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Some Properties of Cyclopropenone Oximes under Beckmann Reaction Conditions

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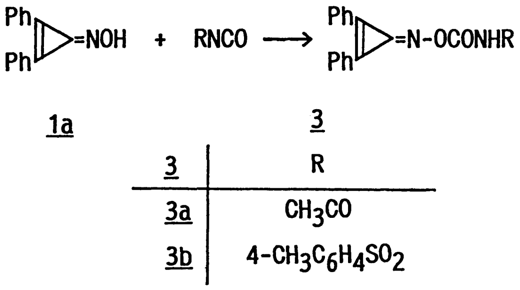
The reaction of diphenylcyclopropenone oxime (**1a**) with acetyl or tosyl isocyanate, carboxylic anhydrides, or nitrohalobenzenes yielded the cyclopropenone *O*-substituted oxime derivatives. Treating with thionyl bromide and chloride **1a** gave 3-haloacrylonitriles. Whereas **1a** as well as other cyclopropenone oximes, were stable under acidic conditions, heating in methanolic sodium hydroxide gave the ring-opened α,α-dimethoxyketones oximes.

In a former paper[1] we reported on the preparation of 2,3-diphenyl-, 2-methy-3-phenyl-, and 2-methyl-3-(4-methylphenyl)cyclopropenone oximes (**1a**—**c**) and their reactions with alkyl and aryl isocyanates, affording 1:2 addition products (Scheme 1). To further explore the chemical nature of these oximes **1**, we investigated the chemical behavior of **1** under Beckmann reaction conditions.[2]

The reaction of **1** with alkyl and aryl isocyanates gives 1:2 adducts **2** in good yields.[1] The failure of the isolation of mono adducts can be explained in terms of the high polarization of cyclopropenone *O*-carbamoyloximes (Scheme 1). In contrast, the reaction of acetyl and tosyl isocyanates with **1a** at room temperature gave 1:1 addition products **3a** and **3b** in 74 and 35% yields, respectively (Scheme 2). No 1:2 adduct was isolated, even when either twice excess of the isocyanates was used or the reactions were performed at higher temperature. The strong electron-attracting acetyl or sulfonyl group might decrease the nucleophilic nature of the imino nitrogen.

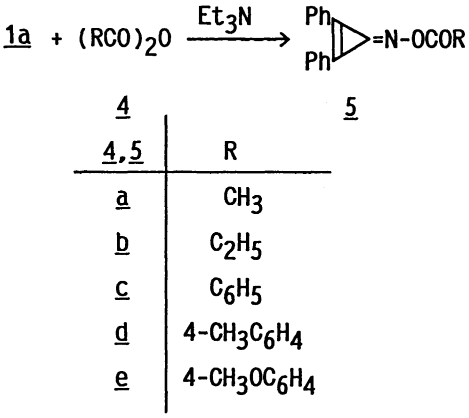
The reaction of **1a** with diphenylketene, dicyclohexyl carbodiimide, or carbon disulfide yielded a complex mixture of the products.

No identifiable products were obtained from the reaction of **1a** with acetyl chloride or tosyl chloride in the presence of triethylamine or pyridine; **1a** with



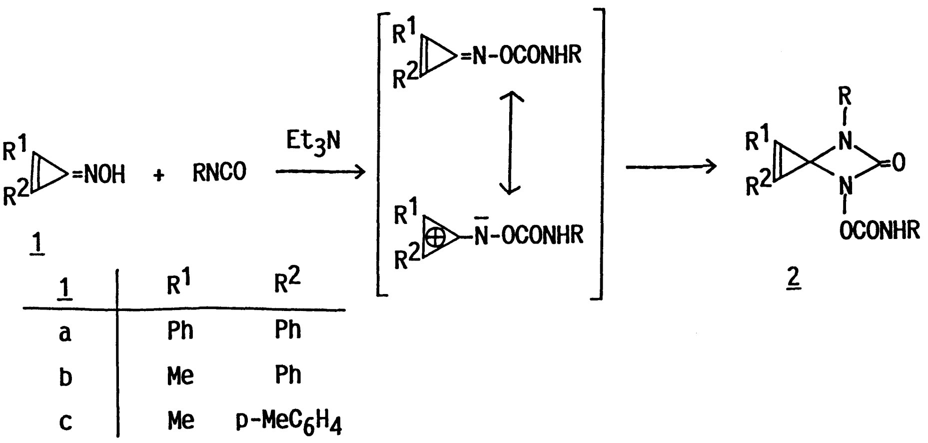
3	R
3a	CH_3CO
3b	$4\text{-}CH_3C_6H_4SO_2$

Scheme 2.



4,5	R
a	CH_3
b	C_2H_5
c	C_6H_5
d	$4\text{-}CH_3C_6H_4$
e	$4\text{-}CH_3OC_6H_4$

Scheme 3.

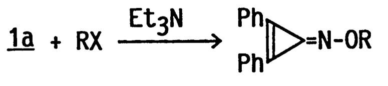


1	R^1	R^2
a	Ph	Ph
b	Me	Ph
c	Me	$p\text{-}MeC_6H_4$

Scheme 1.

Table 1. The Reaction of **1a** with Carboxylic Anhydrides **4**

4	Temp/°C	Product 5	Yield/%
4a	25	**5a**	63
	0	**5a**	71
4b	25	**5b**	23
	0	**5b**	35
4c	0	**5c**	62
4d	0	**5d**	43
4e	0	**5e**	60



6 7

6, 7	RX
a	2,4-$(NO_2)_2C_6H_3F$
b	2,4-$(NO_2)_2C_6H_3Cl$
c	4-$NO_2C_6H_4F$

Scheme 4.

Table 2. The Reaction of **1a** with Aryl Halides **6**

6	Solvent	Time/h	Yield/%
6a	CH_2Cl_2	0.5	21
6a	C_6H_6	1.5	2.9
6b	CH_2Cl_2	3	4.5
6b	C_6H_6	5	0.3
6c	CH_2Cl_2	24	0

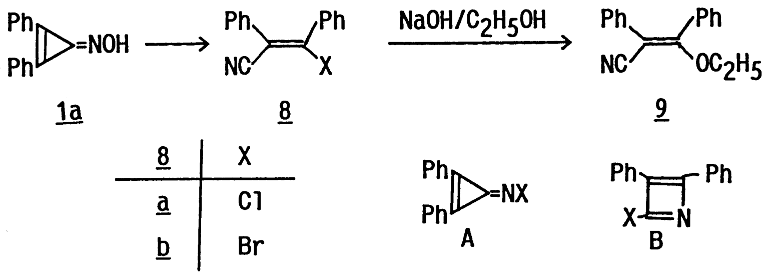
acetic anhydride **4a** in the presence of triethylamine at 0 °C **1a**, however, yielded cyclopropenone *O*-acetyloxime **5a** in a 71% yield (Scheme 3). This yield decreased when the reaction was carried out at room temperature. A similar treatment of **1a** with carboxylic anhydrides **4** produced the corresponding cyclopropenone *O*-acyloximes **5** in moderate yields, as summarized in Table 1.

The treatment of **1a** with typical alkylating reagents such as methyl iodide, methyl fluorosulfonate, or Meerwein reagent resulted in the formation of tarry mixtures, while 2,4-dinitrofluoro- or 2,4-dinitrochlorobenzene reacted with **1a** at ambient temperature, giving the cyclopropenone *O*-2,4-dinitrophenyloxime **7** in small yields (Scheme 4 and Table 2). Attempted thermal and photochemical transformations of these cyclopropene derivatives (**3**, **5**, and **7**) were unsuccessful, yielding only unidentifiable mixtures of tarry products.

As shown in Scheme 5 and Table 3, the reaction of **1a** with halogenating reagents afforded a ring-opened

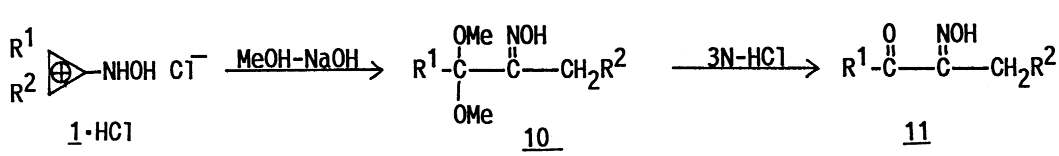
Table 3. The Reaction of **1a** with Halogenating Reagents

Reagent	Reaction conditions			Product (Yield/%)
	Solvent	Temp	Time/h	
$SOCl_2$	—	Reflux	3	**8a**(64)
$SOCl_2$	$CHCl_3$	25 °C	60	**8a**(44)
$SOBr_2$	C_6H_6	Reflux	6	**8b**(51)
PCl_3	C_6H_6	Reflux	24	**8a**(Trace)
PCl_5	CCl_4	25 °C	3	**8a**(66)
PCl_5	CCl_4	0 °C	24	**8a**(63)
PBr_3	C_6H_6	Reflux	24	**8b**(Trace)



8	X
a	Cl
b	Br

Scheme 5.



1·HCl, 10, 11	R^1	R^2
a	Ph	Ph
b	Me	Ph
c	Me	p-MeC_6H_4

Scheme 6.

Table 4. The Reaction of **1** in NaOH–Methanol

1	Reaction conditions		Product (Yield/%)
	Temp/°C	Time/h	
1a	25	24	**10a**(19)
	0	24	**10a**(41)
1b	0	5	**10b**(40)
1c	0	5	**10c**(64)

Table 5. Acidic Hydrolysis of **10** at Room Temperature

10	Product (Yield/%)
10a	**11a**(88)
10b	**11b**(62)
10c	**11c**(68)

product, 3-haloacrylonitrile (**8**), as a single isolable product. The structure of **8** was comfirmed on the basis of spectroscopic studies and chemical transformation. Thus, upon treating with basic ethanol **8a** and **8b** afforded 3-ethoxyacrylonitrile (**9**) in 92 and 35% yields, respectively (Scheme 5). No intermediates, such as the *N*-haloiminocyclopropene (**A**) or azacyclobutadiene (**B**), could be isolated, even at 0 °C.

The oximes **1a** and arylmethylcyclopropenone oximes, **1b** and **1c** were fairly stable in the form of hydrochlorides which can be stored for a long time without decomposition. Upon treating with sodium hydroxide in methanol, however hydrochloride of **1** were readily converted to α,α-dimethoxyketones oximes (**10**) in moderate yields (Scheme 6 and Table 4). The acidic hydrolysis of **10** gave the corresponding diketone monoximes **11** (Table 5). No crystalline products were obtained from **1** in either basic ethanol or propanol. A plausible mechanism for the generation of **10** is shown in Scheme 7. An initial addition of methanol to the cyclopropenone oxime **1** gives the methoxycyclopropanone oxime, which undergoes a reversible thermally allowed conrotatory ring-opening to afford the 2-nitrosoallyl anion, followed by the addition of another molecule of methanol. The allyl anion is presumably sufficiently stabilized to facilitate the formation of the benzyl ketone oximes **10**. Low yields of **10** might suggest that the process is governed by the steric effects.

Experimental

General. Melting points were uncorrected. The ^{13}C NMR spectra were recorded either on a JEOL JNM FX-90Q (22.49 MHz) or a JEOL JNM EX-90 (22.50 MHz) and ^{1}H NMR spectra on a Hitachi R-24B (60 MHz). The IR spectra were recorded on a JASCO A-3 spectrometer.

Preparation of Cyclopropenone Oxime Hydrochloride (1a—c·HCl). The salts **1a—c**·HCl were prepared according to a previously described method[1] and used without purification.

The Reaction of 1a with Acetyl Isocyanate. To a well stirred mixture of **1a** (0.52 g, 2.0 mmol) and triethylamine (0.28 cm^3, 2.0 mmol) in dichloromethane (20 cm^3) was added acetyl isocyanate (5.0 mmol in ether)[3] at 0 °C. After 6 h the solution was poured onto cold water and the organic layer was separated. The extract was dried over $MgSO_4$, concentrated in vacuo, and recrystallized from dichloromethane-ether while affording 2,3-diphenylcyclopropenone *N*-acetylcarbamoyloxime (**3a**) in a 35% yield.

3a: Mp 140—143 °C; IR (KBr) 1870, 1760, and 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.50 (s, 3H, CH_3), 7.3—8.2 (m, 10H, Ph), and 9.3 (bs, 1H, NH); M$^+$, 306. Found: C, 70.51; H, 4.69; N, 9.03%. Calcd for $C_{18}H_{14}N_2O_3$:C, 70.57; H, 4.60; N, 9.14%.

The Reactin of 1a with Tosyl Isocyanate. A similar process as that described above using 1.2-times excess of tosyl isocyanate gave 2,3-diphenylcyclopropenone *N*-tosylcarbamoyloxime (**3b**) in 74% yield.

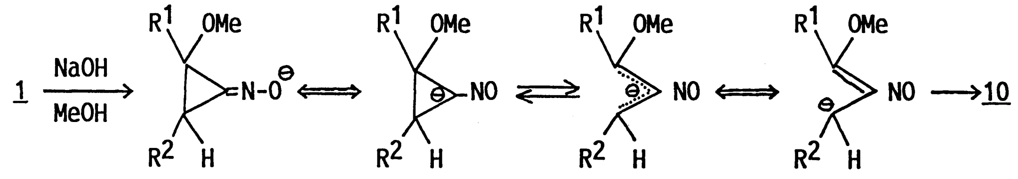
3b: Mp 97—99 °C; IR (KBr) 1870, 1740, and 1350 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.40 (s, 3H, CH_3), 7.1—8.2 (m, 14H, Arom), and 9.3 (bs, 1H, NH); MS *m/z* 220 (M$^+$—TosNH). Found: C, 65.97; H, 4.41; N, 6.73%. Calcd for $C_{23}H_{18}N_2O_4S$: C, 66.01; H, 4.33; N, 6.69%.

The Reaction of 1a, with Carboxylic Anhydrides (4). General Procedure. A mixture of **1a** (2.0 mmol), triethylamine (2.2 mmol), and carboxylic anhydride **4** (2.1 mmol) in dichloromethane (15 cm^3) was stirred at an appropriate temperature until the disappearance of **1a** by checking the reaction mixture with TLC (silica gel, chloroform: ethyl acetate: petroleum ether=2:3:2). The solution was then treated as described in the reaction with isocyanates. The results are shown in Table 1. The physical properties are as follows.

5a: Mp 165—167 °C; IR (KBr) 1870 and 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.30 (s, 3H, CH_3) and 7.2—8.3 (m, 10H, Ph); ^{13}C NMR ($CDCl_3$) δ=19.9 (q), 122.4 (s), 122.5 (s), 127.3 (d), 129.1 (d), 131.5 (d), 131.9 (d), 132.2 (d), 132.4 (d), 132.8 (d), 135.9 (s), and 169.5 (s); MS *m/z*, 220 (M$^+$—CH_3CO). Found: C, 77.59; H, 4.78; N, 5.23%. Calcd for $C_{17}H_{13}NO$: C, 77.55; H, 4.97; N, 5.31%.

5b: Mp 168—170 °C; IR (KBr) 1870 and 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.75 (t, 3H, *J*=7 Hz CH_3), 1.25 (q, 2H, *J*=7 Hz, CH_2), and 7.3—8.5 (m, 10H, Ph); M$^+$, 277. Found: C, 77.98; H, 5.42; N, 4.97%. Calcd for $C_{18}H_{15}NO_2$: C, 77.95; H, 5.45; N, 5.05%.

5c: Mp 122—125 °C; IR (KBr) 1870 and 1730 cm^{-1};



Scheme 7.

^{1}H NMR ($CDCl_3$) δ=7.3—8.4 (m, Arom); ^{13}C NMR ($CDCl_3$) δ=122.6 (s), 122.7 (s), 128.0 (s), 128.3 (d), 129.3 (d), 130.3 (d), 132.2 (d), 132.4 (d), 132.5 (d), 132.7 (d), and 165.6 (s); M$^+$, 325. Found: C, 81.07; H, 4.73; N 4.23%. Calcd for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.64; N, 4.30%.

5d: Mp 133—136 °C; IR (KBr) 1870 and 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.45 (s, 3H, CH_3) and 7.1—8.3 (m, 14H, Arom); ^{13}C NMR ($CDCl_3$) δ=21.5 (q), 122.7 (s), 127.5 (d), 128.0 (s), 129.1 (d), 129.4 (d), 131.6 (d), 132.2 (d), 132.4 (d), 132.7 (d), 143.1 (s), and 165.7 (s); M$^+$, 339. Found: C, 81.46; H, 5.01; N, 4.25%. Calcd for $C_{23}H_{17}NO_2$: C, 81.39; H, 5.04; N, 4.12%.

5e: Mp 129—131 °C; IR (KBr) 1870 and 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.90 (s, 3H, CH_3) and 6.9—8.6 (m, 14H, Arom); ^{13}C NMR ($CDCl_3$) δ=55.3 (q), 113.6 (d), 122.6 (s), 122.7 (s), 128.1 (s), 129.25 (d), 129.34 (d), 131.2 (d), 131.5 (s), 132.2 (d), 132.3 (d), 132.6 (d), 132.9 (s), 136.6 (s), 163.0 (s), and 165.4 (s); M$^+$, 355. Found: C, 77.66; H, 4.89; N, 3.87%. Calcd for $C_{23}H_{17}NO_3$: C, 77.73; H, 4.82; N, 3.94%.

The Reaction of 1a, with Aryl Halides. General Procedure. A mixture of **1a** (2 mmol), aryl halide (2.2 mmol), and triethylamine (2.2 mmol) in an appropriate solvent (15 cm^3) was stirred in an ice bath until the disappearance of the starting **1a**. The reaction mixture was treated as mentioned above; the results are shown in Table 2. 2,3-Diphenylcyclopropenone *O*-2,4-dinitrophenyloxime **7a**: Mp 138—141 °C; IR (KBr) 1860 cm^{-1}; ^{1}H NMR ($CDCl_3$+CF_3CO_2H) δ=7.0—9.0 (m, Arom); ^{13}C NMR ($CDCl_3$+CF_3CO_2H) δ=95.5 (s), 108.1 (s), 120.8 (s) , 121.5 (d), 122.2 (d), 128.3 (s), 128.8 (d), 129.2 (s), 129.4 (d), 130.3 (s), 131.8 (s), 133.4 (d), and 135.6 (d); M$^+$, 387. Found: C, 65.21; H, 3.32; N, 10.89%. Calcd for $C_{21}H_{13}N_3O_5$: C, 65.11; H, 3.38; N, 10.84%.

The Reaction of 1a with Halogenating Reagets. General Procedure. A mixture of **1a** and a halogenating reagent in an appropriating solvent was stirred at the respective temperature. The resulting mixture was treated as above. The results are collected in Table 3. The physical properties are as follows.

8a: Mp 104—108 °C; IR (KBr) 2170 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.7—7.8 (m, Ph); ^{13}C NMR ($CDCl_3$) δ=114.0 (s), 117.3 (s), 128.4 (d), 129.0 (d), 129.2 (d), 129.3 (d), 130.4 (d), 132.4 (s), and 146.9 (d); M$^+$, 239. Found: C, 75.08; H, 4.26; N, 5.80%. Calcd for $C_{15}H_{10}ClN$: C,75.16; H, 4.20; N, 5.84%.

8b: Mp 108—112 °C; IR (KBr) 2200 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.7—8.1 (m, Ph); ^{13}C NMR ($CDCl_3$) δ=115.4 (d), 128.6 (s), 128.9 (d), 129.5 (d), 130.9 (d), 134.8 (s), 138.3 (s), and 142.3 (s); M$^+$, 283. Found: C, 63.32; H, 3.59; N, 4.87%. Calcd for $C_{15}H_{10}BrN$: C, 63.39; H, 3.54; N, 4.92%.

Alcoholysis of 8a and 8b. A solution of **8a** (1 mmol) and NaOH (5 mmol) in ethanol (15 cm^3) was refluxed for one day. The mixture was neutralized by HCl and extracted with dichloromethane. Condensation and recrystallization from petroleum ether afforded 2-ethoxy-1,2-diphenylacrylonitrile **9** in a 92% yield.

9: Mp 79—82 °C; IR (KBr) 2200 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.15 (t, 3H, *J*=7 Hz, CH_3), 3.75 (q, 2H, *J*=7 Hz, CH_2) and 6.9—7.8 (m, 10H, Ph); ^{13}C NMR ($CDCl_3$) δ=51.1 (q), 67.5 (t), 97.5 (s), 119.9 (s), 127.6 (d), 128.2 (d), 128.7 (d), 128.9 (d), 130.6 (s), 132.1 (d), 132.6 (s), and 168.1 (s); M$^+$ 249. Found: C, 81.94; H, 5.98; N, 5.62%. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.61%.

Similar treatment of **8b** yielded **9** in a 35% yield.

Methanolysis of 1 under Basic Conditions. General Procedure. A solution of **1** (2 mmol) and NaOH (4 mmol) in methanol (10 cm^3) was reacted at an appropriate temperature until the disappearance of **1**, observed by checking TLC. The product was treated in the usual manner. The results are collected in Table 4. The physical properties are as follows.

10a: Mp 128—130 °C; IR (KBr) 3230 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.05 (s, 6H, CH_3), 3.55 (s, 2H, CH_2), 7.0—7.7 (m, 10H, Ph), and 9.1 (bs, 1H, OH); ^{13}C NMR ($CDCl_3$) δ=31.4 (t), 49.6 (q), 102.7 (s), 125.7 (d), 127.3 (s), 127.7 (d), 128.0 (d), 128.3 (d), 130.5 (d), 136.6 (s), 138.2 (s), and 156.4 (s); MS *m/z* 268 (M$^+$−OH). Found: C, 71.58; H, 6.67; N, 4.87%. Calcd for $C_{17}H_{19}NO_3$: C, 71.55; H, 6.71 ; N, 4.90%.

10b: Mp 78—80 °C; IR (KBr) 3270 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.31 (s, 3H, CH_3), 3.20 (s, 6H, CH_3O), 3.81 (s, 2H, CH_2), 7.1—7.5 (m, 5H, Ph), and 9.2 (bs, 1H, OH); ^{13}C NMR ($CDCL_3$) δ=22.4 (q), 30.7 (t), 49.1 (q), 101.3 (s), 126.0 (d), 128.2 (d), 129.2 (d), 136.8 (s), and 158.0 (s); MS *m/z* 206 (M$^+$−OH). Found: C, 64.46; H, 7.73; N, 6.20%. Calcd for $C_{12}H_{17}NO_3$: C, 64.55; H, 7.67; N, 6.27%.

10c: Mp 106—110 °C; IR (KBr) 3250 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.28 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 3.17 (s, 6H, CH_3O), 3.75 (s, 2H, CH_2), 6.9—7.4 (s, 4H, Arom), and 8.9 (bs, 1H, OH); M$^+$, 237. Found: C, 65.88; H, 7.93; N, 5.92%. Calcd for $C_{13}H_{19}NO_3$: C, 65.80; H, 8.07; N, 5.90%.

Hydrolysis of 10 in Aqueous Acid. A mixture of **10** (1 mmol) in chloroform (10 cm^3) and conc HCl (3 cm^3) was stirred at room temperature for a day. The product was isolated in the usual manner and recrystallized from benzene. The physical properties of **11** are as follows.

11a: Mp 129—131 °C (lit,[4] mp 126 °C); IR (KBr) 3250, 1665, and 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=4.08 (s, 2H, CH_2), 7.0—7.9 (m, 10H, Ph), and 8.51 (s, 1H, OH); ^{13}C NMR ($CDCl_3$) δ=30.0 (t), 126.5 (d), 128.1 (d), 128.5 (d), 129.2 (d), 130.1 (d), 132.9 (d), 135.7 (s), 136.5 (d), 158.0 (s), and 191.5 (s); M$^+$, 239. Found: C, 75.22; H, 5.41; N, 5.88%. Calcd for $C_{15}H_{13}O_2$: C, 75.29; H, 5.47; N, 5.85%.

11b: Mp 82—84 °C; IR (KBr) 3310, 1690, and 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.38 (s, 3H, CH_3), 3.92 (s, 2H, CH_2), 7.2—7.5 (m, 5H, Ph), and 8.4 (bs, 1H, OH); M$^+$, 177. Found: C, 67.62; H, 6.26; N, 7.82%. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.25; N, 7.90%.

11c: Mp 80—82 °C; IR (KBr) 3200, 1670, and 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.33 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 3.89 (s, 2H, CH_2), 7.0—8.3 (m, 4H, Arom), and 8.4 (bs, 1H, OH); M$^+$, 191. Found: C, 69.21; H, 6.73; N, 7.39%. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32%.

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