# Reaction of 6-Bromobenzocyclohepten-5-one with Amines

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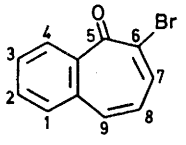
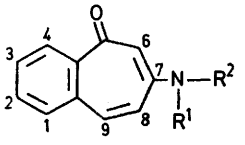
Several examples of *cine*-substitution of the benzocycloheptenone (benzotropone) system are reported. Under mild conditions, substituted benzotropones afford tricyclic amino-derivatives. It is also shown that cleavage of the troponoid ring of benzotropones with appropriate amines constitutes a new method of preparation of aromatic lactams.

THE extent of studies confirms the increasing interest in tropone chemistry in the 1960s,[1] and several more recent reports have been concerned with the synthesis, reactivity, and physical properties of derivatives of cyclohepta-2,4,6-trien-1-one.[1,2] In spite of this work, little is known about the reactivity of bromo-benzocycloheptenones (bromo-benzotropones) towards nucleophilic reagents. This work reports the treatment of the bromobenzotropone (1)[3] with various amines. A tentative inpretation for the formation of the new compounds obtained is also proposed.



(1)

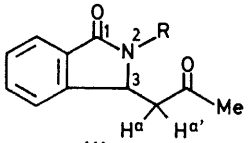


(2)

a; $R^1 = R^2 = Me$
b; $R^1 = H, R^2 = Et$
c; $R^1 = H, R^2 = Pr^i$
d; $R^1 = H, R^2 = CH_2CH_2OH$
e; $R^1 = R^2 = H$
f; $R^1 = R^2 = Me$
g; $R^1R^2 =$ 
h; $R^1 = H, R^2 = [CH_2]_2NMe_2$
i; $R^1 = H, R^2 = [CH_2]_3NMe_2$

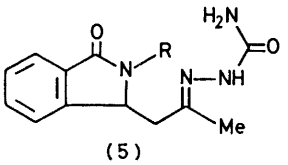
(3)

a; R = Me
b; R = Et
c; R = $Pr^i$
d; R = $CH_2CH_2OH$



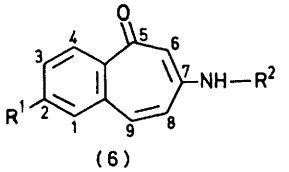
(4)

a; R = Me
b; R = Et
c; R = $Pr^i$



(5)

a; R = Me
b; R = Et



(6)

a; $R^1$ = Cl, $R^2$ = H
b; $R^1$ = OMe, $R^2$ = Me

Reaction of the bromobenzotropone (1) with methylamine affords the methylamino-derivative (2a) in 53% yield, together with the imine (3a) (8%) and the keto-lactam (4a) (23%).

The n.m.r. properties of the methylamino-benzotropone (2a) in Table 1 support its structure. The tricyclic derivative (3a), which gave a crystalline picrate, showed a very intense u.v. maximum at 218 nm, and the n.m.r. data in Table 2 confirm its structure. In particular, the vinylic protons at C-8 and C-7 appeared as doublets of doublets in the δ 6.3—6.9 region. The keto-lactam (4a) exhibited two intense u.v. absorption bands at 222 and 229 nm. The presence of a methyl ketone group was established by the iodoform test and

TABLE 1

N.m.r. data for 6-, 8-, and 9-H for compounds (2a—i) [a]

| Compd. | δ 6-H (d) | δ 8-H (dd) | δ 9-H (d) | $J_{6,8}$/Hz [b] |
|---|---|---|---|---|
| (2a) [c] | 5.73 | 6.49 | 7.18 | 2.5 |
| (2b) [d] | 6.11 | 6.37 | 7.10 | 2.5 |
| (2c) | 6.08 | 6.34 | 7.00 | 3 |
| (2d) [e] | 5.45 | 6.57 | 7.10 | 3 |
| (2e) [d,f] | 6.35 | 6.62 | 7.37 | 3 |
| (2f) | 6.17 | 6.65 | 7.10 | 3 |
| (2g) [d] | 6.25 | 6.53 | 7.10 | 3 |
| (2h) | 6.04 | 6.26 | 7.03 | 3 |
| (2i) | 6.00 | 6.22 | 7.00 | 2.5 |

[a] Recorded for solutions in deuteriochloroform on a HA–100 spectrometer unless otherwise stated. [b] $J_{8,9}$ 12 Hz. [c] [$^2H_6$]-Dimethyl sulphoxide solution. [d] T–60 instrument. [e] [$^2H_4$]-Methanol–[$^2H_6$]dimethyl sulphoxide solution. [f] [$^2H_4$]-Methanol solution.

TABLE 2

N.m.r. data for 6-, 7-, 8-, and 9-H for compounds (3a—d) [a]

| Compd. | δ 6-H (d) | δ 7-H (dd) | δ 8-H (dd) | δ 9-H (d) | $J_{6,7}$/Hz | $J_{7,8}$/Hz | $J_{8,9}$/Hz |
|---|---|---|---|---|---|---|---|
| (3a) | 4.04 | 6.12 | 6.72 | 4.40 | 2 | 5 | 2 |
| (3b) | 4.17 | 6.18 | 6.77 | 4.54 | 2.5 | 5.5 | 2.5 |
| (3c) | 4.35 | 6.31 | 6.90 | 4.77 | 2.8 | 5.5 | 2.8 |
| (3d) [b] | 4.20 | 6.25 | 6.83 | 4.60 | 3 | 6 | 3 |

[a] Recorded for solutions in deuteriochloroform on a HA–100 spectrometer unless otherwise stated. [b] T–60 instrument.

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TABLE 3

Selected n.m.r. data for (4a) and (4b) [a]

| Compd. | δ N–R | 3-H (dd) | $H^a$, $H^{a'}$ (each dd) |
|---|---|---|---|
| (4a) | 3.05 (s) | 4.83 | 2.71, 3.04 |
| (4b) | 3.12 (m), 3.99 (m) 1.22 (t, *J* 7 Hz) | 5.07 | 2.69, 3.01 |

[a] Recorded for solutions in deuteriochloroform on a HA–100 spectrometer. $J_{3,a} = 7$ Hz, $J_{3,a'} = 5$ Hz, $J_{a,a'} = 17$ Hz for (4a) and (4b).

confirmed by the i.r. band at 1 710 $cm^{-1}$, as well as n.m.r. data (see Table 3) which showed a three-proton signal at 2.20. Additionally, compound (4a) gives a crystalline semicarbazone (5a).

Similarly, reaction of the bromobenzotropone (1) with ethylamine and isopropylamine provides the corresponding 7-amino-derivatives (2b) and (2c), as well as the lactams (4b) and (4c) and the imines (3b) and (3c), respectively. The n.m.r. data in Tables 1—3 confirm these structural assignments.

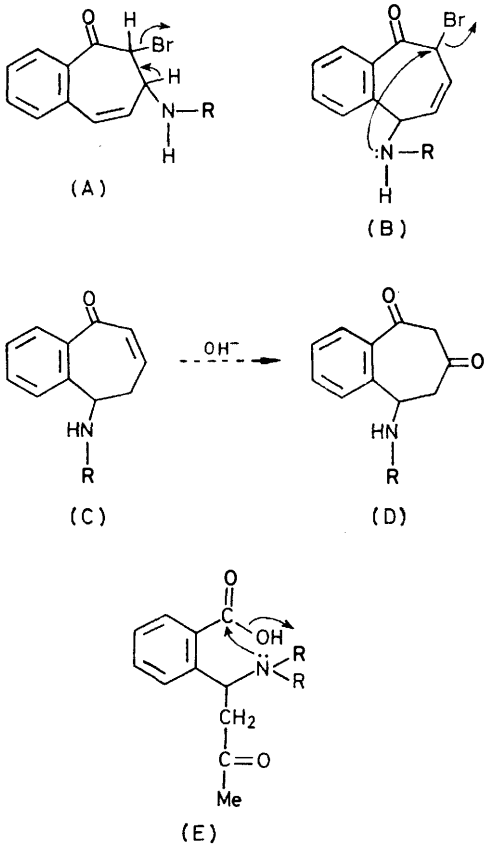
Reactions of the bromobenzotropone (1) with ammonia, ethanolamine, dimethylamine, morpholine, and analogous amines yield the corresponding 7-substituted benzotropones (2d—i). The aminobenzotropones (6a) and (6b) substituted on the benzene ring have also been obtained by similar procedures.

The 7-substituted benzotropones (2) and (6) are probably formed by 1,4-addition at position 7 of compound (1), followed by elimination of bromide ion (A).

Substitution of the bromine in the benzotropone (1) by amines to give compounds (2) is a *cine*-substitution, since the entering group takes a position adjacent to that vacated by the leaving group. This type of reaction has been observed with various tropones.[4] It is conceivable that the addition–elimination mechanism occurs more readily in the seven-membered ring, because there is less strain than in six-membered systems.[5]

The tricyclic derivatives (3a—c) presumably result from 1,6-addition reactions of the amines at position 9 of the substituted tropone (1), followed by displacement of the bromine by attack from the nitrogen, all groups in structure (B) most probably being in a favourable geometry.

The keto-lactams (4a—c) are probably formed by base hydrolysis of the 1,6-addition intermediate (C), which is converted into the β-diketone (D). The transformation (C) ⟶ (D) requires hydroxide ion, followed by an oxidative process. As these reactions were performed in the presence of air for a long period (neither drying conditions nor an inert atmosphere were used), it is conceivable that moisture provides the hydroxide ion and air is the oxidant which reacts readily with the alcohol in the presence of a large excess of base.* This intermediate (D) is then cleaved under alkaline conditions to afford the non-isolated amino-derivative (E), which cyclizes to give the lactams (4); this process thus constitutes a novel synthesis of aryl lactams by fragmentation of aryl tropones.




It is of interest that treatment of compound (1) with ammonia, dimethylamine, morpholine, and similar amines furnishes exclusively the 6-amino-derivatives (2d—i). Conversely, reaction of compound (1) with primary amines ($MeNH_2$, $EtNH_2$, $PrNH_2$) gives similar mixtures of the 7-amino-derivatives (2), the tricyclic products (3), and the lactams (4). Changes in the reaction conditions (*e.g.* different concentrations, longer times) did not modify this pattern.

A salient feature of these reactions is the ready preparation of the not easily accessible tricyclic amino-derivatives (3) and aromatic γ-lactams (4), under rather mild conditions.

## EXPERIMENTAL

Microanalyses were performed by Dr. A. Bernhardt, Max Planck Institut, Mülheim, Germany. M.p.s were determined in capillary tubes with a Mel-Temp Apparatus; they are corrected. T.l.c. was performed with silica gel GF-254 (Merck). I.r. spectra were taken with a Perkin-Elmer Model 21, NaCl prism. U.v. absorption spectra were obtained with a Beckman spectrophotometer, Model DU, for ethanolic solutions. Unless otherwise stated, n.m.r. spectra were recorded with a Varian A-60 spectrometer, for 5—8% (w/v) solutions in deuteriochloroform containing tetramethylsilane as internal reference. Coupling constants are accurate to ±0.5 Hz. Mass spectra were

* Compounds (E) could also be formed during preparative t.l.c., the plate providing the base and air being the oxidant. We thank a referee for this valuable suggestion.

recorded with an Atlas CH-4 spectrometer equipped with an EFO-4B ion source; ionizing energy 70 eV.

*Reaction of* 6-*Bromobenzocyclohepten-5-one* (1) *with Methylamine.*—Methylamine (200 ml) was prepared from the sulphate and aqueous 50% sodium hydroxide, dried with a column packed with sodium hydroxide pellets, condensed and cooled to −30 °C with solid carbon dioxide–acetone. The bromo-ketone (1) [3] (17 g) was added in small portions with stirring and the solution was allowed to reflux (−5 °C) with a solid carbon dioxide–acetone trap for 20 h. The methylamine was then allowed to evaporate off. Crystallization of the residue from ethyl acetate–ether or methanol–ether afforded 7-*methylaminobenzocyclohepten-5-one* (2a) (6.6 g, 53%), m.p. 182—183 °C; $\lambda_{max.}$ 274, 282, and 342 nm (ε 38 900, 41 300, and 8 450); $\nu_{max.}$ 3 300, 1 650, and 1 590 $cm^{-1}$; δ (see also Table 1) 2.73 (d, *J* 5 Hz, NMe), 7.24 (m, NH), 7.4—7.7 (1-, 2-, and 3-H), and 8.39 (m, 4-H); *m/e* 185 ($M^+$), 157 ($M^+$ − CO), and 128 ($M^+$ − NMe − CO) (Found: C, 77.9; H, 6.0; N, 7.6. $C_{12}H_{11}NO$ requires C, 77.8; H, 6.0; N, 7.6%).

Preparative plate chromatography of the mother-liquors from the preparation of (2a) on fluorescent silica gel (solvent system, ethyl acetate–hexane, 4 : 1) furnished two additional compounds. The more-polar component (3 g, 23% yield) was recrystallized from ether, and proved to be 3-*acetonyl*-2-*methylisoindolin*-1-*one* (4a), m.p. 78—79 °C; $\lambda_{max.}$ 222, 229, and 279 nm (ε 10 230, 10 000, and 1 720); $\nu_{max.}$ 1 710, 1 675, and 1 600 $cm^{-1}$; δ (see also Table 3) 2.20 (s, Me-CO) and 7.30—7.90 (m, ArH); *m/e* 203 ($M^+$) (Found: C, 70.7; H, 6.4; N, 6.8. $C_{12}H_{13}O_2N$ requires C, 70.9; H, 6.45; N, 6.9%).

The less-polar component was isolated in 8% yield (0.9 g) and recrystallized from methylene chloride–ether to provide N-*methyl*-6,9-*dihydro*-6,9-*iminobenzocyclohepten*-5-*one* (3a); m.p. 59—60 °C; $\lambda_{max.}$ 218 and 262 nm (ε 19 050 and 4 100); $\nu_{max.}$ 1 695, 1 600, and 1 460 $cm^{-1}$; δ (see also Table 2) 2.48 (s, NMe) and 7.00—7.95 (ArH); *m/e* 185 ($M^+$), 156 ($M^+$ − NMe), and 128 ($M^+$ − NMe − CO) (Found: C, 77.6; H, 5.9; N, 7.3. $C_{12}H_{11}NO$ requires C, 77.8; H, 6.0; N, 7.6%). The *picrate* of (3a) had m.p. 185—187 °C (from ethanol); $\lambda_{max.}$ 356 nm (ε 15 140); $\nu_{max.}$ 1 710, 1 610, 1 565, and 1 545 $cm^{-1}$ (Found: C, 52.1; H, 3.5; N, 13.7. $C_{12}H_{11}NO{\cdot}C_6H_3N_3O_7$ requires C, 52.2; H, 3.4; N, 13.5%).

*Preparation of the Semicarbazone* (5a).—A solution of (4a) in ethanol was heated under reflux for 5 min with an excess of free semicarbazide. Recrystallization from ethanol provided an analytical samples of the *semicarbazone* (5a), m.p. 225—227 °C; $\lambda_{max.}$ 228—229 and 279 nm (ε 20 230 and 1 600); $\nu_{max.}$ 3 440, 3 280, 1 670, and 1 570 $cm^{-1}$; δ[100 MHz; $(CD_3)_2SO$] 1.67 (s, −N=CMe−), 2.63 (dd, *J* 15 and 7 Hz) and 2.90 (dd, *J* 15 and 5 Hz) ($CHCH_2C$=N), 3.00 (s, NMe), 5.00 (dd, *J* 7 and 5 Hz, ArC*H*N), 6.14 ($CONH_2$), 7.30—7.70 (ArH). and 8.99 (N−NHCO); *m/e* 260 ($M^+$), 146 ($M^+$ − $CH_2CMe{:}N{\cdot}NHCONH_2$) (Found: C, 59.7; H, 6.1; N, 21.3. $C_{13}H_{16}N_4O_2$ requires C, 60.0; H, 6.2; N, 21.5%).

*Reaction of* 6-*Bromobenzocyclohepten-5-one* (1) *with Ethylamine.*—To ethylamine (300 ml) cooled to *ca.* −10 °C in acetone–solid carbon dioxide, the bromo-ketone (1) (15 g) was added in small portions with stirring. The solution was allowed to reflux with a solid carbon dioxide trap for 20 h. Ethylamine was then distilled off *in vacuo*. A solution of the residue in methylene chloride was filtered through a column of silica gel (100 g). Evaporation and crystallization from ethyl acetate gave 7-*ethylaminobenzocyclohepten*-5-*one* (2b) (5.8 g, 46%) as yellow plates, m.p. 170—171 °C; $\lambda_{max.}$ 275, 284, and 346 nm (ε 41 300, 44 360, and 9 100); $\nu_{max.}$ 3 200, 1 660, 1 600, and 1 585 $cm^{-1}$; δ (see also Table 1) 1.26 (t, *J* 7 Hz, *Me*$CH_2$), 3.20 (m, MeC*H*$_2$), 5.08 (NH), 7.45—8.45 (ArH), and 8.65 (4-H) (Found: C, 78.3; H, 6.3; N, 7.1. $C_{13}H_{13}NO$ requires C, 78.4; H, 6.6; N, 7.0%).

The mother-liquors from the preparation of (2b) provided a second, less-polar product (700 mg, 5%), following preparative t.l.c. on fluorescent silica-gel plates (solvent system hexane–ethyl acetate, 1 : 1), which proved to be 3-*acetonyl*-2-*ethylisoindolin*-1-*one* (4b), m.p. 61—63 °C; $\lambda_{max.}$ 222, 229, and 278—279 nm (ε 10 000, 9 800, and 1 700); $\nu_{max.}$ 3 450, 1 710, 1 690, and 1 620 $cm^{-1}$; δ (see also Table 3) 2.21 (s, MeCO) and 7.43 (ArH); *m/e* 217 ($M^+$) and 160 ($M^+$ − $CH_2COMe$) (Found: C, 71.8; H, 7.0; N, 6.6. $C_{13}H_{15}NO_2$ requires C, 71.9; H, 7.0; N, 6.45%).

The third less-polar product was also isolated by t.l.c. (100 mg, 0.7%), to provide N-*ethyl*-6,9-*dihydro*-6,9-*iminobenzocyclohepten*-5-*one* (3b), m.p. 64—66 °C; $\lambda_{max.}$ 218 and 262 nm (ε 17 800 and 3 860); $\nu_{max.}$ 3 450, 1 695, and 1 610 $cm^{-1}$; δ (see also Table 2) 1.12 (t, *J* 7 Hz, *Me*$CH_2$), 2.67 (q, *J* 7 Hz, MeC*H*$_2$N), 7.0—7.5 (1-, 2-, and 3-H), and 7.86 (dd, *J* 6.5 and 2.5 Hz, 4-H); *m/e* 199 ($M^+$), 170 ($M^+$ − $C_2H_5$), 156 ($M^+$ − $NC_2H_5$), 142 ($M^+$ − $C_2H_5$ − CO), and 128 ($M^+$ − $NC_2H_5$ − CO).

*Semicarbazone* (5b) *of the Methyl Ketone* (4b).—A solution of (4b) in ethanol was allowed to reflux for 5 min with an excess of semicarbazide hydrochloride and sodium acetate. Recrystallization from ethanol–water provided an analytical sample of the *semicarbazone* (5b), m.p. 195—197 °C; $\lambda_{max.}$ 229 and 279 nm (ε 18 600 and 1 600); $\nu_{max.}$ 3 500, 3 200, 1 700, 1 660, and 1 590 $cm^{-1}$; δ [100 MHz; $(CD_3)SO$] 1.13 (t, *J* 7 Hz, *Me*$CH_2$N), 1.69 (s, −N=CMe−), 2.58 (dd, *J* 15 and 7 Hz) and 2.90 (dd, *J* 15 and 5 Hz) (−$CHCH_2C$=N), 3.24 (dd, *J* 13 and *J* 7 Hz) and 3.80 (dd, *J* 13 and 7 Hz, NC*H*$_2$Me), 5.12 (dd, *J* 7 and 5 Hz, ArC*H*N), 6.13 ($CONH_2$), 7.54 (ArH), and 8.96 (N−NHCO); *m/e* 274 ($M^+$), 160 ($M^+$ − $CH_2CMe{:}N{\cdot}NHCONH_2$), and 132 ($M^+$ − $CH_2CMe{:}N{\cdot}NHCONH_2$ − $C_2H_4$) (Found: C, 61.2; H, 6.6. $C_{14}H_{18}N_4O_2$ requires C, 61.3; H, 6.6%).

*Reaction of* 6-*Bromobenzocyclohepten-5-one* (1) *with Isopropylamine.*—The bromo-ketone (1) (1.1 g) was added in small portions with stirring to isopropylamine (250 ml) kept at −10 °C. The temperature was then allowed to increase to 0 °C and the solution was kept for 20 h at this temperature. The isopropylamine was removed at 40 °C *in vacuo* and the residue was taken up in dilute aqueous hydrochloric acid. The solution was extracted with ether and then treated with 10% sodium hydroxide. The basic material which precipitated was extracted with ethyl acetate. The ethyl acetate was removed *in vacuo* and the residue chromatographed on preparative silica-gel plates using ethyl acetate–hexane (4 : 1) as eluant.

The less-polar amorphous material obtained was N-*isopropyl*-6,9-*dihydro*-6,9-*iminobenzocyclohepten*-5-*one* (3c) (300 mg, 30% yield); $\lambda_{max.}$ 219 and 264 nm (ε 20 400 and 4 600); $\nu_{max.}$ 1 700 and 1 600 $cm^{-1}$; δ (see also Table 2) 1.06 and 1.15 (each d, *J* 6 Hz, NCH*Me*$_2$), 2.89 (s, *J* Hz, NC*H*Me$_2$), 7.00—8.40 (ArH); *m/e* 213 ($M^+$), 198 ($M^+$ − 15), 184 ($M^+$ − CO + H), and 170 ($M^+$ − CO − $CH_3$). Its *picrate* had m.p. 181—182 °C (from methanol); δ 1.55 and 1.65 (each d, *J* 6 Hz, NCH*Me*$_2$), 3.50 (s, OH), 5.07 and 5.53 (each d, *J* 3 Hz, *CH*NC*H*), 6.30 and 6.90 (each dd, *J* 3 and 6 Hz, vinylic-H), and 7.00—8.40 (ArH); *m/e* 213 ($M^+$), 198 ($M^+$ − $CH_3$), 185 ($M^+$ − CO), and 170 ($M^+$ − CO − $CH_3$) (Found: C, 54.2; H, 4.3; N, 12.6. $C_{14}H_{15}NO{\cdot}C_6H_3N_3O_7$ requires C, 54.3; H, 4.1; N, 12.7%).

The more-polar product, isolated using ethyl acetate–hexane (1 : 1) as eluant in 65% yield (0.65 g), was *7-isopropylaminobenzocyclohepten-5-one* (2c) which gave plates from ethyl acetate, m.p. 119—120 °C; $\lambda_{max.}$ 210, 276, 285, and 346 nm (ε 12 300, 28 200, 30 900, and 6 600); $\nu_{max.}$ 1 660, 1 600 (sh), 1 575, 1 535, and 1 475 $cm^{-1}$; δ (see also Table 1) 1.20 (d, *J* 6 Hz, $NCHMe_2$), 3.65 (m, NHC*H*), 5.25 (m, N*H*), 7.60—7.65 (1-, 2-, and 3-H), and 8.58 (m, 4-H); *m/e* 213 ($M^+$), 198 ($M^+ - CH_3$), 185 ($M^+ - CO$), and 170 ($M^+ - CO - CH_3$) (Found: C, 78.65; H, 6.9; N, 6.4. $C_{14}H_{15}NO$ requires C, 78.8; H, 7.1; N, 6.6%).

*7-Aminobenzocyclohepten-5-one* (2e).—A solution of compound (1) (4 g) in anhydrous tetrahydrofuran (500 ml) was slowly added to liquid ammonia (2.5 l) at −33 °C with stirring. After 1 h, the ammonia was evaporated off and the tetrahydrofuran removed *in vacuo*. The residue (2.5 g) was recrystallized from methanol to give the pure *amine* (2e) (1.0 g, 34% yield), m.p. 242 °C (decomp.); $\lambda_{max.}$ 262, 272, 280, and 332 nm (ε 25 700, 32 360, 35 480, and 7 250); $\nu_{max.}$ 3 300—3 100, 1 660, 1 580, and 1 560 $cm^{-1}$; δ (see also Table 1) 7.08—8.00 (m, 1-, 2-, and 3-H) and 8.55 (m, 4-H) (Found: C, 77.4; H, 5.6; N, 7.8. $C_{11}H_9ON$ requires C, 77.2; H, 5.3; N, 8.2%).

*7-Amino-2-chlorobenzocyclohepten-5-one* (6a).—A solution of 6-bromo-2-chlorobenzocyclohepten-5-one (2 g) in anhydrous tetrahydrofuran (100 ml) was slowly added to anhydrous liquid ammonia (1.5 l) with stirring. The ammonia was allowed to evaporate off (stirring was continued during most of this period) and the remaining solvent eliminated *in vacuo*. The crude material crystallized from methanol (700 mg; m.p. 214—220 °C) and was recrystallized from the same solvent to give the *chloro-amine* (6a) (500 mg, 46% yield), m.p. 252—255 °C (decomp.); $\lambda_{max.}$ 214.5, 261, 272.5, and 346 nm (ε 15 140, 44 670, 38 550, and 7 330); $\nu_{max.}$ 3 400, 1 655, 1 600, 1 575, 1 555, and 1 510 $cm^{-1}$; δ [$(CD_3)_2$-SO] 6.07 (d, *J* 2.5 Hz, 6-H), 6.52 (dd, *J* 12 and 2.5 Hz, 8-H), 6.75 ($NH_2$), 7.18 (d, *J* 12 Hz, 9-H), 7.53 (dd, *J* 8 and 2 Hz, 3-H), 7.72 (d, *J* 2 Hz, 1-H), and 8.30 (d, *J* 8 Hz, 4-H); *m/e* 205 ($M^+$) and 177 ($M^+ - CO$) (Found: C, 64.3; H, 4.1; Cl, 17.11; N, 6.5. $C_{11}H_8ClNO$ requires C, 64.2; H, 3.9; Cl, 17.25; N, 6.8%).

The 7-alkylaminobenzocycloheptenones (2d, f—i) and (6b) were obtained by the method already described for the isopropyl derivative (2c). Their physical properties and yields are as follows.

7-(2-Hydroxyethylamino)benzocyclohepten-5-one (2d) had m.p. 199—200 °C (from MeOH–EtOAc); $\lambda_{max.}$ 274, 282—284, and 342 nm (ε 42 270, 42 660, and 8 900); $\nu_{max.}$ 3 200, 3 000, 1 655, and 1 545 $cm^{-1}$; δ (see also Table 1) 1.70 (m, OH), 3.1 (m, $CH_2N$), 3.55 (m, $CH_2O$), 4.70 (m, NH), 7.4—7.8 (1-, 2-, and 3-H), and 8.30 (m, 4-H); *m/e* 215 ($M^+$), 184 ($M^+ - CH_2OH$), 156 ($M^+ - CH_2OH - CO$), and 127 ($M^+ - NHCH_2CH_2OH$–CO); yield, 5%. The corresponding imino-derivative (3d) was obtained by the method described for (3a), and was amorphous, $\lambda_{max.}$ 218 and 260—262 nm (ε 18 800 and 4 150); $\nu_{max.}$ 3 450, 1 700, and 1 620 $cm^{-1}$; δ (see also Table 2) 2.60 (OH), 2.81 (t, *J* 5.5 Hz, $CH_2N$), 3.70 (t, *J* 5.5 Hz, $CH_2O$), 7.0—7.6 (m, 1-, 2-, and 3-H), and 7.93 (dd, *J* 6 and 3 Hz, 4-H); yield, 58%.

*7-Dimethylaminobenzocyclohepten-5-one* (2f) formed pale yellow crystals from ethyl acetate, m.p. 114.5—115.5 °C; $\lambda_{max.}$ 212—214, 282—284, 290, and 358 nm (ε 16 440, 35 480, 36 300, and 10 000); $\nu_{max.}$ 1 645, 1 600, 1 570, and 1 540 $cm^{-1}$; δ (see also Table 1) 3.05 ($NMe_2$), 7.40—7.60 (m, 1-, 2-, and 3-H), and 8.50 (m, 4-H); *m/e* 199 ($M^+$) and 171 ($M^+ - CO$); yield, 54% (Found: C, 78.6; H, 6.7; N, 6.9. $C_{13}H_{13}NO$ requires C, 78.4; H, 6.6; N, 7.0%).

*7-Morpholinobenzocyclohepten-5-one* (2g) had m.p. 147—148 °C (from EtOAc); $\lambda_{max.}$ 286 and 346—348 nm (ε 30 200 and 8 400); $\nu_{max.}$ 1 635 and 1 540 $cm^{-1}$; δ (see also Table 1) 3.25 (t, *J* 5 Hz, $CH_2N$), 3.80 (t, *J* 5 Hz, $CH_2O$), 7.33—7.67 (m, 1-, 2-, and 3-H), and 8.40 (m, 4-H); *m/e* 241 ($M^+$), 213 ($M^+ - CO$), 155 ($M^+ - C_4H_8NO$), and 127 ($M^+ - C_4H_8$-NO − CO); yield, 40% (Found: C, 74.9; H, 6.3; N, 5.8. $C_{15}H_{15}NO_2$ requires C, 74.5; H, 6.25; N, 5.8%).

*2-Methoxy-7-methylaminobenzocyclohepten-5-one* (6b) had m.p. 179—180 °C (from $Et_2O$); $\lambda_{max.}$ 222, 274, and 338—342 nm (ε 12 300, 53 700, and 8 700); $\nu_{max.}$ 3 220, 1 660, and 1 610 $cm^{-1}$; δ (HA-100 instrument) 2.84 (d, *J* 5 Hz, NMe), 3.87 (s, OMe), 5.05 (m, NH), 5.99 (d, *J* 2.5 Hz, 6-H), 6.25 (dd, *J* 2.5 and 12 Hz, 8-H), 6.89 (d, *J* 2.5 Hz, 1-H), 6.96 (d, *J* 12 Hz, 9-H), 7.11 (dd, *J* 2.5 and 9 Hz, 3-H), 8.57 (d, *J* 9 Hz, 4-H); *m/e* 215 ($M^+$), 187 ($M^+ - CO$) and 172 ($M^+ - CO$-$CH_3$); yield, 50% (Found: C, 72.4; H, 6.1; N, 6.4. $C_{13}H_{13}NO_2$ requires C, 72.5; H, 6.1; N, 6.5%).

7-(β-Dimethylaminoethyl)aminobenzocyclohepten-5-ene (2h) had m.p. 116—117 °C (from $Et_2O$); $\lambda_{max.}$ 276, 284, and 342 nm (ε 40 700, 42 700, and 9 100); $\nu_{max.}$ 3 550—3 300, 1 655, 1 545, and 1 510 $cm^{-1}$; δ (see also Table 1) 2.22 (s, $NMe_2$), 2.53 (t, *J* 6 Hz, $NCH_2CH_2NMe_2$), 3.14 (q, *J* 6 Hz, $NCH_2CH_2NMe_2$), 5.33 (m, NH), 7.40—7.60 (m, 1-, 2-, and 3-H), 8.58 (m, 4-H); *m/e* 242 ($M^+$), 184 ($M^+ - 58$), 155 ($M^+ - NHCH_2CH_2NMe_2$), 127 ($M^+ - NHCH_2CH_2NMe_2 -$ CO), and 58 ($CH_2NMe_2$), yield 30%.

The hydrochloride of (2h) had m.p. 218—225 °C (decomp.) (from MeOH); $\lambda_{max.}$ 273, 281, and 334 nm (ε 38 900, 39 800, and 7 400); $\nu_{max.}$ 3 550—3 350, 1 635, and 1 545 $cm^{-1}$; δ ($D_2O$ soln.) 2.88 (s, $NMe_2$), 3.20—3.80 (m, $NH[CH_2]_2$-N), 6.53 (dd, *J* 2.5 and 12 Hz, 8-H), 7.35 (d, *J* 12 Hz, 9-H), and 7.45—8.30 (m, 1-, 2-, 3-, 4-, and 6-H).

7-(3-Dimethylaminopropyl)aminobenzocyclohepten-5-one (2i) had m.p. 117—118 °C (from $CH_2Cl_2$–$Et_2O$ or EtOAc); $\lambda_{max.}$ 276, 284, and 342 nm (ε 39 800, 42 700, and 8 900); $\nu_{max.}$ 3 500, 3 300, 1 655, 1 555, and 1 510 $cm^{-1}$; δ (see also Table 1), 1.75 (m, *J* 6 Hz, $NHCH_2CH_2CH_2N$), 2.22 (s, $NMe_2$), 2.41 (t, *J* 6 Hz, $Me_2NCH_2CH_2CH_2NH$), 3.20 (q, *J* 6 Hz, N*H*), 7.40—7.60 (m, 1-, 2-, and 3-H), and 8.59 (4-H); *m/e* 256 ($M^+$), 198 ($M^+ - 58$), 185 ($M^+ - 72 +$ H), 72 ($CH_2CH_2NMe_2$), and 58 ($CH_2NMe_2$); yield, 33%.

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