Mobile Keto Allyl Systems. 18.[1] Synthesis and Charge-Transfer Interactions of 2-(α-Aminobenzyl)-1-indenones[2]

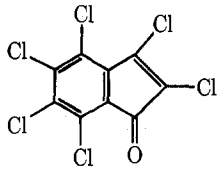
Robert J. Murray and Norman H. Cromwell*

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588

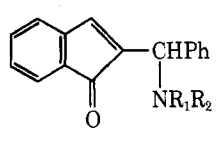
Received May 27, 1975

Several 2-(α-aminobenzyl)-1-indenones variously substituted in the indenone nucleus and on nitrogen were prepared and their absorption spectra recorded. In the trisubstituted amino compounds **12a–c** a discrete band was observed in the visible spectrum energetically well below the low-energy indenone absorption bands found in a concurrent study to occur at ca. 390 nm. The position of this long-wavelength band was dramatically affected by the nature of the substituent in the indenone ring system but was relatively insensitive to changes in solvent polarity. Furthermore, the band was discharged in acid media and was shown to obey Beer's law. An intramolecular CT interaction, of as yet unknown origin, is suggested as being causative of this band.

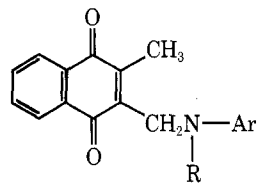
Although molecular complexation between indenones such as **1** and amines have been known since befoe the turn of the century,[3] *intra*molecular charge-transfer (CT) interaction in the indenone system has not been previously reported. The observance of an unusually low-energy band in the 2-(α-aminobenzyl)-1-indenone system **2** previously prepared in our laboratory (λ_{max} 412 nm, $R_1 = R_2 = i\text{-}C_3H_7$)[4] as well as the similarity in structure of **2** to the 2-methyl-3-



1



2



3

aminomethyl-1,4-naphthoquinones **3**, which exhibit intramolecular CT phenomena,[5] has prompted our synthesis of a number of substituted 2-(α-aminobenzyl)-1-indenones and a detailed examination of their electronic spectra in order to determine the possibility of a CT interaction. The results of that study are presented herein.

Results and Discussion

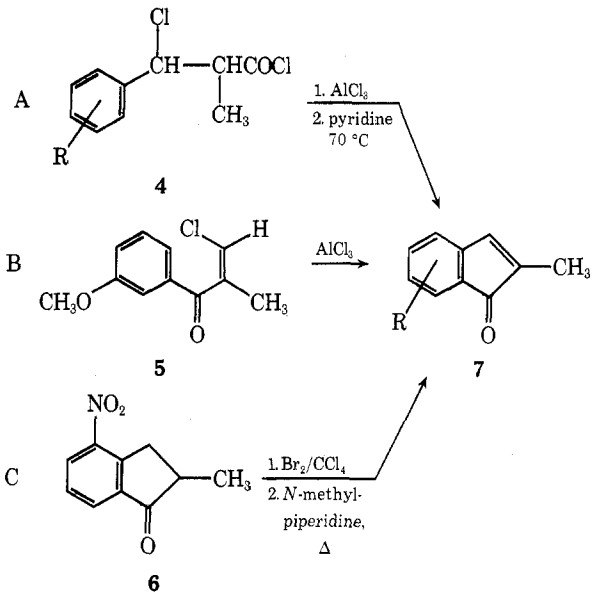
Before undertaking the preparation of analogues of **2** it was deemed important for us first to determine whether the low-energy transition present in the spectrum of **2** could be attributable to any of the separate chromophores present in the 2-(α-aminobenzyl)-1-indenone system.

Although no data were readily available on the electronic spectra of N-alkylated benzylamines as in **2**, it was assumed that their uv–visible spectra would be similar to that of benzylamine itself, which shows no absorption above 265 nm,[6] and thus the contribution of the benzylamine chromophore to the long-wavelength band in question would be negligible.

The contribution of the indenone chromophore, however, was not as easy to neglect. Varied reports are present in the literature regarding the electronic spectra of indenones; some researchers report a band at ca. 330 nm[7] as the longest wavelength band present, while others report a band at ca. 390 nm.[8] In order to clear up this apparent contradiction and, at the same time, to provide spectral data which would be of value in the analogue study envisioned, the synthesis and visible spectral analyses of several 2-methylindenones were undertaken prior to the analogue preparation.

Synthesis and Visible Spectra of Substituted 2-Methylindenones. The 2-methylindenones prepared for this study were synthesized by application or extension of published procedures (Scheme I). Thus 2-methylindenone (**7a**),

Scheme I

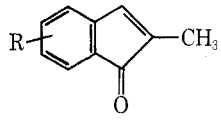


2,4-dimethylindenone (**7b**), and 2,6-dimethylindenone (**7c**) were obtained by cyclization of the appropriate α-methyl-β-aryl-β-chloropropionyl chlorides (**4**)[7c] (Scheme I, pathway A); 2-methyl-6-methoxyindenone (**7d**) was prepared by ring closure of 1-chloro-2-*m*-anisoyl-1-propene (**5**)[9] (pathway B); and finally, 2-methyl-4-nitroindenone (**7e**) was prepared by the bromination–dehydrobromination of 2-methyl-4-nitroindanone (**6**) (pathway C).

The visible spectra of all of the 2-methylindenones showed a band at 330 nm *as well as* a band at ca. 390 nm. The exact position of the longest wavelength band, as can be seen from examination of Table I, depends on the substitution present on the six-membered ring. Substitution by an electron-releasing group such as methyl or methoxyl causes abathochromic shift relative to the parent compound **7a**, whereas substitution by an electron-withdrawing group (**7e**) causes a rather dramatic hypsochromic shift. The substitution of a methyl group, **7c**, by a more electron-releasing methoxyl group, **7d**, causes an additional bathochromic shift.

It can also be seen from examination of Table I that the position of the 390-nm band is very sensitive to solvent po-

Table I. Position of the Long-Wavelength Band in 2-Methylindenones

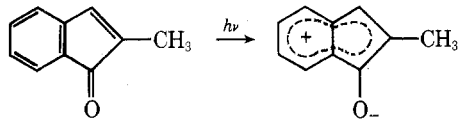


Registry no.	Compd	R	*n*-Hexane λ_{max}, nm (ϵ)	$CHCl_3$ λ_{max}, nm (ϵ)	MeOH λ_{max}, nm (ϵ)
5728-95-0	**7a**	H	392 (550)	400 (430)	400 (415)
60030-93-5	**7b**	4-CH_3	395 (760)	410 (653)	412 (640)
60030-94-6	**7c**	6-CH_3	405 (560)	419 (390)	420 (390)
52102-75-7	**7d**	6-OCH_3	435 (660)		
60030-95-7	**7e**	4-NO_2	357 (1690)	350 (2590)	345 (1750)

Table II. Position of the Long-Wavelength Band in 2-(α-Aminobenzyl)-1-indenones

Registry no.	Compd	*n*-Hexane λ_{max}, nm (ϵ)	$CHCl_3$ λ_{max}, nm (ϵ)	CH_3CN λ_{max}, nm (ϵ)
5387-51-9	**11a**	389 (1000)	390 (400)	
60030-96-8	**11b**	388 (5800)		388 (2800)
60030-97-9	**11c**	385 (5500)	395 (2300)	397 (1950)
60030-98-0	**11d**	393 (1100)		
60030-99-1	**11e**	405 (1700)	405 (850)	405 (500)
60031-00-7	**11f**	405 (2000)	405 (1100)	
60031-01-8	**11g**	395 (2500)		
60031-02-9	**11h**	420 (1050)	425 (850)	
53059-34-0	**12a**	430 (1200)	430 (750)	420 (780)
		407 (s) (1100)	390 (675)	390 (700)
		390 (800)		
60031-03-0	**12b**	455 (1050)	460 (940)	450 (950)
		425 (1330)	425 (s) (1180)	403 (1390)
		405 (1370)		
60031-04-1	**12c**	475 (1035)	470 (910)	470 (890)
		440 (s) (1250)	390 (2100)	387 (2200)
		415 (s) (1700)		
		392 (1845)		
60031-05-2	**12a** HCl			388
60031-06-3	**12b** HCl			395
60031-07-4	**12c** HCl			390

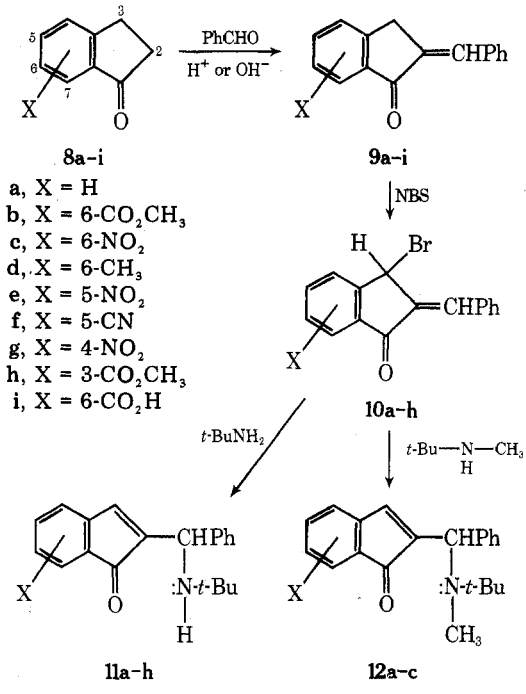
larity. The fact that the long-wavelength band experiences a bathochromic shift upon changing to a polar solvent indicates that the transition responsible for the absorption at 390 nm probably involves a polar excited state such as that pictured below. Therefore, any group capable of supporting the



positive charge would lead to lengthened conjugation and a resultant red shift, whereas substitution by an electron-withdrawing group might be expected to show a slight blue shift.

Synthesis and Visible Spectra of Substituted 2-(α-Aminobenzyl)-1-indenones. The syntheses of the new substituted 2-(α-aminobenzyl)-1-indenones were carried out by a method analogous to one reported in the literature for **2**[4] (Scheme II). Thus, condensation of the appropriately substituted indanone **8**, prepared by existing literature procedures, with benzaldehyde in the presence of acid or base gave the 2-benzal-1-indanone derivative **9** in good yield. Free-radical bromination of **9** with *N*-bromosuccinimide in CCl_4 or $CHCl_3$ produced the 3-bromo-2-benzal-1-indanone derivatives **10**. In some cases the bromo ketones **10** could not be separated from the succinimide coproduct and were used impure in the next reaction. Treatment of **10** with *tert*-butylamine and *N*-methyl-*tert*-butylamine at room temperature in benzene solution afforded the corresponding 2-(α-*tert*-butylaminobenzyl)-1-indenones (**11**) and 2-(α-*N*-methyl-*tert*-butylaminobenzyl)-1-indenones (**12**) in yields of 23–80%.

Scheme II



The proof of structure for compounds **11** and **12** was based on the NMR and ir spectral data of freshly recrystallized samples. In no case was there evidence of the formation of the isomeric 3-amino-2-benzal-1-indanones.

All of the 2-(α-aminobenzyl)-1-indenones prepared in this

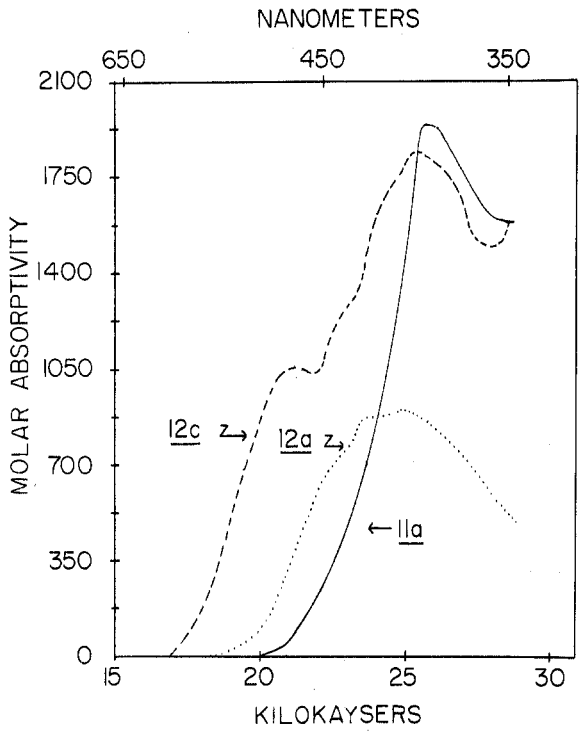


Figure 1. The visible spectra of selected 2-(α-aminobenzyl)-1-indenones in *n*-hexane.

study possess a band at ca. 390 nm as well as the typical indenone absorption bands at lower wavelength with the exact position of the lowest energy band being dependent upon the substitution present in the indenone ring system and on nitrogen (Table II).

The position of the long-wavelength band in the N-disubstituted compounds (**11b–h**) was found to vary in an unpredictable manner from that in the parent compound **11a.** While substitution in the 6 position of the indenone nucleus by electron-withdrawing groups such as carbomethoxy (**11b**) or nitro (**11c**) caused a slight hypsochromic shift relative to **11a,** substitution in the 3, 4, or 5 position by the same or other electron-withdrawing groups caused a bathochromic shift of from 6 (**11g**) to 31 nm (**11h**). Furthermore, substitution by an electron-releasing group such as methyl (**11d**) also resulted in a slight bathochromic shift. The extinction coefficients of these bands were on the order of $1–2 \times 10^3$, with notable exceptions being those for compounds **11b** and **11c,** where the values were 5×10^3 and 5.5×10^3, respectively.

This apparent lack of correlation between the position of the long-wavelength band and the substitution present in the indenone ring system in compounds **11** and thus lack of conformance to CT theory as described by Mulliken[10] is believed to be the result of (1) overlap of the CT band with the low-energy indenone absorption band present at ca. 390 nm and (2) in those compounds which displayed a short λ_{max} and correspondingly large ϵ_{max}, compounds **11b** and **11c,** overlap of the low-energy band(s) with the high-intensity (ϵ 7×10^3 and 1.1×10^4, respectively, see the Experimental Section) band present at 330 nm in those compounds. In short, it is believed that the CT band, if present, is being masked by one or more bands in the visible spectrum, not an uncommon occurrence.[11]

Unfortunately, substantive proof of these claims and thus the determination of the CT bands in compounds **11** by the usual deconvolution techniques or by the calculation of difference spectra where applicable could not be obtained; in no case was a satisfactory band resolution observed.

In lieu of pursuing the search for CT bands in the N-disubstituted amino compounds further, it was thought that it would be much more informative to alter the aminobenzyl side chain via additional substitution on nitrogen in order to "split out" the presumed CT band.

With such additional substitution on nitrogen, compounds **12a–c,** a new absorption band was, indeed, observed in the visible spectrum, energetically well below the indenone low-energy band still present at ca. 390 nm. Furthermore, the energy of this long-wavelength band in **12a–c** was found to vary inversely with the increasing electron-withdrawing power of the substituent in the indenone nucleus (see Figure 1). Such spectral differences are to be expected upon increasing the electron affinity of the acceptor in CT complexes.[10]

The effect of the solvent on the λ_{max} of this band was slight, in keeping with a CT complex involving a neutral ground state.[12] The typical increase in the vibrational fine structure of these bands in nonpolar solvents was noted. The effect on molar absorptivity was quite pronounced, however, and may be due to conformation changes about the aminobenzyl side chain caused by complexing of the nitrogen with the more polar solvents.

Upon further substitution on the nitrogen, via complexing with HCl, the long-wavelength band present in compounds **12** disappeared completely and only the typical indenone absorption bands at higher energy remained. Based upon the above data, coupled with the finding that solutions of compounds **12** obeyed Beer's law over the concentration range $10^{-3}–10^{-5}$, an intramolecular CT interaction seems likely, at least, in compounds **12.** Although several interactions have been considered as being responsible for the CT band observed, including a $\pi \rightarrow \pi^*$ HOMO–LUMO type interaction involving the indenone π system as acceptor and the phenyl ring of the aminobenzyl side chain as donor, as well as an $n \rightarrow \pi^*$ HOMO–LUMO type interaction involving the indenone π system as acceptor and the nitrogen lone pair as donor, to choose one would be presumptuous at this time.

A crystallographic study of these and related compounds is currently underway in order to help resolve this question and will be the subject of a future communication from this laboratory.

Experimental Section[13]

Preparation of Substituted 1-Indanones. Those indanones which have been synthesized by literature methods may be found in Table III. Those reported for the first time are described below.

A. 2-Methyl-4-nitro-1-indanone (6). To 20.0 g (0.096 mol) of α-methyl-*o*-nitrophenylpropionic acid (see Miscellaneous below) was added 12.4 g (7.5 ml, 0.104 mol) of thionyl chloride. After the initial vigorous reaction had subsided, the clear solution was heated on a steam bath for 2 h. Subsequent removal of the excess thionyl chloride at the water pump gave the acid chloride as a light yellow oil.

The crude acid chloride was dissolved in 100 ml of carbon disulfide and 14.0 g (0.105 mol) of aluminum chloride was added in portions over a 30-min period. The yellow solution was then stirred at reflux for 3 h. The carbon disulfide was removed by distillation. The resulting bronze syrup was poured slowly onto 20 ml of concentrated sulfuric acid and 200 g of ice. Benzene (500 ml) was added and the organic layer was separated, washed with 10% sulfuric acid solution (250 ml), water (250 ml), 5% sodium bicarbonate solution (2×200 ml), and water (2×200 ml), and then dried over magnesium sulfate. Evaporation of the solvent at reduced pressure, dissolution of the resulting yellow oil in an ether–petroleum ether mixture, and subsequent cooling provided 12.8 g (70.0%) of **6** as a cream-colored, crystalline solid: mp 74–75 °C; ir (CCl_4) 1730 cm^{-1} (C=O); NMR ($CDCl_3$)[14] δ 8.43 (dd, J = 1.5, 8 Hz, 1 H, C_7 proton), 8.08 (dd, J = 1.5, 8 Hz, 1 H, C_5 proton), 7.63 (m, 1 H, C_6 proton), 4.08 (dd, J = 8, 19 Hz, 1 H, C_3 proton cis to C_2 proton), 3.22 (dd, J = 4, 19 Hz, 1 H, C_3 proton trans to C_2 proton), 2.91–2.57 (m, 1 H, C_2 proton), 1.32 (d, J = 7 Hz, 3 H, $-CH_3$).

Anal. Calcd for $C_{10}H_9NO_3$: C, 62.82; H, 4.74; N, 7.33. Found: C, 62.76; H, 4.71; N, 7.29.

B. 2-Bromo-2-methyl-4-nitro-1-indanone. To 1.0 g (0.0052 mol) of **6** dissolved in 10 ml of carbon tetrachloride was added dropwise 0.84

Table III. Synthesis of 1-Indanones

Compd	Yield, %	Mp, °C
6-Nitro-1-indanone (8c)	35	72–73 (lit.[a] 72)
6-Methyl-1-indanone (8d)	95	60–62 (lit.[b] 62–63)
5-Nitro-1-indanone (8e)	7	131–133 (lit.[c] 128–130)
5-Cyano-1-indanone (8f)	31	131–132 (lit.[d] 131–132)
4-Nitro-1-indanone (8g)	52	100–102 (lit.[e] 101–102)
3-Carbomethoxy-1-indanone (8h)	88	40–42 (lit.[f] 44–45)
6-Carboxy-1-indanone (8i)	55	254–256 (lit.[g] 256–257)

[a] C. K. Ingold and H. A. Piggot, *J. Chem. Soc.*, **123**, 1469 (1923). [b] N. P. Buu-Hoi and N. K. Young, *ibid.*, 3499 (1951). [c] M. Tomita and S. Minami, *ibid.*, 183 (1969). [d] N. L. Allinger and E. S. Jones, *J. Org. Chem.*, **27**, 70 (1962). [e] C. A. Grob and O. Weissbach, *Helv. Chim. Acta*, **44**, 1736 (1961). [f] K. V. Levishina, A. I. Gavrillova, and S. I. Sergievskaya, *J. Gen. Chem. USSR (Engl. Transl.)*, **30**, 3601 (1960). [g] G. Baddely and R. Williamson, *J. Chem. Soc.*, 4647 (1956).

g (0.28 ml; 0.0053 mol) of bromine dissolved in 10 ml of carbon tetrachloride. The bromine was added until a slight color persisted. Removal of the solvent at reduced pressure yielded an orange oil which crystallized on treatment with a methanol–water mixture in the cold: yield 0.87 g (62.1%); mp 115–116 °C; ir (CCl_4) 1740 cm^{-1} (C=O); NMR ($CDCl_3$) δ 8.58 (dd, J = 1, 8 Hz, 1 H, C_7 proton), 8.25 (dd, J = 1, 8 Hz, 1 H, C_5 proton), 7.80 (d, J = 8 Hz, 1 H, C_6 proton), 4.13 (d, J = 18 Hz, 2 H, C_3 proton), 2.07 (s, 3 H, $-CH_3$).

Anal. Calcd for $C_{10}H_8NO_3Br$: C, 44.44; H, 2.96; N, 5.19; Br, 29.63. Found: C, 44.42; H, 2.90; N, 5.19; Br, 29.39.

Preparation of 2-Methyl-1-indenones. A. 2-Methyl-1-indenone (7a) was prepared according to the procedure of Floyd and Allen.[6c] From 12.6 g (0.061 mol) of ethyl α-methyl-β-phenylhydracrylate[6c] there was obtained 4.4 g (50%) of **7a** as yellow plates: mp 44–46 °C (lit.[6c] 45–47 °C); ir (CCl_4) 1715 cm^{-1} (C=O); uv (MeOH) λ_{max} (ε) 238 (28 600), 243 (43 600), 325 (1000), 400 nm (415); NMR ($CDCl_3$) δ 7.42–6.78 (m, 5 H, 4 aromatic protons + 1 vinyl proton), 1.82 (d, J = 2 Hz, 3 H, $-CH_3$).

B. 2,4-Dimethyl-1-indenone (7b) was prepared according to the general procedure of Floyd and Allen.[6c] From 12.6 g (0.056 mol) of ethyl α-methyl-β-o-tolylhydracrylate[15] there was obtained 2.7 g (30%) of **7b** as orange crystals from ether–petroleum ether: mp 42–44 °C; ir (CCl_4) 1720 cm^{-1}; uv (hexane) λ_{max} (ε) 237 (38 000), 242 (43 000), 315 (1190), 337 (1515), 341 (1244), 395 nm (760); NMR ($CDCl_3$) δ 7.38–6.91 (m, 4 H, 3 aromatic protons + 1 vinyl proton), 2.10 (s, 3 H, $-CH_3$), 1.82 (d, J = 2 Hz, 3 H, $-CH_3$).

Anal. Calcd for $C_{11}H_{10}O$: C, 83.52; H, 6.37. Found: C, 83.54; H, 6.39.

C. 2,6-Dimethyl-1-indenone (7c) was prepared according to the general procedure of Floyd and Allen.[6c] From 12.6 g (0.057 mol) of ethyl α-methyl-β-p-tolylhydracrylate[16] there was obtained 2.2 g (25%) of **7c** as orange plates from ether–petroleum ether: mp 48–50 °C; ir (CCl_4) 1720 cm^{-1} (C=O); uv (hexane) λ_{max} (ε) 237 (38 400), 242 (41 600), 316 (705), 329 (560), 405 nm (560); NMR ($CDCl_3$) δ 7.38–6.79 (m, 4 H, 3 aromatic protons + 1 vinyl proton), 2.29 (s, 3 H, $-CH_3$), 1.82 (d, J = 2 Hz, 3 H, $-CH_3$); mass spectrum m/e 158.

D. 2-Methyl-6-methoxy-1-indenone (7d) was prepared according to the procedure of Martens and Hoonaert.[9] From 1.0 g (0.0048 mol) of 1-chloro-2-(3-methoxybenzoyl)propene and 0.68 g (0.0051 mol) of $AlCl_3$ there was obtained 0.15 g (18.3%) of **7d** as red plates: mp 78–80 °C (lit.[9] mp 83 °C); ir (CCl_4) 1712 cm^{-1}; uv (hexane) λ_{max} (ε) 245 (38 000), 252 (3200), 288 (900), 300 (750), 435 nm (660); NMR ($CDCl_3$) 7.18–6.73 (m, 4 H, 3 aromatic protons + 1 vinyl proton), 3.78 (s, 3 H, $-OCH_3$), 1.82 (d, J = 2 Hz, 3 H, $-CH_3$).

E. 2-Methyl-4-nitro-1-indenone (7e). To 0.22 g (0.00082 mol) of 2-bromo-2-methyl-4-nitro-1-indanone was added 8.0 g (0.080 mol) of *N*-methylpiperidine and the solution was stirred at room temperature for 2 h. Then 25 ml of ether was added and the precipitated salt filtered. The filtrate was washed with cold 3 N HCl (3 × 100 ml) and H_2O (2 × 100 ml) and dried ($MgSO_4$), and the solvent was evaporated to yield 0.13 g of a yellow solid. Recrystallization from ether–petroleum ether afforded 0.11 g (74.8%) of **7e** as yellow plates: mp 117–119 °C; ir (CCl_4) 1725 cm^{-1}; uv (hexane) λ_{max} (ε) 214 (10 800), 242 (10 150), 274 (11 900), 328 (1690), 342 (2000), 357 nm (1690); NMR ($CDCl_3$) δ 8.18–7.12 (m, 4 H, 3 aromatic protons + 1 vinyl proton), 2.02 (d, J = 2 Hz, 3 H, CH_3).

Anal. Calcd for $C_{10}H_7NO_3$: C, 63.49; H, 3.73; N, 7.40. Found: C, 63.30; H, 3.71; N, 7.38.

Preparation of Substituted 2-Benzal-1-indanones (9). A. Via Aldol Condensation under Acidic Conditions. General Procedure. The appropriately substituted indanone and a twofold excess of benzaldehyde were dissolved in glacial acetic acid. A catalytic amount of concentrated sulfuric acid (a few drops usually) was added and the mixture was stirred at room temperature for 18 h. The resulting precipitate was collected, washed well with cold water, and recrystallized.

1. 6-Nitro-2-benzal-1-indanone (9c) was obtained in 80% yield after recrystallization from chloroform: mp 247–248 °C; ir (KBr) 1685 cm^{-1} (C=O); uv (CH_3CN) λ_{max} (ε) 245 (19 400), 255 (20 600), 327 nm (26 300); mass spectrum m/e 265.

Anal. Calcd for $C_{16}H_{11}NO_3$: C, 72.45; H, 4.18; N, 5.28. Found: C, 72.51; H, 4.21; N, 5.14.

2. 5-Nitro-2-benzal-1-indanone (9e) was obtained in 70% yield after recrystallization from methanol: mp 222–224 °C; ir (KBr) 1695 cm^{-1} (C=O); NMR ($CDCl_3$) δ 8.50–7.31 (m, 9 H, 8 aromatic protons + 1 vinyl proton), 4.15 (d, J = 1.5 Hz, 2 H, C_3 proton).

Anal. Calcd for $C_{16}H_{11}NO_3$: C, 72.45; H, 4.18; N, 5.28. Found: C, 72.27; H, 4.14; N, 5.35.

3. 5-Cyano-2-benzal-1-indanone (9f) was obtained in 65% yield after recrystallization from methanol: mp 218–220 °C; ir ($CHCl_3$) 1695 cm^{-1} (C=O); NMR ($CDCl_3$) δ 8.16–7.43 (m, 9 H, 8 aromatic protons + 1 vinyl proton), 4.10 (d, J = 1.5 Hz, 2 H, C_3 protons).

Anal. Calcd for $C_{17}H_{11}NO$: C, 83.25; H, 4.52; N, 5.71. Found: C, 83.21; H, 4.42; N, 5.69.

4. 4-Nitro-2-benzal-1-indanone (9g) was obtained in 85% yield after recrystallization from carbon tetrachloride: mp 172–174 °C; ir ($CHCl_3$) 1690 cm^{-1}; NMR ($CDCl_3$) δ 8.68 (dd, J = 1, 8 Hz, 1 H, C_7 proton), 8.49 (dd, J = 1,8 Hz, 1 H, C_5 proton), 7.83–7.33 (m, 7 H, 6 aromatic protons + 1 vinyl proton), 4.47 (d, J = 1.5 Hz, C_3 protons).

Anal. Calcd for $C_{16}H_{11}NO_3$: C, 72.45; H, 4.18; N, 5.28. Found: C, 72.25; H, 4.02; N, 5.28.

5. 6-Carboxy-2-benzal-1-indanone (9i) was obtained in 83% yield after recrystallization from ethanol: mp 306–307 °C; ir (KBr) 1680 cm^{-1} (C=O); uv (CH_3CN) λ_{max} (ε) 234 (30 400), 318 nm (26 500).

Anal. Calcd for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58. Found: C, 77.13; H, 4.60.

B. Via Aldol Condensation under Basic Conditions. General Procedure. Equimolar quantities of benzaldehyde and the appropriately substituted indanone were stirred with ice-bath cooling while a 4% ethanolic potassium hydroxide solution was added. The crude product precipitated from the solution, usually within 15 min, and was filtered, washed with cold water, and recrystallized.

1. 2-Benzal-1-indanone (9a) was obtained in 60% yield after recrystallization from a methanol–water mixture, mp 109–111 °C (lit.[17] mp 109–110 °C).

2. 6-Methyl-2-benzal-1-indanone (9d) was obtained in 78% yield after recrystallization from methanol: mp 170.5–172 °C (lit.[18] 165 °C); ir (KBr) 1690 cm^{-1} (C=O); uv (MeOH) λ_{max} (ε) 235 (8000), 325 nm (28 000); NMR ($CDCl_3$) δ 7.75–7.25 (m, 9 H, 8 aromatic protons + 1 vinyl proton), 3.87 (d, J = 1.5 Hz, 2 H, C_3 proton), 2.37 (s, 3 H, $-CH_3$).

C. Miscellaneous. 1. 3-Carboxy-2-benzal-1-indanone was prepared by the procedure of Campbell,[19] using 10% ethanolic potassium hydroxide for the condensation, in 70% yield: mp 167–168 °C (lit.[19] mp 169–170 °C); ir (KBr) 3200–2500 (OH), 1700 cm^{-1} (broad, C=O); uv (MeOH) λ_{max} (ε) 225 (10 500), 323 nm (25 200).

2. 6-Carbomethoxy-2-benzal-1-indanone (9b). 6-Carboxy-2-benzal-1-indanone (**9b**, 72 mg, 0.00027 mol) was refluxed in 80 ml of anhydrous methanol containing 1 ml of concentrated sulfuric acid for 3.5 h. The solution was then reduced in volume to 40 ml by evaporation at reduced pressure and cooled. The precipitate was collected and recrystallized from methanol to yield 52 mg (69.3%) of **9b** as shiny plates: mp 200–201 °C; ir (KBr) 1725 (ester C=O), 1685 cm^{-1} (ketone C=O); uv (CH_3CN) λ_{max} (ε) 234 (3000), 318 nm (25 500).

Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.67; H, 5.06.

3. 3-Carbomethoxy-2-benzal-1-indanone (9h). 3-Carboxy-2-

benzal-1-indanone (1.77 g, 0.0067 mol) was refluxed in 175 ml of methanol containing 2 ml of concentrated sulfuric acid for 10 h. The solution was evaporated at reduced pressure to 20 ml and cooled. The resulting precipitate was collected and recrystallized from methanol to give 1.57 g (83.9%) of **9h** as colorless crystals: mp 106–108 °C; ir ($CHCl_3$) 1725 (ester C=O), 1695 cm^{-1} (ketone C=O); uv (MeOH) λ_{max} (ϵ) 250 (11 900), 230 nm (12 300); NMR ($CDCl_3$) δ 7.75–7.70 (m, 10 H, 9 aromatic protons + 1 vinyl proton), 4.91 (d, J = 1.5 Hz, 1 H, C_3 proton), 3.33 (s, 3 H, $-OCH_3$).

Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.54; H, 5.09.

Preparation of Substituted 3-Bromo-2-benzal-1-indanones. The preparation of 3-bromo-2-benzal-1-indanone (**10a**) has previously been described,[20] and the same general procedure was used to prepare the following bromo ketones.

A. 3-Bromo-2-benzal-1-indanone (10a) was obtained in 52% yield: mp 118–120 °C (lit.[20] mp 119–120 °C); ir (CCl_4) 1706 cm^{-1} (C=O); uv (hexane) λ_{max} (ϵ) 229 (16 200), 234 (s) (15 000), 254 (s) (10 500), 319 (23 500), 330 nm (18 900); NMR ($CDCl_3$) δ 7.83–7.15 (m, 10 H, 9 aromatic protons + 1 vinyl proton), 6.25 (s, 1 H, C_3 proton).

B. 6-Carbomethoxy-3-bromo-2-benzal-1-indanone (10b) was prepared in 50% yield: mp 195–197 °C; NMR ($CDCl_3$) δ 8.50 (d, J = 1 Hz, 1 H, C_7 proton), 8.30 (dd, J = 1, 8 Hz, 1 H, C_5 proton), 7.92–7.33 (m, 7 H, 6 aromatic protons + 1 vinyl proton) 6.17 (bs, 1 H, C_3 proton), 3.92 (s, 3 H, OCH_3).

Anal. Calcd for $C_{18}H_{13}BrO_3$: C, 60.53; H, 3.67; Br, 22.37. Found: C, 60.54; H, 3.61; Br, 22.57.

C. 6-Nitro-3-bromo-2-benzal-1-indanone (10c) was prepared in 50% yield, mp 175–179 °C. Repeated recrystallization failed to purify **10c.** The following data are for impure **10c:** ir ($CHCl_3$) 1710 cm^{-1} (C=O); uv (CH_3CN) λ_{max} (ϵ) 254 (23 300), 333 nm (25 300); NMR ($CDCl_3$) δ 8.50–8.25 (m, 2 H, C_5 and C_7 protons), 7.89–7.28 (m, 7 H, 6 aromatic protons + 1 vinyl proton), 6.25 (bs, 1 H, C_3 proton).

D. 6-Methyl-3-bromo-2-benzal-1-indanone (10d) was prepared in 53% yield: mp 154–155 °C; ir ($CHCl_3$) 1700 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.29–7.25 (m, 9 H, 8 aromatic protons + 1 vinyl proton), 6.27 (bs, 1 H, C_3 proton), 2.43 (s, 3 H, $-CH_3$).

Anal. Calcd for $C_{17}H_{13}OBr$: C, 65.20; H, 4.18; Br, 25.51. Found: C, 64.99; H, 4.16; Br, 25.60.

E. 5-Nitro-3-bromo-2-benzal-1-indanone (10e) was prepared in 43% yield, mp 180–190 °C. Repeated recrystallizations failed to purify **10e.** The following NMR data are for impure **10e:** δ 8.59 (d, J = 1 Hz, 1 H, C_4 proton), 8.42 (dd, J = 1, 8 Hz, C_6 proton), 8.17–7.50 (m, 7 H, 6 aromatic protons + 1 vinyl proton), 6.43 (d, J = 1 Hz, 1 H, C_3 proton).

F. 5-Cyano-3-bromo-2-benzal-1-indanone (10f) was prepared in 45% yield, mp 210–216 °C. Repeated recrystallizations failed to purify **10f.** The following NMR data are for impure **10f:** δ 8.08–7.35 (m, 9 H, 8 aromatic protons + 1 vinyl proton), 6.35 (d, J = 1 Hz, 1 H, C_3 proton).

G. 4-Nitro-3-bromo-2-enzal-1-indanone (10g) was prepared in 48% yield, mp 160–170 °C. Repeated recrystallizations failed to purify this compound, and its thermal instability made it unprofitable to pursue its purification and analysis. The following NMR data are for impure **10g:** δ 8.48 (dd, J = 1, 8 Hz, 1 H, C_7 proton), 8.25 (dd, J = 1, 8 Hz, 1 H, C_5 proton), 7.80–7.31 (m, 7 H, 6 aromatic protons + 1 vinyl proton), 6.45 (bs, 1 H, C_3 proton).

H. 3-Carbomethoxy-3-bromo-2-benzal-1-indanone (10h) was prepared in 40% yield, mp 120–130 °C. Repeated recrystallizations failed to purify **10h.** The following nmr data are for impure **10h:** δ 8.01–7.33 (m, 10 H, 9 aromatic protons + 1 vinyl proton), 3.53 (s, 3 H, $-OCH_3$).

Preparation of Substituted 2-(α-Aminobenzyl)-1-indenones (11 and 12). General Procedure. A solution of the bromo ketone **10** and 2 molar equiv of amine in benzene was allowed to react at room temperature for 20 h. The amine hydrobromide was filtered off and the solvent evaporated under reduced pressure to yield an oil. The oil was dissolved in ether, filtered free of any remaining hydrobromide salt, and the ethereal solution extracted several times with 3 N hydrochloric acid solution. The aqueous phase was neutralized with saturated sodium carbonate solution and then extracted with ether. The ether extracts were dried and evaporated to yield the product as an oil. The oil was then crystallized in *n*-hexane.

A. 2-(α-*tert*-Butylaminobenzyl)-1-indenone (11a). From 1.0 g (0.0033 mol) of bromo ketone **10a** and 0.48 g (0.70 ml, 0.0066 mol) of *tert*-butylamine there was obtained 0.4 g (41.6%) of **11a** as yellow crystals: mp 78–80 °C (lit.[4] mp 83–85 °C); ir (CCl_4) 1725 cm^{-1} (C=O); uv (hexane) λ_{max} (ϵ) 238 (40 000), 244 (41 600), 303 (1100), 314 (1200), 327 (900), 389 nm (1000); NMR ($CDCl_3$) δ 7.61–6.75 (m, 10 H, 9 aromatic protons + 1 vinyl proton), 4.85 (d, J = 1 Hz, benzylic proton), 1.10 (s, 9 H, *tert*-butyl).

B. 6-Carbomethoxy-2-(α-*tert*-butylaminobenzyl)-1-indenone (11b). From 0.50 g (0.0014 mol) of bromo ketone **10b** and 0.20 g (0.29 ml, 0.0028 mol) of *tert*-butylamine there was obtained 0.31 g (63.1%) of **11b** as yellow crystals: mp 158–159 °C; ir (CCl_4) 1740 (ester C=O), 1725 cm^{-1} (ketone C=O); uv (hexane) λ_{max} (ϵ) 240 (28 000), 315 (7100), 327 (7500), 388 nm (5800); NMR ($CDCl_3$) δ 8.13–7.97 (m, 2 H, C_5 and C_7 protons), 7.50–6.97 (m, 7 H, 6 aromatic protons + 1 vinyl proton), 4.88 (d, J = 1.2 Hz, 1 H, benzylic), 1.48 (bs, 1 H, NH), 1.06 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{22}H_{23}NO_3$: C, 75.62; H, 6.63; N, 4.01. Found: C, 75.50; H, 6.52; N, 3.92.

C. 6-Nitro-2-(α-*tert*-butylaminobenzyl)-1-indenone (11c). From 0.50 g (0.00145 mol) of bromo ketone **10c** and 0.24 g (0.35 ml, 0.0032 mol) of *tert*-butylamine there was obtained 0.29 g (59.2%) of **11c** as orange needles: mp 103–104 °C; ir (CCl_4) 1725 cm^{-1} (C=O); uv (hexane) λ_{max} (ϵ) 228 (40 000), 244 (20 600), 330 (11 000), 385 (5500); NMR ($CDCl_3$) δ 8.17–7.92 (m, 2 H, C_5 and C_7 protons), 7.33–6.92 (m, 7 H, 6 aromatic protons + 1 vinyl proton), 4.80 (d, J = 1.2 Hz, 1 H, benzylic), 1.45 (bs, 1 H, NH), 1.06 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.33. Found: C, 71.35; H, 5.97; N, 8.48.

D. 6-Methyl-2-(α-*tert*-butylaminobenzyl)-1-indenone (11d). From 0.50 g (0.0016 mol) of bromo ketone **10d** and 0.23 g (0.33 ml, 0.0032 mol) of *tert*-butylamine there was obtained 0.25 g (50.1%) of **11d** as orange plates: mp 48–50 °C; ir (CCl_4) 1715 cm^{-1} (C=O); uv (hexane) λ_{max} (ϵ) 245 (44 000), 252 (45 500), 306 (700), 320 (1200), 335 (1100), 393 nm (1100); NMR ($CDCl_3$) δ 7.53–6.75 (m, 9 H, 8 aromatic protons + 1 vinyl proton), 4.88 (d, J = 1.2 Hz, 1 H, benzylic), 2.27 (s, 3 H, $-CH_3$), 1.42 (bs, 1 H, NH), 1.06 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{21}H_{23}NO$: C, 82.59; H, 7.59; N, 4.59. Found: C, 82.61; H, 7.61; N, 4.46.

E. 5-Nitro-2-(α-*tert*-butylaminobenzyl)-1-indenone (11e). From 0.15 g (0.00044 mol) of bromo ketone **10e** and 0.06 g (0.09 ml, 0.00090 mol) of *tert*-butylamine there was obtained 0.10 g of **11e** as yellow cyrstals: mp 130–132 °C; ir (CCl_4) 1725 cm^{-1} (C=O); uv (hexane) λ_{max} (ϵ) 225 (15 200), 242 (13 000), 253 (12 000), 275 (12 000), 315 (2700), 350 (2000), 405 nm (1700); NMR ($CDCl_3$) δ 8.19–7.74 (m, 2 H, aromatic protons), 7.58–7.22 (m, 7 H, 6 aromatic protons + 1 vinyl proton), 4.90 (d, J = 1.2 Hz, 1 H, benzylic), 1.60 (bs, 1 H, NH), 1.06 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.33. Found: C, 71.35; H, 5.97; N, 8.33.

F. 5-Cyano-2-(α-*tert*-butylaminobenzyl)-1-indenone (11f). From 0.25 g (0.00077 mol) of bromo ketone **10f** and 0.11 g (0.16 ml, 0.0015 mol) of *tert*-butylamine there was obtained 0.14 g (56.2%) of **11f** as canary yellow crystals: mp 137–138 °C; ir (CCl_4) 1725 cm^{-1} (C=O); uv (hexane) λ_{max} (ϵ) 246 (31 000), 254 (32 000), 310 (3750), 320 (3800), 333 (4000), 405 nm (2000); NMR ($CDCl_3$) δ 7.48–7.11 (m, 9 H, 8 aromatic protons + 1 vinyl proton), 4.88 (d, J = 1.2 Hz, 1 H, benzylic), 1.42 (bs, 1 H, NH), 1.07 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{21}H_{20}N_2O$: C, 79.72; H, 6.37; N, 8.85. Found: C, 79.53; H, 6.18; N, 8.67.

G. 4-Nitro-2-(α-*tert*-butylaminobenzyl)-1-indenone (11g). From 0.40 g (0.0012 mol) of bromo ketone **10g** and 0.20 g (0.28 ml, 0.0027 mol) of *tert*-butylamine there was obtained 0.25 g (65.1%) of **11g** as fine yellow needles: mp 109–111 °C; ir (CCl_4) 1725 cm^{-1} (C=O); uv (hexane) λ_{max} (ϵ) 240 (13 300), 277 (10 900), 345 (4500), 395 nm (2500); NMR ($CDCl_3$) δ 8.25 (d, J = 1 Hz, 1 H, C_7 proton), 8.03 (dd, J = 1, 8 Hz, C_5 proton), 7.67–7.09 (m, 7 H, 6 aromatic protons + 1 vinyl proton), 4.91 (d, J = 1.1 Hz, 1 H, benzylic), 1.45 (bs, 1 H, NH), 1.07 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.33. Found: C, 71.36; H, 6.02; N, 8.30.

H. 3-Carbomethoxy-2-(α-*tert*-butylaminobenzyl)-1-indenone (11h). From 0.50 g (0.0014 mol) of bromo ketone **10h** and 0.20 g (0.29 ml, 0.0027 mol) of *tert*-butylamine there was obtained 0.25 g (50.2%) of **11h** as red crystals: mp 73–75 °C; ir (CCl_4) 1740 (ester C=O), 1715 cm^{-1} (ketone C=O); uv (hexane) λ_{max} (ϵ) 244 (27 500), 248 (31 000), 325 (2400), 420 nm (1050); NMR ($CDCl_3$) δ 7.66–7.16 (m, 9 H, aromatic), 5.60 (s, 1 H, benzylic), 4.00 (s, 3 H, $-OCH_3$), 1.42 (bs, 1 H, NH), 1.07 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{22}H_{23}NO_3$: C, 75.62; H, 6.63; N, 4.01. Found: C, 75.50; H, 6.70; N, 3.90.

I. 2-(α-*N*-methyl-*tert*-butylaminobenzyl)-1-indenone (12a). The physical data for **12a** have already been reported.[29]

J. 6-Carbomethoxy-2-(α-*N*-methyl-*tert*-butylaminobenzyl)-1-indenone (12b). From 0.25 g (0.00070 mol) of bromo ketone

10b and 0.12 g (0.0014 mol) of *N*-methyl-*tert*-butylamine there was obtained 0.16 g (63.0%) of **12b** as fine red-orange needles: mp 93–95 °C; ir (CCl_4) 1735 (ester C=O), 1728 cm^{-1} (ketone C=O); uv (hexane) λ_{max} (ϵ) 245 (30 000), 307 (1500), 320 (1500), 335 (1200), 405 (1370), 425 (1300), 455 (1050); NMR ($CDCl_3$) δ 8.13–7.97 (m, 2 H, C_5 and C_7 protons), 7.50–6.97 (m, 7 H, 6 aromatic protons + 1 vinyl proton), 5.50 (d, J = 0.8 Hz, 1 H, benzylic), 2.26 (s, 3 H, $-CH_3$), 1.17 (s, 9H, *tert*-butyl).

Anal. Calcd for $C_{23}H_{25}NO_3$: C, 76.01; H, 6.93; N, 3.85. Found: C, 76.08; H, 6.98; N, 3.74.

K. 6-Nitro-2-(α-*N*-methyl-*tert*-butylaminobenzyl)-1-indenone (12c). From 0.55 g (0.0016 mol) of bromo ketone **10c** and 0.28 g (0.0032 mol) of *N*-methyl-*tert*-butylamine there was obtained 0.10 g (17.9%) of **12c** as magenta needles: mp 95–97 °C; ir (CCl_4) 1725 cm^{-1} (C=O); uv (hexane) λ_{max} (ϵ) 225 (26 200), 273 (16 000), 322 (3505), 335 (2800), 392 (1845), 415 (1700), 440 (1250), 475 (1035); NMR ($CDCl_3$) δ 8.17–7.92 (m, 2 H, C_5 and C_7 protons), 7.40–7.12 (m, 7 H, 6 aromatic protons + 1 vinyl proton), 5.48 (d, J = 0.8 Hz, 1 H, benzylic), 2.27 (s, 3 H, $-CH_3$), 1.17 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{21}H_{22}N_2O_3$: C, 71.98; H, 6.33; N, 7.99. Found: C, 72.23; H, 6.49; N, 7.91.

L. The hydrochloride salts of 12a–c were prepared by the addition of dry HCl gas to an ethereal solution of the respective free base. Owing to their hydroscopic nature, the salts were dissolved in acetonitrile immediately after filtration and their uv–visible spectra recorded.

Miscellaneous. A. Preparation of α-Methyl-β-*o*-nitrophenylpropionic Acid. In a 1-l. three-neck round-bottom flask equipped with a reflux condenser, dropping funnel, and mechanical stirrer were placed 9.0 g (0.370 mol) of magnesium, 20 ml of 100% ethanol, and 3 ml of carbon tetrachloride. After the evolution of hydrogen had subsided, the reaction mixture was diluted with 120 ml of 100% ethanol and 63.0 g (0.362 mol) of diethyl methylmalonate was added dropwise over a 1-h period. The mixture was then stirred under reflux for 18 h until all of the magnesium had reacted.

After cooling somewhat, a solution of 50.0 g (0.292 mol) of *o*-nitrobenzyl chloride dissolved in 75 ml of hot 100% ethanol was added all at once and the solution was heated under reflux and mechanical stirring for 40 h. The reaction mixture was then treated with a solution of 38 ml of concentrated sulfuric acid in 250 ml of water and steam distilled (500 ml). The residue was extracted with ether (3 × 100 ml), and the ether solution was dried over magnesium sulfate and evaporated to yield a thick red oil. A mixture of 250 ml of 20% hydrochloric acid and 250 ml of concentrated acetic acid was added and the heterogeneous mixture refluxed for 16 h. The resulting brown homogeneous solution was evaporated to yield a solid. The solid was heated briefly with 500 ml of an ether saturated potassium bicarbonate mixture and filtered. The aqueous phase of the filtrate was acidified with concentrated hydrochloric acid to yield 40.1 g (65.5%) of crude acid as a brown solid.

The crude acid was dissolved in 500 ml of anhydrous methanol, 5 ml of concentrated sulfuric acid was added, and the mixture was refluxed for 48 h. The solution was then cooled, evaporated to small volume (50 ml), and extracted with ether (3 × 150 ml), and the ether was washed with water (1 × 100 ml), and saturated sodium bicarbonate (2 × 100 ml), dried, and evaporated to yield a red oil. Distillation at reduced pressure gave 28.3 g (65.9%) of methyl α-methyl-β-*o*-nitrophenylpropionate as a colorless liquid: bp 116–118 °C (0.5 mm); NMR ($CDCl_3$) δ 8.11–7.3 (m, 1 H, aromatic proton ortho to nitro), 7.84–7.20 (m, 3 H, aromatic), 3.62 (s, 3 H, $-OCH_3$), 3.41–2.77 (m, 3 H, CH_3C-), 1.21 (d, 3 H, CH_3-).

Anal. Calcd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87; N, 6.27. Found: C, 59.15; H, 5.78; N, 6.43.

To 8.0 g (0.036 mol) of the above ester was added 50 ml of water and 80 ml of concentrated hydrochloric acid and the mixture was refluxed for 16 h. After cooling, the solution was extracted with ether (2 × 150 ml), and the ether was washed with water (2 × 100 ml), dried over magnesium sulfate, and evaporated to yield a yellow il. Recrystallization from methanol–water afforded 6.7 g (89.3%) of pure acid as colorless crystals: mp 88–90 °C; NMR ($CDCl_3$) δ 11.11 (bs, 1 H, OH), 8.11–7.94 (m, 1 H, aromatic proton-ortho to nitro groups), 7.61–7.20 (m, 3 H, aromatic), 3.41–2.43 (m, 3 H, $-CH_2CH$), 1.21 (d, J = 6 Hz, 3 H, CH_3-).

Anal. Calcd for $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30; N, 6.78. Found: C, 57.40; H, 5.35; N, 6.80.

Acknowledgment. This investigation was supported by Grant CA-02931 of the National Cancer Institute, U.S. Public Health Service.

Registry No.—6, 51927-25-4; **8c,** 24623-24-3; **8d,** 24623-20-9; **8e,** 22246-24-8; **8f,** 25724-79-2; **8g,** 24623-25-4; **8i,** 60031-08-5; **9b,** 60031-09-6; **9c,** 60031-10-9; **9d,** 60031-11-0; **9e,** 60031-12-1; **9f,** 60031-13-2; **9g,** 60031-14-3; **9h,** 60031-26-7; **9i,** 60031-15-4; **10a,** 5387-50-8; **10b,** 60031-16-5; **10c,** 60031-17-6; **10d,** 60031-18-7; **10e,** 60031-19-8; **10f,** 60031-20-1; **10g,** 60031-21-2; **10h,** 60031-22-3; α-methyl-*o*-nitrophenylpropionic acid, 60031-23-4; α-methyl-*o*-nitrophenylpropionic acid chloride, 60031-24-5; 2-bromo-2-methyl-4-nitro-1-indanone, 60031-25-6; benzaldehyde, 100-52-7; *tert*-butylamine, 75-64-9; *N*-methyl-*tert*-butylamine, 14610-37-8; diethyl methylmalonate, 609-08-5; *o*-nitrobenzyl chloride, 612-23-7; methyl α-methyl-β-*o*-nitrophenylpropionate, 60031-27-8; 3-carboxy-2-benzal-1-indanone, 60031-28-9.

References and Notes

(1) For part 17 in this series, see M. C. Eagen and N. H. Cromwell, *J. Org. Chem.*, **39,** 3863 (1974).
(2) Presented in part at the 9th Midwest Regional Meeting of the American Chemical Society, Lawrence, Kans., Oct 1973.
(3) T. Zincke and H. Gunter, *Justus Liebigs Ann. Chem.*, **272,** 243 (1893).
(4) G. Maury, E.-M. Wu, and N. H. Cromwell, *J. Org. Chem.*, **33,** 1900 (1968).
(5) R. Carruthers, F. M. Dean, L. E. Houghton, and A. Ledwith, *Chem. Commun.*, 1206 (1967).
(6) A. Manchka, M. Stein, and W. Trauner, *Monatsh. Chem.*, **85,** 168 (1954).
(7) (a) C. S. Marvel and C. W. Hinman, *J. Am. Chem. Soc.*, **76,** 5438 (1954); (b) E. Campaigne, G. F. Bulbenko, W. E. Kreighbaum, and D. R. Maulding, *J. Org. Chem.*, **27,** 4428 (1962); (c) M. F. Floyd and G. R. Allen, *ibid.*, **35,** 2647 (1970).
(8) E. D. Bergmann, A. Heller, and H. Weiler-Feilchenfeld, *Bull. Soc. Chim. Fr.*, 635 (1959); d. Kananatsios and C. H. Eugster, *Helv. Chim. Acta*, **48,** 471 (1965); G. Korbrich and H. Trapp, *Chem. Ber.*, **101,** 2660 (1968).
(9) H. Martens and G. Hoonaert, *Synth. Commun.*, **2,** 147 (1972).
(10) R. S. Mulliken, *J. Am. Chem. Soc.*, **74,** 811 (1952); *J. Phys. Chem.*, **56,** 801 (1952).
(11) See for example, M. Oki and K. Mutai, *Tetrahedron*, **26,** 1181 (1970).
(12) E. Kosower, *Prog. Phys. Org. Chem.*, **3,** 93 (1965).
(13) Melting points were taken by the capillary method in a Mel-Temp melting point apparatus and are uncorrected. Ultraviolet–visible spectra were recorded on a Cary Model 14 spectrometer. Infrared spectra were measured with a Perkin-Elmer 237 or 621 spectrometer. Proton magnetic resonance spectra were obtained on a Varian A-60D spectrometer and are reported in parts per million (δ) relative to internal Me_4Si (0.0). Mass spectra were obtained with a Hitachi Model RMU-6D spectrometer. Microanalyses were performed by Micro-Tech Laboratory, Skokie, Ill.
(14) Proton assignments in the ABX system were made based on those reported for 2-methyl-1-indanone: G. Agahagin, H. Plant, and G. D. Vickers, *Anal. Chem.*, **39,** 1583 (1967).
(15) M. S. Gibson, *J. Chem. Soc.*, 808 (1956).
(16) L. Ruzicka and M. Liguori, *Helv. Chim. Acta*, **15,** 140 (1932).
(17) F. S. Kipping, *J. Chem. Soc.*, **65,** 480 (1894)
(18) J. Braun, G. Manz, and E. Reinsch, *Justus Liebigs Ann. Chem.*, **468,** 277 (1898).
(19) N. Campbell and H. G. Heller, *J. Chem. Soc.*, 3006 (1962).
(20) B. D. Pearson, R. P. Ayer, and N. H. Cromwell, *J. Org. Chem.*, **27,** 3038 (1962).
(21) R. J. Murray and N. H. Cromwell, *J. Org. Chem.*, **39,** 3939 (1974).