Product Studies. A. Cyclobutylcarbinyl Brosylate (4-OBs). Cyclobutylcarbinyl brosylate (5 mmol) was dissolved in sufficient solvent (containing 7.5 mmol of urea) to give 25 ml of solution. Five-milliliter aliquots were transferred to 10 ml ampoules, sealed under N_2 and immersed in a constant temperature bath at 55°. After 10 half-lives, the ampoule contents were poured into 50 ml of water and the resultant mixture was extracted once with a 5-ml portion of methylene chloride. The extract was washed four times with 10-ml portions of cold water and dried over magnesium sulfate. The crrude extract on analysis by gas chromatography (50°, 50 ml/min He flow rate) gave rise to two peaks, A (2.2 min retention time) and B (6.3 min retention time), with 1:1 relative peak areas, in addition to the air and solvent peaks. Peak A was identified as cyclopentene by comparison of retention time with that of an authentic sample. Peak B was identified as cyclopentyl 2,2,2-trifluoroethyl ether by nmr analysis: δ 3.70 (q, 2 H, OCH_2CF_3)[3d,10,16] and 1.5–2.0 (broad 8 H, ring protons).

B. Cyclopentylcarbinyl Brosylate (5-OBs). Cyclopentylcarbinyl brosylate was solvolyzed as in section A. After 10 half-lives, the ampoule contents were poured into 50 ml of water and the resultant mixture was extracted three times with 25-ml portions of methylene chloride. The combined extracts were washed three times with 30-ml portions of cold water and dried over anhydrous sodium sulfate, and most of the solvent was removed by distillation with a Nester-Faust NFA-200 autoannular still. The residue on analysis by gas chromatography (60°, 40 ml/min He flow rate) gave rise to two peaks, A (2.5 min retention time) and B (7.8 min retention time), with 1.9:1.0 relative peak areas, in addition to the air and solvent peaks. Peak A was identified as cyclohexene by comparison of retention time with that of an authentic sample. Peak B was identified by nmr analysis as cyclohexyl 2,2,2-trifluoroethyl ether: δ 3.73 (q, 2 H, OCH_2CF_3)[3d,10,16] and 3.2–3.5 (broad, 1 H, $C_2CHOCH_2CF_3$).[3d]

C. Cyclohexylcarbinyl Brosylate (6-OBs). Cyclohexylcarbinyl brosylate was solvolyzed and worked up as in section B. The residue on analysis by gas chromatography (60°, 40 ml/min He flow rate) gave rise to four peaks, A (3.0 min retention time), B (3.3 min retention time), C (9.3 min retention time), and D (12.4 min retention time), with 2.8:1.4:6.6:1.0 relative peak areas, in addition to the air and solvent peaks. Peaks A and B were identified as methylenecyclohexane and 1-methylcyclohexene respectively by comparison of retention times with those of authentic samples. Peak C was isolated by preparative gas chromatography and identified by nmr analysis as 1-methylcyclohexyl 2,2,2-trifluoroethyl ether: δ 3.70 (q, 2 H, OCH_2CF_3)[3d,10,16] and 1.1 (s, 3 H, CCH_3). Peak D was identified as cyclohexylmethyl 2,2,2-trifluoroethyl ether on the basis of retention time and nmr analysis of peak C fraction.

D. Cyclohexyl Tosylate. Cyclohexyl tosylate was solvolyzed as in section B. The solvolysis solution was then injected into the gas chromatograph, giving two peaks, A and B, with 4.0:1.0 relative peak areas, in addition to a very large solvent peak. By comparison with the chromatograms obtained in section B, A and B were identified as cyclohexene and cyclohexyl 2,2,2-trifluoroethyl ether, respectively.

Registry No.—4-OBs, 51108-24-8; 5-OBs, 38806-24-5; 6-OBs, 51108-25-9; c-$C_6H_{11}OTs$, 953-91-3.

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Mobile Keto Allyl Systems. XVI.[1] The Thermal Decomposition of 2-(α-*N*-Methyl-*tert*-butylaminobenzyl)-1-indenone A Deamination–Rearrangement

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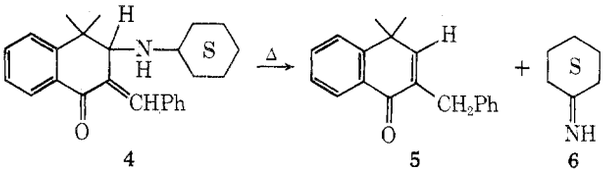
The first reported thermal decomposition of a β-keto allyl amine resulting in a deamination–rearrangement was that by Maury and Cromwell[2] in which 2-(α-diisopropylaminobenzyl)-1-indenone (**2a**) was found to form 2-benzal-1-indanone (**3**) upon heating and what was tentatively identified by vpc as diisopropylamine. Since that initial report Glaros and Cromwell[3,4] have studied extensively the thermal decomposition of the related β-keto allyl amine **4** and have shown that the decomposition proceeds *via* a retroene mechanism producing α,β-unsaturated ketone **5** and presumably imine **6.** In view of these previous results a rein-



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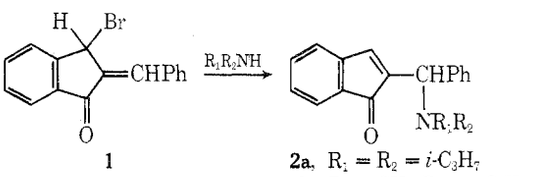
vestigation of the thermal rearrangment of compounds related to **2a** was undertaken. The results of this study for 2-(α-*N*-methyl-*tert*-butylaminobenzyl)-1-indenone (**2b**) are the subject of the present paper.

When **2b,** prepared by the reaction of *N*-methyl-*tert*-butylamine with 3-bromo-2-benzal-1-indanone[5] (**1**), was heated in a sealed tube at 130° for 3 hr 2-benzal-1-indanone (**3**) was isolated in 85% yield. In addition evidence was obtained for the existence of *N*-methylene-*tert*-butylamine (**7**) as a coproduct. Treatment of the decomposition



1 2a, $R_1 = R_2 = i\text{-}C_3H_7$
b, $R_1 = CH_3$; $R_2 = t\text{-}C_4H_9$

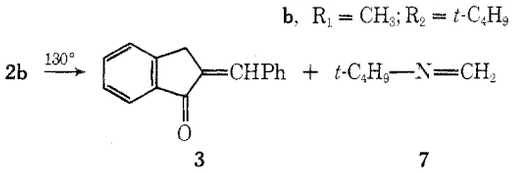


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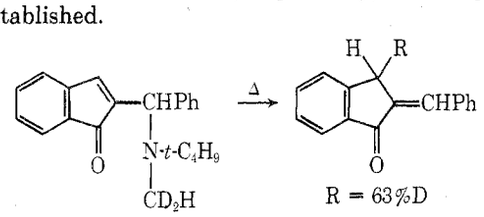
Table I
Kinetic Data for 2b and 4 in Isooctane

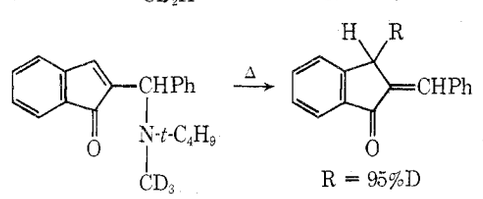
Temp, °C	K^a, sec^{-1} 2b	4
105	3.1×10^{-5} (± 0.1)[b]	
111	5.3×10^{-5} (± 0.4)	
120	1.2×10^{-4} (± 0.1)	2.3×10^{-5} (± 0.1)
130	2.7×10^{-4} (± 0.2)	
135		1.5×10^{-4} (± 0.1)
150		1.9×10^{-4} (± 0.4)
	E_a = 25.8 kcal	E_a = 25.4 kcal
	ΔS^+ = −13 eu at 135°	ΔS^+ = −17 eu at 135°

[a] Average of three runs at each temperature unless otherwise noted. [b] Average of two runs.

mixture with aqueous hydrogen chloride, followed by evaporation of the aqueous extract, afforded *tert*-butylamine hydrochloride in 30% yield, obviously resulting from the acid hydrolysis of imine **7**. Additional evidence to support the formation of **7** was provided by following the course of the decomposition in a sealed nmr tube. Two new absorptions appeared at δ 1.17 (d, J = 2 Hz) and 3.90 (d, J = 1.2 Hz), which increased in intensity with time at the expense of the absorptions of **2b** at δ 1.10 and 5.40. The new low-field absorption was assigned to the resonance for the benzal proton in **3** while the high-field adsorption was assigned to the resonance of the *tert*-butyl group in **7** based upon comparison with a pure sample. The methylene protons of **7**, although not readily discernible, were found by integration to lie under the aromatic multiplet.

The formation of α,β-unsaturated ketone **2** and imine **7** appears to be the result of a retroene reaction being operative. Additional proof of this hypothesis was found in a deuterium labeling experiment. Not only does a retroene reaction demand the formation of imine **7**, but also it requires that the hydrogen α to the nitrogen in the amino moiety be transferred to the benzylic position. Indeed when 2-(α-*N*-methyl-d_2-*tert*-butylaminobenzyl)-1-indenone and 2-(α-*N*-methyl-d_3-*tert*-butylaminobenzyl)-1-indenone were allowed to decompose in the usual manner an 63 and 95% deuterium transfer, respectively, to the 3 position was established.





Although an extensive kinetic investigation was not carried out, a comparison of the first-order kinetic results obtained with those of Glaros and Cromwell[4] for **4** shows a marked similarity (Table I). The difference in the entropies of activation we feel may be the result of a more crowded transition state for **4**. It is therefore believed that both **2b** and **4** decompose by a similar retroene reaction mechanism, one which may best be explained as "a concerted reaction passing through a dipolar transition state."[4]

Experimental[6] Section

Preparation of *N*-Methyl-*tert*-butylamine and Related Compounds. A. *N*-Methyl-*tert*-butylamine. The procedure of Heath and Mattocks[7] was employed with modification. To 22.0 g (0.579 mol) of lithium aluminum hydride suspended in 300 ml of dry ether was added 23.0 g (0.227 mol) of *N*-*tert*-butylformamide (Frinton Laboratories) over a 0.5-hr period. The mixture was refluxed for 2.5 hr and then allowed to stir overnight at room temperature. It was next cooled in an ice bath and the excess lithium aluminum hydride decomposed by the careful dropwise addition of water. The resulting aluminum salts were filtered and washed well with ether. The filtrate was dried over magnesium sulfate and distilled through a 10-cm Vigreux column. The fraction boiling at 50–70° was collected and redistilled to yield 5.0 g (24.8%) of *N*-methyl-*tert*-butylamine as a colorless liquid, bp 64–66° (lit.[8] bp 58–60°): nmr ($CDCl_3$) 2.33 (s, 3 H, $-CH_3$), 1.43 (bs, 1 H, NH), 1.10 (s, 9 H, *tert*-butyl). The forerun, bp 33–50°, was treated with dry HCl gas and gave 9.9 g (35.8%) of *N*-methyl-*tert*-butylamine hydrochloride as colorless plates, mp 254–256° (lit.[7] mp 252–254°).

B. *N*-Methyl-d_2-*tert*-butylamine. The same procedure as in (A) above was used and lithium aluminum deuteride was employed in lieu of lithium aluminum hydride. From 2.0 g (0.047 mol) of lithium aluminum deuteride and 4.0 g (0.039 mol) of *N*-*tert*-butylformamide, there was obtained 0.52 g (15.3%) of product, bp 65–66°: nmr ($CDCl_3$) δ 2.31 (m, 1 H CHD_2), 1.46 (bs, 1 H, NH), 1.10 (s, 9 H, *tert*-butyl); mass spectrum 97.4% d_2.

C. *N*-Methyl-*N*-nitroso-*tert*-butylamine. The procedure of Heath and Mattacks[7] was employed without variation. From 18.0 g (0.261 mol) of sodium nitrite and 12.0 g (0.098 mol) of *N*-methyl-*tert*-butylamine hydrochloride there was obtained 10.1 g (88.0%) of the *N*-nitroso amine as a lemon-yellow oil, bp 31–33° (0.2 mm) (lit.[7] bp 66° (5 mm)); nmr ($CDCl_3$) δ 3.00 (s, 3 H, CH_3), 1.53 (s, 9 H, *tert*-butyl).

D. *N*-Methyl-d_3-*N*-nitroso-*tert*-butylamine. To 2.0 g (0.017 mol) of *N*-methyl-*N*-nitroso-*tert*-butylamine was added 45 ml of 1.3 *M* sodium deuterioxide in deuterium oxide and 20 ml of methanol-d_1 (for solubility). The resulting mixture was heated under reflux for 18 hr. The reaction mixture was cooled and extracted with ether (4 × 50 ml). The ether extracts were dried and evaporated to yield 1.9 g of a yellow oil: nmr ($CDCl_3$) δ 3.00 (m, <1 H, CD_3), 1.53 (s, 9 H, *tert*-butyl); mass spectrum 82.8% d_3.

Recycling of the above product with fresh sodium deuterioxide solution and proceding as above gave 1.7 g (85.0%) of a yellow oil: mass spectrum 94.8% d_3.

E. *N*-Methyl-d_3-*tert*-butylamine Hydrochloride. Into a solution of the above trideuterated nitroso amine (1.7 g, 0.014 mol) in 35 ml of dry ether was passed dry HCl gas until a permanent dark yellow color resulted. The reaction mixture was then stirred at room temperature for 1 hr. It was then filtered and the precipitate washed well with dry ether and air dried. Recrystallization from ethanol gave 1.0 g (55.6% of the amine hydrochloride salt), mp 254–256°: nmr ($CDCl_3$). δ 1.42 (s); mass spectrum 94.8% d_3.

F. *N*-Methylene-*tert*-butylamine (7). The procedure of Hurwitz[9] was utilized without variation. From 13.0 g (1.40 mol) of *tert*-butylamine and 125 ml (1.60 mol) of 37% formaldehyde solution there was obtained 79.8 g (66.9%) of the Schiff base as a colorless liquid, bp 64–66° (lit.[9] bp 63–65°): nmr ($CDCl_3$) δ 7.37 (d, J = 2 Hz, 2 H, $N=CH_2$), 1.17 (d, J = 2 Hz, 9 H, *tert*-butyl).

Preparation of 2-(α-Aminobenzyl)-1-indenones. The preparation of several aminoindenones has already been described in the literature.[10] The same general procedure was employed to prepare the following indenones.

A. 2-(α-*N*-Methyl-*tert*-butylaminobenzyl)-1-indenone (2b). From 0.50 g (0.0017 mol) of 3-bromo-2-benzal-1-indanone and 0.29 g (0.0033 mol) of *N*-methyl-*tert*-butylamine was obtained 0.40 g (77.2%) of **2b** as orange crystals, mp 66–67°; ir (CCl_4) 1715 cm^{-1} (C=O); uv (hexane) λ_{max} (ϵ) 240 (30,000), 307 (1800), 317 (1600), 333 (1040), 390 (800), 407 (1000), 430 nm (1,200); nmr ($CDCl_3$) δ 7.63–6.85 (m, 10 H, 9 aromatic protons + 1 vinyl proton), 5.42 (d, J = 0.8 Hz, benzylic), 2.26 (s, 3 H, $-CH_3$), 1.10 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{21}H_{23}NO$: C, 82.59; H, 7.59; N, 4.59. Found: C, 82.61; H, 7.54; N, 4.46.

B. 2-(α-*N*-Methyl-d_2-*tert*-butylaminobenzyl)-1-indenone was obtained in 80% yield as orange crystals, mp 65–67°: nmr ($CDCl_3$) δ 7.57–6.97 (m, 10 H, 9 aromatic protons + 1 vinyl proton), 5.40 (bs, 1 H, benzylic), 2.25 (m, 1 H, $-CD_2H$), 1.10 (s, 9 H, *tert*-butyl); mass spectrum 97% d_2.

C. 2-(α-*N*-Methyl-d_3-*tert*-butylaminobenzyl)-1-indenone was obtained in 50% yield as orange crystals, mp 65–67°: nmr ($CDCl_3$) δ 7.57–6.97 (m, 10 H, 9 aromatic protons + 1 vinyl proton), 5.40 (bs, 1 H, benzylic), 1.10 (s, 9 H, *tert*-butyl); mass spectrum 94.2% d_3.

The thermal decomposition and kinetic method employed were as previously described,[3,4] except the concentration of **2b** was determined spectrophotometrically at λ 321, 323, 325, and 327 nm.

Trapping Experiment. The decomposition procedure was repeated as before except that when the decomposition solution was evaporated, the distillate was condensed by means of a Dry Ice–acetone trap and then refluxed with aqueous hydrochloric acid for 2 hr. Evaporation gave a 30% yield of *tert*-butylamine hydrochloride, mp 270–285° (lit.[11] mp 270–280°).

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Registry No.—**1**, 5387-50-8; **2b**, 53059-34-0; **3**, 5706-12-7; **7**, 13987-61-6; *N*-methyl-*tert*-butylamine, 14610-37-8; *N*-*tert*-butylformamide, 2425-74-3; *N*-methyl-d_2-*tert*-butylamine, 53059-35-1; *N*-methyl-*N*-nitroso-*tert*-butylamine, 2504-18-9; *N*-methyl-d_3-*N*-nitroso-*tert*-butylamine, 53059-36-2; *N*-methyl-d_3-*tert*-butylamine hydrochloride, 53059-37-3; 2-(α-*N*-methyl-d_2-*tert*-butylaminobenzyl)-1-indenone, 53059-38-4; 2-(α-*N*-methyl-d_3-*tert*-butylaminobenzyl)-1-indenone, 53059-39-5.

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Hexenopyranose Derivatives Obtained by Allylic Bromination of 6,8-Dioxabicyclo[3.2.1]oct-2-ene and 6,8-Dioxabicyclo[3.2.1]oct-3-ene and Subsequent Basic Solvolysis of the Product

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The preparation from acrolein of the two isomeric bicyclic olefins 6,8-dioxabicyclo[3.2.1]oct-3-ene (**1**, Scheme I)[3,4] and 6,8-dioxabicyclo[3.2.1]oct-2-ene (**2**)[4] has permitted the formation of the corresponding epoxides **3** and **4** from which a number of 2- and 4-monodeoxy-[3,4] and dideoxy-DL-hexopyranoses[5,6] have been prepared. Rearrangement of the epoxide **3** to the allylic alcohol **7** with *n*-butyllithium has led to the preparation of DL-glucose,[7,8] DL-allose, and DL-galactose.[9] More recently,[10] the epoxides **3** and **4** have been converted by standard procedures to the epoxides **5** and **6** respectively. Reaction of *n*-butyllithium with epoxide **4** and of lithium diethylamide with the epoxides **5** and **6** gave the allylic alcohols **9**, **8**, and **10** respectively,[10] compounds which then by well-established procedures could provide the remaining isomeric DL-aldohexoses.

The reactions employed in converting **3** to **7** and **8**, and **4** to **9** and **10**, have permitted the introduction of a functional group (OH) not only at each of the olefinic carbon atoms in **1** and **2** but also at the saturated carbon atoms C-2 and C-4 in **1** and **2**, respectively. We have now examined the allylic bromination of olefins **1** and **2** and, as well, the reaction of the resulting allyl bromide with base to determine the value of such a scheme in producing one or more of the compounds **7–10**. This paper describes the results of our findings.

Results and Discussion

The benzoyl peroxide catalyzed reaction of *N*-bromosuccinimide (NBS) with either **1** or **2** in carbon tetrachloride gave, by final distillation, an excellent yield of 4-*exo*-bromo-6,8-dioxabicyclo[3.2.1]oct-2-ene[11] (**12**, Scheme II) of better than 98% purity according to the elemental analysis and both 100- and 220-MHz pmr spectra. Thin-layer chromatography showed only one spot. Accordingly only traces of impurity or of another isomer could be present. Analysis of the 100-MHz pmr spectrum, by double irradiation, identified the signals due to each proton and proved conclusively that the double bond was located between C-2 and C-3 of **12**. Furthermore, the narrow signal at δ 5.56 of $W/2 \approx 3.5$ Hz ($J_{5,4} \approx 0.5$ Hz, $J_{5,3} \approx 1.8$ Hz) due to the anomeric proton at C-5 provided good evidence that the proton at C-4 was endo. Thus, the Dreiding model of structure **12** showed a dihedral angle of about 85° between protons on C-4 and C-5. A small coupling is expected when the dihedral angle is in the neighborhood of 90° especially if the carbon atoms involved are also attached to highly electronegative elements. Unfortunately there was no access to the epimer of **12**, in which the proton is exo and in which the dihedral angle between the protons at C-4 and C-5 is about 35°; hence we were unable to corroborate our view concerning the exo disposition of the bromine atom at C-4, by comparison of the $J_{5,4}$ coupling in these two cases. However, we have recently prepared[10] the epimers **7** and **8** (Scheme I) by unequivocal routes. The anomeric proton of **7** at C-5 formed a dihedral angle of ~85° with the proton at C-4 and gave a narrow signal $W/2 \approx 4$ Hz ($J_{5,4} \approx 1.0$ Hz, $J_{5,3} \approx 2.0$ Hz) while the anomeric proton of **8** formed a dihedral angle of about 35° with the proton on C-4 and provided a signal which was clearly a triplet with $W/2 \approx 6.5$ Hz, $J_{5,4} \approx 3.0$ Hz, and $J_{5,3} \approx 2.0$ Hz. This comparison lends support to our view that the bromine atom in our product is exo as shown in **12**.

The benzoyl peroxide catalyzed bromination was clean and was completed well within 3 hr. The same product was obtained by heating the reactants in the absence of the peroxide, but these latter conditions required extensive heating for as long as 48 hr, involving a clearly apparent induction period, and resulted in concurrent polymerization and lower yields of the bromide **12**. The results obtained indicate that the reaction involves a free-radical mechanism, a view which is supported by the observation that the introduction of traces of hydroquinone markedly retards the reaction and leads to extensive decomposition during the longer heating period. The formation of apparently only one of the four possible isomers indicates a highly selective process in which **11b** (Scheme II) is the important radical species and that the endo approach of the brominating agent to C-4 is strongly inhibited by the rigidly attached 1,3-dioxolane ring.

Reaction of **12** with sodium methoxide in methanol was slow, requiring as long as 80 hr of continuous heating under reflux for completion. Shorter times gave unchanged bromide. Gas–liquid chromatography (glc) of the crude reac-