

## Steric Hindrance in the Benzylation of Anilines

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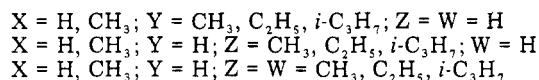
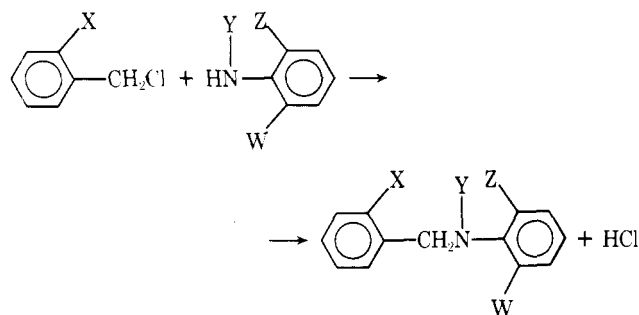
Second-order rate constants and activation parameters for the reactions of benzyl and 2-methylbenzyl chlorides with 2-, 2,6-, and *N*-alkylanilines (methyl, ethyl, and isopropyl) were measured in ethanol solution. The observed reactivity is dependent on the increasing steric hindrance of alkyl groups rather than on basicity of anilines. Satisfactory linear free-energy correlations are found with Charton's steric  $\nu$  parameters. The decreased reactivity of alkylanilines by comparison with the unsubstituted compound is ascribed to a prevailing steric inhibition in the transition-state solvation.

Although the correlation analysis of steric effects has afforded some progress by the critical works of Shorter<sup>1</sup> and Charton,<sup>2</sup> a comprehensive rationalization of steric effects on chemical reactivity is still waiting for a successful approach.

The Taft-Pavelich equation<sup>3</sup> is still applied up to now to separate polar and steric effects, although some controversy has risen because the statistical examination of this relationship has pointed out that  $\sigma^*$  values are not a good measure of polar effects,<sup>4</sup> particularly in alkyl groups.<sup>5</sup>

Moreover, it has been ascertained that the reaction rate in the nucleophilic substitutions to the carbonyl carbon atom can depend on steric or a combination of steric and polar effects;<sup>2</sup> on the contrary, in the substitutions at the saturated carbon atom, for instance in  $XCH_2Cl$  substrates, the reactivity prevalently depends only on steric effects of the X groups.<sup>6</sup>

A dearth of information exists on the role of steric effects of alkyl groups in nucleophilic reagents, apart from the classical paper on the reactions of alkyl halides with ortho-substituted pyridines.<sup>7</sup> Therefore, in connection with our previous works on the kinetics and mechanism of aniline benzylation,<sup>8,9</sup> we now report kinetic data for the reactions of benzyl and 2-methylbenzyl chlorides with a homogeneous series of sterically hindered nucleophiles, i.e., anilines bearing alkyl groups on the nitrogen atom or in the ortho position of the aromatic ring.



The aim of this work is to verify if polar effects of alkyl groups are of relevance in addition to the expected steric effects.

## Results and Discussion

The reactions of benzyl and 2-methylbenzyl chlorides with a large excess of substituted anilines in absolute ethanol were followed by titration of the acid produced (Experimental Section). Kinetics were first order with respect to the substrate to at least 75% completion. The plot of pseudo-first-order rate constants ( $k_1$ ) against aniline concentrations was linear, showing that the reaction is also first order with respect to the

aniline. The second-order overall rate constants ( $k_2$ ) were calculated from the slopes of these plots, according to

$$k_1 = k_{\text{solv}} + k_2[\text{aniline}] \quad (1)$$

*N*-Benzylanilines are the main products because the solvolysis rate is much lower with respect to the aminolysis ( $k_{\text{solv}}$  is about  $10^{-7} \text{ s}^{-1}$ ). In Tables I and II are reported  $k_2$  values and the activation parameters for the reactions of benzyl and 2-methylbenzyl chlorides, respectively.

In agreement with previous data,<sup>8,10</sup> 2-methylbenzyl chloride reacts faster than the unsubstituted compound, because the electrical effects of the methyl group accelerate the chloride ion departure from the  $S_N2$  transition state.

Ortho-substituted anilines, instead, were found to be always less reactive than aniline. Figure 1 shows that the decreased reactivity can be ascribed to the presence of steric effects. In fact, a linear Brønsted plot has been obtained for the reactions of benzyl chloride with meta- and para-substituted anilines,<sup>8</sup> while remarkable negative deviations from this plot are now observed with ortho-substituted anilines; this is in agreement with the general observation that steric interferences usually cause deviations from linear free-energy relationships.<sup>11</sup>

Also *N*-substituted anilines, except the *N*-methyl derivative, are less reactive than aniline, notwithstanding the higher  $pK_a$  values (Figure 1).

The observed reactivity seems to be influenced by the increased steric hindrance of alkyl groups rather than by basicity of anilines; in fact satisfactory linear correlations are found between  $\log k_2$  and the steric  $\nu$  parameter, according to the Charton equation<sup>2</sup>

$$\log k_2 = \psi\nu + h \quad (2)$$

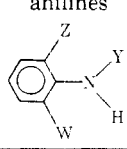
where the  $\nu$  values are a linear function of the van der Waals radii in the case of spherically symmetric groups and are independent of electrical effects. Table III reports the results of the correlations for benzyl and 2-methylbenzyl chloride reactions. Furthermore, additivity of  $\nu$  values is verified in the reactions of ortho-disubstituted anilines.

Steric effects are more evident in the reactions of 2-methylbenzyl chloride; in fact the  $\psi$  values for the reactions with 2-substituted anilines are much greater than the corresponding  $\psi$  values of the reactions with benzyl chloride. The correlations of the *N*-substituted anilines provide similar  $\psi$  values for both substrates. The latter values are greater than that of 2-substituted anilines because of the proximity of the alkyl groups to the reaction center. Moreover, it can be observed that  $\psi$  values always decrease on increasing temperature.

These findings suggest that the steric effects appear relatively more important in the most hindered systems.

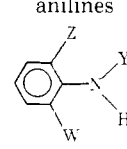
The activation parameters are diagnostics to elucidate considerable steric effects.<sup>13</sup>  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values do not change meaningfully in the reactions of benzyl chloride with 2-substituted anilines and with *N*-methyl- and *N*-ethylani-

**Table I. Rate Constants and Activation Parameters for the Reactions of Benzyl Chloride with Anilines in Ethanol**

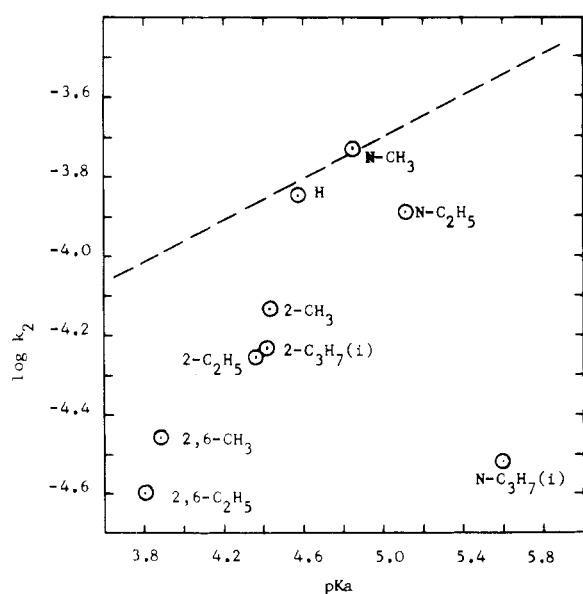
anilines 	registry no.	pK <sub>a</sub> <sup>a</sup> (H <sub>2</sub> O, 25 °C)	Σ <sub>ν<sub>Y+Z+W</sub></sub> <sup>b</sup>	10 <sup>5</sup> k <sub>2</sub> , L mol <sup>-1</sup> s <sup>-1</sup>			ΔH <sup>‡,c</sup> kcal mol <sup>-1</sup>	ΔS <sup>‡,d</sup> cal mol <sup>-1</sup> K <sup>-1</sup>
				40 °C	50 °C	60 °C		
Y = Z = W = H	62-53-3	4.58	0.00	6.55	14.2	26.7	14.0	-33.0
Y = CH <sub>3</sub> ; Z = W = H	100-61-8	4.85	0.52	9.40	18.6	37.5	13.7	-33.4
Y = C <sub>2</sub> H <sub>5</sub> ; Z = W = H	103-69-5	5.11	0.56	5.95	12.8	25.1	14.4	-32.0
Y = C <sub>3</sub> H <sub>7</sub> (i); Z = W = H	768-52-5	5.50	0.76	1.23	3.02	8.60	19.5	-19.0
Y = W = H; Z = CH <sub>3</sub>	95-53-4	4.44	0.52	3.20	7.30	13.3	14.1	-34.0
Y = W = H; Z = C <sub>2</sub> H <sub>5</sub>	578-54-1	4.37	0.56	2.68	5.58	11.2	14.2	-34.0
Y = W = H; Z = C <sub>3</sub> H <sub>7</sub> (i)	643-28-7	4.42	0.76	2.23	5.38	9.81	14.7	-33.5
Y = H; Z = W = CH <sub>3</sub>	87-62-7	3.89	1.04	1.35	3.48	8.49	18.4	-22.2
Y = H; Z = W = C <sub>2</sub> H <sub>5</sub>	579-66-8	3.81	1.12	0.944	2.52	6.28	19.0	-21.0
Y = H; Z = W = C <sub>3</sub> H <sub>7</sub> (i)	24544-04-5		1.52	0.551	1.56	4.60	21.3	-14.8

<sup>a</sup> A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases", Wiley, New York, 1962, p 144; P. D. Bolton and F. M. Hall, *Aust. J. Chem.*, **20**, 1797 (1967); *J. Chem. Soc. B*, 1047 (1969); B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **76**, 357 (1957); R. P. Bell and P. De Maria, *J. Chem. Soc. B*, 1038 (1969). <sup>b</sup> Reference 2. <sup>c</sup> Standard error ±0.5 kcal mol<sup>-1</sup>. <sup>d</sup> Standard error ±2 cal mol<sup>-1</sup> K<sup>-1</sup>.

**Table II. Rate Constants and Activation Parameters for the Reactions of 2-Methylbenzyl Chloride with Anilines in Ethanol**

anilines 	10 <sup>5</sup> k <sub>2</sub> , L mol <sup>-1</sup> s <sup>-1</sup>			ΔH <sup>‡,a</sup> kcal mol <sup>-1</sup>	ΔS <sup>‡,b</sup> cal mol <sup>-1</sup> K <sup>-1</sup>
	40 °C	50 °C	60 °C		
Y = Z = W = H	20.5	39.4	70.4	12.1	-36.7
Y = CH <sub>3</sub> ; Z = W = H	27.3	56.4	107	13.5	-31.8
Y = C <sub>2</sub> H <sub>5</sub> ; Z = W = H	16.2	40.8	82.8	16.3	-23.9
Y = C <sub>3</sub> H <sub>7</sub> (i); Z = W = H	4.47	11.9	33.5	20.2	-14.0
Y = W = H; Z = CH <sub>3</sub>	9.63	20.2	40.3	14.2	-31.7
Y = W = H; Z = C <sub>2</sub> H <sub>5</sub>	8.98	17.3	34.6	13.4	-34.3
Y = W = H; Z = C <sub>3</sub> H <sub>7</sub> (i)	3.56	8.89	24.3	19.4	-17.2
Y = H; Z = W = CH <sub>3</sub>	1.77	6.53	13.2	20.1	-15.8
Y = H; Z = W = C <sub>2</sub> H <sub>5</sub>	1.58	5.69	11.9	20.4	-15.4
Y = H; Z = W = C <sub>3</sub> H <sub>7</sub> (i)	0.756	3.30	7.12	22.7	-9.4

<sup>a</sup> Standard error ±0.5 kcal mol<sup>-1</sup>. <sup>b</sup> Standard error ±2 cal mol<sup>-1</sup> K<sup>-1</sup>.



**Figure 1.** Failure of the Brønsted plot for the reaction of benzyl chloride with ortho- and N-substituted anilines in ethanol at 50 °C. (Dotted line: Brønsted plot for the same reaction with meta- and para-substituted anilines.)

line, while noticeable differences are observed in the reactions with 2,6-disubstituted and N-isopropylaniline. Remarkable variations of activation parameters, instead, are already observed in the reactions of 2-methylbenzyl chloride with 2-isopropyl- and N-ethylanilines.

Enthalpic and entropic changes clearly increase on increasing steric hindrances. Both parameters are mutually dependent, as pointed out by the isokinetic relationship

$$\Delta H^\ddagger = \Delta H^\ddagger_0 + \beta \Delta S^\ddagger \quad (3)$$

The results of this correlation, reported in Table IV, indicate that the reaction mechanism is constant in both series, as it is required in order to correctly apply linear free-energy relationships.<sup>14</sup>

The decreasing of the reaction rate could be ascribed to a frontal strain between the reagents or to a steric inhibition to solvation of the transition state. Both possibilities can be distinguished considering ΔS<sup>‡</sup> values, because the frontal strain should lower ΔS<sup>‡</sup>, while steric inhibition to solvation should increase it.<sup>13</sup> The observed trend of ΔS<sup>‡</sup> values suggests a prevalent steric inhibition to solvation in the transition state.

Nevertheless the activation parameters must be regarded with some caution since other effects can contribute to ΔH<sup>‡</sup> and ΔS<sup>‡</sup> values; steric inhibition to reagent solvation and

Table III. Results of the Correlations with Charton's Equation

	ortho-substituted anilines			N-substituted anilines		
	40 °C	50 °C	60 °C	40 °C	50 °C	60 °C
	reactions of benzyl chloride					
$R^a$	0.993	0.991	0.984	0.998	0.999	0.995
$\psi$	-0.73	-0.63	-0.49	-3.60	-3.24	-2.56
$h$	-4.15	-3.84	-3.62	-2.18	-2.06	-2.13
$s_\psi^b$	0.04	0.04	0.04	0.21	0.13	0.27
$s_h^c$	0.04	0.04	0.04	0.13	0.08	0.17
	reactions of 2-methylbenzyl chloride					
$R^a$	0.983	0.987	0.991	0.991	0.999	0.998
$\psi$	-1.03	-0.75	-0.70	-3.13	-2.77	-2.06
$h$	-3.60	-3.38	-3.10	-1.98	-1.82	-1.92
$s_\psi^b$	0.09	0.05	0.04	0.41	0.12	0.11
$s_h^c$	0.08	0.05	0.04	0.26	0.07	0.07

<sup>a</sup> Correlation coefficient. <sup>b</sup> Standard deviation of  $\psi$ . <sup>c</sup> Standard deviation of  $h$ .

Table IV. Results of the Isokinetic Relationships<sup>a</sup>

reactions of	registry no.	$N$	$R$	$\Delta H^\ddagger_0$	$\beta$	$s_{\Delta H^\ddagger_0}$	$s_\beta$
benzyl chloride	100-44-7	10	0.994	26.9	0.38	0.4	0.01
2-methylbenzyl chloride	552-45-4	10	0.995	25.9	0.38	0.3	0.01
benzyl and 2-methylbenzyl chloride		20	0.986	26.0	0.37	0.4	0.01

<sup>a</sup>  $N$  = number of points,  $R$  = correlation coefficient.  $s_{\Delta H^\ddagger_0}$  and  $s_\beta$  = standard deviation of the estimated value.

steric inhibition to resonance, in fact, cannot be elucidated by kinetic work.

The obtained results confirm the prevalence of steric effects in nucleophilic substitutions to the saturated carbon atom with hindered alkyanilines. The lack of noticeable polar effects of alkyl groups on the nucleophilic reagent is in accord with the reactions of 2-substituted pyridines with methyl iodide,<sup>7,15</sup> and with the substitutions in  $XCH_2Cl$  substrates.<sup>6</sup>

A dependence of both polar and steric effects, instead, has been found for the reactions of 2-thiophenesulfonyl chloride with sterically hindered anilines,<sup>16</sup> but in the latter case the reaction mechanism (addition-elimination pathway on sulfonyl sulfur atom) is very different from the substitution to the saturated carbon atom, which proceeds by a synchronous  $S_N2$  mechanism.

### Experimental Section

**Materials.** Benzyl chloride, 2-methylbenzyl chloride, and anilines (except *N*-isopropylaniline), commercially available samples, were distilled before use. Ethanol containing 0.5% water (Carlo Erba) was used throughout.

***N*-Isopropylaniline** was prepared by adding 41 g (0.33 mol) of 2-bromopropane and 28 g of sodium bicarbonate to a solution containing 31 g (0.33 mol) of aniline in 100 mL of ethanol. The reaction solution was refluxed for 24 h and then filtered off. After evaporation of the solvent, the residue was distilled under vacuum: bp 42 °C (0.07 mm) [lit.<sup>17</sup> bp 212–213 °C (760 mm)]; yield 85–90%; NMR  $\delta$  1.13 (doublet, 6 H, methyl), 3.85 (multiplet, CH), 6.87 (multiplet, 5 H, phenyl).

**Kinetic Procedure.** Rate measurements were carried out potentiometrically by continuous titration of the acid produced, with 0.1 M sodium hydroxide, following the procedure and the apparatus already described.<sup>8,18</sup> The reagent concentrations were ca. 0.002 mol L<sup>-1</sup> for benzyl or 2-methylbenzyl chloride and 0.1–0.5 mol L<sup>-1</sup> for the anilines.

Pseudo-first-order rate constants ( $k_1$ , s<sup>-1</sup>) were obtained from the slope of the conventional plots of  $\log(a-x)$  against time, using the least-squares method. The estimated precision for  $k_2$ , calculated from  $k_1$  values against at least three different aniline concentrations, is  $\pm 7\%$ .

**Reaction Products.** Ethanol solutions of benzyl or 2-methylbenzyl chloride (0.03 mol) and anilines (0.065 mol) were refluxed for 2–24 h, depending on the reaction rates. Ethanol was evaporated and the residue treated with anhydrous ether; the solution, separated from the anilinium chloride precipitate, was evaporated and the residue was crystallized or distilled under vacuum, yield ca. 85%.

***N*-Benzylanilines** (Y, Z, W, mp or bp (°C)/mm): H, H, H, 36–37;<sup>19</sup> CH<sub>3</sub>, H, H, 112/0.13;<sup>20</sup> C<sub>2</sub>H<sub>5</sub>, H, H, 105/0.06;<sup>21</sup> *i*-C<sub>3</sub>H<sub>7</sub>, H, H, 110/0.15;<sup>22</sup> H, CH<sub>3</sub>, H, 60;<sup>23</sup> H, C<sub>2</sub>H<sub>5</sub>, H, 110/0.04;<sup>22</sup> H, *i*-C<sub>3</sub>H<sub>7</sub>, H, 135/0.11;<sup>22</sup> H, CH<sub>3</sub>, CH<sub>3</sub>, 73/1;<sup>22</sup> H, C<sub>2</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>5</sub>, 75/0.6;<sup>22</sup> H, *i*-C<sub>3</sub>H<sub>7</sub>, *i*-C<sub>3</sub>H<sub>7</sub>, 167/0.75;<sup>22</sup> ***N*-2-Methylbenzylanilines:**<sup>22</sup> H, H, H, 135/0.7; CH<sub>3</sub>, H, H, 140/0.34; C<sub>2</sub>H<sub>5</sub>, H, H, 135/0.13; *i*-C<sub>3</sub>H<sub>7</sub>, H, H, 53; H, CH<sub>3</sub>, H, 79–80; H, C<sub>2</sub>H<sub>5</sub>, H, 126/0.04; H, *i*-C<sub>3</sub>H<sub>7</sub>, H, 143–144; H, CH<sub>3</sub>, CH<sub>3</sub>, 56/0.02; H, C<sub>2</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>5</sub>, 110/0.06; H, *i*-C<sub>3</sub>H<sub>7</sub>, *i*-C<sub>3</sub>H<sub>7</sub>, 152/0.32.

Satisfactory combustion analytical data for C, H, N, ( $\pm 0.25\%$ ) were obtained for the benzylanilines synthesized here. The compounds were always checked by NMR spectroscopy.

**Acknowledgment.** We thank the Consiglio Nazionale delle Ricerche (Rome) for the financial support.

**Registry No.**—*N*-Benzylaniline, 103-32-2; *N*-methyl-*N*-benzylaniline, 614-30-2; *N*-ethyl-*N*-benzylaniline, 92-59-1; *N*-isopropyl-*N*-benzylaniline, 38577-69-4; 2-methyl-*N*-benzylaniline, 5405-13-0; 2-ethyl-*N*-benzylaniline, 68950-92-5; 2-isopropyl-*N*-benzylaniline, 35452-49-4; 2,6-dimethyl-*N*-benzylaniline, 16819-50-4; 2,6-diethyl-*N*-benzylaniline, 68950-93-6; 2,6-diisopropyl-*N*-benzylaniline, 68950-94-7; *N*-2-methylbenzylaniline, 50625-79-1; *N*-methyl-*N*-2-methylbenzylaniline, 28059-65-6; *N*-ethyl-*N*-2-methylbenzylaniline, 68950-95-8; *N*-isopropyl-*N*-2-methylbenzylaniline, 68950-96-9; 2-methyl-*N*-2-methylbenzylaniline, 68950-97-0; 2-ethyl-*N*-2-methylbenzylaniline, 68950-98-1; 2-isopropyl-*N*-2-methylbenzylaniline, 68950-99-2; 2,6-dimethyl-*N*-2-methylbenzylaniline, 68951-00-8; 2,6-diethyl-*N*-2-methylbenzylaniline, 68951-01-9; 2,6-diisopropyl-*N*-2-methylbenzylaniline, 68951-02-0; 2-bromopropane, 75-26-3.

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- $\psi$  values are negative because reactivity decreases on increasing steric

- effects. Space filling models confirm the greater hindrance and conformation restrictions in the transition state of 2-methylbenzyl chloride.
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- (15) For this reaction satisfactory linear correlation is obtained between  $\log k_2$  and  $\nu$  parameters (substituents:  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_7(\text{l})$ ,  $\text{C}_4\text{H}_9(\text{t})$ ;  $R = 0.993$ ;  $\psi = -4.45$ ).
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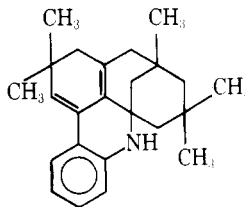
## Isophorone–Aniline Condensation Product

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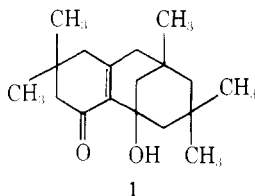
Isophorone, aniline, and hydrogen chloride, as catalyst, when heated together give a novel heterocyclic compound (I), mp 153–155 °C. Isophorone anil, when heated with HCl as catalyst, gives the same product. Cyclohexylamine,



I

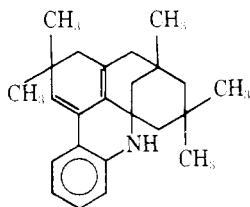
isophorone, and HCl as catalyst gives imine but no dimeric products. A reaction mechanism is proposed for the formation of I.

It is known that isophorone is dimerized by basic catalysts, such as alkali hydroxides<sup>1–3</sup> or sodium amide,<sup>4,5</sup> to give a dimer of structure<sup>6</sup> 1. Acidic catalysts have not been reported



1

to give this product. Surprisingly, we find that isophorone and aniline, using acidic catalysts, such as hydrogen chloride or *p*-toluenesulfonic acid, give a novel heterocyclic compound 2, which has a structure similar to the above dimer 1. This



2

product is also obtained when isophorone anil is heated with acids.

This structural assignment is based on the infrared spectrum (KBr), which possesses absorptions at 3330 (secondary amine),<sup>7</sup> 1630 (conjugated double bond), 1310 (secondary aromatic amine), and 755 (ortho-substituted aromatic ring)  $\text{cm}^{-1}$ . The chemical ionization mass spectrum of 2 shows a strong molecular ion at  $m/e$  333. It also shows a strong  $M + 1$ , which indicates a stable molecule. The proton NMR spectrum in deuteriochloroform has absorptions at 0.6–1.4 (19 H,

large singlets and small multiplets,  $\text{CH}_3$  and  $\text{CH}_2$ ), 1.7–2.4 (6 H, group of multiplets,  $\text{C}=\text{CCH}$  and  $\text{CH}$ ), 3.47 (1 H, singlet,  $\text{N}-\text{H}$ ), 5.26 (1 H, singlet,  $\text{C}=\text{CH}$ ), and 6.3–7.2 (4 H, multiplet,  $\text{Ar}-\text{H}$ ) ppm downfield from internal  $\text{Me}_4\text{Si}$ . Table I contains the <sup>13</sup>C NMR spectral data of 2. It shows that 2 has a total of five aromatic and olefinic carbons which are not attached to hydrogen atoms. Two of these are carbons which are in the aromatic nucleus, and the other three are in the conjugated diene. There are four aromatic carbons and one olefinic carbon which are substituted with a hydrogen atom. In the aliphatic region, there are four carbon atoms which do not contain hydrogens, five methylene carbons, and five methyl carbons.

