

# Mesoionic Compounds VIII. Synthesis of 3-Phenylsydnonyl Substituted Alkenes. Some New Photochromic Sydnones (1a).

Claude V. Greco (1b) and Bernard P. O'Reilly (1c)

Department of Chemistry, St. John's University, Jamaica, N. Y. 11432

Received August 11, 1971

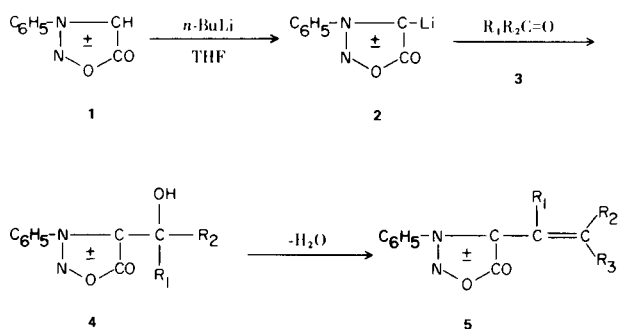
The reactions of 3-phenylsydnonyllithium with a variety of ketones to afford tertiary carbinols **4a-4i** and their subsequent dehydration to 4-(3-phenylsydnonyl) alkenes **5a-5i** are discussed. Among the alkenes, 2-[4-(3-phenylsydnonyl)]propene (**5b**) and 1-[4-(3-phenylsydnonyl)]-1-cyclohexene (**5i**) were photochromic. A Wittig reaction between ethyl-4-(3-phenylsydnonyl)-ketone and methylenetriphenylphosphorane afforded the photochromic 2-[4-(3-phenylsydnonyl)]-1-butene (**5j**).

After the report on the photochromic behavior of 3-(3-pyridyl)sydnone (2), several investigators (3,4) examined the effect of substituents on the pyridylsydnone photochromism. A reversible color transformation by the solids, on exposure to uv radiation, was not exhibited by any of these substituted pyridylsydnones.

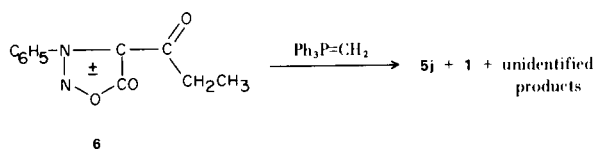
Studies on the photochromism and esr absorption of 3-(3-pyridyl)sydnone indicated the property resulted from color centers analogous to those of alkali halides (5,6). Metz and co-workers (7) favored the formation of a metastable intermediate by uv excitation characterized by color center formation. However, the photochromic behavior could not be related to structural parameters. Indications were that the property might be a general phenomenon of the mesoionic ring. As a continuation of our search for other photochromic sydnones (4) to support this latter hypothesis coupled with our interest in the chemistry of organometallic derivatives of sydnones (1,8) we chose to synthesize some sydnonyl substituted alkenes.

The ketones **3a-3i** (see Scheme I and Table I) on treatment with 3-phenylsydnonyllithium (2) (8b) readily

SCHEME I



SCHEME II



afforded the respective 4-(3-phenylsydnonyl)carbinols (**4a-4i**) (9). In aqueous acetic acid, these tertiary carbinols were dehydrated to the alkenes **5a-5i** by heating one hour on a steam bath (consult Table II). The structures of carbinols **4a**, **4b**, **4d**, **4h**, and **4i** preclude isomerism based on the position of the double bond in the alkene. Therefore, these carbinols yielded only **5a**, **5b**, **5d**, **5h**, and **5i**, respectively. With **4c**, **4e**, and **4f** where isomerism due to the position of the double bond was possible, the most stable alkene predominated, i.e. the more highly substituted. Thus, in aqueous acetic acid **4c** gave a mixture of **5c** and 2-[4-(3-phenylsydnonyl)]-1-butene (**5j**). Likewise, **4e** gave a mixture of **5e** and 2-[4-(3-phenylsydnonyl)]-1-pentene (**5k**) while **4f** afforded **5f** and 4-methyl-2-[4-(3-phenylsydnonyl)]-1-pentene (**5l**). The components of these mixtures were not separated. An nmr analysis in deuteriochloroform (or deuterioacetone) showed a 3:2 ratio of Saytzeff alkene to vinylidene olefin in each mixture. The nmr spectra of these same mixtures examined in TFA portrayed chemical shifts and proton counts consistent with only the most highly substituted alkenes, **5c**, **5e**, and **5f** (see Table IV). The latter were then prepared, uncontaminated with the related vinylidene olefin, by dehydrating **4c**, **4e**, and **4f** in TFA (cf. Experimental and Table II). The carbinol **4g** was dehydrated in aqueous acetic acid to yield only **5g**, the vinylidene olefin without producing any of the Saytzeff alkene, 3-methyl-2-[4-(3-phenylsydnonyl)]-2-butene (**5m**). It was also possible to

TABLE I  
Reactions of Ketones with 3-Phenylsydnonyllithium

Ketone Reactant	Substituents Carbinol Product	R <sub>1</sub>	R <sub>2</sub>	Recrystd. from: (a)	M.p., °C	Yield % (b)	Carbinol Formula	Analysis % C	Found H	(Required) N
<b>3a</b>	<b>4a</b>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	A	146-147	42.8	C <sub>16</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>	67.90 (68.08)	5.04 (5.00)	9.72 (9.92)
<b>3b</b>	<b>4b</b>	CH <sub>3</sub>	CH <sub>3</sub>	B	139-140	52.6	C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub>	59.96 (59.99)	5.61 (5.49)	12.51 (12.72)
<b>3c</b>	<b>4c</b>	CH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub>	A	127-128	60.9	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>	61.61 (61.53)	6.06 (6.02)	11.86 (11.96)
<b>3d</b>	<b>4d</b>	CH <sub>3</sub> CH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub>	A	135-136	59.4	C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	62.91 (62.89)	6.35 (6.50)	11.35 (11.28)
<b>3e</b>	<b>4e</b>	CH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	C	87-89	54.8	C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	62.92 (62.89)	6.30 (6.50)	11.40 (11.28)
<b>3f</b>	<b>4f</b>	CH <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub>	B	100-102	42.7	C <sub>14</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub>	64.22 (64.11)	7.01 (6.92)	10.52 (10.68)
<b>3g</b>	<b>4g</b>	CH <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> CH	D	113-114	28.8	C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	62.74 (62.89)	6.57 (6.50)	11.20 (11.28)
<b>3h</b>	<b>4h</b>	-CH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> -		--	117-121 (c)	65.1 (c)	C <sub>13</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>	-----	----	-----
<b>3i</b>	<b>4i</b>	-CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> -		C	125-126	56.9	C <sub>14</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	64.77 (64.60)	6.03 (6.20)	10.63 (10.76)

(a) Recrystallization Solvents: A = benzene, B = 2-propanol-hexane, C = benzene-hexane, D = methanol-water; (b) Based on 3-Phenylsydnone; (c) Crude product could not be further purified, no elemental analysis.

TABLE II  
Preparation of 3-Phenylsydnonyl Alkenes

Alkene	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Recrystd. from: (a)	M.p., °C	Yield % (b)	Formula	Analysis C	%	Found H	(Required) N
<b>5a</b>	C <sub>6</sub> H <sub>5</sub>	H	H	C	103-105	71.7	C <sub>16</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	72.68 (72.72)		4.68 (4.58)	10.52 (10.62)
<b>5b</b>	CH <sub>3</sub>	H	H	E	109-110	83.8	C <sub>11</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub>	65.19 (65.34)		4.11 (4.98)	14.02 (13.85)
<b>5c(c)</b>	CH <sub>3</sub>	H	CH <sub>3</sub>	E	114-116	86.2	C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	66.42 (66.65)		5.50 (5.59)	12.75 (12.95)
<b>5d</b>	CH <sub>3</sub> CH <sub>2</sub>	H	CH <sub>3</sub>	E	110-112	93.5	C <sub>13</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>	67.85 (67.81)		6.24 (6.13)	12.35 (12.17)
<b>5e(c)</b>	CH <sub>3</sub>	H	CH <sub>3</sub> CH <sub>2</sub>	E	66-67	81.0	C <sub>13</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>	67.65 (67.81)		6.10 (6.13)	12.14 (12.17)
<b>5f(c)</b>	CH <sub>3</sub>	H	(CH <sub>3</sub> ) <sub>2</sub> CH	E	48-50	72.8	C <sub>14</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>	68.63 (68.83)		6.53 (6.60)	11.47 (11.47)
<b>5g</b>	(CH <sub>3</sub> ) <sub>2</sub> CH	H	H	E	104-106	92.0	C <sub>13</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>	67.72 (67.81)		6.23 (6.13)	12.34 (12.17)
<b>5h</b>	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	H	H	E	128-130	83.7	C <sub>13</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	68.29 (68.41)		5.19 (5.30)	12.24 (12.27)
<b>5i</b>	-CH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> -	H	H	E	117-119	83.9	C <sub>14</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>	69.55 (69.41)		5.82 (5.82)	11.72 (11.56)
<b>5j</b>	CH <sub>3</sub> CH <sub>2</sub>	H	H	B	101-102	8.01	C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	66.81 (66.65)		5.74 (5.59)	12.76 (12.95)

(a) Recrystallization Solvents: C = benzene-hexane, E = ethanol-water, B = 2-propanol-hexane; (b) Based on carbinol **4** having same small subscript letter, e.g. **5a** from **4a** etc.;  
(c) Obtained by dehydration with trifluoroacetic acid. All others dehydrated with acetic acid except **5j** obtained by Wittig reaction.

TABLE III

## Spectral Data — Carbinols

Substance	Ir, $\nu$ KBr max OH C=O $\mu$	Uv, $\lambda$ MeOH max nm (log $\epsilon$ )	Solvent (a)	Nmr (ppm) $\delta$	(Multiplicity (b), No. of Protons, Assignment)
<b>4a</b>	2.99 5.79	308 (4.17) 214 (4.41)	A	7.12 6.18 1.96	(s, 10, two C <sub>6</sub> H <sub>5</sub> ) (s, 1, OH) (s, 3, CH <sub>3</sub> )
<b>4b</b>	2.96 5.89	308 (4.30) 212 (3.86)	A	7.67 5.21 1.46	(s, 5, C <sub>6</sub> H <sub>5</sub> ) (s, 1, OH) (s, 6, two CH <sub>3</sub> )
<b>4c</b>	2.95 5.87	307 (4.27) 213 (4.15)	B	7.57 3.26 1.74 1.44 0.85	(s, 5, C <sub>6</sub> H <sub>5</sub> ) (broad s, 1, OH) (q, 2, -CH <sub>2</sub> -) (c) (s, 3, CH <sub>3</sub> ) (t, 3, CH <sub>3</sub> ) (c)
<b>4d</b>	2.97 5.86	306 (4.34) 212 (4.21)	B	7.53 2.96 1.78  0.85	(s, 5, C <sub>6</sub> H <sub>5</sub> ) (broad s, 1, OH) (m, 4, two-CH <sub>2</sub> -) (d) (t, 6, two CH <sub>3</sub> ) (d)
<b>4e</b>	2.95 5.77	310 (4.05) 212 (4.16)	B	7.58 3.19 1.47 1.50 1.00-1.40 0.84	(s, 5, C <sub>6</sub> H <sub>5</sub> ) (broad s, 1, OH) (s, 3, CH <sub>3</sub> ) (m, 2, -CH <sub>2</sub> -) (e) (m, 2, -CH <sub>2</sub> -) (e) (t, 3, CH <sub>3</sub> ) (f)
<b>4f</b>	2.95 5.83	308 (4.01) 213 (4.17)	B	7.58 3.28 1.57 1.20 1.48 0.86	(s, 5, C <sub>6</sub> H <sub>5</sub> ) (broad s, 1, OH) (m, 2, -CH <sub>2</sub> -) (c) (m, 1, -CH-) (s, 3, CH <sub>3</sub> ) (d, 6, two CH <sub>3</sub> ) (f)
<b>4g</b>	2.96 5.87	308 (4.08) 212 (4.18)	B	7.56 3.22 2.10 1.38 0.89 0.86	(s, 5, C <sub>6</sub> H <sub>5</sub> ) (s, 1, OH) (septet, 1, CH) (d) (s, 3, CH <sub>3</sub> ) (d, 3, CH <sub>3</sub> ) (d) (d, 3, CH <sub>3</sub> ) (d)
<b>4h</b>			No Spectral Data		
<b>4i</b>	3.05 5.89	310 (4.34) 212 (4.43)	B	7.59 3.23 1.2-2.2	(s, 5, C <sub>6</sub> H <sub>5</sub> ) (s, 1, OH) (broad m, 10, CH <sub>2</sub> ) (e)

(a) A = DMSO; B = deuteriochloroform; (b) s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet; (c) J = 7.5 Hz; (d) J = 7.0 Hz; (e) These multiplets were not adequately resolved to allow determination of coupling constants. A more accurate assignment of the sets of methylene protons was, therefore, not possible; (f) J = 6.0 Hz.

obtain the nmr spectrum of **5g** in TFA without isomerization to **5m**. Only after 24 hours in TFA did the nmr spectrum of **5g** show 20% isomerization to **5m**.

In addition to the isomerism based on the position of the double bond, alkenes **5c-5f** possessed geometrical isomerism. The olefinic protons of these alkenes found in the downfield range of 5.48-6.08  $\delta$  were considered

oriented *cis* to the 3-phenylsydnonyl substituent. We had several reasons for assigning this configuration to these alkenes based on nmr spectral data: (i) the proton at 5.97  $\delta$  of **5a** would have a *cis* relationship to the phenyl group since it would be more deshielded (12) than the proton *cis* to the 3-phenylsydnonyl group (5.75  $\delta$ ); (ii) the protons of **5b** (5.42  $\delta$ ), **5g** (5.68  $\delta$ ), and **5j** (5.18  $\delta$ )

TABLE IV  
 Spectral Data — Alkenes

Substance	Ir, $\nu_{\text{max}}$ KBr C=O $\mu$ = CH <sub>2</sub> or = CHR	Uv, $\lambda_{\text{max}}$ MeOH nm (log $\epsilon$ )	Solvent (a)	Nmr (ppm) $\delta$	(Multiplicity (b), No. of Protons, Assignment)		
<b>5a</b>	5.75	330 (3.79)	C	7.42	(s, 5,	N-C <sub>6</sub> H <sub>5</sub> )	
	11.1	230 (4.14)		7.15	(s, 5,	C <sub>6</sub> H <sub>5</sub> )	
				5.97	(s, 1,	vinyllic)	
				5.75	(s, 1,	vinyllic)	
<b>5b</b>	5.80	327 (3.96)	B	7.62	(s, 5,	C <sub>6</sub> H <sub>5</sub> )	
	11.2	230 (3.99)		5.42	(s, 1,	vinyllic)	
				5.21	(s, 1,	vinyllic)	
				1.73	(s, 3,	CH <sub>3</sub> )	
<b>5c</b>	5.80	330 (3.85)	B	7.62	(s, 5,	C <sub>6</sub> H <sub>5</sub> )	
	11.53, 12.05	232 (3.94)		6.08	(q, 1,	vinyllic) (c)	
				1.74	(d, 3,	CH <sub>3</sub> ) (c)	
				1.58	(s, 3,	CH <sub>3</sub> )	
<b>5d</b>	5.73	327 (3.90)	C	7.69	(s, 5,	C <sub>6</sub> H <sub>5</sub> )	
	11.61, 11.90	232 (4.04)		6.07	(q, 1,	vinyllic) (c)	
				2.14	(q, 2,	-CH <sub>2</sub> -) (d)	
				1.83	(d, 3,	CH <sub>3</sub> ) (c)	
				0.88	(t, 3,	CH <sub>3</sub> ) (d)	
<b>5e</b>	5.75	330 (3.91)	B	7.60	(s, 5,	C <sub>6</sub> H <sub>5</sub> )	
	11.50, 12.35	233 (4.01)		5.87	(t, 1,	vinyllic) (e)	
				2.08	(p, 2,	-CH <sub>2</sub> -) (e)	
				1.63	(s, 3,	CH <sub>3</sub> )	
				0.92	(t, 3,	CH <sub>3</sub> ) (e)	
<b>5f</b>	5.70	330 (3.90)	B	7.57	(s, 5,	C <sub>6</sub> H <sub>5</sub> )	
	11.45, 11.94	232 (4.02)		5.48	(d, 1,	vinyllic) (e)	
				2.48	(m, 1,	-CH)	
				1.68	(s, 3,	CH <sub>3</sub> )	
				0.88	(d, 6,	two CH <sub>3</sub> ) (c)	
<b>5g</b>	5.75	324 (3.96)	C	7.70	(s, 5,	C <sub>6</sub> H <sub>5</sub> )	
	11.30	230 (4.05)		5.68	(s, 1,	vinyllic)	
				5.50	(s, 1,	vinyllic) (c)	
				2.18	(septet, 1,	-CH) (c)	
				1.02	(d, 6,	two CH <sub>3</sub> )	
<b>5h</b>	5.79	340 (4.08)	C	7.55	(s, 5,	C <sub>6</sub> H <sub>5</sub> )	
	12.35	237 (4.06)		6.38	(broad s, 1,	vinyllic)	
				1.7-2.6	(m, 6,	-CH <sub>2</sub> -)	
<b>5i</b>	5.79	330 (4.03)	C	7.70	(s, 5,	C <sub>6</sub> H <sub>5</sub> )	
	11.90, 12.50	234 (4.11)		6.32	(broad s, 1,	vinyllic)	
				1.5-2.3	(m, 8,	-CH <sub>2</sub> -)	
<b>5j</b>	5.80	324 (3.87)	D	7.64	(s, 5,	C <sub>6</sub> H <sub>5</sub> )	
	11.1, 12.8	228 (4.03)		5.18	(s, 1,	vinyllic)	
				5.04	(s, 1,	vinyllic)	
				2.18	(q, 2,	-CH <sub>2</sub> -) (c)	
				0.99	(t, 3,	CH <sub>3</sub> -) (c)	

(a) B = deuteriochloroform, C = TFA, D = carbon tetrachloride; (b) Same meaning as in Table III; (c) J = 7.0 Hz; (d) J = 7.5 Hz; (e) J = 8.0 Hz.

would therefore be assigned a *cis* orientation to the 3-phenylsydnonyl group since in these alkenes they would be the more deshielded. Furthermore, it has been reported

(13) that protons in alkenes bearing a vicinal methyl substituent have the hydrogen oriented *trans* to this methyl group appearing further downfield from the *cis* oriented

proton; (iii) the cycloalkenes **5h** and **5i** which must have the olefinic proton *cis* to the sydnone group have chemical shift values downfield at 6.38  $\delta$  and 6.32  $\delta$ , respectively.

One explanation for the results of our dehydrations is that although extensive hyperconjugative stabilization existed in the transition states preceding Saytzeff olefin formation, it was not sufficient to overcome the destabilization imparted by eclipsing substituents. The transition states having a minimum of steric interaction from eclipsing substituents were therefore the more stable and in those cases the formation of vinylidene olefin was kinetically favored. Only after continued heating in aqueous acetic acid, or more rapidly in TFA at room temperature, was isomerization to the thermodynamically more stable Saytzeff alkene made possible. Even in the formation of the latter olefins the steric factors favored transition states leading to the geometric isomer in which the 3-phenylsydnonyl group was *cis* to the vinylic hydrogen.

Among the alkenes prepared in this study, **5b** and **5i** exhibited a color change from light yellow to blue-green on exposure to ultraviolet radiation (320-400 nm, Blak-Ray Model UVL-22). Alkene **5b** recovered its original color slowly in the dark (10-15 minutes) while **5i** recovered its original color in about 2-4 minutes after ceasing exposure. As previously stated in this article, carbinol **4c** dehydrated in acetic acid to a mixture of **5c** and **5j**. On irradiation the mixture exhibited photochromism. The olefin **5c** obtained in the pure state by TFA dehydration of **4c** was not the responsible component. In order to verify **5j** as the phototropic entity in the mixture, a pure sample was prepared by application of the Wittig reaction (10) to ethyl-4-(3-phenylsydnonyl)ketone (**6**, Scheme II) (12). Treatment of **6** with methylenetriphenylphosphorane at room temperature yielded 8% of **5j** and 28% of **1**. This reaction was repeated at reflux temperature and 7% of **5j** and 37% of **1** were isolated. However, the mechanism for deacylation of **6** in this reaction has not yet been studied. To be certain the sydnone ring itself was not reacting with the phosphorane, sydnone **1** was treated with methylenetriphenylphosphorane to afford an 85% recovery of **1**. The pure crystalline **5j** on exposure to uv light (320-400 nm) changed from light yellow to blue-green which was reversible at room temperature within 1-2 minutes.

A significant conclusion drawn from these observations is that the mesoionic ring may be a necessary but not a sufficient structural feature for photochromism to occur otherwise all of the alkenes would have exhibited color changes. We are presently examining the effect of molecular modifications on the photochromism of compounds **5b**, **5i**, and **5j** as a preliminary study to elucidating the photochemical mechanism.

## EXPERIMENTAL

All melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Microanalysis were performed by Alfred Bernhardt Microanalytical Laboratory, West Germany. The infrared spectra were measured on a Perkin-Elmer Infracord Model 137, and the ultraviolet spectra were obtained with a Bausch and Lomb 505 spectrophotometer. All nmr spectra were determined on a Varian A-60-A using tetramethylsilane as internal reference with chemical shifts reported in ppm ( $\delta$ ). Reagents.

*N*-Phenylglycine (Eastman Kodak, White Label) was used without further purification in the preparation of 3-phenylsydnone. The tetrahydrofuran (Fisher, ACS grade) was stored over molecular sieve (Linde Type 4A). All ketones (Fisher ACS grade), except benzophenone, were dried over calcium chloride and distilled. The *n*-butyllithium was purchased from Foote Mineral, Easton, Pa. and assayed as 1.47 *M* by double titration. All reactions with *n*-butyllithium were performed under a nitrogen atmosphere.

### General Procedure for the Preparation of Carbinols.

Equimolar amounts of *n*-butyllithium and 3-phenylsydnone in tetrahydrofuran (THF) at  $-20^\circ$  were stirred one hour and then treated with 1.5 molar equivalents of the ketone which had been dissolved in a small amount of tetrahydrofuran. After stirring 2 hours at  $-30^\circ$ , the reaction solution was poured into water (3X the volume of THF employed) containing a 25% molar excess of acetic acid. The mixture was extracted with three portions of benzene, the combined extracts dried (magnesium sulfate), filtered and evaporated *in vacuo* to yield crude carbinol. Three recrystallizations from the designated solvent gave the analytical sample in the yields shown in Table I.

### General Procedure for Preparation of 4-(3-Phenylsydnonyl) Alkenes.

Two g. of the carbinol was dissolved in a solution of 10 ml. of acetic acid and 2 ml. of water and heated on a steam bath for 1 hour (with **4a**, **4b**, **4d**, **4g**, **4i**) or left in 10 ml. of trifluoroacetic acid for 4 hours at room temperature (with **4c**, **4e**, **4f**). The precipitate formed on addition of the reaction solution to 200 ml. of cold water was filtered, washed three times with cold water and recrystallized once to give analytically pure alkenes (Table II).

### Wittig Reaction on Ethyl-4-(3-Phenylsydnonyl) Ketone.

To a 250 ml. three neck flask containing triphenylmethylphosphonium bromide (3.57 g., 0.010 mole) and 50 ml. of dry THF was added *n*-butyllithium (7.0 ml., 0.010 mole) at room temperature. After stirring 2 hours, ethyl-4-(3-phenylsydnonyl) ketone (**6**) (11) (2.18 g., 0.010 mole) in 5 ml. of THF was added in 10 minutes. The reaction mixture was stirred 18 hours, poured into 100 ml. of water, extracted three times with benzene and the benzene extracts washed three times with water. The extract was evaporated under vacuum to 3.2 g. of a red oil, which was chromatographed on a column of 100 g. silica gel (Fisher S-157). The fractions eluted with 10% ethyl acetate in benzene were recrystallized from 2-propanol-hexane to yield **5j** (0.173 g., 8.01%) m.p. 100-102°. A recrystallization from 2-propanol-hexane yielded the pure alkene **5j** (0.120 g., 5.65%) m.p. 101-102°.

The fractions eluted with 20% ethyl acetate in benzene upon recrystallization from benzene yielded 3-phenylsydnone (0.452 g., 27.9%). The fractions eluted with 30-100% ethyl acetate yielded a crude oily residue that was unidentified.

## REFERENCES

- (1a) Mesoionic Compounds VII, C. V. Greco and B. P. O'Reilly, *Tetrahedron Letters*, 3057 (1971); (b) To whom correspondence should be addressed; (c) Taken from the predoctoral dissertation research of B. P. O'Reilly, St. John's University.
- (2) J. M. Tien and I. M. Hunsberger, *J. Am. Chem. Soc.*, **77**, 6604 (1955).
- (3) M. Ohta and M. Masaki, *Bull. Chem. Soc. Japan*, **33**, 649 (1960).
- (4a) C. V. Greco and I. M. Hunsberger, *J. Heterocyclic Chem.*, **7**, 761 (1970); (b) J. M. Tien and I. M. Hunsberger, *J. Chin. Chem. Soc. (Taipei)*, **15**, 163 (1968).
- (5) H. S. Gutowsky, R. L. Rutledge and I. M. Hunsberger, *J. Chem. Phys.*, **29**, 1183 (1958).
- (6) T. Mill, A. van Roggen and C. F. Wahlig, *J. Chem. Phys.*, **35**, 1139 (1961).
- (7) F. I. Metz, W. C. Servoss and F. E. Welsh, *J. Phys. Chem.*, **66**, 2446 (1962).
- (8a) C. V. Greco and M. Pesce, *J. Heterocyclic Chem.*, **6**, 259 (1969); (b) Cf. also, C. V. Greco, M. Pesce and J. M. Franco, *ibid.*, **3**, 391 (1966).
- (9) Carbinols **4b** and **4c** were previously reported to have been obtained from 3-phenylsydnonylmagnesium bromide. Cf., M. Ohta and H. Kato, *Nippon Kagaku Zasshi*, **78**, 1653 (1957); *Chem. Abstr.*, **54**, 1503 (1960), and C. H. Wang, *Bull. Inst. Chem. Acad. Sinica*, **12**, 46 (1966), *Chem. Abstr.*, **66**, 94964 (1967).
- (10) G. Wittig and U. Schoellkopf, *Organic Syntheses*, **40**, 66 (1966).
- (11) C. V. Greco, J. Tobias and L. B. Kier, *J. Heterocyclic Chem.*, **4**, 160 (1967).
- (12) L. M. Jackman and S. Sternhell, "Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, N. Y. 1969, pp. 222-225.
- (13) H. O. House, D. D. Traficante, and R. A. Evans, *J. Org. Chem.*, **28**, 248 (1963). Cf. also, R. B. Bates and D. M. Gale, *J. Am. Chem. Soc.*, **82**, 5479 (1960).