Single Electron Transfer as a Mechanistic Feature in the Alkylation of Vicinal Dianions

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Abstract: The vicinal dianion **1** formed by reducing benzophenone anil in tetrahydrofuran with alkali metals is alkylated in 60–80% total yield by *tert*-butyl halides, 1- and 2-bromoadamantane, 1-bromobicyclo[2.2.2]octane, and neopentyl halides. The alkyl group is introduced at the benzylic carbon or at the para position of a phenyl group attached to this carbon. Alkylation experiments using 1,3-dihalo-3-methylbutane followed by product studies demonstrate that the tertiary halide of the alkylating agent reacts faster than the primary by a factor of at least 6. These observations support an alkylation mechanism based on single electron transfer (SET) from **1** to the alkyl halide followed by coupling of the radical anion–alkyl radical pair so produced.

The reduction of unsaturated compounds in aprotic solvents by alkali metals can produce a variety of anionic products[1,2] among which the most common are radical anions, and monomeric and dimeric dianions. Of these, the monomeric dianions are especially interesting since, in a formal sense, they can be regarded as having adjacent anionic centers. In addition, they can be visualized as reacting not only as nucleophilic reagents but also by single electron transfer (SET), a process which is a reversal of their formation. It is the purpose of this report to show that a SET mechanism can be operative in alkylation reactions of monomeric vicinal dianions.

The dianion **1**, derived from benzophenone anil, was selected since several studies of this organometallic derivative[3] have been made. We were persuaded to examine the mechanistic question for two reasons. First, an earlier alkylation study of **1** by secondary halides[3a] revealed a complex and highly variable alkylation pattern which was awkward to rationalize on the basis of nucleophilic substitution. Second, compelling evidence has accumulated that radical anions[4,5] react with alkyl halides by SET mechanisms and other organometallic derivatives[6,7] undergo addition reactions by SET mechanisms as well.

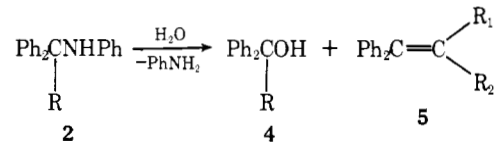
In the present study alkyl halides were selected which can be expected to be poor alkylating agents (in a nucleophilic sense) because of dehydrohalogenation and/or low reaction rates, but which can be expected to form radicals in a SET reaction. Tertiary alkyl halides are such a class of compounds; alkylation of carbanions are unfavorable[8] yet tertiary radicals are regarded[9] as more stable members of the alkyl radical series.

Results

Consequently, the three tertiary bromides, *tert*-butyl, 1-adamantyl, and 1-bicyclo[2.2.2]octyl,[10] were examined as alkylating agents for **1**. As Table I shows, alkylation products were obtained in 65–80% yields under mild reaction conditions. The alkylation products consisted of the benzylic alkylation product, **2**, and the para-alkylated anil, **3**.

Continuing this study, the behavior of sterically hindered secondary and primary halides was examined. 2-Bromoadamantane[11] is known to react sluggishly in nucleophilic substitution reactions but high total yields of alkylation products were produced on reaction with **1**. Similarly neopentyl halides are classic examples of primary halides resistant to nucleophilic substitution reactions; here efficient alkylation of **1** was effected by neopentyl bromide and iodide. (However, neopentyl chloride failed to react while 1-bicyclo[2.2.2]octyl chloride reacted very slowly.)

The alkylation product **2** (eq 1) formed in these last two



2 **4** **5** (1)

reactions was found to readily lose the elements of aniline through solvolysis and/or elimination reactions. This decomposition required only mild acidic conditions such as those present during chromatography on silica gel.

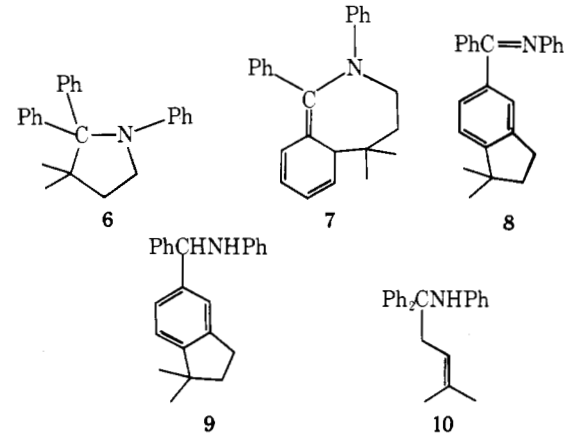
The structures of products **2** and **3** follow from their spectral data. In particular, the similarity of the aromatic region of the NMR spectral and of the aromatic substitution pattern of the IR spectra to the spectra of authentic **3** (R = *t*-Bu) established the para position of the alkyl groups.

In addition to **2** and **3**, small amounts (5–15%) of *N*-benzhydrylaniline and benzophenone anil were formed. In three cases (R = 1-adamantyl, 2-adamantyl, and 1-bicyclo[2.2.2]octyl) dimeric products, R–R, were detected and identified by their spectral properties. Two of these dimers are known compounds.[12,13]

Having ascertained that tertiary halides alkylated **1**, it was of interest to determine the relative rate of reaction of **1** with a tertiary vs. a primary alkyl halide. Qualitatively, this was assessed through alkylation of **1** with 1,3-dihalo-3-methylbutane followed by a structural determination of the products. Since it had been shown previously that alkylation of **1** occurs stepwise,[3,14] first at the benzylic carbon (or in the ortho or para position of an attached phenyl group), the products' structures will establish the preferred reacting site of the dihalide.

The reaction mixture proved complex and was found to contain compounds **6**, **7**, **8**, **9**, and **10** (Scheme I) with the

Scheme I. Reaction Products of **1** with 1,3-Dihalo-3-methylbutanes

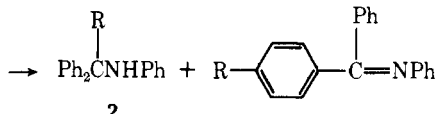


6 **7** **8** **9** **10**

Table I. Alkylation of 1 with Tertiary Halides[a]

$(Ph_2CNPh)^{2-}\ 2Na^+ + RBr$

1



2 3

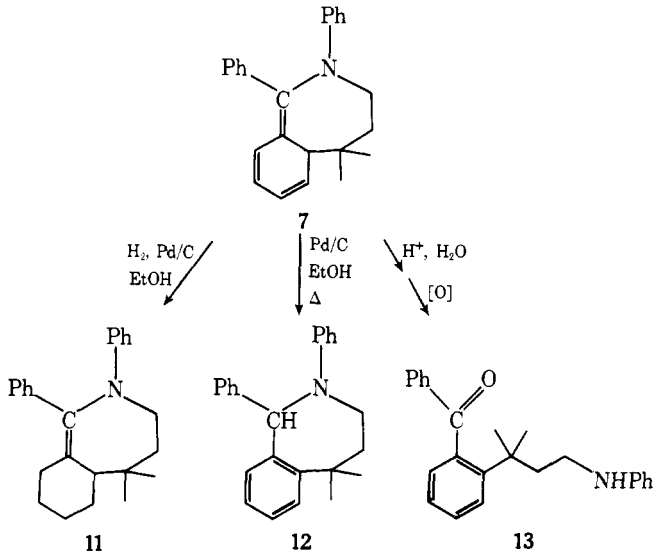
R	% yield of 2	% yield of 3
t-Bu	35	35
1-Ad[b]	23	43
1-Bicyclo[c]	27	53
2-Ad[b]	55	27
t-$BuCH_2$	71	11
t-$BuCH_2$[d]	66	22

[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 represents the 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-triphenylpyrrolidine[14] (3.79 δ). Similarly compound **7** showed a $N\text{-}CH_2$ 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 aromization 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 $Eu(fod)_3$ 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.

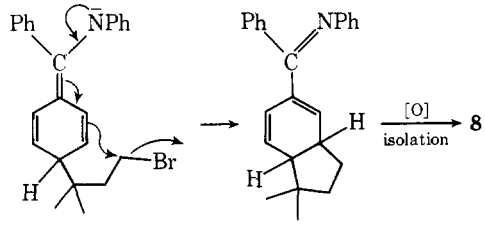
Discussion

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 mechanism[4] 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 ± 0.1) and iodides ($E_{1/2}$[18] -1.6 ± 0.1). Alkyl chlorides are borderline cases with *tert*-butyl chloride ($E_{1/2}$[18] −2.60) reacting but neopentyl chloride ($E_{1/2}$ −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.

$A^{2-} + RX \longrightarrow A^{-\cdot} + R\cdot + X^-$ followed by $A^{-\cdot} + R\cdot \longrightarrow (A\text{-}R)^-$



(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 density[19] is highest at the benzhydrylic 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 benzhydrylic site. This effect is clearly seen in the results of Table I where benzhydrylic alkylation decreases in the order neopentyl > 2-adamantyl > *tert*-butyl[21] > 1-adamantyl ≈ 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 disproportionates[22] and leads to benzophenone anil and *N*-benzhydrylaniline 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.

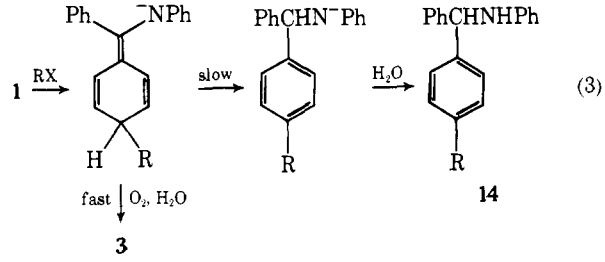
Do primary alkyl halides react by a SET mechanism? The failure of neopentyl chloride to react can be rationalized by its inability to be reduced[23] by the dianion **1**. The successful alkylations with neopentyl bromide and iodide suggest the SET mechanism. We attempted to resolve this question using 5-hexenyl halides as has Garst in related studies with the radical anions from naphthalene[4] and benzophenone.[5] Since the 5-hexenyl radical cyclizes to the cyclopentylmethyl radical with a rate constant[24] 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's[36] 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 and the amine **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



(3)

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 tube[26] and 100 ± 10 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.[3d] The solution was then drained from the excess metal into a nitrogen-filled flask, cooled to −78 °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-methylbutanes[30] 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*-benzhydrylaniline, **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 (CCl_4) 3410 (NH), 1645 (C=C), 1600, 1500, 1315, 910, 695 cm^{-1}; NMR 1.3 (m, CH_2, 4), 1.9 (m, CH_2, 2), 2.5 (m, CH_2, 2), 4.33 (s, NH, 1), 4.9 (m, $=CH_2$, 2), 5.7 (broad m, =CH, 1), 6.3-7.7 (m, Ph, 15). Anal. Calcd. for $C_{25}H_{27}N$: 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 (CCl_4) 3420 (NH), 1600, 1500, 1450, 1315, 695 cm^{-1}; NMR (CCl_4) 1.36 (s, CH_3, 3), 1.56 (s, CH_3, 3), 3.19 (d, CH_2, 2), 4.54 (broad s, NH, 1), 4.93 (broad t, =CH, 1), 6.2-7.7 (m, Ph, 15). Anal. Calcd. for $C_{24}H_{25}N$: C, 88.01; H, 7.71; N, 4.28. Found: C, 88.31; N, 7.60; N, 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 (CCl_4) 3475 (NH), 1600, 1500, 1315, 700, 690 cm^{-1}; NMR (CCl_4) 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 $C_{23}H_{25}N$: 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 (CCl_4) 3440 (NH), 1600, 1505, 1315, 1270, 700, 690 cm^{-1}; NMR (CCl_4) 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 $C_{23}H_{25}N$: 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 (CCl_4) 1620 (C=N), 1595, 1485, 1315, 1295, 960, 835, 690 cm^{-1}; NMR (CCl_4), 1.29, 1.33 (s'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 $C_{23}H_{23}N$: 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 prepared[32] from *p-tert*-butylbenzophenone[33] and aniline and reduced to amine **14** (R = *t*-Bu) with $LiAlH_4$. 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 (CCl_4) 3470 (NH), 2900, 1600, 1500, 1310m 690 cm^{-1}; NMR 1.4-1.8 (m, CH_2, 12), 1.96 (broad s, bridgehead H, 3), 4.35 (broad s, NH, 1), 5.93-8.05 (m, aromatic, 15). Anal. Calcd. for $C_{29}H_{31}N$: 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 (CCl_4) 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 $C_{29}H_{29}N$: 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 (CCl_4) 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 $C_{27}H_{29}N$: C, 88.23; H, 7.95; N, 3.81. Found: C, 88.47; H, 7.97; N, 3.85.

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

Cation of **1**	*t*-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
	I	1	25[c]	45
		2	27	42
Li	Cl	1	17 ± 1	30 ± 2
		2	16	22
	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.

Two recrystallizations of **3** (R = bicyclo) from ethanol gave an analytical sample, mp 169-170 °C; IR (CCl_4) 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 $C_{27}H_{27}N$: 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 (CCl_4) 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 $C_{29}H_{31}N$: 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** (R_1, R_2 = 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 (CCl_4) 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 $C_{29}H_{29}N$: 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** (R_1, R_2 = 2-adamantylidene) recrystallized twice from absolute ethanol, mp 104-105 °C; IR (CCl_4) 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 $C_{23}H_{24}$: 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 (CCl_4) 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 $C_{23}H_{26}O$: 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 (CCl_4) 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 $C_{23}H_{24}O$: 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 ^{1}H NMR spectra of the individual chromatographic fractions.

2 (R = neopentyl), mp (from ethanol) 79–80 °C; IR (CCl_4) 3480 (NH), 2950, 1600, 1500, 1445, 1305, 1250, 1030, 700 cm^{-1}; NMR 0.75 (s, *t*-Bu, 9), 2.50 (s, CH_2, 2), 6.2–7.7 (m, aromatic, 15), 4.05 (broad s, NH, 1). Anal. Calcd. for $C_{24}H_{27}N$: 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 (CCl_4) 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, CH_2, 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** (R_1 = H, R_2 = *t*-Bu), an oil, had the following spectral properties: IR (CCl_4) 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 (H_2SO_4–HNO_3) to give the known 3,3-dimethyl-1,1-di(4-nitrophenyl)butane, mp 157–159 °C (reported[34] 156 °C).

Compound **4** (R = neopentyl) after recrystallization from hexane had mp 70.5–71.5 °C; IR (CCl_4) 3610 (OH), 2950, 1600, 1490, 1475, 1465, 1445, 1360, 1170, 1060, 1030, 985, 690 cm^{-1}; NMR ($CDCl_3$) 0.85 (s, *t*-C_4H_9, 9), 2.00 (s, OH, 1), 2.43 (s, CH_2, 2), 7.1–7.7 (m, aromatic, 10). Anal. Calcd. for $C_{18}H_{22}O$: 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 (CCl_4) 2950, 1660 (C=O), 1600, 1300, 1270, 930, 915, 850, 690 cm^{-1}; NMR 0.94 (s, *t*-Bu, 9), 2.59 (s, CH_2, 2), 7.1–8.0 (m, aromatic, 9). Anal. Calcd. for $C_{18}H_{20}O$: 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 (CCl_4) 2950, 1600, 1495, 1310, 1290, 1190, 1030, 685 cm^{-1}; NMR (220 MHz) 0.89 (s, CH_3, 3), 1.05 (s, CH_3, 3); $NCH_2{}^ACH_2{}^B$, A_2BB^1 pattern, 1.59 (d of t, H_B, J_{BB^1} = 16 Hz, J_{AB} = 4 Hz), 2.00 (d of t, H_{B^1}, J_{AB^1} = 7 Hz), 3.79 (d of d, H_A's, 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 $C_{24}H_{25}N$: 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 (CCl_4) 2950, 1600, 1505, 1485, 1330, 1155, 1040, 690 cm^{-1}; NMR 0.77 (s, CH_3, 6), 2.04 (t, *J* = 7 Hz, CH_2, 2), 3.92 (t, *J* = 7 Hz, CH_2, 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 $C_{24}H_{25}N$: 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 (CCl_4) 3440 (NH), 2960, 1600, 1505, 1430, 1315, 700, 690 cm^{-1}; NMR 1.22 (s, CH_3, 6), 1.85 (t, *J* = 7 Hz, CH_2, 2), 2.80 (t, *J* = 7 Hz, CH_2, 2), 4.11 (s, NH, 1), 5.40 (s, CH, 1), 6.3–7.5 (m, aromatic, 13). Anal. Calcd. for $C_{24}H_{25}N$: 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 (CCl_4) 2960, 1615 (C=N), 1590, 1485, 1445, 1315, 900, 690 cm^{-1}; NMR 1.21, 1.30 (s's, CH_3, 6) (compound exhibits syn-anti isomerism), 1.95 (m, CH_2, 2), 2.85 (m, CH_2, 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 $NaHCO_3$ solution, water, and drying ($MgSO_4$) 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, CH_3, 6), 1.98 (t, *J* = 7 Hz, CH_2, 2), 2.94 (t, *J* = 7 Hz, CH_2, 2), 7.2–7.9 (m, aromatic, 8); mass spectrum, *m/e* (rel. intensity) 250 (15, M$^+$), 235 (77), 105 (100). Anal. Calcd. for $C_{18}H_{18}O$: 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-2*H*-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 (CCl_4) 2960, 1600, 1500, 1405, 1320, 1250, 1030, 990, 690 cm^{-1}; NMR (220 MHz) 1.14 (s, CH_3, 3), 1.32 (s, CH_3, 3); $NCH_2{}^ACH_2{}^B$, AA^1BB^1 pattern, 1.37 (half of d of quartets, H_{B^1}, $J_{A^1B^1}$ = 2.5 Hz, J_{AB^1} = 4.5 Hz, 0.5), 2.06 (overlapping dd, H_B, J_{AB} = 12.5 Hz, J_{A^1B} = 5 Hz, J_{BB^1} = 15 Hz), 3.38 (d of q, H_{A^1}, J_{AA^1} = 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 $C_{24}H_{25}N$: 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 (CCl_4) 3420 (NH), 2940, 1675 (C=O), 1600, 1505, 1450, 690 cm^{-1}; NMR (CCl_4) 1.32 (s, CH_3, 6), 1.91 (t, *J* = 8 Hz, CH_2, 2), 2.89 (t, *J* = 8 Hz, CH_2, 2), 3.30 (s, NH, 1), 6.1–8.0 (m, aromatic, 14). Anal. Calcd. for $C_{24}H_{25}NO$: 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-2*H*-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 (CCl_4) 2940, 1595, 1500, 1355, 1310, 1295, 1225, 690 cm^{-1}; NMR (220 MHz) 0.95, 0.96 (two s, CH_3, 6), 1.18–1.93 (m, CH_2'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) (NCH_2), 6.55–6.73 (m, aromatic, 3), 7.01–7.36 (m, aromatic, 7). Anal. Calcd. for $C_{24}H_{29}N$: 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 $C_{16}H_{26}$: C, 87.98; H, 12.02. Found: C, 88.15; H, 12.15.

Preparation of 5-Benzoyl-1,1-dimethylindan and 5-(α-Anilinobenzyl)-1,1-dimethylindan, 9. 5-Nitro-1,1-dimethylindan[15] (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 (NH_2), 2950, 1620, 1500, 1330, 850, 810 cm^{-1}; NMR (CCl_4) 1.20 (s, 6, CH_3's), 1.85 (t, J = 8 Hz, 2, CH_2), 2.78 (t, J = 8 Hz, 2, benzylic CH_2), 3.30 (s, 2, NH_2), 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 (CCl_4) 2950, 2210 (C≡N), 1480, 1460, 1360, 1070, 880, 830 cm^{-1}; NMR (CCl_4) 1.25 (s, 6, CH_3's), 1.92 (t, J = 6.5 Hz, 2, CH_2), 2.91 (t, J = 6.5 Hz, 2, benzylic CH_2), 7.15 (d, J = 7 Hz, 1, 7-H), 7.3–7.5 (m, 2, 4, and 6 H). Anal. Calcd. for $C_{12}H_{13}N$: 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 NH_4Cl, 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 converted[32] 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 $LiAlH_4$ 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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References and Notes

(1) N. L. Holy, *Chem. Rev.*, **74**, 243 (1974).
(2) M. V. George and V. Kalyanaraman, *J. Organomet. Chem.*, **47**, 225 (1973).
(3) (a) J. G. Smith and R. A. Turle, *J. Org. Chem.*, **37**, 126 (1972); (b) J. G. Smith, I. Ho, and G. E. F. Simpson, *Ibid.*, **40**, 495 (1975); (c) J. G. Smith and G. E. F. Simpson, *ibid.*, **41**, 2878 (1976); (d) J. G. Smith and C. D. Veach, *Can. J. Chem.*, **44**, 2245 (1966).
(4) J. F. Garst, *Acc. Chem. Res.*, **4**, 400 (1971).
(5) J. F. Garst and C. D. Smith, *J. Am. Chem. Soc.*, **98**, 1520 (1976).
(6) E. C. Ashby, J. D. Buhler, I. G. Lopp, T. L. Wiesemann, J. S. Bowers, Jr., and J. T. Laemmle, *J. Am. Chem. Soc.*, **98**, 6561 (1976), and earlier papers cited.
(7) H. O. House and C-Y. Chu, *J. Org. Chem.*, **41**, 3083 (1976), and earlier papers cited.
(8) H. O. House, "Modern Synthetic Reactions", W. A. Benjamin, Menlo Park, Calif., 1972, p 530.
(9) G. A. Russell in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 7.
(10) P. v. R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 2700 (1961).
(11) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2540 (1970).
(12) (a) H. F. Reinhardt, *J. Org. Chem.*, **27**, 3258 (1962); (b) P. H. Owens, G. J. Gleicher, and L. M. Smith, Jr., *J. Am. Chem. Soc.*, **90**, 4122 (1968).
(13) J. A. Van Zorge, J. Strating, and H. Wynberg, *Recl. Trav. Chim. Pays-Bas*, **89**, 781 (1970).
(14) J. G. Smith and C. D. Veach, *Can. J. Chem.*, **44**, 2245 (1966).
(15) (a) L. M. Stock and P. E. Young, *J. Am. Chem. Soc.*, **94**, 4247 (1972). A key intermediate, 3,3-dimethyl-6-nitroindan-1-one, is incorrectly termed a 5-nitro derivative in this paper; (b) C. F. Koelsch and C. D. Le Claire, *J. Org. Chem.*, **6**, 516 (1941).
(16) By a factor of 10^{-5} relative to 80% ethanol. S. G. Smith, A. H. Feinberg, and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).
(17) Half-wave reduction potential for $A^{-}\cdot|A^{2-}$ (A^{2-} = 1) vs. SCE in DMF of −2.83 V, M. Uehara and J. Nakaya, *Nippon Kagaku Kāishi*, 2440 (1974).
(18) L. Meites and P. Zuman, "Electrochemical Data", Part 1, Vol. A, Wiley, New York, N.Y., 1974. The $E_{1/2}$ values were measured in DMF vs. SCE.
(19) Standard Hückel molecular orbital calculation with McLachlan configurational interactions for radicals was used assuming a coplanar arrangement of all aromatic rings. The "frontier electron theory" of Fukui[20] gave qualitatively similar results.
(20) K. Fukui, T. Yonezawa, and H. Singu, *J. Chem. Phys.*, **20**, 722 (1952).
(21) D. S. Kristol, R. C. Parker, H. D. Perlmutter, K-C. H. Chen, D. H. Hawes, and G. H. Wahl, Jr., *J. Org. Chem.*, **41**, 3205 (1976), report that the *tert*-butyl group is sterically smaller than the two bridge-head alkyl groups.
(22) A. G. Evans and J. C. Evans, *J. Chem. Soc. B*, 271, (1966).
(23) Neopentyl chloride has $E_{1/2}$ = −2.83, F. L. Lambert and G. B. Ingall, *Tetrahedron Lett.*, **26**, 3231 (1974).
(24) D. Lal, D. Griller, S. Husband, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6355 (1974).
(25) By analogy with the allylic chlorination of 3-methyl-1-butene, C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).
(26) J. W. B. Reesor, J. G. Smith, and G. F. Wright, *J. Org. Chem.*, **19**, 940 (1954).
(27) (a) G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Am. Chem. Soc.*, **86**, 964 (1964); (b) N. Kornblum and D. C. Iffland, *ibid.*, **77**, 6653 (1955).
(28) (a) K.-I. Morita and T. Kobayaski, *J. Org. Chem.*, **31**, 229 (1967); (b) Z. Suzuki and K.-I. Morita, *ibid.*, **32**, 31 (1967).
(29) C. D. Smith, Ph.D. Thesis, University of Georgia.
(30) J. Tanaka, T. Katagiri, and K. Takabe, *Yuki Gosci Kagaku Kyokai Shi*, **28**, 764 (1970); *Chem. Abstr.*, **73**, 98321k (1970).
(31) This reagent was kindly supplied by Dr. V. Snieckus of this department.
(32) G. Reddelien, *Chem. Ber.*, **46**, 2718 (1913).
(33) E. D. Hughes, C. K. Ingold, and N. Taher, *J. Chem. Soc.*, 940 (1940).
(34) L. Schmerling, J. P. Lurisi, and R. W. Welch, *J. Am. Chem. Soc.*, **77**, 1774 (1955).
(35) H. T. Clarke and R. R. Read, "Organic Syntheses", Collective Vol. I, 2nd ed, H. Gilman and A. H. Blatt, Ed., Wiley, New York, N.Y., 1967, p 514.
(36) R. M. Magid, E. C. Nieh, and R. D. Gandour, *J. Org. Chem.*, **36**, 2099 (1971); R. M. Magid and E. C. Nieh, *ibid.*, **36**, 2105 (1971).