Chemical Society, to the U.S. Army Research Office, and to the Marathon Oil Co. for support of this research.

Registry No. *cis*-1, 79722-23-9; *trans*-1, 79722-24-0; *cis*-**2a**, 79722-25-1; *trans*-**2a**, 79722-26-2; **2b**, 79722-28-4; **2c**, 79722-29-5; **3**, 1119-87-5; **4**, 79722-30-8; **5**, 79722-31-9; *cis*-**6**, 79722-32-0; *trans*-**6**, 79722-33-1; 5-chloro-2-pentanone, 5891-21-4; quinuclidine, 100-76-5; 1-(4-oxopentyl)pyridinium hexachloroplatinate, 79735-25-4; piperonal, 120-57-0; piperonylic acid, 94-53-1; 2,2,2-trichlorotoluene, 98-07-7; benzoic acid, 65-85-0.

Substituent Effect Behavior in the Antiaromatic Inden-1-yl Cation System

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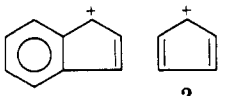
Studies of the rate-accelerating effects in solvolysis produced by 5-methyl and 5-methoxy substituents on the benzene ring and a 3-methyl substituent on the double bond of the inden-1-yl 3,5-dinitrobenzoate system have been carried out. In both 80% aqueous acetone and in 2,2,2-trifluoroethanol, the rate accelerations observed in the inden-1-yl system were approximately the same as those found in model cyclopenten-3-yl and indan-1-yl systems. From these results, it is concluded that delocalization of charge into both the benzene ring and double bond of the 8π-electron inden-1-yl carbocation is taking place and is apparently undiminished by antiaromatic effects.

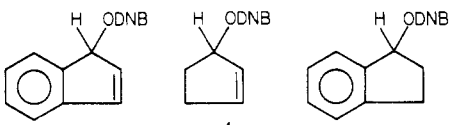
Introduction

Several years ago, we initiated a study[1] directed toward obtaining experimental information under normal solvolytic conditions concerning the structural and chemical consequences of potential antiaromaticity[2] in the 8π electron inden-1-yl cation system (1). Our interest in this



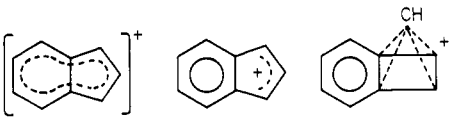
1 2

specific system was because of its close relationship to the classic 4π-electron cyclopentadienyl cation (2). However, in contrast to the latter,[3] its precursors are easier to handle and its formation requires somewhat less drastic conditions. Thus, the rates of solvolysis of inden-1-yl 3,5-dinitrobenzoate (3) and suitable model compounds including 4 and 5 were investigated in 80% aqueous acetone or in 2,2,2-trifluoroethanol. At 80 °C, 3 was found to be approximately 10^{11}-fold retarded in rate as compared to what would be predicted for the compound in the absence of destabilizing antiaromatic interactions in its activated complex for ionization.



3 4 5

We have now turned our attention toward obtaining evidence under solvolytic conditions of the structure of the inden-1-yl cation intermediate. For example, by analogy to similar questions which have been raised concerning the structure of the cyclopentadienyl cation 2,[4] is the inden-1-yl cation a completely delocalized ground-state triplet as in 6, a partially delocalized ground-state singlet as in 7, or possibly even a square-pyramidal species such as 8? For the case of the parent unsubstituted cyclopentadienyl cation 2 generated by treatment of 5-bromocyclopentadiene with SbF_5 at 78 K, EPR studies have shown[5] that it is a planar, regular pentagonal triplet in its ground state. The pentaphenylcyclopentadienyl cation, on the other hand, is a ground-state singlet.[6]



6 7 8

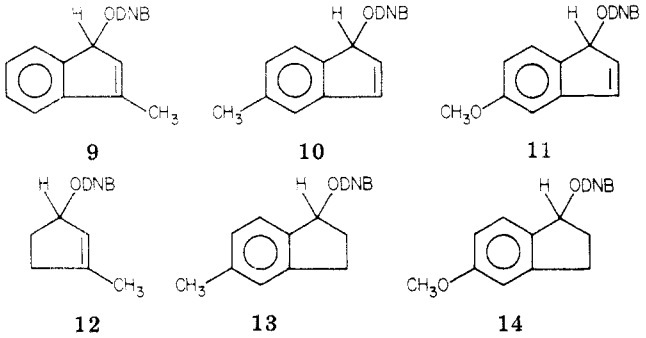
To obtain information as to the structure of the inden-1-yl cation we examined the effects upon its ease of formation of adding electron-releasing substituents on both the double bond and benzene ring sides of the molecule. It was anticipated that this should reveal the extent of charge delocalization at various positions in the activated complex leading to the inden-1-yl cation intermediate. For example, if the substituent causes a much smaller or no accelerating effect when compared to that observed in a suitable delocalized model system, then it can be concluded that diminished or no delocalization of charge at that carbon is occurring. The results of this study are described below.

Results and Discussion

For the study of the delocalization in the inden-1-yl cation system, it was necessary to prepare compounds 9, 10, and 11 for use in kinetic substituent effect comparisons with 3. Also, compounds 12, 13, and 14 were prepared as model systems whose kinetic behaviors were to be compared with 4 and 5 to assess the magnitudes of the substituent effects to be expected when normal charge delocalization is taking place.

(1) Friedrich, E. C.; Taggart, D. B. *J. Org. Chem.* **1978**, *43*, 805.
(2) Breslow, R. *Acc. Chem. Res.* **1973**, *6*, 393.
(3) Breslow, R.; Hoffman, J. M., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 2110.
(4) (a) Breslow, R.; Mazur, S. *J. Am. Chem. Soc.* **1973**, *95*, 584. (b) Kollmar, H.; Smith, H. O.; Schleyer, P. v. R. *Ibid.* **1973**, *95*, 5834. (c) Dewar, M. J. S.; Haddun, R. C. *Ibid.* **1973**, *95*, 5836. (d) Hehre, W. J.; Schleyer, P. v. R. *Ibid.* **1973**, *95*, 5837. (e) Bauld, N. L.; Welsher, T. L.; Cessac, J.; Holloway, R. L. *Ibid.* **1978**, *100*, 6920. (f) Borden, W. T.; Davidson, E. R. *Ibid.* **1979**, *101*, 3771. (g) Olah, G. A.; Prakash, G. R. S.; Liang, G.; Westerman, P. W.; Kunde, K.; Chandrasekhar, J.; Schleyer, P. v. R. *Ibid.* **1980**, *102*, 4485.
(5) Saunders, M.; Berger, R.; Jaffe, A.; McBride, J. M.; O'Neill, J.; Breslow, R.; Hoffman, J. M., Jr.; Perchonock, C.; Wasserman, E.; Hutton, R. S.; Kuck, V. J. *J. Am. Chem. Soc.* **1973**, *95*, 3017.
(6) Breslow, R.; Chang, H. W.; Hill, R.; Wasserman, E. *J. Am. Chem. Soc.* **1967**, *89*, 1112.

0022-3263/82/1947-0315$01.25/0

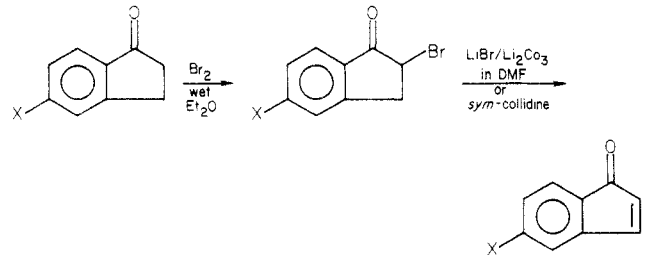


9 10 11

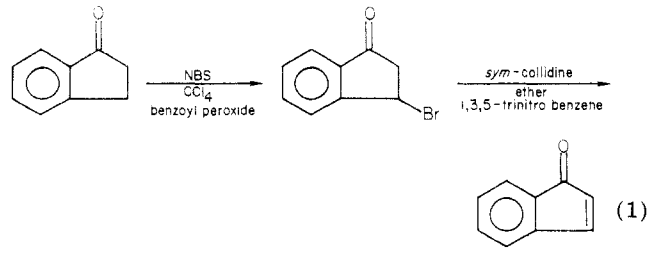
12 13 14

Preparations of compounds **9** and **12** were straightforward as their alcohol precursors had previously been synthesized in our laboratory as part of other studies.[7] The ketone precursor of **13** was readily prepared by literature procedures,[8] and the ketone precursor of **14** was commercially available. However, syntheses of the 5-methyl- and 5-methoxyinden-1-yl systems **10** and **11** presented considerable difficulties.

Our initial approaches to the inden-1-one precursors of **10** and **11** involved attempts at preparation and dehydrobromination of the corresponding 2-bromoindan-1-ones. The preparations[9] of the 2-bromoindan-1-ones as mixtures consisting of the desired 2-bromo ketone together with considerable 2,2-dibromo ketone and unreacted starting material were successful. However, dehydrobromination of the 2-bromo ketone containing mixture with lithium bromide and lithium carbonate in dimethylformamide[10] or with *sym*-collidine either gave no reaction under mild conditions or polymeric products under more vigorous conditions.

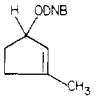
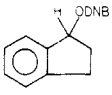
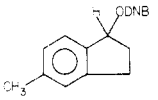
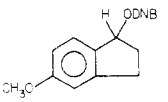
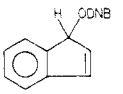
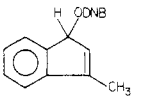
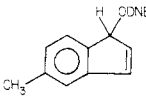
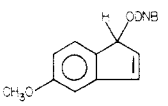


Owing to the problems encountered in preparation and dehydrobromination of the 2-bromoindanones, it was then decided to investigate the 3-bromoindanone route developed by Marvel and Hinman[10] for the synthesis of inden-1-one shown in eq 1. With this method, the 5-methyl- and 5-methoxyinden-1-ones were obtained. These were reduced to the corresponding inden-1-ols which were converted into their 3,5-dinitrobenzoates **10** and **11** without any difficulties.



(1)

Table I. Rates of Hydrolysis of Some 3,5-Dinitrobenzoates in 80% Aqueous Acetone at Various Temperatures

compd	temp, °C (±0.05 °C)	$10^5 k_1$, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
	80.0	116 ± 5[a]		
	60.0	13.7 ± 0.7[a]	21.9	−11.1
	39.5	1.25 ± 0.08		
	21.2	(0.132)		
	21.2	150 ± 10[b]		
	80.0	(91 000)[c]		
	100.0	30.6 ± 0.4[a]		
	80.0	4.53 ± 0.4[a]	25.5	−7.2
	60.0	0.429 ± 0.018		
	21.2	(2.36 × 10^{-5})		
	80.0	(99.8)		
	60.1	113 ± 0.5	24.9	−2.1
	39.5	0.889 ± 0.042		
	21.2	(0.0692)		
	80.0	(35 000)[d]		
	21.2	39.0 ± 2.3		
	100.0	<0.01[a]		
	80.0	(10^{-5})		
	125	0.59 ± 0.07		
	101.2	0.0806 ± 0.0047	23.9	−23.5
	80.0	(0.0112)		
	21.2	(1.01 × 10^{-5})		
	125	0.51 ± 0.07		
	101.2	0.0461 ± 0.0059	28.7	−11.2
	80.0	(0.004 28)		
	21.2	(9.94 × 10^{-7})		
	125	(12.8)		
	100.1	1.08 ± 0.13	28.5	−5.3
	80.3	0.119 ± 0.025		
	21.0	(2.82 × 10^{-5})		

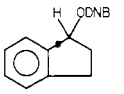
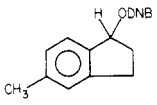
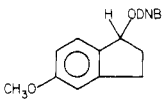
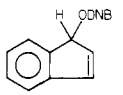
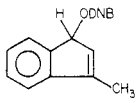
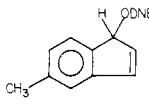
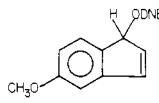
[a] Data of E. C. Friedrich and D. B. Taggart (*J. Org. Chem.* **1978**, *43*, 805). [b] Based on five one-point runs calculated using two experimental infinities from separate runs. [c] Estimated using a $\Delta H^{\ddagger}$ value of 21.9 kcal mol^{-1}. [d] Estimated using a $\Delta H^{\ddagger}$ value of 23 kcal mol^{-1}.

Having prepared the necessary 3,5-dinitrobenzoate ester starting materials for the kinetic substituent effect studies, we next examined their rates of hydrolysis in 80% aqueous acetone. All of the esters exhibited good first-order kinetic behaviors and gave nearly theoretical production of acid after 10 half-lives for reaction. The kinetic data are summarized in Table I together with some data for comparison from our earlier study.[1]

Since, when dealing with systems having low reactivities in aqueous acetone problems due to bimolecular nucleophilic displacements by water or to slow production of acid

(7) (a) Friedrich, E. C.; Taggart, D. B.; Saleh, M. A. *J. Org. Chem.* **1977**, *42*, 1437. (b) Friedrich, E. C.; Saleh, M. A. *J. Am. Chem. Soc.* **1973**, *95*, 2617.
(8) Mayer, F.; Muller, P. *Chem. Ber.* **1927**, *60*, 2278.
(9) House, H. O.; McDaniel, W. C. *J. Org. Chem.* **1977**, *42*, 2155.
(10) Marvel, C. S.; Hinman, C. W. *J. Am. Chem. Soc.* **1954**, *76*, 5435.

Table II. Solvolysis Rates of Some 3,5-Dinitrobenzoates in 2,2,2-Trifluoroethanol at Various Temperatures

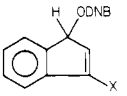
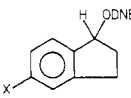
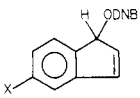
compd	temp, °C (±0.05 °C)	$10^5 k_1$, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
	80.0	(1440)		
	39.5	21.9 ± 0.9	22.0	−5.0
	21.0	2.10 ± 43		
	80.0	(343)[a]		
	60.0	49.6 ± 1.1[a]		
	39.9	5.59 ± 0.28[a]	21.9[a]	−8.4[a]
	21.0	(0.550)		
	21.1	52.1 ± 3.9[b]		
	21.2	8700 ± 1700[c]		
	125.0	0.110 ± 0.005[a]		
	100.0	0.0104 ± 0.0003[a]	27.1	−14.1
	80.0	(0.001 24)[a]		
	21.0	(4.44 × 10^{-7})		
	99.9	6.67 ± 0.43	25.3	−10.5
	80.1	0.811 ± 0.0293		
	21.0	(4.78 × 10^{-4})		
	101.1	0.211 ± 0.056	23.4	−22.3
	80.3	0.0313 ± 0.0023		
	21.0	(3.11 × 10^{-5})		
	99.9	160 ± 14[c]	25.7	−2.8
	80.2	21.8[d]		
	21.0	(0.0113)		

[a] Data of E. C. Friedrich and D. B. Taggart (*J. Org. Chem.* 1978, *43*, 805). [b] Based on two one-point runs calculated using two experimental infinities determined in separate runs. [c] Based on three one-point half-life runs calculated using the theoretical infinities. Experimental infinities determined in separate runs were close to theoretical. [d] Determined from the slope of the best line drawn visually through the points.

by oxidation of the acetone may exist, the rates of solvolysis of a number of the systems were also investigated for comparison in 2,2,2-trifluoroethanol where neither of these problems should exist. The results of the kinetic studies in 2,2,2-trifluoroethanol are summarized in Table II. All of the compounds which had convenient rates for accurate measurements exhibited good first-order kinetic behaviors and gave experimental infinities which were close to theoretical.

Before commenting on the conclusions which may be drawn from the kinetic studies in 80% aqueous acetone and in 2,2,2-trifluoroethanol, we need to mention the results of several other related studies. The products of hydrolysis of both the 3-methyl- and 5-methoxyinden-1-yl 3,5-dinitrobenzoates in 80% aqueous acetone at 100 °C were the alcohols corresponding to the starting 3,5-dinitrobenzoates and their allylic rearrangement isomers. Thus, it is clear that both compounds must be solvolyzing via an S_N1 ionization process, and that at least some allylic delocalization through the double bond is occurring. NMR examination of a sample of 1-deuterioinden-1-yl 3,5-dinitrobenzoate which had been heated in 2,2,2-trifluoroethanol at 125 °C for a period sufficient for 30% acid production and then reisolated showed that less than 5% of 3-deuterioinden-1-yl 3,5-dinitrobenzoate had been formed. This indicated that the relative rates which were determined are not complicated by differential ion-pair return via a delocalized or equilibrating allylic cation intermediate. The details of both of these studies are given in the Experimental Section.

Table III. Rate Accelerations Produced by Substituents in Various 3,5-Dinitrobenzoates in 80% Aqueous Acetone and in 2,2,2-Trifluoroethanol

system	rate ratio	80% aq acetone 21 °C	80% aq acetone 80 °C	trifluoroethanol 21 °C	trifluoroethanol 80 °C
	k_{CH_3}/k_H	1100	780		
	k_{CH_3}/k_H		1100	1100	650
	k_{CH_3}/k_H	29	22	92	
	k_{CH_3O}/k_H	16600	7700	16000	
	k_{CH_3}/k_H		400	70	25
	k_{CH_3O}/k_H		12000	25000	17600

The rate acceleration produced by the substituents in solvolyses in both 80% aqueous acetone and in 2,2,2-trifluoroethanol for the 3,5-dinitrobenzoates studied are summarized in Table III. It is seen that the rate ratios observed for the various systems are of the same order of magnitude in both 80% aqueous acetone and in 2,2,2-trifluoroethanol. This provides evidence that the rates measured are those for unimolecular ionization in both solvents, and that any contributions from bimolecular nucleophilic displacements by solvent in 80% aqueous acetone must be very small, if present at all. Also, the results obtained indicate that both in 80% aqueous acetone and in 2,2,2-trifluoroethanol the magnitudes of the rate accelerations produced by the substituents in the model cyclopenten-1-yl and indan-1-yl systems are approximately the same as those observed in the antiaromatic inden-1-yl system even though the actual rate differences between the model and inden-1-yl systems are 10^6 to 10^8. Thus, delocalization of charge into both the benzene ring and double bond of the inden-1-yl cation as in **6** must be taking place even though antiaromatic destabilization is present. However, the observation that the magnitudes of the substituent effects were so very similar for both the model

and inden-1-yl systems was unexpected.

The Hammett $\rho\sigma$ treatment[11] provides a way to quantitatively describe the magnitudes of substituent effects in reacting systems. Thus, it was found for both the unsubstituted and 5-methyl- and 5-methoxy-substituted indan-1-yl and inden-1-yl systems that plots of log k vs. σ^+ values gave good straight line fits. The ρ values obtained for the substituted indan-1-yl 3,5-dinitrobenzoates in 80% aqueous acetone and in 2,2,2-trifluoroethanol at 21 °C were −5.3 and −5.5, respectively. For the substituted inden-1-yl 3,5-dinitrobenzoates, ρ is −6.0 in 80% aqueous acetone at 80 °C and is −5.4 at 80 °C and −5.6 at 21 °C in 2,2,2-trifluoroethanol. Thus, in both solvent systems, both the indan-1-yl and inden-1-yl systems are experiencing similar high electron deficiencies at the reaction sites in their rate-determining steps.

In conclusion, the results of the present study indicate that similar electronic effects are operating in the reactions of both the indan-1-yl or 2-cyclopenten-1-yl and inden-1-yl systems. Delocalization into the benzene ring and double bond in the inden-1-yl cation system appears to be undiminished by antiaromatic effects.[12] It is suggested, as a consequence of the present study, that rate-accelerating substituent effects may be used for increasing the reactivity of cyclopentadienyl cation precursors into an experimentally convenient range for studies under normal solvolytic conditions. Work resulting from this suggestion is in progress.

Experimental Section

General Procedures. Melting and boiling points are uncorrected. Infrared spectra were run on a Perkin-Elmer Model 237B instrument. NMR spectra were run on Varian Associates A-60A or EM 360 instruments, and chemical shifts are reported in parts per million (δ) downfield from a Me_4Si internal standard. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

3-Methylcyclopent-2-en-1-yl 3,5-Dinitrobenzoate. This was prepared by reaction of 3-methylcyclopent-2-en-1-ol[7b] with 3,5-dinitrobenzoyl chloride in pyridine at 0 °C. Recrystallization of the crude product from a 5:2 mixture of mixed hexanes and chloroform gave a 31% yield of the dinitrobenzoate as white crystals, mp 135 °C dec. The crystals dissolved readily in deuterated chloroform to give a clear solution which, however, after about 15 min began to deposit 3,5-dinitrobenzoic acid: NMR ($CDCl_3$) δ 1.6 (3 H, s, CH_3), 2.0 (4 H, m, CH_2), 5.3 (1 H, m, CH=C), 5.7 (1 H, m, CHODNB), 9.0 (3 H, s, aromatic).

Anal. Calcd for $C_{13}H_{12}O_6N_2$: C, 53.42; H, 4.11. Found: C, 53.03; H, 3.99.

5-Methylindan-1-yl 3,5-Dinitrobenzoate. A 2.5-g (0.017 mol) sample of 5-methylindan-1-one, prepared following the method of Mayer and Muller[8] except using 1,2-dichloroethane instead of carbon disulfide as the Friedel–Crafts acylation solvent, was reduced with 0.34 g (0.0086 mol) of lithium aluminum hydride in ether to give 1.6 g (63% yield) of 5-methylindan-1-ol as a white solid, mp 68–71 °C. Reaction of the alcohol with 2.5 g (0.011 mol) of 3,5-dinitrobenzoyl chloride in pyridine at −15 °C followed by workup and recrystallization from a 2:1 mixture of mixed hexanes and toluene gave 1.7 g (49% yield) of the dinitrobenzoate as a white solid: mp 122–124 °C; NMR ($CDCl_3$) δ 2.4 (3 H, s, CH_3), 2.5 (2 H, m, CH_2CHODNB), 3.0 (2 H, m, aromatic CH_2), 6.7 (1 H, s, CHODNB), 7.2 (3 H, m, aromatic), and 9.0 (3 H, m, aromatic).

Anal. Calcd for $C_{17}H_{14}N_2O_6$: C, 59.65; H, 4.12. Found: C, 59.78; H, 4.25.

5-Methoxyindan-1-yl 3,5-Dinitrobenzoate. A 2.1-g (0.013 mol) sample of 5-methoxyindan-1-one (Aldrich) was reduced with 0.3 g (0.008 mol) of lithium aluminum hydride in ether. The light yellow liquid remaining after workup and removal of the ether was reacted with 3.0 g (0.013 mol) of 3,5-dinitrobenzoyl chloride in pyridine at −15 °C. Recrystallization of the yellow solid obtained after workup from a 2:1 mixture of mixed hexanes and toluene gave 2.6 g (56% yield) of a yellow powder: mp 109 °C dec; NMR ($CDCl_3$) δ 2.5 (2 H, m, CH_2CHODNB), 3.0 (2 H, m, aromatic CH_2), 3.9 (3 H, s, OCH_3), 6.7 (1 H, m, CHODNB), 6.9–7.5 (3 H, m, aromatic), 9.1 (3 H, s, aromatic).

Anal. Calcd for $C_{17}H_{14}N_2O_7$: C, 56.99; H, 3.94. Found: C, 57.18; H, 4.12.

3-Methylinden-1-yl 3,5-Dinitrobenzoate. This was prepared by reaction of 3-methylinden-1-ol[7a] with 3,5-dinitrobenzoyl chloride in pyridine at −25 °C. Recrystallization of the crude product from a 2:1 mixture of chloroform and mixed hexanes gave a 51% yield of the dinitrobenzoate as yellow needles: mp 181–182 °C; NMR ($CDCl_3$) δ 2.2 (3 H, s, CH_3), 6.1 (1 H, m, CHODNB), 6.4 (1 H, m, CH=C), 7.2 (3 H, m, aromatic), 9.1 (3 H, s, aromatic).

Anal. Calcd for $C_{17}H_{12}N_2O_6$: C, 60.00; H, 3.55. Found: C, 60.26; H, 3.75.

5-Methylinden-1-yl 3,5-Dinitrobenzoate. To 12 g (0.082 mol) of 5-methylindan-1-one dissolved in 90 mL of CCl_4 was added 0.05 g of benzoyl peroxide and one-third of 15 g (0.082 mol) of *N*-bromosuccinimide. A 275-W sunlamp was shined onto the solution which was heated to reflux. The remaining *N*-bromosuccinimide was added in equal parts after 20 and 40 min, and the mixture was refluxed for 2 h. The succinimide formed was removed by filtration and the filtrate washed with water, dried, and concentrated uner reduced pressure to give a brown-red liquid containing about 25% of 3-bromo-5-methylindanone: NMR (CCl_4) δ 2.5 (3 H, s, CH_3), 3.2 (2 H, m, CH_2C=O), 5.7 (1 H, m, CHBr), 7.5 (3 H, m, aromatic).

The mixture prepared above was dissolved in 100 mL of anhydrous ether, a few crystals of 1,3,5-trinitrobenzene and 120 mL of *sym*-collidine were added, and the resulting solution was stirred for 1.5 h at room temperature and refluxed for 3 h at 50 °C. The collidine hydrobromide was removed by filtration and the filtrate was cooled in an ice bath and acidified to congo red paper, using a cold 1:1 mixture of concentrated HCl and water. The ether solution was separated, washed with water and saturated aqueous Na_2CO_3, and dried over $MgSO_4$, and the ether was removed by distillation to give a brown liquid containing about 22% 5-methylinden-1-one: NMR (CCl_4) δ 2.5 (3 H, s, CH_3), 5.9 (1 H, d, J = 6 Hz, CHC=O), 7.1 (4 H, m, =CH–aromatic H).

The 5-methylinden-1-one containing mixture prepared as described above was reduced, using 1.3 g (0.033 mol) of $LiAlH_4$ in ether at 0 °C for 15 min. Workup by addition of saturated NH_4Cl solution followed by drying of the ether solution and removal of the ether by distillation gave a brown liquid containing about 30% of 5-methylinden-1-ol: NMR (CCl_4) δ 2.2 (3 H, s, CH_3), 3.5 (1 H, s, OH), 4.8 (1 H, m, CHOH), 6.4 (1 H, d of d, J = 6, 2 Hz, =CHCHOH), 6.7 (1 H, d, J = 6 Hz, aromatic =CH), 7.0 (3 H, m, aromatic).

Reaction of the alcohol-containing mixture produced above with 5.5 g (0.023 mol) of 3,5-dinitrobenzoyl chloride in pyridine at −15 °C for 2 h followed by workup and recrystallization from a 3:1 mixture of petroleum ether and chloroform gave 3.6 g (13% yield overall from 5-methylindan-1-one) of a yellow powder found to be a mixture of both the 5-methylinden-1-yl and 5-methylindan-1-yl 3,5-dinitrobenzoate. After several additional recrystallizations from a 2:1 mixture of *n*-pentane and toluene and considerable loss in yield the material, mp 147–150 °C, still contained about 20% of the 5-methylindan-1-yl 3,5-dinitrobenzoate. However, as this should not interfere in kinetic studies, further attempts at purification were not done. NMR ($CDCl_3$) δ 2.3 (3 H, s, CH_3), 6.5 (2 H, m, =CHCHODNB), 7.0 (1 H, d of d, J = 6, 2 Hz, aromatic =CH), 7.2 (3 H, m, aromatic), 9.1 (3 H, s, aromatic).

Anal. Calcd for $C_{17}H_{12}N_2O_6$: C, 60.00; H, 3.55. Found: C, 59.55; H, 3.48.

5-Methoxyinden-1-yl 3,5-Dinitrobenzoate. Following a procedure similar to that described above for preparing the analogous 5-methyl compound, 5.8 g (0.036 mol) of 5-methoxyindan-1-one (Aldrich) was reacted with 6.4 g (0.036 mol) of *N*-bromosuccinimide and 0.10 g of benzoyl peroxide in 110 mL of CCl_4 under UV irradiation at reflux for 2 h. The reddish liquid product attained after workup contained about 50% of the desired 3-bromo-5-methoxyindan-1-one: NMR (CCl_4) δ 3.1 (2 H, m,

(11) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1957**, *79*, 1913.
(12) Whitman, D. W.; Carpenter, B. K. *J. Am. Chem. Soc.* **1980**, *102*, 4272.

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.

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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