was added. The mixture was evaporated to dryness. After water was added (25 ml) the residue was extracted several times with ethyl acetate. The extract was dried with anhydrous sodium sulfate and the solvent was evaporated. The substances can be purified by column chromatography or preferentially by preparative tlc on silica plates using the following solvent systems: compound **4b** in chloroform–methanol (85:15), yield 35%; **4c** and **4d** in chloroform–methanol (90:10), yield 34 and 70%, respectively.

O-(*p*-Nitrophenyl) *N*-(5′-Deoxyadenosyl) 3′,5′-Cyclic Phosphoramidates (6b–d). With Pyridine–Ammonia.—The respective diester amidate **4b–d** (1 mmol) in a mixture of pyridine–concentrated ammonia–water (2:5:3) (300 ml) was kept at 45° for 2 hr. The solvent was removed *in vacuo*, and the residue was washed with weakly alkaline (pH 9) water.

With Aqueous NaOH–Methanol.—The respective diester amidate **4b–d** (1 mmol) was dissolved in 100 ml of methanol, and after addition of 1 *N* NaOH (20 ml) the mixture was kept at room temperature for 2 hr. After neutralization with dilute acetic acid, the mixture was evaporated to dryness and some weakly alkaline water (pH 9) was added. Further work-up of the two procedures is identical; the yields are approximately the same.

Crude compounds of type **6** were purified by column chromatography or preferentially by preparative tlc on silica plates with the following solvent systems: compound **6b** in chloroform–methanol (85:15), yield 91%; **6c** and **6d** in chloroform–methanol (90:10); yield 91% each. Compound **6b** can be crystallized from methanol by adding ethyl acetate; **6c** and **6d** were obtained as a colorless powder.

Direct Synthesis of *N*-(5′-Deoxyadenosyl) 3′,5′-Cyclic Phosphoramidates (7b–d) from 4.—The respective diester amidate **4b–d** (1 mmol) was dissolved in a pyridine–concentrated ammonia–water mixture (100 ml, 3:5:2) and kept at 40° for 7 days; 1 *N* NaOH (3 ml) was added and the solvent was removed *in vacuo*. The residue was dissolved in methanol (10 ml) and filtered. After addition of acetone (300 ml), the desired cyclophosphoramidates **7b–d** precipitated. The precipitate was washed with acetone.

Further purification was carried out on a DEAE cellulose column using the following conditions for the individual compounds.

7b: DE 52 (HCO_3^- form); volume 75 ml for 3000 OD, 0.2 mmol; linear gradient water → 0.1 *M* triethylammonium bicarbonate, 2 l. each; fraction 15 ml; between fraction 58 and 70, 0.022–0.26 *M*; yield 50%.

7c: DE 52 (HCO_3^- form); volume 40 ml for 400 OD, 0.026 mmol; linear gradient water → 0.1 *M* triethylammonium bicarbonate, 1 l. each; fraction 9 ml; between fraction 21 and 39, 0.01 and 0.02 *M*; yield 55%.

7d: DE 52 (HCO_3^- form); volume 40 ml for 400 OD, 0.026 mmol; linear gradient water → 0.1 *M* triethylammonium bicarbonate, 1 l. each; fraction 9 ml; between fraction 45 and 62, 0.02–0.028 *M*; yield 53%.

Conversion of 6 into 7.—Identical conditions as described for conversion of **4** into **7** were used for converting **6** into **7**.

Stability of Compounds 7a–d in Various Buffer Solutions.—Compounds **7a–d** (20 OD each) were incubated in buffer solution (pH 5, pH 7, and pH 9, 200 μl) at 37° for 5 hr (Table II). Then the mixture was separated on paper chromatography in solvent A. The extent of cleavage was determined spectroscopically.

TABLE II
PERCENTAGE CLEAVAGE OF 7 IN BUFFER

Compd	pH 5, %	pH 7, %	pH 9, %
7a	98	15	0
7b	100	40	0
7c	90	9	0
7d	45	4	0

Registry No.—**2b**, 30765-10-7; **2b** HI, 30461-85-9; **3c**, 30765-12-9; **3d**, 30765-13-0; **3e**, 30765-14-1; **4a**, 29845-63-4; **4b**, 29845-64-5; **4c**, 30765-17-4; **4d**, 30826-38-1; **5a**, 30765-18-5; **6b**, 29845-65-6; **6c**, 30765-20-9; **6d**, 30765-21-0; **7a**, 29845-61-2; **7b** Na salt, 30765-23-2; **7c** Na salt, 30765-24-3; **7d** Na salt, 30765-25-4.

Acknowledgment.—The authors thank Dr. H. M. Schiebel, Stöckheim, for recording the nmr and mass spectra and for helpful discussions. We are also indebted to Mrs. T. Krebs and Mr. F. Tlatlik for skillful technical assistance.

Mobile Keto Allyl Systems. X.[1a] The Thermal Decomposition of 2-(*o*-Methylbenzal)-3-amino-4,4-dimethyl-1-tetralones[1b]

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Several 2-(*o*-methylbenzal)-3-amino-4,4-dimethyl-1-tetralones (**4**) have been prepared and those possessing a hydrogen atom α to the nitrogen in the amino moiety were found to decompose thermally to yield 2-(*o*-methylbenzyl)-1,4-dihydro-4,4-dimethyl-1-ketonaphthalene (**8**). By the use of deuterium-labeling experiments, it has been shown that this α hydrogen atom is transferred to the benzylic position. Possible mechanisms are discussed.

In connection with other work, it was necessary to prepare several 2-(*o*-methylbenzal)-3-amino-4,4-dimethyl-1-tetralones and to study their thermal stability. Condensation of *o*-tolualdehyde with 4,4-dimethyl-1-tetralone yielded *trans*-2-(*o*-methylbenzal)-4,4-dimethyl-1-tetralone[2] (**1**) in high yield. Bromination[3] with *N*-bromosuccinimide gave 2-(α-bromo-*o*-methylbenzyl)-1,4-dihydro-4,4-dimethyl-1-ketonaphthalene (**2**). When **2** was allowed to react with cyclohexylamine, isopropylamine, and *tert*-butylamine in solvent benzene at room temperature, two products were obtained as had been observed in a similar case.[3] Besides the corresponding 2-[α-(amino)-*o*-methylbenzyl]-1,4-dihydro-4,4-dimethyl-1-ketonaphthalenes (**3**), the desired 2-(*o*-methylbenzal)-3-amino-4,4-dimethyl 1-tetralones (**4**) were obtained. It is the thermal decomposition of these compounds **4** with which this paper is concerned.

Results

While compounds **3a–c** and **4c** were stable to column chromatography, compounds **4a** and **4b** decomposed.

(1) (a) For paper IX in this series, see N. H. Cromwell, K. Matsumoto, and A. D. George, *J. Org. Chem.*, **36**, 272 (1971). (b) Presented at the 1970 Midwest Regional Meeting of the American Chemical Society, Lincoln, Nebr., Oct 1970, Abstract No. 502.

(2) A. Hassner and N. H. Cromwell, *J. Amer. Chem. Soc.*, **80**, 893 (1958).

(3) N. H. Cromwell and E. M. Wu, *J. Org. Chem.*, **33**, 1895 (1968).

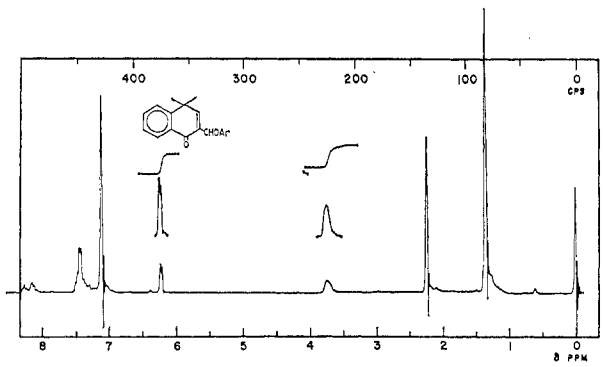
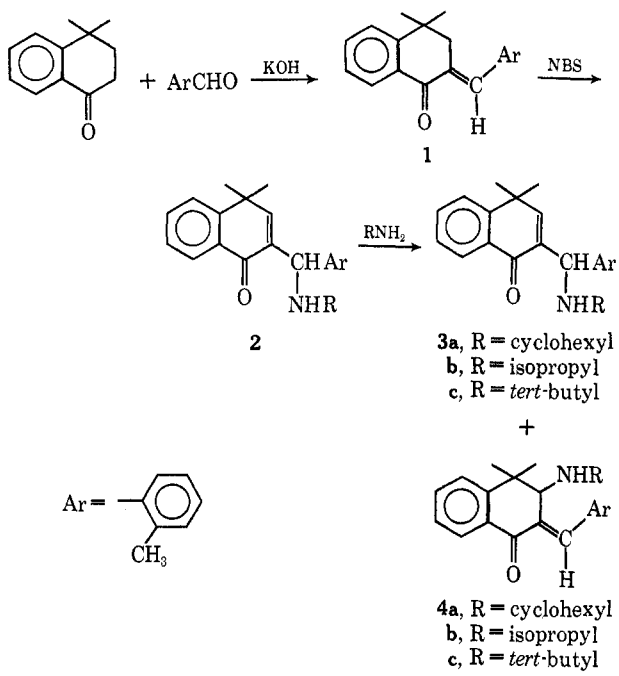
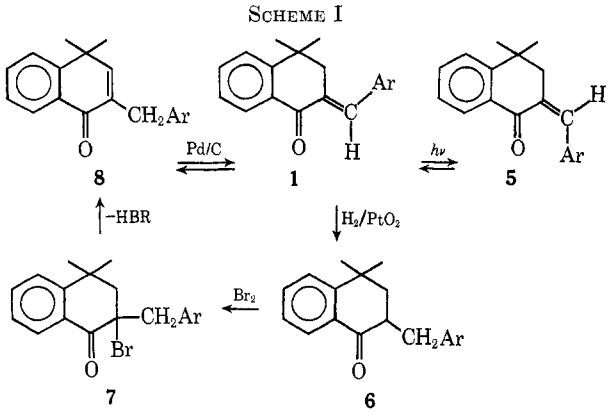


Figure 1.—Nmr spectrum of 2-(*o*-methylbenzyl)-1,4-dihydro-4,4-dimethyl-1-ketonaphthalene.



The product of decomposition was found to contain no nitrogen. From the spectral data and by comparison with *cis*-2-(*o*-methylbenzal)-4,4-dimethyl-1-tetralone[4] (**5**) as well as with 2-(*o*-methylbenzyl)-1,4-dihydro-4,4-dimethyl-1-ketonaphthalene[2] (**8**) prepared by published procedures, the isolated compound was identified as **8** (Scheme I, Figure 1).

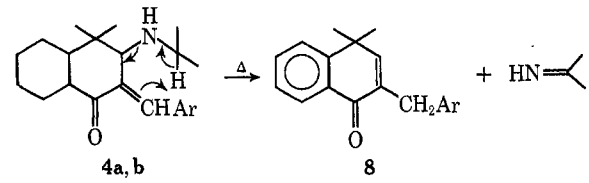
SCHEME I



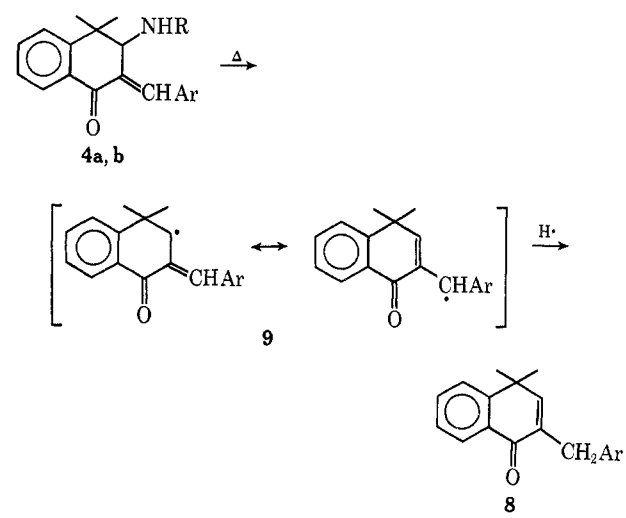
A pure sample of **4b** was obtained by precipitating it from the decomposition product **8** after column chromatography. Compound **4a** could be isolated by triturating the mixture of **3a** and **4a** and filtering the solid which formed. Because **4a** could be obtained in this manner, most of the work was done on this compound, but **4b** behaved similarly.

If **4a** or **4b** was heated to 135° in a sealed tube for 3 hr, the same product **8** could be obtained in high yield. The reaction occurred either neat or with dry benzene which had been deoxygenated with dry nitrogen. No other compounds could be readily isolated.

Two possible mechanisms come to mind immediately. The first one involves a six-membered transition state in which a ketimine and **8** are formed. This may be considered to be a retro ene reaction and can be depicted as follows.



A second mechanism is a homolytic scission of the carbon–nitrogen bond to give a radical **9** which can abstract a hydrogen atom to yield the observed product **8**.



Retro Ene Mechanism.—We have called this a retro ene reaction and have drawn a six-membered cyclic transition state only for convenience. It is recognized that the reaction may be concerted or stepwise and these possibilities are discussed later. Attempts were made to trap the imine by extraction of the decomposition solution with water and reacting the aqueous extracts with a solution of 2,4-dinitrophenylhydrazine. A small amount of the 2,4-dinitrophenylhydrazone of cyclohexanone was obtained, mp 156–157° (lit.[5] 160°), which lends support to the retro ene mechanism being operative. The small yield of cyclohexanone did not rule out the possibility that the cyclic mechanism was only a side reaction and the main reaction occurs by another pathway. The 2,4-dinitrophenylhydrazone was not of **8** since **8** did not react with 2,4-dinitrophenylhydrazine solution.

(4) D. N. Kevill, E. D. Weiler, and N. H. Cromwell, *J. Org. Chem.*, **29**, 1276 (1964).

(5) "Dictionary of Organic Compounds," 45h ed, Vol. 2, Oxford University Press, New York, N. Y., 1965, p 785.

Compound **4c** has no hydrogen α to the nitrogen in the amino moiety (hereafter referred to as the α hydrogen) and is stable. The retro ene reaction requires that the α hydrogen be transferred to the benzylic position. It was felt, therefore, that a deuterium labeling experiment would be of value in providing more insight into the mechanism of this decomposition. Cyclohexylamine-d_1 was prepared by the sodium and methanol-d_1 reduction[6] of cyclohexanone oxime.[7] The cyclohexylamine-d_1 was allowed to react with **2**. The product **4a** was isolated by trituration of the product mixture, recrystallized, and decomposed in the normal manner. Mass spectrometric analysis showed **4a** to contain 98% atom/molecule of deuterium. The product **8** isolated after chromatography had mp 85.5–86.5°, the same as that for **8** obtained previously. The nmr spectrum (Figure 2) of **8** obtained from the decomposition of 2-(*o*-methylbenzal)-3-(1′-deuteriocyclohexylamino)-4,4-dimethyl-1-tetralone was identical with that obtained previously (Figure 1) except for the vinyl and methylene proton signals. The methylene signal appeared as a broad singlet at 229 Hz which integrated to 1.01 protons and the vinyl signal appeared as a doublet at 378 Hz (J = 1.4 Hz) and integrated to 1.00 protons. Mass spectral analysis showed **8** in this case to contain 98% atom/molecule of deuterium, and the nmr spectrum is consistent with a structure having one atom/molecule of deuterium in the benzylic position. The fact that the signal at 229 Hz is a broad singlet is probably due to unresolved coupling to the deuterium which has a spin of one and J_{CH-D} 2.4 Hz.[8]

As a control experiment, the proton on the nitrogen of **4a** was exchanged with deuterium oxide and the resultant *N*-deuterio compound containing 60% atom/molecule of deuterium by mass spectrometric analysis was decomposed. The resultant **8** showed no deuterium by nmr. The ratio of intensities of the vinyl to methylene signals was one to two and the spin–spin splitting pattern was a triplet and a doublet, respectively (Figure 1).

Radical Mechanism.—The radical produced in the homolytic scission might be expected to be relatively stable due to the high degree of resonance stabilization available to it. Therefore, attempts were made to trap and observe it. It was thought that the radical trap that offered the best possibility was 2-methyl-2-nitrosopropane.[9]

When 2-methyl-2-nitrosopropane was added to a sample of **4a** at the time it was thought to be half-decomposed and perhaps had the highest steady-state concentration of radicals present; only an esr signal due to di-*tert*-butyl nitroxide was observed. This radical is observed because 2-methyl-2-nitrosopropane decomposes to form di-*tert*-butyl nitroxide either thermally or photochemically.[10]

(6) The procedure was essentially that of W. H. Lycan, S. V. Puntambeker, and C. S. Marvel, "Organic Syntheses," Collect. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1943, p 318.

(7) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, Wiley, New York, N. Y., 1956, p 255.

(8) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966, p 1092.

(9) For recent examples of the use of 2-methyl-2-nitrosopropane as a radical trapping agent, see S. Terabe and R. Konaka, *J. Amer. Chem. Soc.*, **91**, 5655 (1969), and references therein.

(10) G. R. Chalfont, M. J. Perkins, and A. Horsfield, *ibid.*, **90**, 7141 (1968).

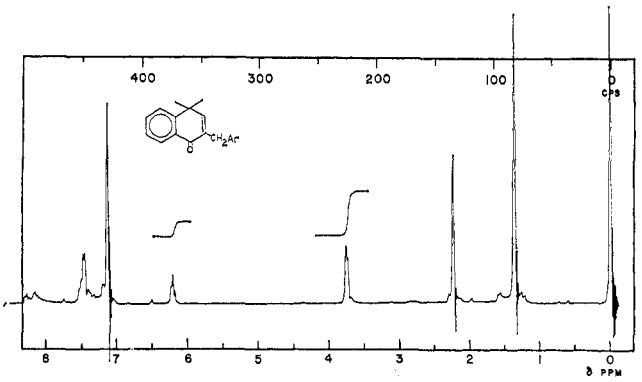
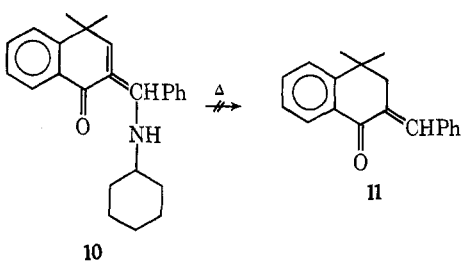


Figure 2.—Nmr spectrum of 2-(α-deuterio-*o*-methylbenzyl)-1,4-dihydro-4,4-dimethyl-1-ketonaphthalene.

Since **4a** was stable at room temperature and most radical traps decompose at elevated temperatures, no direct evidence could be obtained to support the radical mechanism.



10 11

In another experiment 2-[α-(cyclohexylamino)-benzyl]-1,4-dihydro-4,4-dimethyl-1-ketonaphthalene (**10**) was subjected to the same decomposition conditions for 6 hr, but nmr analysis showed no evidence of decomposition. In this case, the unsubstituted benzyl compound was used since it could be obtained more easily due to no reaction giving rearranged product, as well as the fact that **10** is a solid and **3a** is an oil.

Discussion

The complete transfer of the α deuterium to the benzylic position, the absence of deuterium transfer from the nitrogen, and the formation of cyclohexanone when water is added to the decomposition mixture argues against the radical mechanism as described above and supports the retro ene reaction as the most likely pathway. The driving force of the retro ene reaction has often been considered to be the energy gained from the formation of the new bonds minus the energy required to break the old bonds.[11] It is known that in the 4,4-dimethyl-1-tetralone system the endocyclic 2-benzyl isomer is thermodynamically more stable than the exocyclic 2-benzal isomer.[12] The greater stability of the endocyclic isomer must provide an important driving force for the decomposition of **4a** and **4b**.

By referring to this decomposition as a retro ene reaction, we do not mean to imply that the transition state is one of a truly concerted reaction. The retro ene reaction is an example of a symmetry-allowed 1,5

(11) H. M. R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).

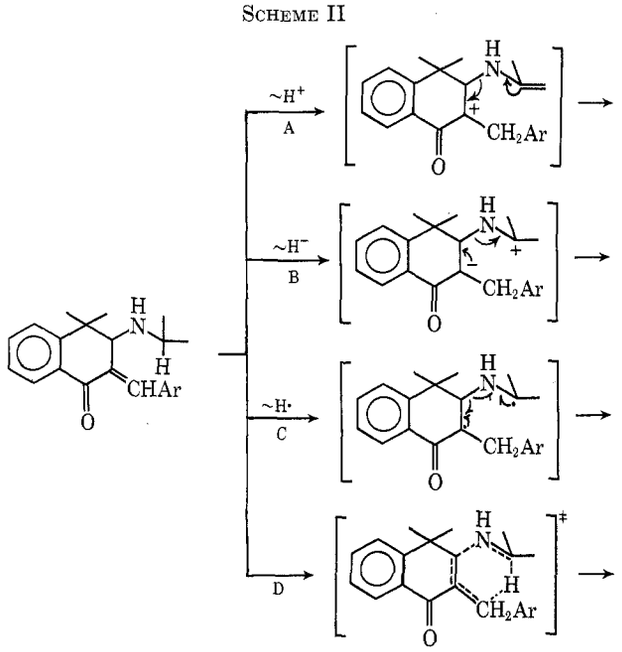
(12) N. H. Cromwell, R. P. Ayer, and P. W. Foster, *J. Amer. Chem. Soc.*, **82**, 130 (1960).

TABLE I

Compd	Mp, °C	Calcd, % C	H	N	X	Found, % C	H	N	X	Ir, cm⁻¹ C=O	C=C	Ar
1	108–109	86.92	7.29			86.71	7.47			1675	1620, 1610	1600
2	140–145 dec	67.61	5.39		22.49[a]	67.37	5.41		22.77[a]	1660	1645	1600
3a	129–131 dec[b]	68.72	7.10	3.08	17.58[a,b]	68.85	7.17	2.85	17.68[a]	1655	1640	1600
3b	236–237 dec[c]	74.67	7.62	3.78	9.58[c,d]	74.46	7.78	3.61	9.63[d]	1660	1640	1600
3c	121–122	82.95	8.41	4.03		82.66	8.45	4.03		1675	1660	1610
4a	116–117	83.60	8.37	3.75		83.38	8.35	3.69		1670	1620	1600
4b	96–97	82.84	8.16	4.20		82.70	8.25	4.36		1665	1610	1600
4c	127–128[e] 223–224[e]	62.49[e]	5.59[e]	9.72[e]		62.72[e]	5.63[e]	9.75[e]		1675	1625	1610
10	77.5–78.5	83.52	8.13	3.90		83.60	8.21	4.01		1660	1645	1600
5	62–64	86.92	7.29			87.15	7.32			1675	1625	1600
6	102–103	86.28	7.97			86.19	8.02			1675		1600
7	127–128	67.22	5.92		22.36[a]	66.93	5.94		22.31[a]	1680		1600
8	83–85	86.92	7.29			86.81	7.38			1660		1600

[a] Bromine. [b] Hydrobromide salt. [c] Hydrochloride salt. [d] Chlorine. [e] Picrate.

SCHEME II



hydrogen shift[13] and may be concerted, but a stepwise process cannot be excluded.[11]

There are several mechanistic extremes which may be considered and which are illustrated in Scheme II. Path A would involve a rate-determining proton transfer, path B a hydride transfer, path C a hydrogen atom transfer, while path D involves a concerted cyclic transition state. All of these possibilities would account for complete transfer of the α hydrogen as well as the products observed. The proton transfer, path A, might be unfavorable since the dipolar intermediate formed would possess a negative charge adjacent to a nitrogen atom with its lone pair and a positive charge adjacent to a carbonyl group. In contrast, the dipolar intermediate formed in path B, by the hydride transfer, would possess a negative charge stabilized by the adjacent carbonyl group as well as a positive charge adjacent to the stabilizing nitrogen atom. While the reaction may be more or less concerted, path B should have favorable energy characteristics. Thus, a concerted reaction with ionic character, *via* path B, appears to be a likely possibility. The data at hand does not allow us to exclude any of these possibilities. Kinetic experiments, particularly solvent effects and substituent effects on the rate and isotope effects, will be undertaken in order to further elucidate the mechanism of this reaction. The generality of this type of retro ene reaction is being explored.

(13) R. B. Woodward and R. Hoffman, *J. Amer. Chem. Soc.*, **87**, 2511 (1965).

Experimental Section[14]

trans-**2-(*o*-Methylbenzal)-4,4-dimethyl-1-tetralone**[15] (**1**) was prepared from 4,4 dimethyl-1-tetralone[16] and *o*-tolualdehyde according to a published procedure.[2] Recrystallization from ethanol yielded a pale yellow crystalline compound in 93% yield.

2-(α-Bromo-*o*-methylbenzyl)-1,4-dihydro-4,4-dimethyl-1-ketonaphthalene (**2**)[15] was prepared by a published procedure.[3] Recrystallization from CCl_4 yielded **2** as a white crystalline compound in 78% yield. Nmr, tlc, and elemental analysis showed this compound to be pure with no aromatic bromination or bromomethyl compound present.

Reaction of 2 with Amines.[17]—All reactions were carried out in benzene solution at room temperature as previously described.[3] After 3–5 days, the solvent was removed and the residue digested with ether. The solution was then filtered free of amine hydrobromide. The ethereal solution was then saturated with dry HCl gas to precipitate the amino products. The hydrochlorides were filtered from the solution and dissolved in ethanol. The free bases were released from their salts with aqueous $NaHCO_3$ and the resulting basic solution was extracted with ether. The ether was dried over anhydrous $MgSO_4$, filtered, and evaporated to yield an oil. An nmr spectrum was taken of this oil to determine the ratio of products.

2-*o*-Methylbenzal-3-(cyclohexylamino)-4,4-dimethyl-1-tetralone (**4a**) **and 2-[α-(Cyclohexylamino)-*o*-methylbenzyl]-1,4-dihydro-4,4-dimethyl-1-ketonaphthalene** (**3a**).[15]—The crude oil containing **3a** and **4a** in a ratio of 33 to 67 was triturated with a drop of petroleum ether (bp 30–60°) to yield a yellow solid which could be filtered after additional petroleum ether was used to dissolve the remaining oil. The yellow solid was recrystallized from ethanol to yield pure **4a** in 25% yield, mp 116–117°.

The solution remaining after the initial filtration was passed through a column of Florisil, eluting with benzene. The benzene

(14) Melting points were taken by the capillary method in a Mel-Temp melting point apparatus and are uncorrected. Infrared spectra were obtained as CCl_4 solutions using a Perkin-Elmer Model 237 spectrophotometer. Ultraviolet spectra were taken on a Cary Model 14 recording spectrophotometer. Proton magnetic resonance spectra were obtained on a Varian A-60 or A-60D spectrometer employing $CDCl_3$ solutions and are reported in hertz relative to internal TMS (0.0 Hz). Mass spectra were obtained with a Hitachi Model RMU-6D spectrometer, and electron spin resonance spectra were taken on a Joelco Model JES 3BSX spectrometer. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

(15) Analytical and ir data are presented in Table I for all compounds. Nmr and uv data are presented in Table II.

(16) R. D. Campbell and N. H. Cromwell, *ibid.*, **77**, 5169 (1955).

(17) Isolated yields are not reported for all compounds since they decomposed while being isolated. Relative ratios of products given are by nmr analysis of the mixture.

TABLE II

Compd	λ_{max}	$\epsilon \times 10^{-3}$	Nmr[a,b] $(CH_3)_2C$	CH_3Ph	$-CH_2-$	$CH=$	$-CH-$	Amino
1	228 sh	6.3[c]						
	282	8.97	77	139	d, 168, $J = 1.5$	480		
	295	8.98						
2	245	14.1[d]	93	153		?[e]	d, 409, $J = 2$	
	292 sh	2.98						
	302	2.08						
3a	257	9.55[c]	84, 86	147		?[e]	322	m, 50–170, cyclohexyl
	303 sh	2.37						
3b	257	10.4[c]	83, 85	150			325	85 NH; d, 65, $J = 6$;[f] d, 67, $J = 6$;[f] m, 169, $CH(CH_3)_2$
	300 sh	2.79						
3c	258	12.0[c]	85, 88	153		?[e]	325	s, 66
	300 sh	3.86						
4a	277	12.3[c]	85, 93	142		479	236	m, 10–130
	297	11.6						
4b	275	12.6[c]	89, 94	139		m, 488–503	239	139 NH; d, 24, $J = 6$;[f] CH_3-; d, 40, $J = 7$;[f] CH_3 plus NH; m, 139, $CH(CH_3)_2$
	297 sh	11.0				503		
4c	273	11.8[c]	86, 95	138		469	250	s, 41
	302	11.6						
10	257	11.0[c]	85, 88			?[e]	308	154, NH; m, 50–130, cyclohexyl
	300 sh	3.8						
5	270	12.4[c]	85	135	d, 164, $J = 1.5$	m, 408		
	300 sh	8.65						
6	251	12.8[c]	75, 83	142	m, 100–240			
	292	2.06						
7	258	11.3[d]	80, 98	149	229,[g] 151			
	295	2.76						
8	255	11.0	82	134	d, 226, $J = 1.5$	t, 374 $J = 1.5$		

[a] All nmr spectra were taken in $CDCl_3$ and chemical shifts are reported in hertz relative to internal TMS. [b] All compounds exhibited a multiplet downfield of the aromatic region assigned to the ring proton β to the carbonyl [see G. Glaros and N. H. Cromwell, *J. Chem. Educ.*, 46, 854 (1969), for spectra of similar compounds] (483–504 Hz) and aromatic protons in the region 400–465 Hz. [c] 95% ethanol. [d] Isooctane. [e] Buried under aromatic protons. [f] Nonequivalent methyl on isopropyl moiety. [g] Benzylic methylene.

fraction contained **4a** which had not crystallized out of the oily mixture plus the decomposition product **6**. Elution with ethyl acetate gave **3a** in 16% yield as a white oil.

2-*o*-Methylbenzal-3-(isopropylamino)-4,4-dimethyl-1-tetralone (4b) and 2-[α-(isopropylamino)-*o*-methylbenzyl]-1,4-dihydro-4,4-dimethyl-1-ketonaphthalene (3b).[15]—The mixed hydrochlorides were obtained in 86% yield in a 50/50 ratio. Trituration of the mixture of **3b** and **4b** was unsuccessful, so the mixture was chromatographed on a column of Florisil eluting with benzene. The benzene fractions were combined and the benzene was removed under reduced pressure. Nmr analysis showed this fraction to contain **4b** and **8**. This mixture was dissolved in ether; the ethereal solution was saturated with HCl to precipitate **4b** as its hydrochloride; the hydrochloride was isolated, dissolved in ethanol, and neutralized with aqueous $NaHCO_3$. The basic solution was extracted with ether, the ether dried ($MgSO_4$), and the solvent removed to yield an oil which slowly crystallized. Recrystallization gave pure **4b**, mp 96–97°, suitable for complete analysis (Tables I and II). Further elution with ethyl acetate provided **3b** as an oil, mp (HCl salt) 236–237°.

2-*o*-Methylbenzal-3-(*tert*-butylamino)-4,4-dimethyl-1-tetralone (4c) and 2-[α-(*tert*-Butylamino)-*o*-methylbenzyl]-1,4-dihydro-4,4-dimethyl-1-ketonaphthalene (3c).[15]—The crude oil obtained in 52% yield was shown by nmr analysis to contain **3c** and **4c** in a ratio of 15 to 85. Chromatography of the crude oil on a column of Florisil eluting with benzene afforded **4c** as an oil, mp (HCl salt) 127–128°, analyzed as its picrate, mp 223–224° (Tables I and II). Further elution with ethyl acetate gave **3c**, mp 121–122°, as a white solid.

2-[α-(Cyclohexylamino)benzyl]-1,4-dihydro-4,4-dimethyl-1-ketonaphthalene (10)[15] was prepared as previously described[3] from 3.4 g (0.01 mol) of 2-(α-bromobenzyl)-1,4-dihydro-4,4-dimethyl-1-ketonaphthalene, mp 117–118 (lit.[3] 115–116°). Only one compound was detected by nmr analysis. Recrystallization from ethanol give 0.97 g (28%) pure **10**, 92–93°.

***cis*-2-*o*-Methylbenzal-4,4-dimethyl-1-tetralone (5).**[15]—Irradiation of a solution of 0.9 g (0.0033 mol) of **2** in 100 ml of methanol using a B-100A Blakray source as previously described[4] produced **5** as deep yellow plates. Recrystallization from ethanol yielded 0.55 g (62%) of **5**, mp 62–64°.

2-(*o*-Methylbenzyl)-1,4-dihydro-4,4-dimethyl-1-ketonaphthalene (8).[15]—This compound could not be isolated in pure form except by decomposition of **4a** or **4b**. The following procedures yielded **8** contaminated with **1**. Column chromatography with alumina, silica gel, and Florisil, as well as tlc with silicic acid, silicic acid–$AgNO_3$, and Florisil, all failed to separate the two isomers **8** and **1**. In each case, however, the nmr spectra was the same as **1** and the decomposition product **8**.

A. Rearrangement with Palladium.—The procedure followed was that reported in the literature.[12] The product was shown by nmr analysis to contain 77% endo isomer **8** and 23% exo isomer **1**.

B. Dehydrohalogenation.—The scheme followed was that recorded in the literature.[2] Hydrogenation for 15 min at 40 psi of 2.76 g (0.01 mol) of **2** in methanol with PtO_2 yielded 2.3 g (83%) 2-*o*-methylbenzyl-4,4-dimethyl-1-tetralone (**6**), mp 102–103°.

Bromination[2] of 2.08 g (0.0075 mol) of **6** in $CHCl_3$ yielded, after the usual work-up, 2.1 g (79%) of 2-bromo-2-(*o*-methylbenzyl)-4,4-dimethyl-1-tetralone as white crystals, mp 127–128°.

Dehydrohalogenation of **7** gave a mixture of exocyclic isomer **1**, as well as endocyclic isomer **8**. This was shown by nmr when cyclohexylamine[18] or silver nitrate[12] was used as the dehydrobromination agent.

Thermal Decomposition.—The usual procedure involved adding the desired volume (2.5–5.0 ml) of benzene which had been dried over sodium to a weighed amount of **4a** in a test tube which has a constriction. This solution was deoxygenated by passing dry N_2 through it. The tube was then sealed and covered with Al foil to exclude light. The tube was suspended over boiling xylene (*ca.* 135°) for at least 3 hr. It was then opened, and the solvent was removed under reduced pressure. The product was a yellow oil which crystallized slowly and could be recrystallized from ethanol. Isolation was made easier by

(18) A. Hassner and N. H. Cromwell, *J. Amer. Chem. Soc.*, **80**, 901 (1958).

passing the decomposition solution through a small column of Florisil (2 mm × 4 cm in a small filter stem) to remove the colored material. Isolated yields were approximately 85–90% working on a scale of 40–150 mg of **4a**. Recrystallization of the solid formed gave white crystals, mp 83–85°.

Trapping Experiments. A.—The decomposition procedure described above was repeated, except that when the tube was opened, water was added and the mixture shaken well. Several extractions with water were performed and the aqueous extracts placed togenter in a flask containing freshly prepared 2,4-dinitrophenylhydrazine solution.[19] An immediate precipitate formed which was redissolved by heating the solution on a steam bath. The solution was allowed to cool and filtered to give the 2,4-dinitrophenylhydrazone, mp 156–157° (lit.[5] 160°).

B.—The decomposition tube was attached to a stopcock. After 1.5 hr, the stopcock was opened and a 1-ml sample (0.9 *M*) of 2-methyl-2-nitrosopropane in benzene was added. The tube cooled, and a sample was placed in an esr tube. The spectrum consisted of a triplet, $J \approx 15.5$ G.

2-Methyl-2-nitrosopropane was synthesized using literature methods illustrated in the reaction scheme below.

$$(CH_3)_3CNH_2 \xrightarrow{KMnO_4} (CH_3)_3CNO_2{}^{20}$$

$$(CH_3)_3CNO_2 \xrightarrow[Zn]{NH_4Cl} (CH_3)_3CNHOH{}^{21}$$

$$(CH_3)_3CNHOH \xrightarrow[OH^-]{Br_2} (CH_3)_3CNO{}^{22}$$

(19) Reference 7, p 111.
(20) N. Kornblum, *Org. React.*, **12**, 133 (1962).
(21) F. D. Greene and J. F. Pazos, *J. Org. Chem.*, **34**, 2269 (1969).
(22) W. D. Emmons, *J. Amer. Chem. Soc.*, **79**, 6522 (1957).

Control Experiments.—The same decomposition conditions were applied to **3c**, **4c**, and **10**. Analysis by nmr of the crude reaction mixture showed no decomposition.

In another experiment, 100 mg of **4a** was dissolved in benzene, and the solution was extracted five times with 1 ml of D_2O. The benzene layer was dried over $MgSO_4$ and the solvent removed. The product was recrystallized from CH_3OD. Mass spectral analysis showed it to contain 60% deuterium atom/molecular. A 52-mg sample of this *N*-deuterio-**4a** was dissolved in 1 ml of benzene and decomposed as described above. The nmr spectrum of the decomposition product was identical with that obtained from normal **4a** (see Figure 1).

Registry No.—**1**, 30765-45-8; **2**, 30765-46-9; **3a** HBr, 30765-47-0; **3b** HCl, 30765-48-1; **3c**, 30765-49-2; **4a**, 30765-50-5; **4b**, 30765-51-6; **4c** HCl, 30765-52-7; **4c** picrate, 30765-53-8; **5**, 30765-54-9; **6**, 30765-55-0; **7**, 30765-56-1; **8**, 30768-30-0; **8-*d***, 30768-31-1; **10**, 30768-32-2.

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Carbon–Sulfur Cleavage of 1-Adamantyl Sulfides[1]

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Acid-catalyzed carbon–sulfur cleavage at the bridgehead of some 1-adamantyl sulfides was encountered. β-(1-Adamantanethio)ethylamine and ε-(1-adamantanethio)pentylamine were converted by boiling hydrochloric acid to 1-chloroadamantane (80–90%) and the corresponding ω-mercaptoalkylamine. A similar cleavage was exhibited by *S*-(1-adamantyl)isothiuronium bromide and several amidine derivatives of β-(1-adamantanethio)-ethylamine. By direct contrast, 1-methyl- and 1-ethylthioadamantane were recovered quantitatively under these conditions. 1-Adamantyl alkyl ethers were converted by hydrochloric acid at 25° to 1-chloroadamantane, irrespective of the nature of the substituent in the alkyl side chain. Whereas 1-adamantanol was transformed to 1-chloroadamantane (92%) by cold concentrated hydrochloric acid, 1-adamantanethiol remained unchanged even on boiling with this acid.

During an attempted acid-catalyzed hydrolysis of the thiosulfate group in the α-amidinium Bunte salt **20** to the corresponding thiol by means of hot concentrated hydrochloric acid, cleavage of the sulfide moiety took place and 1-chloroadamantane (**1**) was isolated in 75% yield. This unexpected displacement at the 1-adamantane bridgehead prompted us to investigate this type of reaction further. In view of the facile solvolysis of 1-adamantyl ethers and sulfonates,[2-4] it was of further interest to compare the relative stability of similarly constituted 1-adamantyl ethers and sulfides and related systems toward hydrochloric acid.

The behavior of 1-adamantanol (**2**) and the corresponding thiol **12** toward hot concentrated hydrochloric acid was investigated first. Reaction of **2** furnished 1-chloroadamantane (**1**, 94%) after 0.5 hr, while **12** was recovered quantitatively even after 3 hr. This conversion of **2** to **1** appeared to be a simpler procedure than the one reported previously using thionyl chloride.[4]

Some simple ethers and thioethers in this series were examined next. It had been found that on shaking with cold concentrated hydrochloric acid for a short time, 1-methoxyadamantane (**3**) yielded **1** (96.5%),[3] but it was claimed that a similar cleavage of the ethyl analog **4** was more difficult.[3] We have found that **4**[2] was converted quantitatively to **1** by cold concentrated

(1) Support for this work by the U. S. Army Medical Research and Development Command (Contract DADA 17-69-C-9110) is gratefully acknowledged.
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