine, 3cf.** Following the general procedure, 0.25 g (1 mmol) of complex **1a** and 0.37 g (1 mmol) of sulfilimine **2ce** gave (no irradiation was required) after oxidation of the crude imidate and Florisil chromatography (hexane/ethyl acetate (1:1)) 0.18 g (75%) of imidate **3cf** as a pale yellow oil: ^1H NMR δ 1.90 (s, 3H, CH_3),

3.37 (s, 3H, OCH_3), 3.41 (t, 2H, J = 6.0 Hz, CH_2SO_2), 3.59 (t, 2H, J = 6.0 Hz, CH_2N), 7.40–7.95 (m, 5H, arom); ^{13}C NMR δ 162.8 (C=N), 133.4, 129.1, 127.0, 124.7 (arom), 57.4 (CH_2SO_2), 52.1 (OCH_3), 43.3 (CH_2N), 15.0 (CH_3); IR (Cl_3CH) ν 1665 (C=N) cm^{-1}. Anal. Calcd for $C_{11}H_{15}SNO_3$: C, 54.75; H, 6.27; N, 5.81; S, 13.26. Found: C, 54.56; H, 6.48; N, 6.04.

***N*-(2-Cyanoethyl)methoxybenzylideneamine, 3cg.** Following the general procedure, 0.31 g (1 mmol) of complex **1c** and 0.25 g (1 mmol) of sulfilimine **2cf** gave (no irradiation was required) after oxidation of the crude imidate and Florisil chromatography (hexane/ethyl acetate (1:1)) 0.12 g (62%) of imidate **3cg** as a pale yellow oil: ^1H NMR δ 2.57 (t, 2H, J = 6.6 Hz, CH_2CN), 3.53 (t, 2H, J = 6.6 Hz, CH_2N), 3.82 (s, 3H, OCH_3), 7.20–7.45 (m, 5H, arom); ^{13}C NMR δ 162.9 (C=N), 131.5, 129.8, 128.4, 127.7 (arom), 118.8 (CN), 53.3 (OCH_3), 45.5 (CH_2N), 20.5 (CH_2CN); IR (Cl_3CH) ν 2225 (CN), 1670 (C=N) cm^{-1}. Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.18; H, 6.43; N, 14.89. Found: C, 70.23; H, 6.50; N, 15.01.

***N*-(*p*-Anisyl)methoxybenzylideneamine, 3ea.** Following the general procedure, 0.31 g (1 mmol) of complex **1c** and 0.18 g (1 mmol) of sulfilimine **2ag** were irradiated for 15 h. After oxidation the crude imidate was purified by vacuum bulb to bulb distillation: yellow oil; yield 0.17 g (71%); ^1H NMR δ 3.67 (s, 3H, *p*-OCH_3), 3.92 (s, 3H, OCH_3), 6.62–6.70 (dd, 4H, arom), 7.19–7.24 (m, 5H, arom); ^{13}C NMR δ 159.3 (C=N), 155.2, 141.4, 132.0, 129.6, 129.1, 127.8, 122.4, 113.9 (arom), 55.2 (*p*-OCH_3), 53.7 (OCH_3); IR (Cl_3CH) ν 1665 (C=N) cm^{-1}. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.65; H, 6.27; N, 5.81. Found: C, 74.72; H, 6.45; N, 6.11.

***N*-(*p*-Anisyl)-1-(benzyloxy)ethylideneamine, 3eb.** Following the general procedure, 0.32 g (1 mmol) of complex **1d** and 0.18 g (1 mmol) of sulfilimine **2ag** were irradiated for 16 h. After oxidation the imidate was obtained as an analytically pure compound. Pale brown oil. Yield 0.21 g (85%); ^1H NMR δ 1.89 (s, 3H, CH_3), 3.79 (s, 3H, OCH_3), 5.21 (s, 2H, CH_2), 6.71 (d, 2H, arom), 6.85 (d, 2H, arom), 7.35–7.43 (m, 5H, arom); ^{13}C NMR δ 161.8 (C=N), 155.6, 145.1, 142.1, 128.4, 128.1, 127.8, 122.0, 114.2 (arom), 67.5 (OCH_2), 55.4 (OCH_3), 16.2 (CH_3); IR (Cl_3CH) ν 1670 (C=N) cm^{-1}. Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.26; H, 6.72; N, 5.49. Found: C, 75.55; H, 6.47; N, 5.12.

***N*-(*p*-Anisyl)-1-(allyloxy)ethylideneamine, 3ec.** Following the general procedure, 0.26 g (0.94 mmol) of complex **1e** and 0.17 g (0.94 mmol) of sulfilimine **2ag** were irradiated for 15 h. After oxidation the crude imidate was purified by Florisil chromatography (hexane/ethyl acetate (9:1)): yellow oil; yield 0.11 g (54%); ^1H NMR δ 1.83 (s, 3H, CH_3), 3.75 (s, 3H, OCH_3), 4.66 (dt, 2H, J = 5.7, 1.4 Hz, CH_2), 5.22 (ddd, 1H, J = 10.5, 3.1, 1.4 Hz, *cis*-CH_2=), 5.34 (ddd, 1H, J = 17.1, 3.1, 1.4 Hz, *trans*-CH_2=), 6.03 (ddd, 1H, J = 17.1, 10.5, 5.7 Hz, CH=), 6.66 (d, 2H, arom), 6.82 (d, 2H, arom); ^{13}C NMR δ 161.0 (C=N), 155.5, 142.1, 121.9, 114.2 (arom), 133.2 (CH=), 117.4 (H_2C=), 66.3 (OCH_2), 55.3 (OCH_3), 16.0 (CH_3); IR (Cl_3CH) ν 1670 (C=N), 1610 (C=C) cm^{-1}. Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.21; H, 7.37; N, 6.83. Found: C, 70.00; H, 7.44; N, 6.57.

***N*-(*p*-Anisyl)-1-(3-butynyloxy)ethylideneamine, 3ed.** Following the general procedure, 0.29 g (1 mmol) of complex **1f** and 0.18 g (1 mmol) of sulfilimine **2ag** were irradiated for 15 h. After oxidation the crude imidate was purified by Florisil chromatography (hexane/ethyl acetate (1:1)): yellow oil which crystallized upon standing at room temperature; mp 50 °C; yield 0.11 g (50%); ^1H NMR δ 1.82 (s, 3H, CH_3), 2.00 (t, 1H, J = 2.7 Hz, CH), 2.60 (dt, 2H, J = 2.7, 6.9 Hz, CH_2CCH), 3.76 (s, 3H, OCH_3), 4.26 (t, 2H, J = 6.9 Hz, CH_2O), 6.65 (d, 2H, arom), 6.81 (d, 2H, arom); ^{13}C NMR δ 161.1 (C=N), 155.5, 142.0, 121.8, 114.2 (arom), 81.2 (*C*CH), 69.4 (OCH_2), 63.3 (*C*HC), 55.4 (OCH_3), 18.8 (CH_2), 15.9 (CH_3); IR (Cl_3CH) ν 2420 (CC), 1675 (C=N) cm^{-1}. Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.85; H, 6.96; N, 6.45. Found: C, 71.55; H, 6.97; N, 6.29.

***N*-(*p*-Anisyl)cyclopropylmethoxymethylideneamine, 3ee.** Following the general procedure, 0.27 g (1 mmol) of complex **1g** and 0.18 g (1 mmol) of sulfilimine **2ag** were irradiated for 16 h. After oxidation the crude imidate was purified by silica gel flash chromatography (hexane/ethyl acetate (10:1)): colorless oil; yield 0.13 g (63%); ^1H NMR δ 0.60–0.67 (m, 2H, CH_2), 0.96–1.01 (m, 2H, CH_2), 1.46–1.55 (m, 1H, CH), 3.70 (s, 3H, OCH_3), 3.77 (s, 3H, *p*-OCH_3), 6.75–6.90 (m, 4H, arom); ^{13}C NMR δ 164.3 (C=N), 155.3, 142.0, 122.5, 114.2 (arom), 55.4 (*p*-OCH_3), 52.9 (OCH_3), 9.5 (CH), 6.6 (2 CH_2); IR (Cl_3CH) ν 1655 (C=N) cm^{-1}. Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.21; H, 7.37; N, 6.83. Found: C, 69.87; H, 6.98; N, 7.11.

***N*-(*p*-Anisyl)-1-methoxy-3-phenyl-2-propenylideneamine, 3ef.** Following the general procedure, 0.34 g (1 mmol) of complex **1h** and 0.18 g (1 mmol) of sulfilimine **2ag** were irradiated for 20 h. After oxidation the imidate was obtained as an analytically pure compound: pale brown oil; yield 0.23 g (85%); ^1H NMR δ 3.79 (s, 3H, *p*-OCH_3), 3.90 (s, 3H, OCH_3), 6.40 (d, 1H, J = 16.2 Hz, PhCH=C*H*), 6.77 (d, 2H, arom), 6.85 (d, 2H, arom), 7.37 (d, 1H, J = 16.2 Hz, PhC*H*), 7.24–7.41 (m, 5H, Ph); ^{13}C NMR δ 158.2 (C=N), 138.5 (PhC*H*), 114.5 (PhCH=*C*H), 155.7, 141.2, 135.4, 129.1, 128.7, 127.4, 122.7, 114.1 (arom), 55.3 (*p*-OCH_3), 53.1 (OCH_3); IR (Cl_3CH) ν 1655 (C=N), 1615 (C=C) cm^{-1}. Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.37; H, 6.41; N, 5.24. Found: C, 76.52; H, 6.68; N, 5.11.

***N*-(*p*-Anisyl)-1-methoxy-3-(trimethylsilyl)propynylideneamine, 3eg.** Following the general procedure, 0.33 g (1 mmol) of complex **1i** and 0.18 g (1 mmol) of sulfilimine **2ag** gave (no irradiation was required) after oxidation the crude imidate, which was purified by chromatography (hexane/ethyl acetate (10:1)): light color oil; yield 0.15 g (59%); ^1H NMR δ 0.07 (s, 9H, $SiMe_3$), 3.74 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 6.81 (d, 2H, arom), 6.93 (d, 2H, arom); ^{13}C NMR δ 145.6 (C=N), 156.4, 140.3, 122.7, 113.6 (arom), 98.8 (*C*C=N), 93.1 (CSiMe_3), 55.4 (*p*-OCH_3), 53.9 (OCH_3), 0.94 (TMS); IR (Cl_3CH) ν 2400 (CC), 2170 (CC), 1630 (C=N) cm^{-1}. Anal. Calcd for $C_{14}H_{19}NO_2Si$: C, 64.36; H, 7.28; N, 5.36; Si, 10.73. Found: C, 64.45; H, 7.29; N, 5.35.

(+)-*N*-(*p*-Anisyl)-1-((1(*R*)-phenylbutyl)oxy)ethylideneamine, 3eh. Following the general procedure, 0.37 g (1 mmol) of complex **1j** and 0.18 g (1 mmol) of sulfilimine **2ag** were irradiated for 9 h. After oxidation the crude imidate was purified by chromatography (hexane/ethyl acetate (10:1)) in Florisil: colorless oil; yield 0.21 g (70%); ^1H NMR δ 0.93 (t, 3H, J = 7.2 Hz, CH_3CH$_2$), 1.20–1.40 (m, 4H, 2 × CH_2), 1.81 (s, 3H, CH_3), 3.71 (s, 3H, OCH_3), 6.02 (t, 1H, J = 6.6 Hz, CH), 6.53 (d, 2H, arom), 6.76 (d, 2H, arom), 7.20–7.37 (m, 5H, Ph); ^{13}C NMR δ 160.2 (C=N), 155.2, 142.3, 142.0, 128.0, 127.0, 126.5, 121.7, 114.0 (arom), 75.5 (O-CH), 55.2 (OCH_3), 38.6 (CH_2CH), 18.7 (CH_2CH_3), 16.2 (CH_3C=N), 13.9 (CH_3CH_2); IR (Cl_3CH) ν 1680 (C=N) cm^{-1}; $[\alpha]^{24}_D$ = +115.1° (c = 0.218). Anal. Calcd for $C_{19}H_{23}NO_2$: C, 76.72; H, 7.80; N, 4.71. Found: C, 76.53; H, 7.71; N, 4.92.

(−)-*N*-(*p*-Anisyl)-1-(menthyloxy)ethylideneamine, 3ei. Following the general procedure, 0.37 g (1 mmol) of complex **1k** and 0.18 g (1 mmol) of sulfilimine **2ag** were irradiated for 9 h. After oxidation the crude imidate was purified by silica gel flash chromatography (hexane/ethyl acetate (40:1)): colorless oil which crystallized upon standing at room temperature; mp 59–60 °C; yield 0.30 g (98%); ^1H NMR δ 0.83 (d, 3H, J = 6.9 Hz, CH_3), 0.89 (d, 3H, J = 5.1 Hz, CH_3), 0.91 (d, 3H, J = 5.4 Hz, CH_3), 0.86–1.14 (m, 3H, CH, CH_2), 1.32–1.44 (m, 1H, CH), 1.44–1.56 (m, 1H, CH), 1.60–1.70 (m, 2H, CH_2), 1.76 (s, 3H, CH_3C=N), 1.92–2.04 (m, 1H, CH), 1.96–2.25 (m, 1H, CH), 3.75 (s, 3H, OCH_3), 4.94 (ddd, 1H, J_1 = 4.2 Hz, J_2 = 10.8 Hz, CHO), 6.63 (d, 2H, arom), 6.79 (d, 2H, arom); ^{13}C NMR δ 160.8 (C=N), 155.3, 142.7, 121.8, 114.1 (arom), 73.7 (CHO), 55.4 (OCH_3), 47.6, 40.5, 34.5, 31.2, 26.5, 23.6, 22.1, 20.7, 16.7 (CH_3C=N), 16.3; IR (Cl_3CH) ν 1660 (C=N) cm^{-1}; $[\alpha]^{24}_D$ = −45.1° (c = 0.122). Anal. Calcd for $C_{19}H_{29}NO_2$: C, 75.19; H, 9.64; N, 4.62. Found: C, 75.31; H, 9.84; N, 4.53.

(−)-*N*-(*p*-Anisyl)-1-(1(*R*)-myrtenyloxy)ethylideneamine, 3ej. Following the general procedure, 0.37 g (1 mmol) of complex **1l** and 0.18 g (1 mmol) of sulfilimine **2ag** were irradiated for 15 h. After oxidation the crude imidate was purified by Florisil chromatography (hexane/ethyl acetate 2%): yellow oil; yield 0.12 g (40%); ^1H NMR δ 0.84 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.81 (s, 3H, CH_3C=N), 2.06–2.12 (m, 1H, CH), 2.16–2.21 (m, 2H, CH_2), 2.24–2.32 (m, 2H, CH_2), 2.37–2.43 (m, 1H, CH), 3.76 (s, 3H, OCH_3), 4.51–4.53 (m, 2H, CH_2O), 5.56–5.59 (m, 1H, CH=), 6.65 (d, 2H, arom), 6.80 (d, 2H, arom); ^{13}C NMR δ 161.5 (C=N), 155.4, 142.4, 121.9, 114.2 (arom), 143.9 (C=), 120.1 (CH=), 68.1 (CH_2O), 55.4 (OCH_3), 43.6, 40.7, 38.0, 31.5, 31.3, 26.1, 21.0, 16.1 (CH_3C=N), IR (Cl_3CH) ν 1675 (C=N, C=C) cm^{-1}; $[\alpha]^{24}_D$ = −15.9° (c = 0.044). Anal. Calcd for $C_{19}H_{25}NO_2$: C, 76.21; H, 8.42; N, 4.68. Found: C, 76.43; H, 8.56; N, 4.80.

(−)-*N*-(*p*-Anisyl)-1-((1*S*)-*endo*-bornyloxy)ethylideneamine, 3ek. Following the general procedure, 0.15 g (0.4 mmol) of complex **1m** and 0.07 g (0.4 mmol) of sulfilimine **2ag** were irradiated for 15 h. After oxidation the crude imidate was purified by Florisil chromatography (hexane/ethyl acetate 5%): yellow oil which crystallized upon standing at room temperature; mp 54–55 °C; yield 0.08 g (66%); ^{1}H NMR δ 0.87 (s, 3H, CH_3), 0.90 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), 1.03 (dd, 1H, J_1 = 3.5 Hz, J_2 = 13.7 Hz, CH), 1.19 (t, 1H, J = 7.5 Hz, CH), 1.21–1.35 (m, 2H, CH_2), 1.66 (t, 1H, J = 4.3 Hz, CH), 1.80 (s, 3H, CH_3C=N), 2.01–2.10 (m, 1H, CH), 2.37–2.45 (m, 1H, CH), 3.76 (s, 3H, OCH_3), 4.96 (dt, 1H, J_1 = 1.8 Hz, J_2 = 2.6 Hz, J_3 = 9.6 Hz, CHO), 6.65 (d, 2H, arom), 6.81 (d, 2H, arom); ^{13}C NMR δ 161.6 (C=N), 155.3, 142.9, 121.9, 114.1 (arom), 80.0 (CHO), 55.4 (OCH_3), 48.7, 47.5, 44.9, 37.1, 28.1, 27.2, 19.8, 19.0, 16.3 (CH_3C=N), 13.7; IR (Cl_3CH) ν 1665 (C=N) cm^{-1}; $[\alpha]^{24}_D$ = −65° (*c* = 0.100). Anal. Calcd for $C_{19}H_{27}NO_2$: C, 75.70; H, 9.03; N, 4.65. Found: C, 75.81; H, 9.15; N, 4.65.

***N*-(2-Ethoxyethyl)benzamide, 4a.** Following the general procedure, 0.09 g (0.29 mmol) of complex **1c** and 0.09 g (0.29 mmol) of sulfilimine **2ca** were irradiated for 17 h. After oxidation the crude amide was purified by silica gel flash chromatography (ethyl acetate): yellow oil; yield 0.03 g (50%); ^{1}H NMR 1.20 (t, 3H, J = 6.9 Hz, CH_3), 3.52 (q, 2H, J = 6.9 Hz, CH_2CH_3), 3.60 (t, 2H, J = 6.4 Hz, CH_2O), 3.62 (q, 2H, J = 4.8 Hz, CH_2NH), 6.56 (broad s, 1H, NH), 7.30–7.80 (arom); ^{13}C NMR 167.4 (CO), 134.6, 131.4, 128.5, 126.9 (arom), 69.0 (CH_2O), 66.5 (CH_2O), 39.9 (CH_2N), 15.1 (CH_3); IR (Cl_3CH) 3400 (NH), 1660 (CO) cm^{-1}. Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.35; H, 7.83; N, 7.25. Found: C, 68.20; H, 8.03; N, 7.29.

***N*-(2-Acetoxyethyl)benzamide, 4b.** Following the general procedure, 0.087 g (0.28 mmol) of complex **1c** and 0.08 g (0.28 mmol) of sulfilimine **2cb** were irradiated for 17 h. After oxidation of crude amide was purified by silica gel flash chromatography (ethyl acetate): yellow oil; yield 0.03 g (50%); ^{1}H RMN δ 2.10 (s, 3H, CH_3), 3.73 (q, 2H, J = 5.5 Hz, CH_2NH), 4.30 (t, 2H, J = 5.5 Hz, CH_2O), 6.59 (broad s, 1H, NH), 7.40–7.80 (m, 5H, arom); ^{13}C RMN δ 171.4 ($COCH_3$), 167.6 (CONH), 134.3, 131.6, 128.6, 127.0 (arom), 63.3 (CH_2O), 39.6 (CH_2NH), 20.8 (CH_3); IR (Cl_3CH) ν 3360 (NH), 1735 ($COCH_3$), 1660 (CONH) cm^{-1}. Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.74; H, 6.33; N, 6.76. Found: C, 63.52; H, 6.12; N, 6.89.

***N*-(2-(Ethoxycarbonyl)ethyl)benzamide, 4c.** Following the general procedure, 0.31 g (1 mmol) of complex **1c** and 0.30 g (1 mmol) of sulfilimine **2cc** were irradiated for 17 h. After oxidation the crude amide was purified by silica gel flash chromatography (hexane/ethyl acetate (1:1)): pale yellow oil; yield 0.12 g (55%); ^{1}H NMR δ 1.26 (t, 3H, J = 7.2 Hz, CH_3), 2.63 (t, 2H, J = 6.0 Hz, CH_2CO), 3.71 (q, 2H, J = 6.0 Hz, CH_2NH), 4.16 (q, 2H, J = 7.2 Hz, CH_2O), 6.88 (broad s, 1H, NH), 7.38–7.77 (m, 5H, arom); ^{13}C NMR 172.8 (CO), 167.3 (CONH), 134.4, 131.4, 128.5, 126.8 (arom), 60.7 (CH_2O), 35.3 (CH_2O), 33.9 (CH_2N), 14.1 (CH_3); IR (Cl_3CH) ν 3400 (NH), 1730 (COO), 1660 (CONH) cm^{-1}. Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.13; H, 6.84; N, 6.33. Found: C, 64.98; H, 7.01; N, 6.50.

***N*-[2-(1,3-Dioxolan-2-yl)ethyl]benzamide, 4d.** Following the general procedure, 0.31 g (1 mmol) of complex **1c** and 0.30 g (1 mmol) of sulfilimine **2cd** were irradiated for 17 h. After oxidation the crude amide was purified by silica gel flash chromatography (hexane/ethyl acetate (1:1)): yellow oil; yield 0.22 g (98%); ^{1}H NMR δ 1.99 (dt, 2H, J_1 = 6.0 Hz, J_2 = 4.2 Hz, CH_2CH), 3.59 (q, 2H, J = 6.0 Hz, CH_2NH), 3.83–3.99 (m, 4H, 2 × CH_2O), 4.97 (t, 1H, J = 4.2 Hz, CH), 7.22 (broad s, 1H, NH), 7.30–7.85 (m, 5H, arom); ^{13}C NMR δ 167.0 (CO), 134.4, 131.0, 128.2, 126.6 (arom), 103.4 (CH), 64.6 (2 × CH_2O), 34.9 (CH_2N), 32.3 (CH_2C); IR (Cl_3CH) ν 3420 (NH), 1655 (CO) cm^{-1}. Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.13; H, 6.84; N, 6.33. Found: C, 65.31; H, 6.69; N, 6.22.

***N*-(2-(Phenylsulfonyl)ethyl)benzamide, 4e.** Compound **4e** was prepared as compound **3ce** except for the crude reaction mixture after oxidation was led to stand at room temperature for 24 h. The crude amide thus obtained was purified by silica gel flash chromatography (hexane/ethyl acetate (1:1)): white crystalline solid; mp 102–104 °C (hexane/Cl_3CH); yield 0.28 g (96%); ^{1}H NMR δ 3.42 (t, 2H, J = 6.3 Hz, CH_2SO_2), 3.85 (q, 2H, J = 6.3 Hz, CH_2NH), 7.10 (broad s, 1H, NH), 7.34–7.81 (m, 10H, arom); ^{13}C NMR δ 167.4 (C=O), 138.7, 133.9, 133.5, 131.6, 129.4, 128.4, 127.7, 126.9 (arom), 55.0 (CH_2SO_2), 33.8 (CH_2NH); IR (Cl_3CH) ν 3400 (NH), 1655 (C=O) cm^{-1}. Anal. Calcd for $C_{15}H_{15}SNO_3$: C, 62.27; H, 5.23; N, 4.84; S, 11.06. Found: C, 62.18; H, 5.44; N, 4.92; S, 10.94.

***N*-(2-(Phenylsulfonyl)ethyl)acetamide, 4f.** Compound **4f** was prepared as compound **3cf** except that the crude reaction mixture after oxidation was led to stand at room temperature for 24 h. The crude amide thus obtained was purified by silica gel flash chromatography (hexane/ethyl acetate (1:1)): pale yellow oil; yield 0.16 g (70%); ^{1}H NMR δ 1.93 (s, 3H, CH_3), 3.31 (t, 2H, J = 6.0 Hz, CH_2SO_2), 3.66 (q, 2H, J = 6.0 Hz, CH_2N), 6.49 (broad s, 1H, NH), 7.55–7.91 (m, 5H, arom); ^{13}C NMR δ 170.3 (CO), 138.7, 134.0, 129.4, 127.7 (arom), 55.1 (CH_2SO_2) 33.2 (CH_2N), 22.9 (CH_3); IR (Cl_3CH) ν 3250 (NH), 1675 (C=N). Anal. Calcd for $C_{10}H_{13}SNO_3$: C, 52.85; H, 5.77; N, 6.17; S, 14.08. Found: C, 52.69; H, 5.57; N, 5.96; S, 14.26.

***N*-(2-Cyanoethyl)benzamide, 4g.** Compound **4g** was prepared as compound **3cg** except that the crude reaction mixture after oxidation was led to stand at room temperature for 24 h. The crude amide thus obtained was purified by silica gel flash chromatography by (EtOAc): pale yellow oil; yield 0.14 g (80%); ^{1}H NMR δ 2.71 (t, 2H, J = 6.3 Hz, CH_2CN), 3.67 (q, 2H, J = 6.3 Hz, CH_2NH), 7.13 (broad s, 1H, NH), 7.38–7.79 (m, 5H, arom); ^{13}C NMR δ 168.0 (CO), 133.5, 131.9, 128.6, 127.0 (arom), 118.3 (CN), 36.1 (CH_2NH), 18.3 (CH_2CN); IR (Cl_3CH) ν 3550 (NH), 2225 (CN), 1650 (CO) cm^{-1}. Anal. Calcd for $C_{10}H_{10}N_2O$: C, 68.93; H, 5.79; N, 16.09. Found: C, 69.12; H, 5.64; N, 15.92.

Reaction of *N*-Haloimidates 2d and Diphenyl Sulfide. Synthesis of *N*-Benzoylsulfilimine 5. Following the general procedure, 0.31 g (1 mmol) of complex **1c** and 0.28 g (1 mmol) of *N*-chloro- (**2da**) or *N*-bromosulfilimine (**2db**) was irradiated for 48 h. Analytically pure *N*-benzoylsulfilimine, **5**, was obtained after purification of the crude mixture by silica gel flash chromatography (Cl_3CH/CH_3OH (20:1)): yield 0.18 g (60%); mp 126–127 °C (benzene) (lit.[33] mp 126–127 °C).

Isolation of $(CO)_5CrNCMe$, 6. Following the experimental procedure described for the synthesis of amide **4b**, from 0.17 g (0.59 mmol) of sulfilimine **2cb** and 0.17 (0.53 mmol) of complex **1c**, 0.04 g (40%) of complex **6** was obtained by flash chromatography (pentane) of the crude reaction mixture obtained prior to oxidation, as a very unstable yellow oil: ^{1}H NMR δ 2.19 (s, 3H, CH_3); ^{13}C NMR δ 286.1 (CN), 219.1 (*trans*-CO), 213.9 (*cis*-CO), 4.0 (CH_3); IR (Cl_3CH) ν 1980 (*trans*-CO), 1940 (*cis*-CO), 1900 (s) cm^{-1}.

Isolation of $(CO)_5CrSMe_2$. Following the experimental procedure described for the synthesis of imidate **3ag**, complex **1a** (0.25 g, 1 mmol) and sulfilimine **2ag** (0.18 g, 1 mmol) were irradiated in ether, under CO atmosphere (CO, balloon) for 9 h. Silica gel chromatography (pentane) of the crude reaction mixture obtained prior to oxidation yields 0.07 g (25%) of complex as an unstable deep yellow oil: ^{1}H NMR δ 2.32 (s, 6H, Me_2); ^{13}C NMR δ 220.9 (*trans*-CO), 214.8 (*cis*-CO), 27.2 (Me_2); IR (Cl_3CH) ν 2070 (*trans*-CO), 1930 (*cis*-CO), 1430, 1220 cm^{-1}.

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