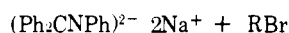


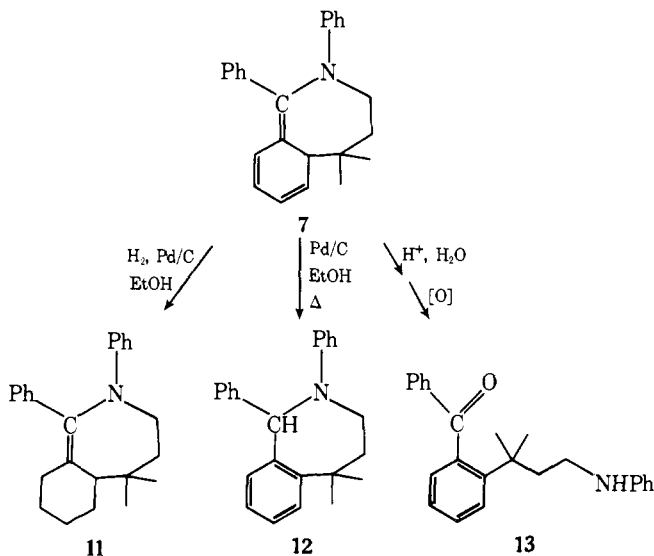
Table I. Alkylation of **1** with Tertiary Halides^a

R	% yield of	
	2	3
<i>t</i> -Bu	35	35
1 -Ad ^b	23	43
1 -Bicyclo ^c	27	53
2-Ad ^b	55	27
<i>t</i> -BuCH ₂	71	11
<i>t</i> -BuCH ₂ ^d	66	22

^a One mole of alkyl halide. Reaction conditions, 1 h at -78°C , 3 h at 20°C , tetrahydrofuran as solvent. ^b Ad represents the adamantyl group. ^c 1-Bicyclo[2.2.2]octyl group. ^d Neopentyl iodide.

amounts relatively insensitive to reaction conditions (see Table III, Experimental Section) except for the ratio of **8** to **9**.

The structure of **6** follows from its spectral data; in particular the chemical shift of the NCH_2 triplet (3.92 δ) agrees with that of the corresponding group of 1,2,2-triphenylpyrrolidine¹⁴ (3.79 δ). Similarly compound **7** showed a N-CH_2 multiplet at 3.79 δ and the diallylic proton at 3.45 δ was shown to be coupled to the vinylic protons at 5.8 δ . The chemical transformations shown in Scheme II further support the assigned

Scheme II. Chemical Transformation of **7**

structure. Hydrogenation of two double bonds of **7** was readily effected to give **11** while aromatization to **12** occurred on heating with palladium. Hydrolysis of **7** (an enamine) was effected under acidic conditions to form the substituted benzophenone **13**.

Compound **10** was formed in such small quantities that an analytically pure sample could not be isolated from the reaction mixture. It was identified by comparison of its spectral properties with those of an authentic sample prepared by alkylating **1** with 1-bromo-3-methyl-2-butene.

Compounds **8** and **9** were interrelated by hydrogenation of the former to the latter. Their NMR spectra clearly established the indan-related structures but left unresolved the question of the positional substitution. Hydrolysis of **8** to its corresponding benzophenone, 5-benzoyl-1,1-dimethylindan, was

effected and further structural studies done on the ketone. Treatment of the ketone with $\text{Eu}(\text{fod})_3$ demonstrated that four protons ortho to the carbonyl were present and established that the five-membered ring was fused at positions meta and para to the carbonyl. Coupling was demonstrated to exist between the isolated ortho proton (a broad singlet in the 220-MHz spectrum) and the broadened triplet due to the benzylic methylene group. This strongly suggested the substitution pattern shown in **8** with the quaternary carbon attached para to the carbonyl (or C=N) rather than the isomeric compound with the quaternary carbon meta. Final confirmation of the structure was accomplished by the synthesis of 5-benzoyl-1,1-dimethylindan and of **9** beginning with the known 1,1-dimethyl-5-nitroindan.¹⁵

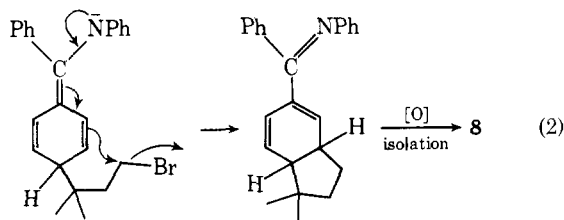
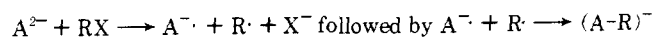
The results of this last alkylation experiment demonstrates a marked preference by **1** for alkylation by tertiary halides over primary halides. Assuming all of **10** arose by initial reaction of the primary halide site (dehydrohalogenation of the dihalide prior to alkylation cannot be excluded), the results summarized in Table III show a minimum relative reactivity of tertiary to primary of 6 to 1.

Discussion

In summary, the results demonstrate that dianion **1** can be alkylated by tertiary halides, by bridge-head halides, and by sterically hindered primary and secondary halides. The relative rate of alkylation of **1** by tertiary halides exceeds by at least a factor of 6 the rate of alkylation of the dianion by primary halides. On this basis, a bimolecular nucleophilic substitution mechanism can be discarded.

A unimolecular mechanism is considered unlikely as well. First, the reaction medium, tetrahydrofuran, is a poor solvent for promoting such dissociative processes.¹⁶ Second, four of the alkyl bromides examined (*tert*-butyl, 1- and 2-bromoadamantane, and 1-bromobicyclo[2.2.2]octane) show a range of reactivity of 10^6 in their solvolysis reactions^{10,11} (*tert*-butyl bromide being the most reactive). Under the mild reaction conditions employed here, significant differences in the extent of alkylation would be expected but none were seen (Table I) and all four reagents instantly discolored the red-violet solution of **1** at -78°C .

A SET mechanism⁴ satisfactorily accommodates the observations made in this study. On the basis of half-wave reduction potentials,^{17,18} the dianion **1** ($E_{1/2}^{17} -2.83$) is capable of reducing alkyl bromides ($E_{1/2}^{18} -2.5 \pm 0.1$) and iodides ($E_{1/2}^{18} -1.6 \pm 0.1$). Alkyl chlorides are borderline cases with *tert*-butyl chloride ($E_{1/2}^{18} -2.60$) reacting but neopentyl chloride ($E_{1/2}^{18} -2.83$) not reacting under the reaction conditions used. Electron transfer from dianion **1** to the alkyl halide leads to rapid dissociation of the latter thus forming a radical-radical anion pair. The close spatial proximity of these intermediates results in efficient capture of the alkyl radical by the radical anion to form a monoalkylated monoanion. Subsequent reaction of this last anion is by conventional nucleophilic routes. Thus with 1,3-dihalo-3-methylbutane, dialkylation can occur, one such reaction being shown in eq 2.



Coupling of the radical-radical anion pair can be expected to be influenced by two factors, the spin-density distribution

in the radical anion and the steric bulk of the alkyl radical itself. In the case of the radical anion, spin density¹⁹ is highest at the benzydrylic carbon and, to a lesser degree, at the para and the ortho positions. The greater the steric size of the alkyl radical, the less likely it is that alkylation will occur at the benzydrylic site. This effect is clearly seen in the results of Table I where benzydrylic alkylation decreases in the order neopentyl > 2-adamantyl > *tert*-butyl²¹ > 1-adamantyl \approx 1-bicyclo[2.2.2]octyl.

Considering the size of the alkyl groups used in this study, it is not surprising that ortho-substituted products were not observed. The exception to this is the alkylation products formed from 1,3-dihalo-3-methylbutane where a substantial amount of the ortho (tertiary-substituted) derivative **7** is formed. This suggests some orientation of the radical-radical anion pair during coupling. A possible explanation might be a dipole-dipole interaction between the amine anion-cation pair and the primary carbon-bromine dipole which positions the tertiary radical so as to favor ortho substitution.

Escape of members of the radical-radical anion pair from the solvent cage must occur to some extent. The radical anion disproportionates²² and leads to benzophenone anil and *N*-benzydrylaniline as products while the alkyl radical would form the hydrocarbon and the alkyl dimer.⁴ The former, because of their volatility, would escape detection by the procedures used here. The latter, as already mentioned, were detected in three cases.

The product mixture formed via an SET mechanism might be expected to be insensitive to the halide leaving group since this is not involved in the product-forming step. The results summarized in Table II (Experimental Section) for *tert*-butyl halides show that any effect is less than the experimental error of our analytical method. However, a cation effect can be seen in the decrease in the extent of alkylation when lithium is the cation.

Do primary alkyl halides react by a SET mechanism? The failure of neopentyl chloride to react can be rationalized by its inability to be reduced²³ by the dianion **1**. The successful alkylations with neopentyl bromide and iodide suggest the SET mechanism. We attempted to resolve this question using 5-hexenyl halides as has Garst in related studies with the radical anions from naphthalene⁴ and benzophenone.⁵ Since the 5-hexenyl radical cyclizes to the cyclopentylmethyl radical with a rate constant²⁴ of 10^5 s^{-1} , products containing the cyclized alkyl group might be expected. However, none were observed.

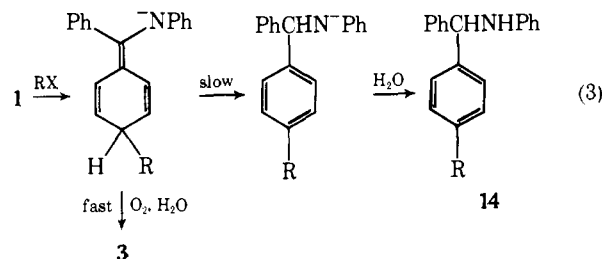
This lack of formation of cyclized products can be explained by assuming a rate of coupling of the radical-radical anion pair far in excess of the rate of cyclization of the 5-hexenyl radical. This is not unreasonable in the proposed SET mechanism since the two reactive intermediates are formed essentially simultaneously and in close spatial proximity.

More difficult to explain is the reaction of **1** with 1-bromo-3-methyl-2-butene. By an SET mechanism, a delocalized allyl radical should be formed. While **10**, the thermodynamically more stable alkene, would be the expected major product,²⁵ some of the isomeric alkene can also be expected. This was not the case. Indeed, the formation of a single product is reminiscent of Magid's³⁶ observation that phenyllithium and either 1-chloro-3-methyl-2-butene or 3-chloro-3-methyl-1-butene produce the same product, 1-phenyl-3-methyl-2-butene.

At the moment, we cannot exclude the possibility that two mechanistic pathways are available for the reaction of **1** with primary halides, bimolecular nucleophilic substitution and SET. In the case of chlorides, unhindered alkyl halides and allyl halides the former mechanism may predominate. When nucleophilic substitution becomes difficult for steric reasons (e.g., neopentyl halides) then the SET mechanism becomes the dominant component of the reaction as it is with the secondary

and tertiary alkyl bromides investigated in the present study.

One aspect of these alkylation reactions is still being examined—the factors controlling the oxidation state of the ring-substituted products. In alkylations with *tert*-butyl halides, this ring-alkylated product was isolated as a mixture of the anil **14** whenever the reaction time at 20 °C greatly exceeded the standard 3 h. It is our working hypothesis that the initial ring-alkylation produces a methylenecyclohexadiene derivative which is rapidly oxidized during isolation to the anil **3** (eq 3). However, if protected from oxidation, the



methylenecyclohexadiene undergoes a thermal [1.5] sigmatropic rearrangement which leads eventually to the amine **14**. More detailed studies are in progress.

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian T-60 or a Perkin-Elmer R12B spectrometer. Certain spectra (as specified) were recorded on a Varian HR-220 spectrometer at the Canadian 220 MHz NMR Centre. Except where specified, CDCl_3 solutions were used; all line positions are reported in δ units relative to tetramethylsilane as internal standard. Infrared (IR) spectra were recorded on a Beckman IR10 spectrometer and ultraviolet (UV) spectra on a Unicam SP800B spectrophotometer. Mass spectra were measured on an AEI MS-30 double beam, double focusing spectrometer at 70 eV with perfluorokerosene in the reference beam. Elemental analyses were performed by MHW Laboratories, Garden City, Mich. Thin layer chromatography (TLC) was performed on Eastman 13181 Silica Gel or 13252 Alumina Chromagram sheets.

General Procedure. All reductive metalations and reactions of dianion **1** were performed under nitrogen purified by bubbling through a refluxing solution of sodium benzophenone ketyl in xylene. Tetrahydrofuran (THF) was dried and purified by distilling from lithium aluminum hydride, storing under nitrogen over LiAlH_4 , and distilling it immediately prior to use.

Benzophenone anil (0.01 mol, 2.57 g) was placed in a nitrogen-flushed modified Schlenk tube²⁶ and $100 \pm 10 \text{ mL}$ of THF distilled in. An excess of freshly cut alkali metal was added (drybox) and the mixture shaken overnight to ensure that the reaction to form the dianion was complete.³⁴ The solution was then drained from the excess metal into a nitrogen-filled flask, cooled to $-78 \text{ }^\circ\text{C}$ and, with vigorous stirring, the alkyl halide injected through a septum. Unless otherwise noted, the cold bath was removed after 1 h, the solution warmed to room temperature for 3 h, and the reaction quenched by injection of excess water. The products were isolated by extracting with ether, drying the extract (MgSO_4), and removing the solvent under vacuum.

Of the alkylating agents, 1- and 2-bromoadamantane (Aldrich) were used as received. The other alkyl halides were distilled immediately prior to use. The neopentyl halides,²⁷ 1-halobicyclo[2.2.2]octane,²⁸ 5-hexenyl halides,²⁹ and 1,3-dihalo-3-methylbutanes³⁰ were prepared by literature procedures.

Since the alkylation product **2** was thermally unstable, column chromatography was utilized for analyses. The reaction mixture was chromatographed on Silica Gel 60 (E. Merck AG) using 3:1 petroleum ether (60–110 °C):benzene graded through benzene to 2:1 benzene:DEE. Each fraction was analyzed by NMR spectroscopy to determine the composition and from these data the composition of the reaction mixture was obtained. Appropriate fractions were combined in order to obtain analytical samples of the individual components. The order of elution was **2**, *N*-benzydrylaniline, **3**, benzophenone anil. In two

cases, the alkylation mixtures formed with the neopentyl halides and with 2-bromoadamantane, solvolysis of the corresponding **2** and partial hydrolysis of the anils **3** to ketones occurred. Chromatography on neutral aluminum oxide (E. Merck AG, activity III) was used to minimize these problems. Analytical results are summarized in Tables I–III. The individual products are described below.

Reaction of 1 with 5-Hexenyl Halides. Preparation of 7-Anilino-7,7-diphenyl-1-heptene. Recrystallization from absolute ethanol gave an analytical sample, mp 54–56 °C; IR (CCl₄) 3410 (NH), 1645 (C=C), 1600, 1500, 1315, 910, 695 cm⁻¹; NMR 1.3 (m, CH₂, 4), 1.9 (m, CH₂, 2), 2.5 (m, CH₂, 2), 4.33 (s, NH, 1), 4.9 (m, =CH₂, 2), 5.7 (broad m, =CH, 1), 6.3–7.7 (m, Ph, 15). Anal. Calcd. for C₂₅H₂₇N: C, 87.93; H, 7.97; N, 4.10. Found: C, 87.93; H, 8.09; N, 3.89.

Yields were 79, 97, and 97% using hexenyl chloride, bromide, and iodide, respectively.

Reaction of 1 with 1-Bromo-3-methyl-2-butene.³¹ Preparation of 5-Anilino-5,5-diphenyl-2-methyl-2-pentene. The title compound was obtained in 92% yield. Two recrystallizations from ethanol gave an analytical sample, mp 73–74.5 °C, IR (CCl₄) 3420 (NH), 1600, 1500, 1450, 1315, 695 cm⁻¹; NMR (CCl₄) 1.36 (s, CH₃, 3), 1.56 (s, CH₃, 3), 3.19 (d, CH₂, 2), 4.54 (broad s, NH, 1), 4.93 (broad t, =CH, 1), 6.2–7.7 (m, Ph, 15). Anal. Calcd. for C₂₄H₂₅N: C, 88.01; H, 7.71; N, 4.28. Found: C, 88.31; N, 7.60; H, 4.18.

Reaction of 1 with *tert*-Butyl Halides. Numerous reactions were performed with the chloride, bromide, and iodide and with different counterions for **1** (Li, Na, and K). Under the standard reaction conditions, the alkylation products were **2** and **3** (R = *t*-Bu). If the reaction time at 20 °C (prior to quenching with water) was extended, an increasing amount of the amine **14** (R = *t*-Bu) was formed at the expense of **3**. The amine **14** eluted after **2** (R = *t*-Bu) and before *N*-benzhydrylaniline.

Recrystallization from methanol gave an analytical sample of **2** (R = *t*-Bu), mp 117.5–118.5 °C; IR (CCl₄) 3475 (NH), 1600, 1500, 1315, 700, 690 cm⁻¹; NMR (CCl₄) 1.01 (s, *t*-Bu, 9), 4.63 (s, NH, 1), 5.8–7.9 (m, Ph, 15); mass spectrum, *m/e* (rel. intensity) 315 (0.06, M⁺), 259 (22), 258 (100), 180 (26). Anal. Calcd. for C₂₃H₂₅N: C, 87.57; H, 7.99; N, 4.44. Found: C, 87.30; H, 8.04; N, 4.37.

Recrystallization from petroleum ether (60–80 °C) gave an analytical sample of **14** (R = *t*-Bu), mp 118–119 °C; IR (CCl₄) 3440 (NH), 1600, 1505, 1315, 1270, 700, 690 cm⁻¹; NMR (CCl₄) 1.25 (s, *t*-Bu, 9), 3.90 (s, NH, 1), 5.28 (s, CH, 1), 6.2–7.3 (m, aromatic, 14); mass spectrum, *m/e* (rel. intensity) 315 (8, M⁺), 224 (21), 223 (100). Anal. Calcd. for C₂₃H₂₅N: C, 87.57; H, 7.99; N, 4.44. Found: C, 87.62; H, 8.09; N, 4.54.

The analytical sample of **3** (R = *t*-Bu), recrystallized from 60–80 °C petroleum ether, had mp 75–76 °C; IR (CCl₄) 1620 (C=N), 1595, 1485, 1315, 1295, 960, 835, 690 cm⁻¹; NMR (CCl₄) 1.29, 1.33 (s, *t*-Bu, 9) (exhibits syn-anti isomerism), 6.4–7.9 (m, aromatic, 14); mass spectrum, *m/e* (rel. intensity) 314 (26, M + 1), 313 (100, M⁺), 256 (21), 236 (21), 180 (19). Anal. Calcd. for C₂₃H₂₃N: C, 88.13; H, 7.40; N, 4.47. Found: C, 88.03; H, 7.28; N, 4.35.

An authentic sample of **3** (R = *t*-Bu) was prepared³² from *p*-*tert*-butylbenzophenone³³ and aniline and reduced to amine **14** (R = *t*-Bu) with LiAlH₄. Identity to the isolated compounds was confirmed by spectral data and by mixture melting point.

Table II summarizes the alkylation results obtained under various reaction conditions. Since reaction times exceeded 4 h in some experiments, mixtures of anil **3** and amine **14** (R = *t*-Bu) were obtained—only total ring alkylation is reported.

Reaction of 1 with 1-Bromoadamantane. The analytical sample of **2** (R = 1-Ad) (from EtOH) had mp 185 °C (dec); IR (CCl₄) 3470 (NH), 2900, 1600, 1500, 1310, 690 cm⁻¹; NMR 1.4–1.8 (m, CH₂, 12), 1.96 (broad s, bridgehead H, 3), 4.35 (broad s, NH, 1), 5.93–8.05 (m, aromatic, 15). Anal. Calcd. for C₂₉H₃₁N: C, 88.50; H, 7.94; N, 3.56. Found: C, 88.36; H, 8.10; N, 3.45.

Recrystallization of **3** (R = 1-Ad) twice from ethanol gave the analytical sample, mp 163–164 °C; IR (CCl₄) 2900, 1620 (C=N), 1600, 1450, 1315, 1300, 960, 840 cm⁻¹; NMR 1.5–2.3 (m, aliphatic, 15), 6.6–7.9 (m, aromatic, 14). Anal. Calcd. for C₂₉H₂₉N: C, 88.96; H, 7.46; N, 3.58. Found: C, 89.18; H, 7.44; N, 3.65.

Reaction of 1 with 1-Bromobicyclo[2.2.2]octane. The crude **2** (R = bicyclo) was recrystallized twice from petroleum ether (30–60 °C). An analytical sample had mp 152–153 °C; IR (CCl₄) 3470 (NH), 2900, 1600, 1500, 1315, 695 cm⁻¹; NMR 1.54 (broad s, aliphatic, 13), 3.63 (broad s, NH, 1), 5.9–8.0 (m, aromatic, 15). Anal. Calcd. for

Table II. Alkylation of **1** with *tert*-Butyl Halides

Cation of 1	<i>t</i> -BuX		% alkylation	
	X	Ratio ^a	Benzylic (2)	Para (3 + 14)
Na	Cl	1	29 ± 2 ^b	35 ± 7
		2	32 ± 2	29 ± 3
	Br	1	35 ± 2	35 ± 4
		2	35 ± 2	30 ± 4
Li	Cl	1	25 ^c	45
		2	27	42
	Br	1	15	25
		2	18	23
K	Cl	1	23	28
		2	30 ± 1	36 ± 2
	Br	1	25	50
		2	34	40

^a Mole ratio *t*-BuX/**1**. ^b Average of three experiments when error is indicated. ^c Single experiment when no error shown.

C₂₇H₂₉N: C, 88.23; H, 7.95; N, 3.81. Found: C, 88.47; H, 7.97; N, 3.85.

Two recrystallizations of **3** (R = bicyclo) from ethanol gave an analytical sample, mp 169–170 °C; IR (CCl₄) 2900, 1615 (C=N), 1595, 1480, 1315, 1295, 960, 835, 690 cm⁻¹; NMR 1.73 (m, aliphatic, 13), 6.6–7.9 (m, aromatic, 14). Anal. Calcd. for C₂₇H₂₇N: C, 88.72; H, 7.45; N, 3.83. Found: C, 88.52; H, 7.58; N, 3.78.

1-Chlorobicyclo[2.2.2]octane did not react under the standard conditions.

Reaction of 1 with 2-Bromoadamantane. Chromatography of the reaction mixture on alumina gave the following products: **2** (R = 2-Ad) mp (from ethanol) 144–145 °C; IR (CCl₄) 3500 (NH), 2900, 1600, 1500, 1445, 1310, 700 cm⁻¹; NMR 1.4–2.0 (m, aliphatic, 12), 2.12 (broad s, 2), 2.83 (s, 1), 4.39 (s, NH, 1), 6.1–7.7 (m, aromatic, 15). Anal. Calcd. for C₂₉H₃₁N: C, 88.50; H, 7.94; N, 3.56. Found: C, 88.59; H, 7.94; N, 3.35.

Treatment of a warm ethanol solution of this compound with a catalytic amount of concentrated HCl effected rapid and quantitative conversion to **5** (R₁, R₂ = 2-adamantylidene).

Compound **3** (R = 2-Ad) could not be obtained pure by recrystallization due to contamination by the ketone (hydrolysis product). A portion of this impure material was purified by preparative TLC on a 1000-μm plate of alumina, mp 141–143 °C; IR (CCl₄) 2900, 1610 (C=N), 1595, 1485, 1450, 1315, 1295, 960, 860 cm⁻¹; NMR 1.5–2.2 (m, aliphatic, 12), 2.49 (broad s, 2), 3.04 (broad s, 1), 6.6–8.0 (m, aromatic, 14). Anal. Calcd. for C₂₉H₂₉N: C, 88.96; H, 7.46; N, 3.58. Found: C, 88.99; H, 7.59; N, 3.45.

Chromatography of the reaction mixture on silica gel resulted in decomposition of **2** and hydrolysis of **3** with the formation of the following products, listed in order of elution:

The fractions containing **5** (R₁, R₂ = 2-adamantylidene) recrystallized twice from absolute ethanol, mp 104–105 °C; IR (CCl₄) 2900, 2840, 1600, 1490, 1440, 1090, 1065 cm⁻¹; NMR 1.7–2.2 (m, aliphatic, 12), 2.78 (broad s, 2), 7.22 (broad s, Ph, 10). Anal. Calcd. for C₂₃H₂₄: C, 91.93; H, 8.07. Found: C, 91.72; H, 8.20.

Ozonolysis converted **5** to benzophenone and 2-adamantanone which were identified by GC/MS and by their IR spectra.

The fraction containing **4** (R = 2-Ad) was recrystallized twice from absolute ethanol, mp 152–153 °C; IR (CCl₄) 3640 (OH), 2900, 1490, 1445, 1090, 1065, 1020, 680 cm⁻¹; NMR 1.3–2.6 (m, aliphatic, 15), 2.76 (s, OH, 1), 7.1–7.7 (m, aromatic, 10). Anal. Calcd. for C₂₃H₂₆O: C, 86.73; H, 8.24. Found: C, 86.67; H, 8.25.

The fractions containing *p*-(2-adamantyl)benzophenone were recrystallized twice from absolute ethanol, mp 116–117 °C; IR (CCl₄) 2900, 1660 (C=O), 1605, 1450, 1315, 1280, 935, 920, 855, 710, 700 cm⁻¹; NMR 1.4–2.1 (m, aliphatic, 12), 2.52 (broad s, 2), 3.08 (broad s, 1), 7.3–8.0 (m, Ph, 9). Anal. Calcd. for C₂₃H₂₄O: C, 87.30; H, 7.64. Found: C, 87.57; H, 7.80.

Reaction with Neopentyl Halides. Neopentyl chloride did not react under standard reaction conditions. From the reaction products obtained with neopentyl bromide or iodide, the following compounds were isolated by chromatography of the reaction mixture on alumina:

Table III. Reaction^a of **1** with 1,3-Dihalo-3-methylbutane

Metal	Halide	Product %				
		6	7	8	9	10
Li	Br	18	32	11	24	0
Na	Br	22	26	2	25	2
K	Br	21	16	2	24	11
Na	Cl	25	23	22	0	6

^a Reaction conditions were those specified above. Analyses were obtained from the ¹H NMR spectra of the individual chromatographic fractions.

2 (R = neopentyl), mp (from ethanol) 79–80 °C; IR (CCl₄) 3480 (NH), 2950, 1600, 1500, 1445, 1305, 1250, 1030, 700 cm⁻¹; NMR 0.75 (s, *t*-Bu, 9), 2.50 (s, CH₂, 2), 6.2–7.7 (m, aromatic, 15), 4.05 (broad s, NH, 1). Anal. Calcd. for C₂₄H₂₇N: C, 87.49; H, 8.26; N, 4.25. Found: C, 87.44; H, 8.50; N, 4.16.

The anil **3** (R = neopentyl) was not isolated in pure form due to contamination by the ketone (hydrolysis product). The following spectral data for the anil were obtained; IR (CCl₄) 2950, 1610 (C=N), 1485, 1364, 1315, 1220, 1140, 955, 850, 690 cm⁻¹; NMR 0.86, 0.95 (s's, *t*-Bu, 9), 2.45, 2.55 (s's, CH₂, 2) (compound exhibits syn-anti isomerism), 6.6–7.9 (m, aromatic, 14). This material was hydrolyzed to *p*-neopentylbenzophenone in aqueous acidic ethanol.

Chromatography of the reaction mixture on silica gel resulted in hydrolysis and decomposition of the preceding products and the following compounds are isolated (listed in order of elution).

Compound **5** (R₁ = H, R₂ = *t*-Bu), an oil, had the following spectral properties: IR (CCl₄) 3020, 2950, 1600, 1490, 1470, 1460, 1440, 1360, 1070, 1030, 880, 690 cm⁻¹; NMR 0.96 (s, *t*-Bu, 9), 6.11 (s, olefinic, 1), 7.13–7.40 (m, aromatic, 10). The identity of **5** was confirmed by hydrogenation (Pd/C) followed by nitration (H₂SO₄-HNO₃) to give the known 3,3-dimethyl-1,1-di(4-nitrophenyl)butane, mp 157–159 °C (reported³⁴ 156 °C).

Compound **4** (R = neopentyl) after recrystallization from hexane had mp 70.5–71.5 °C; IR (CCl₄) 3610 (OH), 2950, 1600, 1490, 1475, 1465, 1445, 1360, 1170, 1060, 1030, 985, 690 cm⁻¹; NMR (CDCl₃) 0.85 (s, *t*-C₄H₉, 9), 2.00 (s, OH, 1), 2.43 (s, CH₂, 2), 7.1–7.7 (m, aromatic, 10). Anal. Calcd. for C₁₈H₂₂O: C, 84.98; H, 8.72. Found: C, 84.87; H, 8.58.

Two recrystallizations of *p*-neopentylbenzophenone provided the analytical sample, mp 58.5–59.5 °C; IR (CCl₄) 2950, 1660 (C=O), 1600, 1300, 1270, 930, 915, 850, 690 cm⁻¹; NMR 0.94 (s, *t*-Bu, 9), 2.59 (s, CH₂, 2), 7.1–8.0 (m, aromatic, 9). Anal. Calcd. for C₁₈H₂₀O: C, 85.66; H, 8.00. Found: C, 85.58; H, 8.12.

Reaction of 1 with 1,3-Dibromo-3-methylbutane. This reaction was performed on twice the usual scale giving, as crude reaction product, 6.58 g of a bright yellow gum. Chromatography on alumina yielded the following products described below in order of their elution. The analytical data on several runs are summarized in Table III.

The first third (**7** could not be purified if significant amounts of **6** were present. Decomposition of **7** occurred if silica gel or silicic acid were used for chromatography.) of the bright yellow lead band containing **7** was recrystallized from ethanol. An analytical sample had mp 110 °C (dec) in air, mp 127–130 °C (tube sealed under nitrogen); IR (CCl₄) 2950, 1600, 1495, 1310, 1290, 1190, 1030, 685 cm⁻¹; NMR (220 MHz) 0.89 (s, CH₃, 3), 1.05 (s, CH₃, 3); NCH₂³ACH₂², A₂BB¹ pattern, 1.59 (d of t, H_B, J_{BB}¹ = 16 Hz, J_{AB} = 4 Hz), 2.00 (d of t, H_B¹, J_{AB}¹ = 7 Hz), 3.79 (d of d, H_A², 2); 3.45 (d, J = 5 Hz, allylic CH, 1), 5.83 (m, vinyl H, 2), 6.15 (m, vinyl H, 1), 6.51 (d, J = 10 Hz, vinyl H, 1), 6.58–7.30 (m, aromatic, 10); mass spectrum, *m/e* (rel. intensity) 327 (27, M⁺), 271 (46), 270 (100), 251 (21), 250 (78), 180 (32), 165 (36); UV (EtOH) λ_{max} (log ε) 252 (4.16), 308 (3.76), 385 nm (4.02). Anal. Calcd. for C₂₄H₂₅N: C, 88.01; H, 7.71; N, 4.28. Found: C, 88.00; H, 7.65; N, 4.46.

Fractions containing **6** were recrystallized twice from ethanol. An analytical sample had mp 116.5–117.5 °C; IR (CCl₄) 2950, 1600, 1505, 1485, 1330, 1155, 1040, 690 cm⁻¹; NMR 0.77 (s, CH₃, 6), 2.04 (t, J = 7 Hz, CH₂, 2), 3.92 (t, J = 7 Hz, CH₂, 2), 6.2–7.7 (m, aromatic, 15); mass spectrum, *m/e* (rel. intensity) 327 (8, M⁺), 271 (44), 270 (100), 250 (10), 195 (7), 180 (24), 165 (20). Anal. Calcd. for C₂₄H₂₅N: C, 88.01; H, 7.71; N, 4.28. Found: C, 88.32; H, 7.99; N, 4.07.

The fraction containing **9** was recrystallized from ethanol, mp

79–81 °C, mixture melting point with authentic material 80–82 °C; IR (CCl₄) 3440 (NH), 2960, 1600, 1505, 1430, 1315, 700, 690 cm⁻¹; NMR 1.22 (s, CH₃, 6), 1.85 (t, J = 7 Hz, CH₂, 2), 2.80 (t, J = 7 Hz, CH₂, 2), 4.11 (s, NH, 1), 5.40 (s, CH, 1), 6.3–7.5 (m, aromatic, 13). Anal. Calcd. for C₂₄H₂₅N: C, 88.01; H, 7.71; N, 4.28. Found: C, 88.01; H, 7.72; N, 4.20.

A fraction containing **9**, **10**, and *N*-benzhydrylaniline was rechromatographed on silica gel using cyclohexane:petroleum ether (60–80 °C) as eluent. This purified **10** had IR and NMR spectra identical with the synthetic material.

The anil **8** was obtained as an amorphous yellow solid by recrystallization from ethanol. Additional recrystallizations would not yield material giving a satisfactory analysis but spectral data were obtained: IR (CCl₄) 2960, 1615 (C=N), 1590, 1485, 1445, 1315, 900, 690 cm⁻¹; NMR 1.21, 1.30 (s's, CH₃, 6) (compound exhibits syn-anti isomerism), 1.95 (m, CH₂, 2), 2.85 (m, CH₂, 2), 6.6–7.9 (m, aromatic, 13); mass spectrum, *m/e* (rel. intensity) 325 (100, M⁺), 310 (18), 269 (24), 256 (12), 248 (37), 235 (47), 218 (18), 180 (72), 105 (43).

Hydrogenation of **8** (Pd/C) gave the amine **9**; mp (from ethanol) 78–80 °C, mixture melting point 79–81 °C.

Preparation of 5-Benzoyl-1,1-dimethylindan. The anil **8** (0.8 g) was refluxed for 12 h in 20 mL of ethanol containing 10% water and 10 drops of concentrated HCl. After extracting from ether, washing with dilute aqueous HCl, saturated NaHCO₃ solution, water, and drying (MgSO₄) the solvent was evaporated. Chromatography of the residue on silica gel (eluent, benzene) separated the impurity (benzophenone) and gave the title ketone as a colorless oil: IR (neat) 2960, 1660, 1600, 1445, 1315, 1275, 1175, 1070, 830, 740, 700 cm⁻¹; NMR (220 MHz) 1.30 (s, CH₃, 6), 1.98 (t, J = 7 Hz, CH₂, 2), 2.94 (t, J = 7 Hz, CH₂, 2), 7.2–7.9 (m, aromatic, 8); mass spectrum, *m/e* (rel. intensity) 250 (15, M⁺), 235 (77), 105 (100). Anal. Calcd. for C₁₈H₁₈O: C, 86.36; H, 7.25. Found: C, 86.46; H, 7.26.

Preparation of 5,5-Dimethyl-1,2-diphenyl-1,3,4,5-tetrahydro-2H-2-benzazepine 12. A solution of **7** (0.34 g, 1.04 mmol) in 50 mL of absolute ethanol and 95 mg of 5% Pd/C was refluxed for 6 h under nitrogen. After cooling, the solution was filtered and the solvent removed in vacuo. The residue was chromatographed on silica gel using benzene as eluent. Collection of the lead band gave (after two recrystallizations from absolute ethanol) 0.22 g of **12**, mp 161–162 °C; IR (CCl₄) 2960, 1600, 1500, 1405, 1320, 1250, 1030, 990, 690 cm⁻¹; NMR (220 MHz) 1.14 (s, CH₃, 3), 1.32 (s, CH₃, 3); NCH₂³ACH₂², AA¹BB¹ pattern, 1.37 (half of d of quartets, H_B¹, J_{A¹B¹} = 2.5 Hz, J_{AB¹} = 4.5 Hz, 0.5), 2.06 (overlapping dd, H_B, J_{AB} = 12.5 Hz, J_{A¹B} = 5 Hz, J_{BB¹} = 15 Hz), 3.38 (d of q, H_{A¹}, J_{AA¹} = 12.5 Hz), 3.55 (d of t, H_A), 6.14 (s, benzylic CH, 1), 6.5–7.7 (m, aromatic, 10); mass spectrum, *m/e* (rel. intensity) 327 (23, M⁺), 251 (21), 250 (100). Anal. Calcd. for C₂₄H₂₅N: C, 88.01; H, 7.71; N, 4.28. Found: C, 88.28; H, 7.94; N, 4.20.

Preparation of 1-Anilino-3,3-dimethyl-3-(*o*-benzoylphenyl)butane, 13. A solution of **7** (130 mg, 0.4 mmol) in benzene containing 10 drops of aqueous acetic acid was refluxed 30 min. After removing the solvent, the residue was chromatographed on silica gel and the second band collected (some **12** also formed in this reaction). This crude **13** was purified by preparative TLC on silica gel using benzene as eluent. The material was an oil; IR (CCl₄) 3420 (NH), 2940, 1675 (C=O), 1600, 1505, 1450, 690 cm⁻¹; NMR (CCl₄) 1.32 (s, CH₃, 6), 1.91 (t, J = 8 Hz, CH₂, 2), 2.89 (t, J = 8 Hz, CH₂, 2), 3.30 (s, NH, 1), 6.1–8.0 (m, aromatic, 14). Anal. Calcd. for C₂₄H₂₅NO: C, 83.91; H, 7.35; N, 4.09. Found: C, 83.66; H, 7.25; N, 3.88.

Preparation of 5,5-Dimethyl-1,2-diphenyl-3,4,5,6,7,8,9,11-octahydro-2H-2-benzazepine 11. An ethyl acetate solution of 174 mg (0.53 mmol) of **7** was hydrogenated at STP over 50 mg of 5% Pd/C for 12 h. The solution was filtered, the solvent removed in vacuo, and the residue recrystallized twice from ethanol to give 140 mg of pure **11**. An analytical sample had mp 128–129 °C; IR (CCl₄) 2940, 1595, 1500, 1355, 1310, 1295, 1225, 690 cm⁻¹; NMR (220 MHz) 0.95, 0.96 (two s, CH₃, 6), 1.18–1.93 (m, CH₂'s, 8), 1.93–2.14 (m, 1), 2.47 (t, J = 8 Hz, 1), 2.55–2.77 (m, 1) (allylic CH's), 3.55–3.70 (m, 1), 3.86–4.05 (m, 1) (NCH₂), 6.55–6.73 (m, aromatic, 3), 7.01–7.36 (m, aromatic, 7). Anal. Calcd. for C₂₄H₂₉N: C, 86.94; H, 8.83; N, 4.23. Found: C, 87.01; H, 9.05; N, 4.20.

Isolation of Alkyl Dimers. Chromatography of the reaction mixtures formed using 1- and 2-bromoadamantane and 1-bromobicyclo[2.2.2]octane disclosed an additional product to those described. These products, formed in 8–10% yield, eluted before any of the nitrogen-containing products and, on the basis of physical properties, were

identified as the alkyl dimers, R-R (R = alkyl group of the bromoalkane).

Bis(1-adamantane), mp 283–285 °C (lit. mp 288–290,^{12a} 280–283 °C^{12b}); NMR and IR spectra agreeing with those described; mass spectrum *m/e* (rel. intensity) 270 (22, M⁺), 135 (100), 134 (32).

Bis(2-adamantane), mp 181–183 °C (lit.¹³ mp 184.5–185.5 °C); NMR, IR, and mass spectra in agreement with those reported.¹³

Bis(1-bicyclo[2.2.2]octane), mp 227–230 °C (sealed tube); NMR 1.3 (broad s); mass spectrum *m/e* (rel. intensity) 218 (100, M⁺), 190 (12), 189 (56), 133 (25), 109 (75), 91 (93). Anal. Calcd. for C₁₆H₂₆: C, 87.98; H, 12.02. Found: C, 88.15; H, 12.15.

Preparation of 5-Benzoyl-1,1-dimethylindan and 5-(α -Anilino-benzyl)-1,1-dimethylindan, 9. 5-Nitro-1,1-dimethylindan¹⁵ (3.73 g, 0.02 mol) in 75 mL of ethanol was hydrogenated over 100 mg of 5% Pd/C for 3 h at 15 °C and 35 psi. After filtration and removal of the solvent, 3.02 g (96%) of 5-amino-1,1-dimethylindan was obtained as a colorless oil: IR (neat) 3440, 3360, and 3210 (NH₂), 2950, 1620, 1500, 1330, 850, 810 cm⁻¹; NMR (CCl₄) 1.20 (s, 6, CH₃'s), 1.85 (t, *J* = 8 Hz, 2, CH₂), 2.78 (t, *J* = 8 Hz, 2, benzylic CH₂), 3.30 (s, 2, NH₂), 6.2–6.4 (m, 2, 4, and 6 H's), 6.81 (d, *J* = 10 Hz, 1, 7-H). The amine was used in the next step without further purification.

The aminoindan derivative was converted to its corresponding nitrile using standard procedures.³⁵ Steam distillation provided the crude nitrile, 0.72 g (21%). Vacuum sublimation (60 °C, 0.1 mm) effected further purification giving a yellow solid, 0.56 g (16%), mp 44–45 °C; IR (CCl₄) 2950, 2210 (C≡N), 1480, 1460, 1360, 1070, 880, 830 cm⁻¹; NMR (CCl₄) 1.25 (s, 6, CH₃'s), 1.92 (t, *J* = 6.5 Hz, 2, CH₂), 2.91 (t, *J* = 6.5 Hz, 2, benzylic CH₂), 7.15 (d, *J* = 7 Hz, 1, 7-H), 7.3–7.5 (m, 2, 4, and 6 H). Anal. Calcd. for C₁₂H₁₃N: C, 84.15; H, 7.67; N, 8.18. Found: C, 84.41; H, 7.43; N, 8.09.

The nitrile (0.56 g, 3.3 mmol) in 5 mL of benzene was added to an ether solution of phenylmagnesium bromide prepared from 0.8 g (5 mmol) of bromobenzene and 0.14 g (5.8 mmol) of magnesium. After 3 h of refluxing, the reaction mixture was hydrolyzed with NH₄Cl, the organic phase separated, washed with water, and the solvent removed. The residue was refluxed for 2 h with 20 mL of 50% aqueous ethanol containing 1 mL of concentrated HCl. The hydrolyzed product was isolated by benzene extraction and purified by chromatography on silica gel using benzene as eluting solvent. The 5-benzoyl-1,1-dimethylindan so purified (0.76 g, 92%) had spectral properties identical with those previously described.

The ketone (0.76 g, 3 mmol) was converted³² to its corresponding anil with excess aniline, the majority of the excess aniline removed by distillation, and the residue reduced by refluxing with 0.5 g of LiAlH₄ in 40 mL of ether for 2 h. After hydrolysis with water, the mixture was filtered, the ether layer evaporated, and the residue chromatographed on silica gel (1:1 benzene:petroleum ether (30–60 °C)) to give 0.50 g of crude **7** (51%), mp 80–82 °C, after two recrystallizations from ethanol. Spectral data were identical with those described earlier.

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