CH_2C=O), 4.0 (3 H, s, OCH_3), 5.6 (1 H, m, CHBr), 7.1-7.8 (3 H, m, aromatic).

Reaction of the bromide containing mixture prepared above with 100 mL of *sym*-collidine in 75 mL of ether containing a few crystals of 1,3,5-trinitrobenzene for 3 h at room temperature and 2 h at 50 °C gave a product after workup which contained about 45% 5-methoxyinden-1-one: NMR (CCl_4) δ 4.0 (3 H, s, OCH_3), 5.9 (1 H, d, J = 6 Hz, =CHC=O), 7.0 (4 H, m, aromatic =CH).

Reduction of the indenone containing mixture with 0.70 g (0.018 mol) of $LiAlH_4$ in ether at 0 °C for 20 min gave after workup a yellow oil which appeared to contain about 50% of 5-methoxyinden-1-ol: NMR (CCl_4) δ 3.9 (3 H, s, OCH_3), 5.1 (1 H, m, CHOH), 6.4 (1 H, d of d, J = 5, 2 Hz, =CHCHOH), 6.7 (3 H, m, aromatic =CH), 7.2 (1 H, m, aromatic).

Reaction of the alcohol mixture prepared as above with 4.3 g (0.018 mol) of 3,5-dinitrobenzoyl chloride in pyridine at -15 °C for 2 h gave after workup and recrystallization first from a 2:1 mixture of petroleum ether and chloroform and second from toluene containing a little pentane gave 1.9 g (16% yield based on starting 5-methoxyindan-1-one) of light yellow powder: mp 149-156 °C; NMR ($CDCl_3$) δ 3.9 (3 H, s, OCH_3), 6.4 (1 H, m, CHODNB), 6.9 (2 H, m, HC=CH), 7.4 (3 H, m, aromatic), 9.1 (3 H, s, aromatic).

Anal. Calcd for $C_{17}H_{12}O_7N_2$: C, 57.30; H, 3.41. Found: C, 57.39; H, 3.65.

1-Deuterioinden-1-yl 3,5-Dinitrobenzoate. Following a procedure similar to that described above and which was also used by Marvel and Hinman,[10] 4.0 g (0.030 mol) of indan-1-one was reacted with 6.5 g (0.037 mol) of *N*-bromosuccinimide. The 3-bromoindan-1-one-containing product was dehydrobrominated with collidine in ether. Reduction of the inden-1-one-containing dehydrobromination product with 0.65 g (0.015 mol) of $LiAlD_4$ in ether gave an alcohol-containing product which was reacted with 3.6 g (0.016 mol) of 3,5-dinitrobenzoyl chloride in pyridine at -15 °C for 2 h. Workup and recrystallization once from a 2:1 mixture of petroleum ether and chloroform and twice from acetone gave about 0.5 g (5% overall yield from starting indan-1-one) of the desired 1-deuterioinden-1-yl 3,5-dinitrobenzoate: mp 143-146 °C (lit.[1] mp 145.5-146.5 °C for nondeuterated material); NMR ($CDCl_3$) δ 6.4 (1 H, d, J = 6 Hz, =CHCDODNB), 6.9 (1 H, d, J = 6 Hz, aromatic =CH), 7.3 (4 H, m, aromatic), 9.1 (3 H, s, aromatic).

Hydrolysis Products from 3-Methylinden-1-yl 3,5-Dinitrobenzoate. A 0.16-g sample of 3-methylinden-1-yl 3,5-dinitrobenzoate and 0.1 g of $CaCO_3$ were added to 5 mL of 80% aqueous acetone and sealed in an ampule. After being heated at 100 °C for 22.5 days (about 5 half-lives for reaction), the reaction mixture was worked up by pouring into ether, washing with saturated aqueous NaCl, and drying over $MgSO_4$. Removal of the ether gave a solid material which was found by NMR examination to consist of 75% 3-methylinden-1-ol and 25% 1-methylinden-1-ol by integration of their respective methyl (δ 2.0 vs. 1.5) and vinylic (δ 5.8 vs. 6.2 and 6.5) proton absorptions.

Hydrolysis Product from 5-Methoxyinden-1-yl 3,5-Dinitrobenzoate. Hydrolysis of a sample of 5-methoxyinden-1-yl 3,5-dinitrobenzoate in 80% aqueous acetone under conditions similar to those used above gave a product found by NMR examination to be a methoxyindenol. Although the evidence is not clear-cut, slight differences in the complex aromatic proton absorption region from that of a pure sample of 5-methoxyinden-1-ol would tend to indicate that the product is a mixture of 5-methoxyinden-1-ol and its 3-methoxyinden-1-ol allylic rearrangement isomer.

Examination for Ion-Pair Return in Reaction of 1-Deuterioinden-1-yl 3,5-Dinitrobenzoate in CF_3CH_2OH. 1-Deuterioinden-1-yl 3,5-dinitrobenzoate (0.02 g) and $CaCO_3$ (0.1 g) were added to 5 mL of 2,2,2-trifluoroethanol, sealed in a Pyrex ampule and heated at 125 °C for 4 days (time for 30% acid product). The contents were poured into water, and the precipitate formed was filtered, dried under vacuum, and analyzed by NMR. Integration of the δ 6.5 (=CHCHODNB) and 6.9 (aromatic =CH) proton regions showed that the isolated dinitrobenzoate still had greater than 95% of one deuterium at the 1-position.

Kinetic Procedures. These were done in manners similar to those described earlier[1] except that titrations of 5-mL aliquots of trifluoroethanol reaction mixtures were done in 25 mL of reagent grade acetone, using a mixed indicator prepared from 0.2 g of bromocresol purple and 0.2 g of bromothymol blue in 60 mL of methanol.

Acknowledgment. We thank the Committee on Research of the University of California, Davis, for a Faculty Research Grant providing partial support for this study.

Registry No. 3, 53820-88-5; 4, 64666-40-6; 5, 61463-15-8; 9, 79827-83-1; 10, 79827-84-2; 11, 79827-85-3; 12, 79827-86-4; 13, 79827-87-5; 14, 79827-88-6; 3-methylcyclopent-2-en-1-ol, 3718-59-0; 5-methylindan-1-ol, 33781-37-2; 5-methoxyindan-1-one, 5111-70-6; 3-methylinden-1-ol, 23417-85-8; 5-methylindan-1-one, 4593-38-8; 3-bromo-5-methylidanone, 28122-16-9; 5-methylinden-1-one, 79827-89-7; 5-methylinden-1-ol, 79827-90-0; 3-bromo-5-methoxyindan-1-one, 79827-91-1; 5-methoxyinden-1-one, 72913-59-8; 5-methoxyinden-1-ol, 79827-92-2; 1-deuterioinden-1-yl 3,5-dinitrobenzoate, 79839-33-1.

Spectroscopic Study of the Interaction of 1-(Di-*n*-propylamino)-2,6-dinitro-4-(trifluoromethyl)benzene with Amines[1]

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The reactions of **4** with amines and amino acids in Me_2SO-H_2O solutions have been studied by NMR and UV-vis spectroscopy, and kinetic parameters have been determined. In the presence of 1 equiv of OH^-, 1:1 σ complexes were formed, but there was no evidence for 1:2 complexes. Spectral and kinetic data indicate that the initial reaction product is a 1,3 σ complex and that in H_2O-rich solvent mixtures this complex is slowly converted into the isomeric 1,1 σ complex. Equilibrium constants for the reactions of **4** with *n*-$BuNH_2$ and with piperidine have been determined.

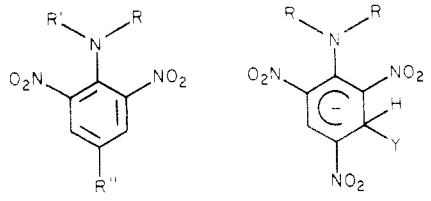
Aromatic amines **1** bearing a variety of substituents on the aromatic ring and on nitrogen are commonly used as plant growth regulators, but little is known about their mechanism of action.[2] It has been suggested that their activity might be due to the electron-deficient nature of the aromatic ring which makes these compounds good

(1) Presented in part at the 2nd Congreso Argentino de Fisico-Quimica, Carlos Paz, Côrdoba, Argentina, 1980.

(2) (a) Ashton, F. M.; Crafts, A. I. "Mode of Action of Herbicides"; Wiley-Interscience: New York, 1973; p 504. (b) Parke, S. J.; Soper, O. F. *Weed Sci.* **1977**, *25*, 79.

0022-3263/82/1947-0319$01.25/0

electrophiles toward biological bases to form Meisenheimer-like compounds.[3]

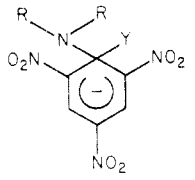


1 2

R = C_2H_5 or CH_3, Y = OH, SO_3^{2-}, or CH_3O

Although the chemistry of Meisenheimer complexes has been extensively studied,[4] the literature regarding reactions of aromatic substrates bearing an amine group as a substituent pertains for the most part to compounds having three nitro groups with OH^-, SO_3^{2-}, and CH_3O^- as nucleophiles.[5] In all cases the preferred site of attachment seems to be the C-3 position to form the 1:1 complex **2**.

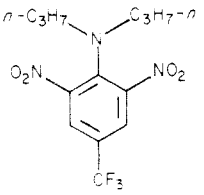
The formation of complex **3** where the nucleophile adds to C-1 was not detected as a stable entity with the above-mentioned nucleophiles, although addition to C-1 is known to lead to the thermodynamically more stable product when there are substituents other than dialkylamino attached to this carbon.[4,6]



3

Transient intermediates of type **3** have been reported in the reaction of picryl ethers with aliphatic amines,[7] and a 1:1 σ complex of type **3** was suggested to be the major reaction product of hydroxylamine with *N*-methyl and *N,N*-dimethylpicramide.[8]

We report here on our studies of the interaction of **4**, which is commonly used as a herbicide, with several amines and amino acids in dimethyl sulfoxide–water.



4

Results

NMR Spectroscopy. The NMR spectrum of **4** in 90% Me_2SO–H_2O shows an aromatic absorption at δ 8.34. Addition of 1 or 2 equiv of *n*-$BuNH_2$, *sec*-$BuNH_2$, piperidine, alanine, or threonine to these solutions does not shift this peak. However, when 1 equiv of KOH is then added to these solutions, the peak at δ 8.34 begins to diminish, and two new peaks at ~5 and ~7 ppm begin to grow (Table I). These new peaks integrate in a ratio of 1:1 and are attributed to H_a and H_b in the Meisenheimer complex **5**.

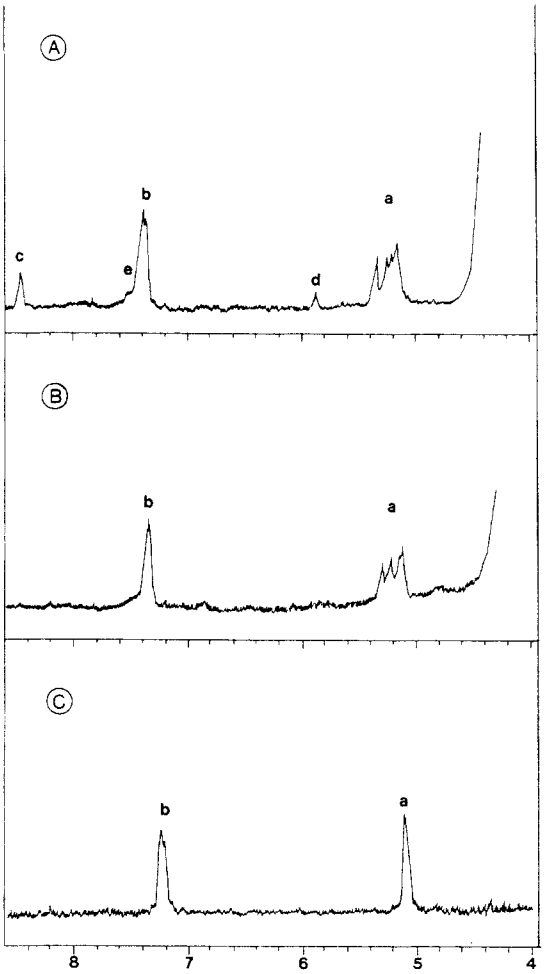
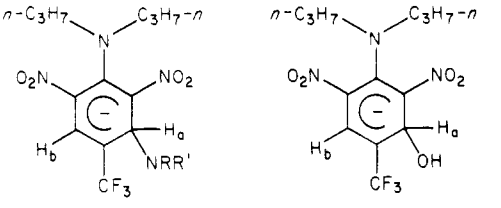


Figure 1. Proton NMR of the aromatic region of the reaction product of alanine and **4** in water–dimethyl sulfoxide (90%) ($[4]_0$ = 0.4 M, $[alanine]_0$ = 0.4 M, $[KOH]_0$ = 0.8 M): (A) 10 min after mixing, a and b are H_a and H_b of **7**, c is unreacted **4**, and d and e are H_a and H_b of **6**; (B) 3 h after mixing; (C) the same as in B but in Me_2SO-d_6–D_2O.



5 6

The possibility that these peaks are due to the hydroxy complex **6** is eliminated because when KOH is added to a solution of **4** in the same solvent, the absorptions of **6** appear at δ 5.83 and 7.44, but after addition of 1 equiv of the amine, they slowly change to the values shown in Table I. These results indicate that the amines can displace hydroxide ion from its complex with **4**. There is a precedent where an aromatic amine displaces methoxide ion from its complex with trinitrobenzene.[9]

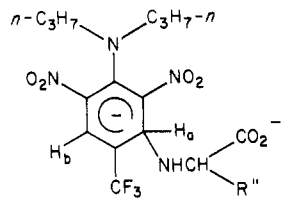
(3) Hall, R. C.; Giam, C. S. *J. Agric. Food Chem.* **1974**, *22*, 461.
(4) For reviews on Meisenheimer complexes see: Buncel, E.; Norris, A. R.; Russell, K. E. *Q. Rev., Chem. Soc.* **1968**, *22*, 123. Crampton, M. R. *Adv. Phys. Org. Chem.* **1969**, *7*, 211. Strauss, M. J. *Chem. Rev.* **1970**, *70*, 667.
(5) Buncel, E.; Hamaguchi, M.; Norris, A. R. *Can. J. Chem.* **1980**, *58*, 1615, 1609 and references cited therein.
(6) (a) Fendler, J. E.; Fendler, J. H.; Griffin, C. E.; Larsen, J. W. *J. Org. Chem.* **1970**, *35*, 287. (b) Bernasconi, C. F. *J. Am. Chem. Soc.* **1971**, *93*, 6975.
(7) Fyfe, C. A.; Damji, S. W. H.; Koll, A. *J. Am. Chem. Soc.* **1979**, *101*, 951.
(8) Grudtsy, I. D.; Gitis, S. S. *J. Org. Chem. USSR (Engl. Transl.)* **1974**, *10*, 1471.
(9) Buncel, E.; Webb, J. G. K. *Can. J. Chem.* **1974**, *52*, 630.

Table I. NMR Parameters of σ Complexes 5[a]

R	shift, δ (J, Hz)	
	H_a	H_b
$CH_3CHCH_2CH_3$	5.25 (10)[b]	7.35
$CH_3(CH_2)_3$	5.10 (8)[b]	7.20
$-(CH_2)_5-$[c]	5.19	7.33
$CH_3CHCO_2^-$	5.25[d]	7.35
$CH_3CHOHCHCO_2^-$	5.04[d]	7.17

[a] R′ = H unless otherwise indicated. [b] Coupling constant of NH-H_a. [c] Piperidine. [d] Two doublets, see text.

With the two butylamine complexes the H_a peak is a doublet with J = 8–10 Hz. This result is unusual because CH–NH coupling is not often seen in protic solvents. When the solvent is Me_2SO-d_6–D_2O, the H_a peak of **5** appears as a singlet as expected. The H_a absorption of the amino acid complexes **7** comprises two poorly resolved doublets with a total separation of 12 Hz. The relative intensity of these doublets changes with time (Figure 1), but the whole peak integrates for one proton. We believe that these two absorptions represent cis and trans conformations of the C–H and the N–H, which are present in roughly equal amounts (see Figure 1). It is known that when rotation about a bond is restricted the hydrogens in the two conformations are not magnetically equivalent and can produce two chemically shifted resonance peaks.[10] It appears that the CO_2^- group in **7** inhibits rotation about the CH–NH bond, which does not occur with the butylamine complexes.



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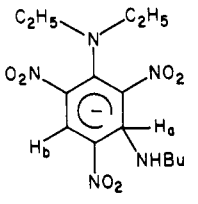
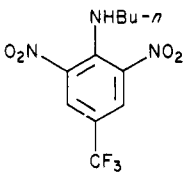


8

For comparison we investigated the NMR of *N,N*-diethylpicramide in the presence of piperidine or *n*-$BuNH_2$. *N,N*-Diethylpicramide has a peak at δ 8.86 in 90% Me_2SO–H_2O. After the addition of 1 equiv of piperidine this peak becomes very broad, is centered at 7.8 ppm, and is not changed by addition of 1 equiv of KOH. Similar broadening of the aromatic absorption is observed in the reactions of picramide with hydroxylamine[8] and of trinitrobenzene with amines in Me_2SO.[9] The addition of 1 equiv of *n*-$BuNH_2$ to a solution of *N,N*-diethylpicramide causes a similar broadening of the aromatic absorption, but after the addition of 1 equiv of KOH, two new absorptions develop at δ 8.36 and 7.73 and are attributed to H_a and H_b of complex **8**. There is no coupling between the CH_a–NH protons, indicating a more rapid exchange with the solvent, probably because of the higher acidity of the amine proton in **8** than in **5** (R = *n*-Bu, R′ = H).

UV–vis Spectroscopy. Solutions of **4** in 10–90% Me_2SO–H_2O have a broad absorption at λ 420–430 nm (ε ~3000 M^{-1} cm^{-1}). Addition of *n*-$BuNH_2$ (1 M) and KOH (10^{-2} M) to a solution of **4** in 10% Me_2SO–H_2O results in formation of a species with λ_{max} at 335 and 425 nm. The absorbance at 425 nm increases with time ($k = 1.2 \times 10^{-4}$ s^{-1}) and shifts to 435 nm. The spectra of solutions of **4** in 20% Me_2SO–H_2O containing *n*-$BuNH_2$ (0.05 M) and KOH (0.05–0.88 M) taken 4–6 min after mixing, before the optical density had been reached maximum, gave a reasonably good isosbestic point at 300 nm.

Solutions containing *n*-$BuNH_2$ (0.509 M) and KOH (0.36 M) show a rapid and complete conversion into the species with λ_{max} at 330 and 425 nm. From the optical density extrapolated to zero time the extinction coefficients we calculated to be 10 500 and 18 200 M^{-1} cm^{-1}, respectively. If these solutions were acidified, the spectra reverted to that of **4**. After the solutions were allowed to stand a while, the absorbances at 330 and 425 nm began to diminish, and after they were allowed to stand overnight there was irreversible formation of a compound with a spectrum similar to that of the product of reaction of **4** with KOH under the same conditions. This spectrum was also essentially identical with that obtained by reaction of 1-chloro-2,6-dinitro-4-(trifluoromethyl)benzene with KOH under these conditions and was different from that of **9**. We believe that these changes represent initial conversion of **4** into the Meisenheimer complex **5** and subsequent conversion of **5** into the phenol **10**.



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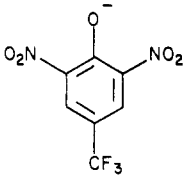


10

Similar slow irreversible changes have been observed in the reaction of *N,N*-dimethylpicramide with methoxide ion in methanol[11] or methanol–dimethyl sulfoxide solutions[5] or with hydroxide ion in water.[12]

In solutions of **4** in 40–70% Me_2SO–H_2O, the species with λ_{max} at 330 and 430 nm attains equilibrium optical density in about 10 min. The increase in absorption at 430 nm with increasing concentration of KOH, with the concentration of *n*-$BuNH_2$ kept constant, was used to determine the equilibrium constant. The spectra in 40% or 50% Me_2SO show a reasonably good isosbestic point, whereas there is no isosbestic point in the spectra in 60% or 70% Me_2SO.

The behavior of solutions containing piperidine (0.1–1 M) and KOH (10^{-2} M) in 20% Me_2SO is similar to that of solutions containing *n*-$BuNH_2$ under similar conditions. A species with λ_{max} at 335 and 425 nm is formed increasingly as the concentration of piperidine increases or when the concentration of piperidine is kept constant and that of KOH is increased. These solutions are rather stable, and the equilibrium absorption is reached 2–3 min after mixing. When the concentration of piperidine is increased from 0.05 to 1 M with KOH 0.5 M, the maximum absorption shifts from 425 to 435 nm, and the extinction coefficient decreases, while the extinction coefficient at 330 nm increases slightly.

In 40% Me_2SO the equilibrium optical density of the species with λ_{max} at 335 and 430 nm is reached quickly, and the solutions are stable for 2–3 h. Spectra taken at constant [piperidine] and increasing [KOH] show an isosbestic point at 296 nm. Similar behavior is observed in 50% Me_2SO; the maximum absorption occurs at the same wavelength, and the isosbestic point is at 300 nm (ε 5000 M^{-1} cm^{-1}).

Kinetic Studies. An attempt was made to determine the kinetics of formation and decomposition of the species formed from **4** and *n*-$BuNH_2$ in 30% Me_2SO–H_2O by using

(10) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy", 2nd ed.; Pergamon Press: 1967; Vol. 1, p 133.

(11) Gold, V.; Rochester, C. H. *J. Chem. Soc.* **1964**, 1697.
(12) Gold, V.; Rochester, C. H. *J. Chem. Soc.* **1964**, 1727.

Table II. Kinetics of the Interaction of 4 with *n*-Butylamine in 30% Me_2SO-H_2O at 25 °C[a]

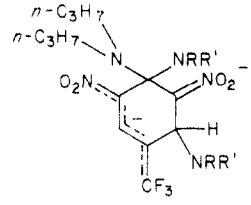
$[n\text{-BuNH}_2]$, M	[KOH], M	$10^2 k_{obsd}$, s^{-1} [b]
0.05	0.100	2.23
0.06	0.100	3.20
0.07	0.100	3.38
0.08	0.100	3.86
0.09	0.100	4.17
0.10	0.100	5.19
0.07	0.039	(11.3)
0.07	0.058	5.42 (12.5)
0.07	0.078	4.20 (10.0)
0.07	0.097	4.00 (9.47)
0.07	0.126	3.88
0.07	0.155	4.07
0.07	0.194	3.96

[a] Ionic strength 0.1 M (KCl as compensating electrolyte), $[4]_0 = 3 \times 10^{-5}$ M [b] "Formation" rate as indicated in the Results. Values in parentheses are lower limits of measured "decomposition" rates.

two methods. One method ("decomposition") involved preparing the σ complex **5** in 90% Me_2SO, adding it to a solution containing the desired quantity of hydroxide ion and *n*-$BuNH_2$, and measuring the rate of relaxation of the system at 420–430 nm. The second method ("formation") involved determining the rate of formation of the species with λ_{max} at 430 nm by adding a solution of **4** to a solution containing the desired quantities of *n*-$BuNH_2$ and KOH. In some cases (see Table II) both methods were used, but there was a factor of 2 difference in the rates measured by the two methods, indicating that there is more than one relaxation time in the system.[13] The rates are quite high, and the range of concentrations we could scan was not wide enough to determine the "decomposition" relaxation time with high precision.

Discussion

The NMR of solutions containing **4**, amine, and KOH in 90% Me_2SO in ratios of 1:1:1 or 1:2:2 is consistent with the formation of Meisenheimer complex **5**. There is no evidence for the formation of 1:2 complexes such as **11** or **12**. This result contrasts with the tendency of *N*,*N*-di-



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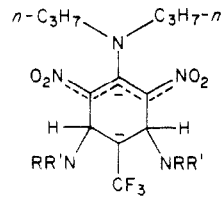
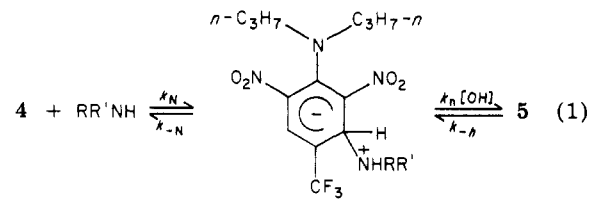


12

alkylpicramides to add 2 mol of nucleophile in high Me_2SO content solutions.[5] The tendency of **5** not to add a second molecule of nucleophile is attributed to the ineffectiveness of the trifluoromethyl group in stabilizing the negative charge localized on a single carbon atom.

A highly basic medium is required for the formation of a detectable amount of complex **5**, which probably occurs as shown in eq 1. The zwitterion **13** is a steady-state intermediate under our reaction conditions.

In 90% Me_2SO solutions containing 2 equiv of amine/equiv of **4** (~0.4 M), **5** is not formed to the limits of our NMR detection (~10%); under these conditions the equilibrium of eq 1 lies to the left, and $k_N \leq 10^{-2}$ M^{-1},[14]



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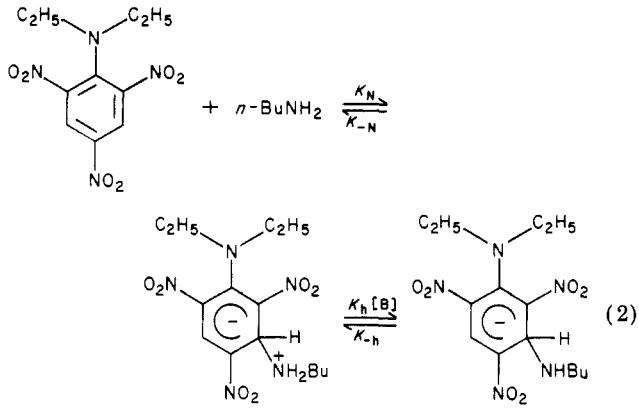
which compares well with values for related compounds.[4,15,16]

The interaction of *n*-$BuNH_2$ with *N*,*N*-diethylpicramide is qualitatively similar to its reaction with **4** (eq 2), but

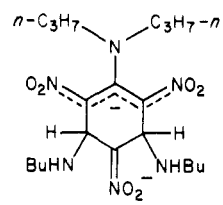


14

(2)

there are differences that reflect the greater stabilizing power of the 4-nitro group compared with the 4-trifluoromethyl group. Even in the absence of KOH a fast exchange occurs, indicating that a substantial amount of **14** is formed under conditions where less than 10% of **5** is formed from **4**. The fact that the overall equilibrium constant of eq 2 is greater than that of eq 1 probably reflects a higher k_N and to some extent also a higher k_h.

In solutions where the molar ratio of *N*,*N*-diethylpicramide, *n*-$BuNH_2$, and KOH was 1:2:2, there was no absorption in the NMR above 5 ppm, which probably indicates the formation of **15**; this complex should absorb in



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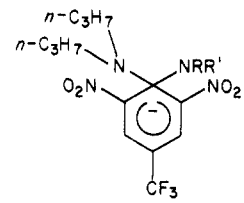


16

the range 4–5 ppm, and this range of absorption is hidden by the solvent. This result confirms the strong tendency of picramides to form 1:2 complexes even in a solvent of high Me_2SO content, which is known to unstabilize such complexes.[17,18]

The UV–vis spectra of solutions containing **4** and piperidine with various concentrations of KOH (Figure 2) is also consistent with the formation of **5**, although the isomeric complex **16** cannot be excluded since it should have about the same spectrum as **5**. Although the spectrum obtained is similar to that reported for **6**,[19] the

(13) Bernasconi, C. F. "Relaxation Kinetics"; Academic Press: New York, 1976; p 142.
(14) For estimation of this value it was assumed that the ratio of acidity constants of **14** and piperidine is equal to 1 as has been suggested for other zwitterionic Meisenheimer complexes.[15]
(15) Bernasconi, C. F.; Muller, M. C.; Schmid, P. *J. Org. Chem.* **1979**, *44*, 3189.
(16) Bernasconi, C. F.; Terrier, F. *J. Am. Chem. Soc.* **1975**, *97*, 7458.
(17) Carmpton, M. R. *J. Chem. Soc.* **1967**, 1341.
(18) Terrier, F.; Millot, F. *Bull. Soc. Chim. Fr.* **1970**, 1743.

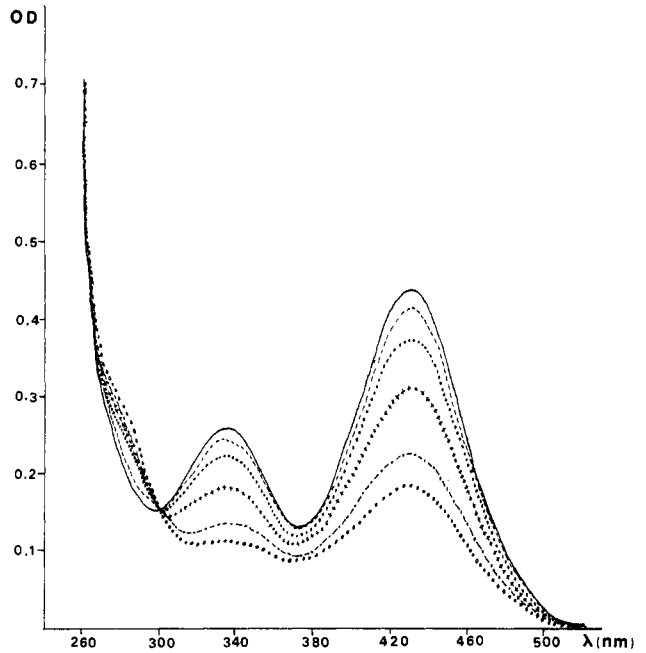


Figure 2. Absorbance of 4 in the presence of piperidine at various potassium hydroxide concentrations with $[4]_0 = 3 \times 10^{-5}$ M and [pip] = 0.051 M: 0.010 (O), 0.022 (- - -), 0.036 (+++), 0.061 (···), 0.074 (- - -), and 0.087 M (—).

Table III. Equilibrium Constants for the Reaction of 4 with n-$BuNH_2$ or Piperidine in Me_2SO-H_2O

Me_2SO, molar fraction	$10^{-3}K_NK_h$,[a] M^{-2}	
	n-$BuNH_2$ (log ϵ)	piperidine
0.060		0.106[b]
0.141	0.331 (4.34)	0.648
0.199	3.06 (4.32)	3.66
0.268	9.72 (4.32)	
0.355	98.5 (4.31)	

[a] Calculated by the nonlinear least-squares method from eq 3 unless otherwise noted. [b] Calculated from a Benessi-Hildebrand plot.

equilibrium constant for the formation of amine complexes is higher than that for hydroxy complexes; accordingly, the spectra in Figure 2 must reflect the formation of **5** and/or **16** rather than **6**. In Me_2SO-rich solutions it was necessary to use low concentrations of reactants, and the possible formation of **6** must be considered. The overall absorbance of solutions of **4** in Me_2SO–H_2O is given by eq 3, where A_0

$$A - A_0 = \frac{(\epsilon_c - \epsilon_4)[OH](K_0 + K_NK_h[RR'NH])[4]_0}{1 + [OH](K_0 + K_NK_h[RR'NH])} \quad (3)$$

is the absorbance of **4** in pure solvent, ϵ_c is the extinction coefficient of the σ complex, K_0 is the equilibrium constant for the formation of **6**, $K_N = k_N/k_{-N}$, and $K_h = k_h/k_{-h}$ (eq 1).

It is apparent from eq 3 that a plot of the reciprocal of the left-hand side against the reciprocal of [KOH] should yield a straight line when the [amine] is constant. From the slope and intercept of such plots, ϵ_c and K_NK_h can be determined, if K_0 is known,[20] by the Benessi-Hildebrand treatment.[21] Alternatively, a nonlinear least-squares

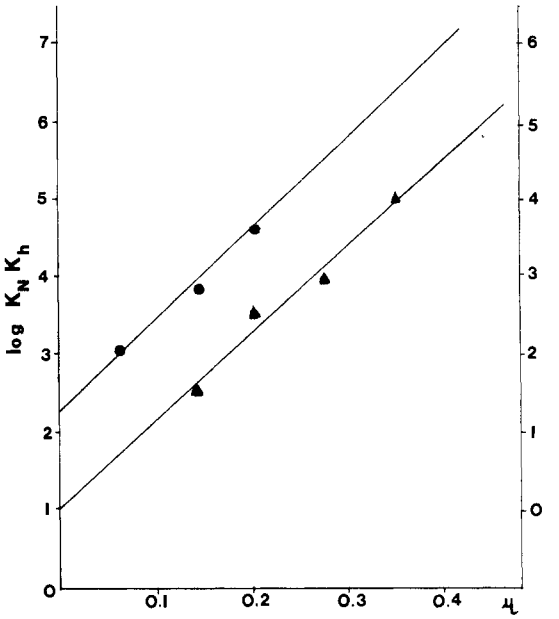


Figure 3. Equilibrium constant for the interaction of 4 with n-butylamine (left ordinate, ▲) and piperidine (right ordinate, ●) against the mole fraction of Me_2SO.

treatment of the parameters in eq 3 gives the product K_NK_h and ϵ_c[22] (see Table III). Both methods give comparable results in solutions with [Me_2SO] greater than 40%, but in 20% Me_2SO solutions the Benessi-Hildebrand plot is not linear with either n-$BuNH_2$ or piperidine. The nonlinear least-squares method gives a moderately good fit at low [KOH], especially with piperidine, and these values are shown in Table III.

Solvent Effect. Figure 3 shows the linear relation between log K_NK_h and the molar fraction of Me_2SO. The overall equilibrium constants for piperidine and n-$BuNH_2$ differ at most by a factor of 2, similar to those of their reactions with trinitrobenzene.[14] The small difference indicates that the decrease in acidity of the piperidine complex compared with the n-$BuNH_2$ complex is almost fully compensated by an increase in the ratio $(K_N)_{pip}/(K_N)_{BuNH_2}$. The solvent dependence of the overall equilibrium constant is determined by the solvent dependence of nucleophile addition (K_N), the acidity constant of complex **13** (K_{13}), and the solvent dependence of the self-ionization constant of water,[23] and our results fit eq 4.

$$\log K_NK_{13} = 1.84\mu + \log K^0{}_NK^0{}_{13} \quad (4)$$

Equation 4 predicts a smaller dependence of K_NK_{13} on the molar fraction of Me_2SO (μ) than is usually found for other Meisenheimer complexes since relations like eq 4 have slopes in the range 8–12.

Kinetics. In 20% Me_2SO–H_2O solutions we can identify three processes, well-differentiated by their rates. The first is fast, reversible, and complete by the time of the first measurement of absorbance. The second, also reversible, is slower and is characterized by an increase in optical density and a shift of the absorption maximum toward longer wavelength (from 425 to 435 nm). The third, irreversible, process is characterized by a decrease in the 435-nm absorption and disappearance of the 335-nm ab-

(19) de Rossi, R. H.; Madoery, O. D.; de Vargas, E. B. *J. Org. Chem.* **1980**, *45*, 649.

(20) The mathematical form of eq 3 would be the same if the absorbing species were **5** and **16** provided that their extinction coefficients are similar. In the derivation of eq 3 it was assumed that the extinction coefficients of **5** (and/or **16**) and **6** are the same since this is true in cases where both can be determined.

(21) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.

(22) A nonlinear least-squares program for a HP 41C calculator was used to compute K_NK_h and ϵ_c. Assistance by Dr. D. Murature in the writing of the program is acknowledged.

(23) Fiordoponti, P.; Rallo, F.; Rodante, F. *Z. Phys. Chem.* **1974**, *88*, 149.

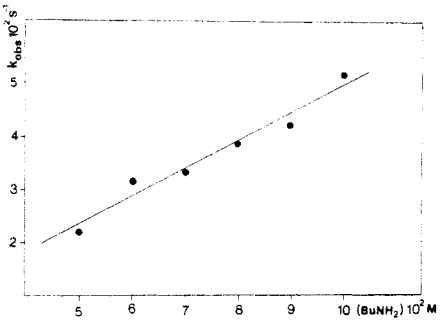
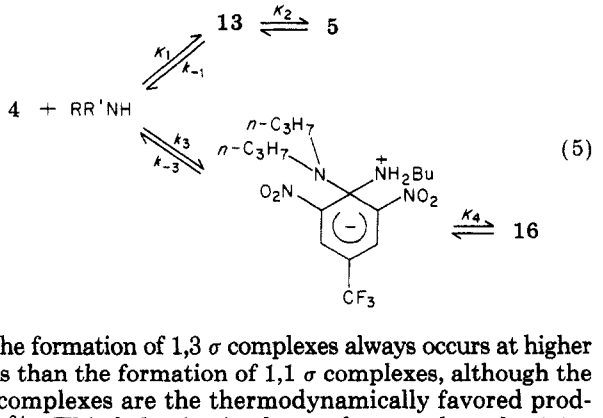


Figure 4. Dependence of the "formation" rate on the *n*-butylamine concentration with $[4]_0 \approx 3 \times 10^{-5}$ M and $[KOH]_0 = 0.1$ M.

sorption. We think that the first process is the formation of complex **5**, on the basis of the NMR results and the behavior of **4** with KOH.[19] We have no direct evidence pertaining to the second process. Although this step might involve formation of **11** or **12**, its kinetic characteristics militate against this possibility. Moreover, the spectral absorbance in equilibrated solutions can be represented by eq 3, which implies a 1:1 reaction, and spectra of 1:2 σ complexes are usually quite different from those of 1:1 complexes. We believe that this step involves formation of complex **16**, the isomer of **5**.

The reaction rates measured by starting from a solution of **4** ("formation") were quite different from those obtained when we added a solution of **5** in 90% Me_2SO to *n*-$BuNH_2$ and KOH ("decomposition"), suggesting that the processes involved in the two determinations were not the same. The possibility that the "formation" rate represented equilibration of **4** with a 1:2 complex (**12**) was eliminated because the UV–vis spectra gave no evidence for **12**. Furthermore, the rate of formation of **12** should have second-order dependence on $[BuNH_2]$, whereas the observed rate is linear with $[BuNH_2]$ (Figure 4).

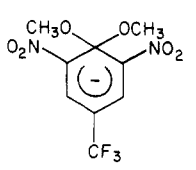
The more likely possibility is that the predominant species being slowly formed in the mainly aqueous solvent is the 1:1 complex **16**, despite the fact that it is only a minor species, if formed at all, in Me_2SO-rich solutions. In this case our system can be represented by eq 5.



(5)

The formation of 1,3 σ complexes always occurs at higher rates than the formation of 1,1 σ complexes, although the 1,1 complexes are the thermodynamically favored products.[24] This behavior is observed even when the 1:1 σ complex has a weak electron-withdrawing group. For example, the complex **17** is more stable than **18** but is formed at a lower rate.

The observed "decompositon" rate is given by eq 6, since the process involving the formation of **5** contributes very little because the equilibrium shown in eq 5 lies mainly to the left. The observed "formation" rate constant is



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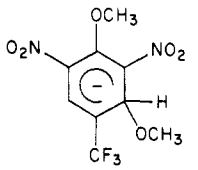

18

given by eq 7, which is consistent with its dependence on $[BuNH_2]$ and $[OH^-]$.[25]

$$k_{obsd} = k_{-1}/K_2[OH^-] \quad (6)$$

$$k_{obsd} = k_3[BuNH_2][OH^-] + k_{-3}/K_4[OH^-] \quad (7)$$

Our analysis implies an unusual behavior of **4** compared with other nitro-substituted aromatic amines: the predominant formation of a C-1 σ complex in water-rich solutions as opposed to the reaction in Me_2SO-rich solvents where the C-3 σ complex predominates. This result is a consequence of the kinetics of the system and is not due to the relative thermodynamic stabilities of **5** and **16** in Me_2SO and in water. The lifetimes of σ complexes increase with the Me_2SO content of the solvent. For example, the lifetime of **17** increases from 4.5 ms in pure methanol to 272 s in 92.6% Me_2SO (w/w).[26] Thus it may well be that complex **5** is formed rapidly in 90% Me_2SO and that the time required for its conversion into **16** is so long that irreversible decomposition intervenes. Perhaps this is the reason that C-1 complexes are not detected by NMR in reactions of nitro-substituted aromatic amines with nucleophiles because in most cases the NMR spectrum is taken in Me_2SO, and solubility problems preclude determinations in other solvents.

Experimental Section

N-*n*-Butyl-2,6-dinitro-4-(trifluoromethyl)aniline (**9**) was prepared from 1-chloro-2,6-dinitro-4-(trifluoromethyl)benzene and *n*-butylamine by standard procedures. The spectra of **9** in 20% Me_2SO H_2O (v/v) in the absence as well as in the presence of KOH (10^{-2} M) are about the same, with only a little increase in the optical density at the maximum [λ 435 nm (ϵ 5200 M^{-1} cm^{-1}) in pure solvent]. With *n*-$BuNH_2$ 1 M and KOH (10^{-2} M), **9** gives rise to species having the characteristic maximum absorption of σ complexes, probably representing addition of *n*-$BuNH_2$ to the 1- or 3-position of **9**.

Trifluraline (**4**) was available from a previous study[18] and was recrystallized from ethanol. Me_2SO was dried on 3-Å molecular sieves and vacuum distilled. Solvent mixtures were made up from the desired number of volumes of Me_2SO in 100 volumes of solution.

^1H NMR studies were carried out on a Varian T 60 spectrophotometer at the probe temperature, and the absorption is reported in δ values relatives to Me_4Si for deuterated solutions, but in solutions of Me_2SO–H_2O the δ values were taken relatives to the peak of the solvent and then corrected for the absorption of the solvent relative to Me_4Si.

Absorbance measurements were obtained with a Beckman 24 spectrophotometer, and the spectra like those of Figure 2 were taken by reading the optical density at 5-nm intervals.

Kinetic measurements were made by rapidly injecting 10–20 μL of a solution of **4** in pure Me_2SO ("formation") or a solution of **4**, *n*-$BuNH_2$, and KOH in 90% Me_2SO ("decomposition") into the thermostated cell of the spectrophotometer containing *n*-$BuNH_2$, KOH, and KCl in Me_2SO–water such that the final concentrations were those shown in Table II. The increase and decrease in absorbance for the "formation" and "decomposition", respectively, were recorded at 430 nm.

(24) Buncel, E.; Norris, A. R.; Russell, K. E.; Sheridan, P. J. *Can. J. Chem.* **1974**, *52*, 25.

(25) In the derivation of eq 7 it was assumed that $K_1K_2[BuNH_2][OH] \ll 1$.

(26) Terrier, F.; Millot, F. *C. R. Hebd. Seances Acad. Sci. Ser. C* **1969**, *268*, 808.

Acknowledgment. This research was supported in part by the Consejo Nacional de Investigaciones Cientificas y Tecnicas and Secretaria de Estado de Ciencia y Tecnologia, Argentina.

Registry No. 4, 1582-09-8; 5·K (R = $CH_3CHCH_2CH_3$; R^1 = H), 79816-18-5; 5·K (R = $CH_3(CH_2)_3$; R^1 = H), 79871-51-5; 5·K (R = R^1 = $-(CH_2)_5-$), 79816-19-6; 5·2K (R = cH_3CHCO_2H; R^1 = H), 79816-20-9; 5·2K (R = $CH_3CHOHCHCO_2H$; R^1 = H), 79827-20-6; 9, 10223-72-0; *sec*-butylamine, 13952-84-6; piperidine, 110-89-4; alanine, 56-41-7; threonine, 72-19-5; *n*-butylamine, 109-73-9.

Supplementary Material Available: Table of UV-vis spectral data on solutions of 4 + piperidine in Me_2SO-H_2O (3 pages). Ordering information is given on any current masthead page.

Electroreductive Cyclopropylcarbonylation of Aromatic Ketones and Their Schiff Bases

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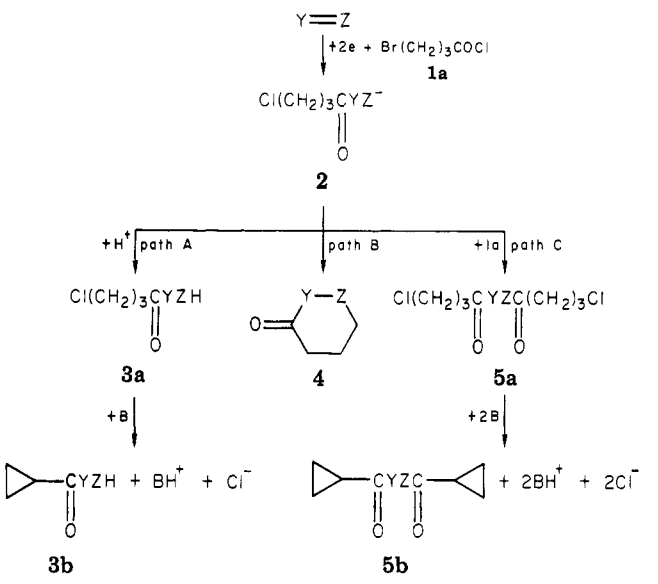
Mono- and dicyclopropylcarbonyl derivatives have been obtained by electroreduction of fluorenone, benzophenone, fluorenone anil, and benzophenone anil in the presence of 1 equiv of 4-bromo(or chloro)butyryl chloride (**1a** or **1b**). The electrolyses are carried out in DMF or MeCN according to two methods. In method A, **1a** (or **1b**) is added dropwise during the electrolysis. In method B, the total amount of **1a** (or **1b**) is added at the beginning of the experiment. The electrogenerated bases which are necessary to perform the cyclopropylcarbonylation reactions are either the radical anions of the depolarizers or their acylated anions. The distribution of the compounds and their yields, which are moderate, depend on two main factors which are the method applied and the solvent. It is shown that the properties of acid chlorides **1a** and **1b** differ in DMF and MeCN. The highest yields of cyclopropyl derivatives are reached in MeCN when method B is applied. However, in this solvent the acylation reaction is less specifically orientated than in DMF, and unexpected propionitrile derivatives are isolated. In the case of the anils, results of chemical reduction by alkali metals and electrochemical reduction are compared.

In a previous publication,[1] we have reported the electrosynthesis in *N,N*-dimethylformamide (DMF) of numerous acylated compounds. During the electrochemical reduction of unsaturated compounds Y=Z in the presence of 1 equiv of 4-bromobutyryl chloride (**1a**), we have obtained,[1] via the intermediate anion **2**, the monoacylated compounds **3a**, the cyclic compounds **4**, and the diacylated compounds **5a** (Scheme I).

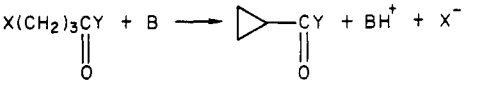
The formation of **3a** is favored if the intermediate acylated anion **2** presents a basic character and the competitive formation of **4** and **5a** occurs when **2** has nucleophilic properties.

In this report, we describe the electrosynthesis of cyclopropyl derivatives **3b** and **5b** (ketones, esters, and amides) during the electrolyses in DMF or acetonitrile (MeCN) of aromatic ketones (fluorenone (**6**), benzophenone) and Schiff bases (fluorenone anil (**7**), benzophenone anil (**8**)) in the presence of 1 equiv of **1a** or 4-chlorobutyryl chloride (**1b**). For the cyclopropylcarbonylation according to Scheme II, strong bases (B) and, in many cases, high temperatures are required.[2-4] We will show that, under in our experimental conditions, strong bases (B) are electrochemically generated which favor the transformation of **3a** to **3b** and that of **5a** to **5b** (Scheme I).

Scheme I



Scheme II[a]



[a] X = halogen; Y = R, OR, X, NR_2.

On the account of the known acidic properties of MeCN, we may anticipate that the nature and the distribution of the electrolysis compounds will depend on the solvent. If

(1) C. Degrand, P.-L. Compagnon, G. Belot, and D. Jacquin, *J. Org. Chem.*, **45**, 1189 (1980).
(2) G. W. Cannon, R. C. Ellis and J. R. Leal in "Organic Syntheses", Collect. Vol. IV, Wiley, New York; 1963, p 597.
(3) B. W. Horrom and L. R. Swett (Abbott Laboratories), U.S. Patent 2 992 269 (1961).
(4) R. E. A. Dear and E. E. Gilbert, *J. Org. Chem.*, **33**, 1690 (1968).

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