of Florisil) and eluted successively with hexane (75 ml), 50% ether–hexane (50 ml), ether (150 ml), and then chloroform (50 ml). The pure oxazolidone was obtained from the ether eluate; it had mp 87–88° (lit.[13] mp 87–87.5°) (0.76 g, 45% yield). Infrared ($CHCl_3$) showed 3520, 3350 (NH), 1760 (carbonyl), 1220, 1070, 970, 695 cm^{-1}.

cis-**Cyclohexano**[*b*]-**2-oxazolidone.**—Prepared by pyrolysis of neat ethyl N-(2-chlorocyclohexyl)carbamate (2.06 g, 0.01 mole) at 180–185°, the crude product in a minimum of chloroform was placed on a Florisil column (1.5 g of crude oxazolidone–30 g of Florisil). Elution successively with hexane (50 ml) and 25% ether–hexane (50 ml) afforded 0.32 g of unconverted starting material. Further elution with 50% ether–hexane (50 ml) and 75% ether–hexane (100 ml) gave a colorless oil. Low-temperature recrystallization from ether–hexane yielded the pure oxazolidone, mp 54–55° (lit.[14] mp 55–56°) (0.76 g, 65% yield). Infrared (CCl_4) showed 3300 (NH), 1760 (carbonyl), 1220, 995, 955 cm^{-1}.

cis- **and** *trans*-**4,5-Diethyl-2-oxazolidone.**—Prepared by neat pyrolysis of an approximately equimolar mixture of *erythro*- and *threo*-ethyl N-(2-chloro-1,2-diethyl ethyl)carbamate (2.08 g, 0.01 mole) at 180–185°, the crude product in a minimum of chloroform was placed on a Florisil column (1.4 g of crude oxazolidone–25 g of Florisil) and eluted successively with hexane (50 ml), 50% ether–hexane (100 ml), and ether (150 ml). The ether eluates on evaporation yielded a colorless oil which was recrystallized from ether–hexane. Crystals were obtained that analyzed perfectly for the expected oxazolidone but the melting range (66–72°) indicated that the product (1.04 g, 70%) was a mixture of *cis* and *trans* isomers. Infrared ($CHCl_3$) showed 3540, 3350 (NH), 1760 (carbonyl), 1230, 985 cm^{-1}.

1-Iodo-2-(N-Carbomethoxy)amino-*n***-dodecane.**—Prepared from 1-dodecene (8.4 g, 0.05 mole) by reaction with preformed iodine isocyanate in tetrahydrofuran at −50° followed by reaction with methanol,[9] the iodocarbamate was recrystallized from 25% ether–hexane (6.5 g, 35% yield), mp 67.5–69°. Infrared (CCl_4) showed 3400 (NH), 1710 (carbonyl), 1510 (amide II), 1250, 1100, 900 cm^{-1}.

4-*n***-Decyl-2-oxazolidone** (**4**).—The iodocarbamate described above (2.5 g, 0.007 mole) was heated at 150° in a nitrogen atmosphere until methyl iodide evolution ceased. The crude reaction product was recrystallized from hexane at −20° (0.8 g, 55% yield), mp 31.5–32.5°. Infrared (CCl_4) showed 3300 (NH), 1760 (carbonyl), 1240, 1050, 940 cm^{-1}.

Anal. Calcd for $C_{13}H_{25}NO_2$: C, 68.7; H, 11.1; N, 6.16. Found: C, 68.6; H, 11.0; N, 6.08.

2-Hydroxy-*n***-dodecylamine.**—1,2-Dodecane epoxide[15,16] (18.4 g, 0.10 mole) in ethanol (500 ml) was added in one portion to a solution of sodium azide (7.8 g, 0.12 mole) and ammonium chloride (6.5 g, 0.12 mole) in water (200 ml), and the solution was refluxed for 48 hr. The reaction mixture was poured into water (800 ml) and extracted with ether (four 100-ml portions). The ether solution was dried over anhydrous sodium sulfate and the ether was removed in a rotary evaporator. The crude residual azidohydrin (21.3 g, 94% yield) was dissolved in ethanol (300 ml) and hydrogenated at room temperature in a stirring autoclave for 48 hr at 780 psi with platinum oxide catalyst (0.50 g). The solution was filtered and evaporated to dryness. The crude amino alcohol was recrystallized from hexane (12.5 g, 62% yield), mp 51–52°. Infrared (CCl_4) showed 3500 (OH), 3400 (NH), 1480, 1070 cm^{-1}.

Anal. Calcd for $C_{12}H_{26}NO$: C, 71.63; H, 13.52; N, 6.96. Found: C, 71.49; H, 13.22; N, 6.70.

5-*n***-Decyl-2-oxazolidone** (**3**).—Prepared from the amino alcohol (5.0 g, 0.025 mole) and diethyl carbonate (10 g, 0.08 mole) by Homeyer's method,[10] the crude product was recrystallized from ethanol (3.6 g, 63% yield), mp 86–87.5°. The product was identical with that from the pyrolysis of N-(2-chloro-*n*-dodecyl)-carbamate already described. Infrared (CCl_4) showed 3300 (NH), 1760 (carbonyl), 1240, 1095, 955 cm^{-1}.

Anal. Calcd for $C_{13}H_{25}NO_2$: C, 68.68; H, 11.08; N, 6.16. Found: C, 68.85; H, 11.05; N, 6.09.

Acknowledgment.—The authors acknowledge with thanks support of this investigation by Public Health Service Research Grants No. CA-07803 and CA-07174 from the National Cancer Institute.

(13) See Table II, footnote *a*.

(14) See Table II, footnote *b*.

(15) D. Swern, G. N. Billen, and J. T. Scanlan, *J. Am. Chem. Soc.*, **68**, 1504 (1946).

(16) Commercial peroxyacetic acid (40%), with sodium acetate added to neutralize sulfuric acid, was employed. The distilled reaction product was >97% 1,2-epoxydodecane (glpc).

Azetidinyl Ketones. II.[1] Synthesis, Epimerization, and Nuclear Magnetic Resonance Spectra of 1-*t*-Butyl-2-phenyl-3-benzoylazetidines

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Received August 8, 1966

trans-α-(Bromomethyl)chalcone (**1**) reacts with *t*-butylamine in solvent pentane to give 2-[α-(N-*t*-butylamino)-benzyl]acrylophenone (**2**) as the kinetically favored product which readily rearranges in more polar solvent media to the thermodynamically more stable α-[(N-*t*-butylamino)methyl]chalcone (**3**) and no evidence for an azetidinyl ketone is observed. When **2** or **3** was treated with hydrogen bromide followed by reaction with base, **2** produced the *cis*-1-*t*-butyl-2-phenyl-3-benzoylazetidine (**4**) while **3** gave *trans* isomer **5**; *cis* isomer **4** is readily converted into *trans* isomer **5** by sodium methoxide in methanol. Spectral studies, especially nmr and deuteration of the azetidines, were employed to assign the configurations. The mechanism and stereochemistry of the reactions leading to these stereospecific cyclizations to produce the arylaroylazetidines in good yield are discussed.

In a preliminary communication[3] concerning the study of mobile ketoallyl systems, it was reported that *trans*-α-(bromomethyl)chalcone (**1**) in solvent pentane reacts with 2 molar equiv of *t*-butylamine to give exclusively, in high yield, the rearranged substitution product, 2-[α-(N-*t*-butylamino)benzyl]acrylophenone (**2**). This compound under the proper conditions may be induced to rearrange quantitatively to the thermodynamically more stable isomeric form, α-[(N-*t*-butylamino)methyl]chalcone (**3**).

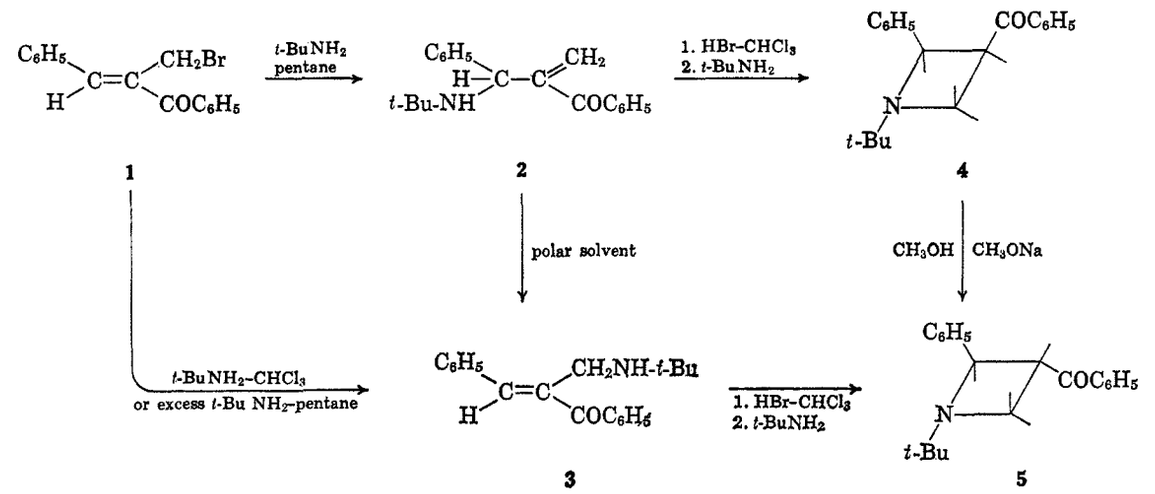
Although **2** is reasonably stable with respect to isomerization either in the crystalline state or in solvent pentane, in solvent chloroform (and other slightly polar solvents) it readily rearranges to **3**. Even in solvent pentane, however, **2** reacts readily with added *t*-butylamine to give **3**. The rearrangement **2** → **3** was then suggested to involve a four-membered-ring dipolar intermediate (X).

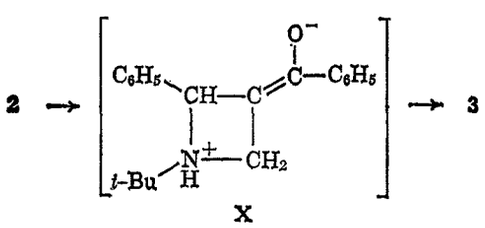
(1) See N. H. Cromwell and Earl Doomes, *Tetrahedron Letters*, **No. 34**, 4037 (1966), for the first announcement of the synthesis of 2-aryl-3-aroylazetidines.

(2) To whom communications concerning this article should be addressed: Department of Chemistry, University of Nebraska, Lincoln, Nebraska.

(3) R. P. Rebman and N. H. Cromwell, *Tetrahedron Letters*, **No. 52**, 4833 (1965).

SCHEME I



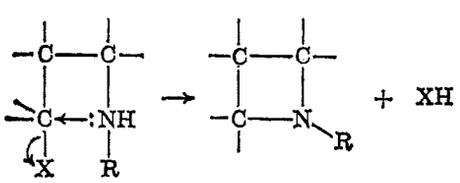


X

Results

Originally, it had been considered possible that under proper conditions C-aroylazetidines would result from the reaction of **1** with primary amines or from the rearrangement of **2**. However, in solvent acetonitrile or methanol, we have followed this rearrangement by nmr and no azetidine has been detected; the formation of **3**[4] is complete without heating in 24 hr but in methanol solution further reactions take place.

The ring closure of a γ-halamine in the presence of base is one of the most commonly used synthesis of azetidines.[5] This reaction involves an internal nucleophilic displacement by an amino group of the halogen atom in the γ position of a three-carbon chain. These



reactions were generally performed by treating the crude bromamine hydrobromide with alkali.

In a preliminary communication[1] it was reported that β-ketoallylamines 2-[α-(N-*t*-butylamino)benzyl]-4′-phenylacrylophenone and α-[(N-*t*-butylamino)methyl]-4′-phenylchalcone reacted with hydrogen bromide to give β-aroyl-γ-bromoallylamine hydrobromides which on treatment with base produced for the first time C-aroylazetidines in high yield. This synthetic scheme has now been applied to the β-ketoallylamines **2** and **3**.

The action of an excess of hydrogen bromide gas on **2** in $CHCl_3$ solution followed by neutralization with *t*-butylamine gave in good yield (80%) the *cis*-1-*t*-butyl-2-phenyl-3-benzoylazetidine (**4**); the same reaction series with chalcone **3** gave only the *trans*-1-*t*-butyl-2-phenyl-3-benzoylazetidine (**5**). Furthermore, **4** was readily converted into *trans* isomer **5** by treatment with sodium methoxide in methanol (see Scheme I).

The assignment of *cis* and *trans* configurations for **4** and **5**, respectively, is based on the following considerations (a–d).

(a) In the corresponding aziridine series it has been shown[6] that *cis*-2-phenyl-3-benzoylaziridines absorb at slightly shorter wavelengths in the ultraviolet and with lower intensity than the *trans* isomers; **4** absorbs at 240 mμ (ϵ 10,900) (isooctane) and **5** absorbs at 242 mμ (ϵ 15,500) (isooctane).

(b) The nmr spectrum of **4** (Figure 1) shows the *t*-butyl group at τ 9.08, the ten aromatic protons between 2.5 and 3.2, then a complex pattern between 5.07 and 6.87, which for ease of discussion can be divided into four groups: (1) a doublet at τ 5.07, 5.22 (one proton), (2) a doublet of doublets τ 5.67 $\ll$ 5.86, (3) a multiplet τ 6.0 $\ll$ 6.17, (4) a doublet of doublets τ 6.63 $\ll$ 6.87 (three protons for 2–4).

As a first approximation one can consider this complex pattern as an ABMX system (Figure 1). The resolution of such a system is quite complicated; however, this can be simplified by considering $J_{AX} \simeq J_{BX} \simeq 0$. Such assumption is reasonable because by replacing H_M by deuterium in **4** (and in **5**) H_X appears as a singlet (Figures 1 and 2). H_X would be expected to appear at lowest field, being deshielded by the nearby N atom and C_6H_5 group, and the lowest field doublet centered at τ 5.15 can be attributed to H_X coupled with H_M and J_{XM} = 9 cps. H_M would be coupled with H_A, H_B, and H_X and, as a first approximation, would give an octet. H_A and H_B would each give a quartet by coupling with each other and then with H_M.

(4) The *trans* structure of this chalcone was shown by nmr (CCl_4 as solvent). For all the *trans*-α-methyl-substituted chalcones the ethylenic hydrogen is near τ 3.0 and no *trans*-allylic coupling is detected. For the *cis*-α-methylchalcones the same hydrogen is at higher field and the *cis*-allylic coupling constant is J = 1.5 cps. The fact that $J_{cis} > J_{trans}$ is not unusual as the allylic coupling constant is the algebraic sum of both σ and π contributions to the coupling (see E. W. Garbisch, *J. Am. Chem. Soc.*, **86**, 5561 (1964)). Furthermore, such sequence was also reported by M. Martin, G. Martin, and P. Caubere, *Bull. Soc. Chim. France*, 3066 (1964).

(5) For a review, see J. A. Moore in "Heterocyclic Compounds with Three and Four-Membered Rings," Part II, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 885.

(6) A. E. Pohland, R. C. Badger, and N. H. Cromwell, *Tetrahedron Letters*, **No. 48**, 4369 (1965).

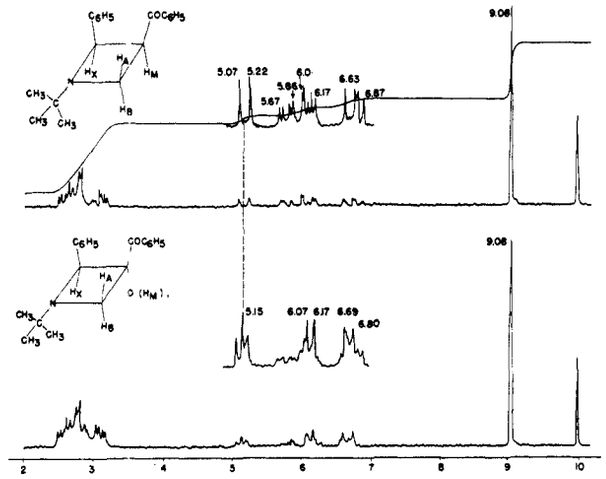


Figure 1.—Upper set of curves for the nmr spectrum of *cis*-azetidine **4**. Lower set for **4** with H_M 50% replaced by deuterium.

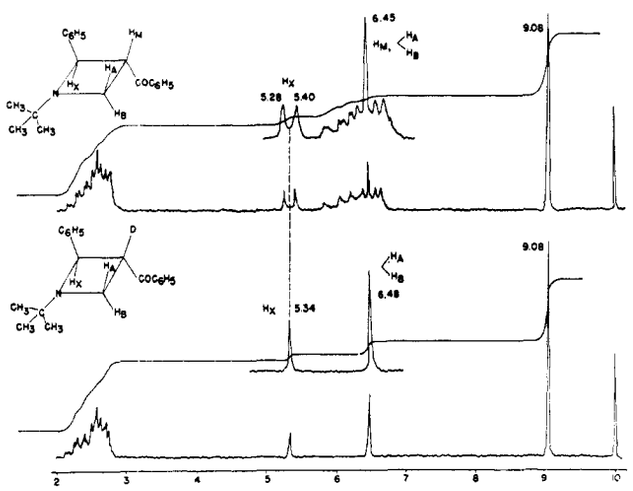


Figure 2.—Upper set of curves for the nmr spectrum of *trans*-azetidine **5**. Lower set for **5** with H_M 100% replaced by deuterium.

To simplify this pattern we have prepared, using deuterium bromide, **4** partially deuterated in the 3 position (D > 50%, Figure 1). H_X gives now a singlet at τ 5.15 and the two geminal protons H_A and H_B are seen now as an AB system, the position of this system being roughly equivalent to the group of signals (3 and 4) in the nondeuterated compound. It can be deduced from the AB system that $J_{AB} = -6.5$ cps, this coupling constant being expected to be negative.[7] Compared to the results generally obtained for J_{gem}[8] this value is quite small, but, as the geminal coupling constant for methylene groups depends on the overlap of the CH bonds with the electron pair on the adjacent heteroatom,[7b] this is not surprising.

The quartet (4) for **4** at higher field corresponds to H_B (or to H_A) and, as we know J_{AB}, it is possible to deduce directly from this pattern that $J_{BM\ (or\ AM)} = 7.5$ cps.

The nmr spectrum of **5** (Figure 2) shows the *t*-butyl group at τ 9.08, ten aromatic protons between 2.15 and 2.82, then a complex pattern between 5 and 6.7 (four protons). In the methylene range, there is first at low field a doublet centered at 5.34 corresponding to the H_X proton coupled with H_M, and $J_{XM} = 7$ cps. For **4**, $J_{XM} = 9$ cps, and it is known for vicinal constants that $J_{cis} > J_{trans}$;[9] by example, for cyclobutanone $J_{cis} = 8.9$ cps, $J_{trans} = 6.5$ cps,[8] in the Δ^2-pyrazoline series $9 < J_{4,5\ cis} < 10.5$ cps and $6 < J_{4,5\ trans} < 7.5$ cps,[10] and in the aziridine series the same order is found.[6,11] So we can deduce that **4** is the *cis* diastereoisomer and **5** the *trans*.

Between τ 5.9 and 6.7 compound **5** shows a complex pattern with a sharp peak at 6.45. The replacement of H_M by deuterium led us to a great simplification (Figure 2): H_X now appeared as a singlet at τ 5.34; H_A and H_B gave a simple peak at 6.48.

(c) The easy isomerization of **4** to **5** shows also that **5** is the more stable azetidine, *i.e.*, the *trans* one. However, in the aziridine series the *cis* compound appears to be more stable than the *trans*[6] but it is difficult to compare these two series. For the aziridine the ring is smaller and this different stability may only indicate that the 1–3 nonbonded interaction is more important than the 2–3. In the azetidine series the situation is different and one can logically expect the 1–3 nonbonded interactions to be less than the 2–3; hence the more stable isomer will be the *trans* one.

(d) The mass spectra of **4** and **5** are quite similar, giving rise to fragments at identical *m/e* values; however, some differences in the relative intensities of the peaks can be noted. Both **4** and **5** show a small peak at *m/e* 293, corresponding to M^+. The complete mass spectral results for the azetidine series will be discussed in a forthcoming publication.

Discussion of the Results

The addition of HBr to **2** and **3** gives, respectively, the hydrobromides **6** and **7**. These two compounds can exist as two diastereoisomers: **6a** and **7a** for the *threo* and **6b** and **7b** for the *erythro* (with respect to C_6H_5 and C_6H_5CO) (see Scheme II).

The cyclization of these γ-halamines must now be treated as a conformational problem and the stereochemistry of these amine hydrobromides is of fundamental interest.

Such a point was made by Grob[12] and by Vaughan[13] but this[1] is the first case where a pair of diastereoisomers of simple azetidines is reported in the literature.[14]

As the cyclization to the azetidine ring involves a nucleophilic displacement of the halogen atom, several competing reactions such as substitution, elimination, dimerization, or fragmentation may also take place.[15] Dimerization is of course unlikely because of the N-*t*-

(7) (a) J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965); (b) T. A. Crabb and R. F. Newton, *Chem. Ind.* (London), 339 (1966).

(8) For cyclobutanone, by example, $J_{gem\ \alpha} = |16\text{–}17|$ cps and $J_{gem\ \beta} = |12|$ cps; B. Braillon, J. Salaün, J. Gore, and J.-M. Conia, *Bull. Soc. Chim. France*, 1981 (1964).

(9) For a review, see A. A. Bothner-By in "Advances in Magnetic Resonance," J. S. Waugh, Ed., Academic Press Inc., New York, N. Y., 1965, p 195.

(10) G. Maury, Doctoral Thesis, Montpellier, 1965.

(11) N. J. Leonard, R. Y. Ning, and R. L. Booth, *J. Org. Chem.*, **30**, 4357 (1965).

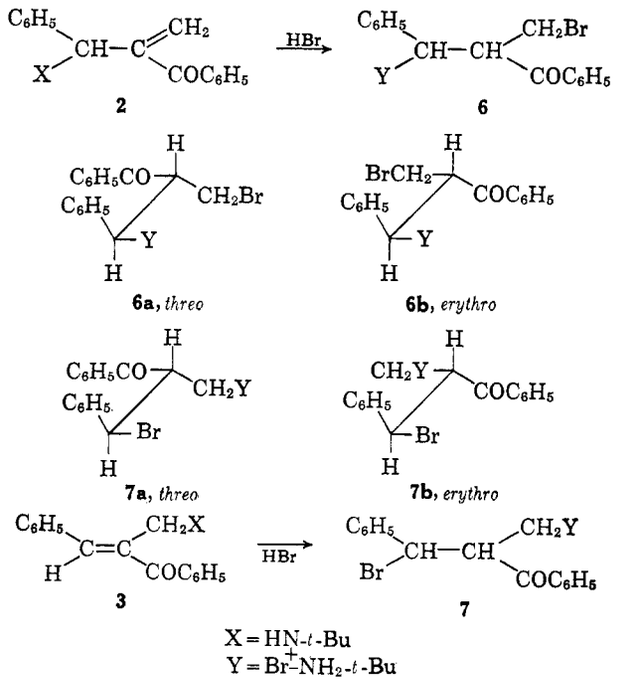
(12) (a) C. A. Grob, *Experientia*, **13**, 126 (1957); (b) C. A. Grob in "Kekule Symposium on Theoretical Organic Chemistry," Butterworth and Co. (Publishers) Ltd., London, 1959.

(13) W. R. Vaughan, R. S. Klonowski, R. S. McElhinney, and B. B. Millward, *J. Org. Chem.*, **26**, 138 (1961).

(14) However, the synthesis of *cis*- and *trans*-7-azabicyclo[4.2.0]octanes (an azetidine fused to a cyclohexane ring) has just been reported in the literature: E. J. Moriconi and P. H. Mazzochi, *ibid.*, **31**, 1372 (1966).

(15) Reference 5, pp 891–896.

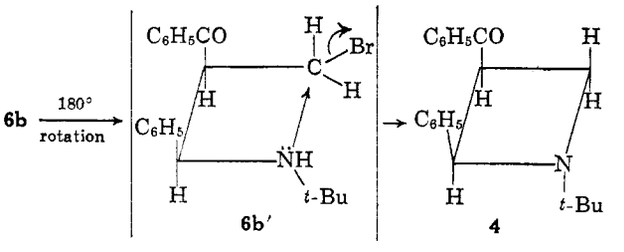
SCHEME II



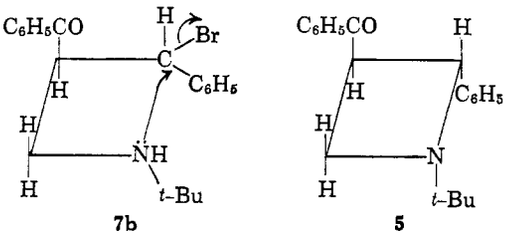
butyl group; fragmentation also is not expected because, when the nitrogen atom is substituted by a bulky group, the stereoelectronic situation is less favorable to fragmentation.[13] Furthermore, the nature of the leaving group is important; if the halogen atom is primary as for **6**, neither fragmentation nor elimination is expected to interfere, but, if it is secondary as for **7**, an SN1 reaction may be favored.[15]

The yield of azetidine does not depend only on the relative ease of ring closure but on the stability of the product as well; and for this one has to consider the influence of the substituents. Vaughan[13] has considered this problem and suggests that a bulky group on the nitrogen and no substituents on carbon represent the most favorable case. Adjacent *threo* substituents will have little effect but *erythro* substituents, which must become eclipsed in the transition state, will retard the rate of cyclization and decrease the stability of the ring.

The cyclization of **6** is expected to be an internal SN2-type reaction which is stereospecific. Since the *cis* azetidine is produced this implies that the *erythro* form of the bromamino ketone hydrobromide **6b** is produced on adding hydrogen bromide to **2**. The conformation **6b** should have less nonbonded interactions than any of the various possible conformations of the *threo* configuration **6a** as shown by Dreiding models. An 180° rotation of **6b** produces the transition state **6b′** with the bulky substituents now eclipsed. Ring closure of the *threo* configuration **6a** would have produced the *trans* azetidine **5**.



The cyclization of **7** gave the *trans* azetidine **5** (60%) and returned 40% of the starting material **3**. This result implies that elimination of hydrogen bromide from **7** competed with the ring closure reaction. This ring closure with a secondary bromide may be either an SN1- or internal SN2-type reaction. The latter mechanism would involve the *erythro* configuration **7b** since the *threo* configuration **7a** would be expected to produce the *cis* azetidine **4** by this mechanism.



The above-described method of synthesizing the heretofore unknown C-aroylazetidines from the readily available β-ketoallylamines seems to be of general applicability and further studies of the effect of substituents on nitrogen and the carbon chain on the course of these cyclizations have been undertaken. The availability of azetidines with a carbonyl functionality attached to a ring carbon suggests the possibility of conversion to other new types through carbonyl derivatives. Ring-cleavage reaction studies and conversion to azetidinium salts are obvious extensions of work in this new series of azetidines.

Experimental Section[16]

2-[α-(N-*t*-Butylamino)benzyl]acrylophenone (**2**).—A 3.0-g sample of *t*-butylamine (0.041 mole) in 50 ml of pentane was added with stirring to a solution of 6.02 g (0.02 mole) of *trans*-α-(bromomethyl)chalcone[3] (**1**) in 500 ml of pentane. The solution was allowed to stand for 48 hr, the *t*-butylamine hydrobromide was removed, and the solvent was evaporated. Recrystallization from hexane gave 4.1 g (70%) of white crystals: mp 69–70° (lit.[3] mp 69°); infrared $\nu_{C=O}^{Nujol}$ 1635 cm^{-1}; ultraviolet $\lambda_{max}^{isooctane}$ 243 mμ (ε 11,900); nmr 8.93 (*t*-butyl), 8.83 (NH), 4.92 (benzyl proton), 4.45, 3.87 (=CH_2), ten aromatic protons between 3.0 and 2.3.

***trans*-α[(N-*t*-Butylamino)methyl]chalcone** (**3**).—This compound was obtained[3] by rearrangement of **2** or by action of *t*-butylamine on **1** in $CHCl_3$ solution.

A. From Reaction of 1 with *t*-Butylamine.—A 3.01-g (0.01 mole) sample of **1** and 1.53 g (0.021 mole) of *t*-butylamine in 25 ml of $CHCl_3$ were refluxed overnight. Evaporation of the solvent and recrystallization from hexane gave 2.80 g (93%) of **3**: mp 104–105° (lit.[3] mp 105°); infrared $\nu_{C=O}^{Nujol}$ 1650 cm^{-1}; ultraviolet $\lambda_{max}^{isooctane}$ 255 mμ (ε 11,500), 283 (ε 16,100); nmr 8.83 (*t*-butyl), 6.38 (CH_2), 2.10–2.80 (ten aromatic protons and =CH).

B. Rearrangement of 2.—A 2.93-g (0.01 mole) sample of **2** was refluxed 24 hr in 25 ml of $CHCl_3$. Evaporation of the solvent and recrystallization from hexane gave 2.61 g (89%) of **3**.

***cis*-1-*t*-Butyl-2-phenyl-3-benzoylazetidine** (**4**).—A 2.93-g (0.01 mole) sample of **2** was dissolved in 100 ml of $CHCl_3$ saturated with hydrogen bromide gas. The solution was kept overnight and neutralized with *t*-butylamine. The *t*-butylamine hydrobromide was then removed and the solvent was evaporated. Extraction of the solid residue with 200 ml of boiling pentane and evaporation of the solvent gave 2.35 g (80%) of a white solid: mp 116–118°

(16) The melting points are corrected. The infrared and ultraviolet measurements were made on Perkin-Elmer Model 21 and Cary Model 11 instruments, respectively. The nmr spectra were determined on a Varian A-60 spectrometer, the spectra being obtained in CCl_4 with tetramethylsilane as internal standard. Chemical shifts are listed as τ values. Assignments were made on the basis of the integrated values obtained for the number of protons. Mass spectra were determined on a Perkin-Elmer Hitachi RMU-6D double-focusing mass spectrometer operating at 70 ev, the all-glass heated inlet system being maintained at approximately 200°.

after recrystallization from heptane followed by sublimation; infrared $\nu_{C=O}^{CCl_4}$ 1688 cm^{-1}; ultraviolet $\lambda_{max}^{isooctane}$ 240 mμ (ε 10,900); the nmr spectrum is presented in the discussion.

Anal. Calcd for $C_{20}H_{23}NO$ (293.39): C, 81.87; H, 7.90; N, 4.77. Found: C, 81.60; H, 8.01; N, 4.89.

Compound 4 Partially Deuterated in the 3 Position.—Deuterium bromide was prepared by action of D_2O on redistilled PBr_3 and the reaction was carried out exactly as for **4**. The nmr spectrum is presented in the discussion.

trans-**1-*t*-Butyl-2-phenyl-3-benzoylazetidine (5). A. From Epimerization of 4.**—A 0.58-g (0.002 mole) sample of **4** and 0.07 g of sodium methoxide in 10 ml of methanol were refluxed for 48 hr. After evaporation of the solvent, the oily residue was extracted with 100 ml of boiling pentane and treated with charcoal. Evaporation of the solvent gave 0.435 g (75%) of **5**: mp 61–63° after recrystallization from heptane and sublimation; infrared $\nu_{C=O}^{CCl_4}$ 1680 cm^{-1}; ultraviolet $\lambda_{max}^{isooctane}$ 242 mμ (ε 15,500); the nmr spectrum is presented in the discussion.

Anal. Calcd for $C_{20}H_{23}NO$ (293.39): C, 81.87; H, 7.90; N, 4.77. Found: C, 81.71; H, 7.88; N, 4.49.

B. From 3 *via* the Bromamino Ketone Hydrobromide.—A 2.93-g (0.01 mole) sample of **3** was dissolved in 100 ml of $CHCl_3$ saturated with HBr and treated exactly as for **4**. The crude extract was analyzed by nmr and showed the presence of 60% **5** and 40% **3**.

C. Compound 5 Deuterated in the 3 Position.—This compound was obtained from **4** as described above using CH_3OD instead of CH_3OH. The nmr spectrum is presented in the discussion.

Anal. Calcd for $C_{20}H_{22}DNO$ (294.39); C, 81.59; H, 7.53; N, 4.75. Found: C, 81.58; H, 7.90; N, 4.50.

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The Decomposition of Hydrazine Derivatives by Their Reaction with Hydroperoxides

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The reactions of triphenylhydrazine, diphenylpicrylhydrazine, *unsym*-diphenylhydrazine, and tetraphenylhydrazine with hydroperoxides were studied. Diphenylamine was isolated as the main reaction product in all reactions except in the case of tetraphenylhydrazine. The progressive production of free-radical species in the reaction systems was followed by an esr technique and the resulting reaction mixtures were analyzed by gas and column chromatography. A reaction mechanism is proposed.

Although it is known that when amines are warmed with hydroperoxides rapid decomposition of the peroxides occurs to provide the corresponding alcohols, the fate of the amines is not clear. Bickel and Kooyman[1] were unable to isolate any definite compounds derived from the amines. De la Mare[2] investigated the oxidation of secondary amines by hydroperoxides to give carbonyl compounds and the lower amine resulting from carbon–nitrogen bond scission. The hydroperoxides were reduced to the corresponding alcohols. A reaction mechanism was tentatively proposed on the basis of the results obtained by Coppinger and Swalen.[3] On the other hand, Ueda and co-workers[4] have studied the decomposition of diphenylpicrylhydrazyl (DPPH) by hydroperoxide using the esr technique and ascribed the change of the original signal shape to complex formation between DPPH and hydroperoxide. However, this was soon disputed by Möbius and Schneider,[5] who reinvestigated the same reaction spectroscopically in the ultraviolet region as well as using the esr technique. They found that the change of esr signal should be ascribed to the formation of diphenyl nitroxide, but they did not isolate any reaction product. As radicals at concentrations as low as about 10^{-10} mole/l. can be detected by the esr technique, the observation of radical species in the reaction system does not necessarily indicate participation of these radicals in the main reaction route. One must be very cautious about the establishment of reaction mechanisms on the basis of esr study alone.

The present authors have studied the reaction of aryl-substituted hydrazine derivatives—triphenylhydrazine, diphenylpicrylhydrazine, *unsym*-diphenylhydrazine and tetraphenylhydrazine—with hydroperoxides—*t*-butyl hydroperoxide and cumyl hydroperoxide—by means of precise analysis of reaction products and by the esr technique in order to clarify unambiguously the mechanism of the reaction of hydrazine derivatives with hydroperoxides.

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Results

Triphenylhydrazine, diphenylpicrylhydrazine, and *unsym*-diphenylhydrazine reacted with *t*-butyl hydroperoxide at a fairly rapid rate, but tetraphenylhydrazine did not (eq 1–4). When triphenylhydrazine dissolved in benzene was mixed with *t*-butyl hydroperoxide at *ca.* 4°, the color changed gradually to violet, and finally to dark brown. After 2 hr the reaction mixture was separated by distillation under a nitrogen atmosphere into a volatile fraction and a brown residue. The volatile fraction was analyzed by gas chromatography and the residue was analyzed by column chromatography. Nitrosobenzene, *t*-butyl alcohol, and acetone were identified as components of the volatile fraction. Diphenylamine and nitrosobenzene were found as the major products in the residue. Diphenylpicrylhydrazine reacted with *t*-butyl hydroperoxide more slowly than did triphenylhydrazine, and reaction occurred at an appreciable rate at a higher temperature (60°) to give diphenylamine and trinitronitrosobenzene as the major reaction products.

unsym-Diphenylhydrazine was decomposed by *t*-butyl hydroperoxide at an appreciable rate at room temperature, and only diphenylamine was found as a major product. Tetraphenylhydrazine did not react at temperatures lower than 5°, but it decomposed quite slowly at 50° to give a reaction mixture which had a slightly violet color. After 2 hr almost all of the tetra-