Philip Tarburton, Lori J. Wolpa, Robert K. Loerch,

Thomas L. Folsom, and Norman H. Cromwell*

Department of Chemistry, The Univeristy of Nebraska, Lincoln, Nebraska 68588

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The synthetic scope of the reaction of primary amines with α,β-dibromochalones to form aroylaziridines is explored and found to require at least one hydrogen on the α-carbon of the amine. Fourteen new epimeric 1-alkyl-2-aryl(alkyl)-3-aroylaziridines are synthesized accordingly. Next, representative aroylaziridines are investigated by infra-red spectroscopy in solvents of ambient polarity to assess the relative populations of the *gauche* and *cisoid* conformers present in the (Z)-(cis) series.

A series of papers, the majority coming from this laboratory (1-4), has dealt with the cyclization reaction of α,β-dibromo ketones with three moles of primary amine to form aroylaziridines. A more recent paper (5) has dealt with a procedure for the reaction with isopropyl-amine or ethylamine to form these aziridines. In general, the first mole of amine does not add to the substrate but acts as a base causing an elimination reaction to afford an elimination reaction to afford an α-bromochalcone in excess of 85% yield (6) which obviates the need to use the dibromo ketone directly (7). The next step involves the addition of the second mole of primary amine to the α-bromo-α,β-unsaturated ketone (1,3,8). This then yields a mixture of d,l-erythro and d,l-threo-α-bromo-β-amino ketones:
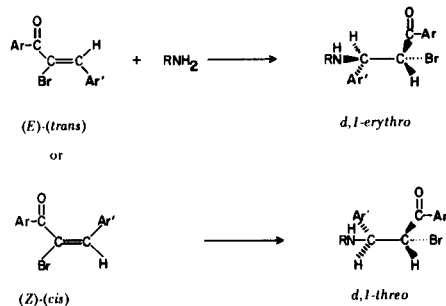
Hence, the second mole of primary amine acts as a nucleophile in this Michael addition to afford the d,l-erythro and d,l-threo-ketones. It would appear that the 1,4-conjugate addition is not stereospecific such that both the (Z)-(cis) and (E)-(trans)-α-bromo-α,β-unsaturated ketones react to give a mixture of the d,l-erythro and d,l-threo-α-bromo-β-amino ketones; see reference 5 for a discussion of the steric controls involved in these Michael additions.

The third mole of an amine again acts as a base by allowing ring closure of the d,l-erythro and d,l-threo-α-bromo-β-amino ketones in a stereospecific fashion:
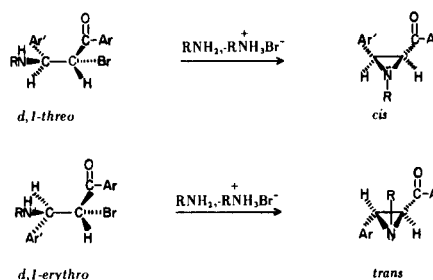
The stereochemistry of ring closure to produce the three-membered ring, and ring opening to reform the α-bromo-β-aminocarbonyl compound have both been shown to involve Walden inversion (8). Hence, the fact ring closure is an internal SN2 type reaction assures that the erythro compound gives only the trans aroylaziridine while the threo affords the cis isomer.

The major limitation of the reaction of α,β-dibromo-chalcones or α-bromochalcones with substrate to afford aziridines is that the nucleophile must be a primary alkyl amine whose α-carbon is not tertiary. That is to say, t-butylamine has been found not to react with α,β-di-bromochalcone (or α-bromochalcone) to afford aziridine (9).

Discussion

Outlined in Table I are the newly synthesized (E)-(trans) and (Z)-(cis)-1-alkyl-2-aryl(alkyl)-3-aroylaziridines. It is important to take note of the fact that irrespective of the substituents on the α-N-alkylcarbon, the prerequisite for ring closure via Walden inversion is the presence of one or more α-hydrogen(s) on the N-alkylcarbon. The reason attributed to this trend may well be rationalized on the basis of recent ^{13}C nmr studies (10) which reveal that the hydrogen of the α-N-alkylcarbon is extended toward the center of the three-ring, and impinges on the C_2 and C_3 substituents (Figure 2). This argument is reinforced

Figure 2. Conformer of aroylaziridine with hydrogen of N-alkylcarbon pointing toward center of aziridine ring.

Table I

Selected (E)- and (Z)-1-Alkyl-2-aryl(alkyl)-3-aroylaziridines

Compound	R_1	R_2	R_3
2E or 2Z	(cyclohexyl)	Ph	Ph
3E or 3Z	(cyclopentyl)	Ph	Ph
4E or 4Z	-CH₂CH₃ *	Ph	Ph-Ph-p
5E or 5Z	-CH(CH₃)₂ *	Ph	Ph-Ph-p
6E or 6Z	-CH₂C(CH₃)₃ *	Ph	Ph
7E or 7Z	-CHPh₂ *	Ph	Ph
8E or 8Z	(thienyl)	CH₃	Ph

by the fact that the small C_1-N-C_2 angle (11) makes it difficult to accommodate any other group (i.e., methyl) "inside" the three-ring. Thus, it makes little difference what N-CHR₄R₅ is because R₄ and R₅ are extended away from the ring. This is borne out by the fact that when R₄=R₅=phenyl the nucleophile is quite space-demanding. However, both 7E and 7Z have been synthesized using the aforementioned procedure. Also the fact that pairs 2 and 3 were synthesized in good yields lends credence to the argument that it is of little importance how space-

demanding the substituents R₄ and R₅ are (12-14).

Infrared studies of selected aroylaziridines were carried out in carbon tetrachloride, acetonitrile and deuterio-chloroform. This work is a direct extension of work done earlier in these laboratories (15). The values obtained for the carbonyl stretching frequencies of 2E, 2Z, 3E, 3Z, 4E, 4Z, 5E and 5Z appear in Table II. In all solvents studied, the (E)-(trans) isomers show a carbonyl stretching band at a considerably lower frequency than that of the saturated ketone analog 9 (Figure 3), i.e. 22-29 cm⁻¹ lower. For the (Z)-(cis)-1-alkyl-2-phenyl-3-aroylaziridines

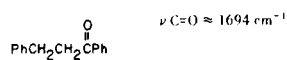Figure 3. Stretching frequency of model ketone 9 in carbon tetrachloride.

under study, 2Z-5Z, there are two carbonyl stretch bands in carbon tetrachloride (one at high frequency similar to the model ketone 9 and one similar to that of the (E)-(trans) isomers) (see Table II). This lowered carbonyl stretching frequency is attributed to three-ring carbonyl hyperconjugation (16) available only in the cisoid conformation (Figure 4). Hence, in the case of the (Z)-(cis)
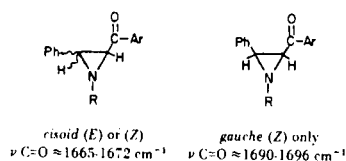

Figure 4. Possible conformers of (E)- and (Z)-1-alkyl-2-aryl-3-aroylaziridines in carbon tetrachloride.

Table II

Carbonyl Stretching Frequencies of Selected Aroylaziridines

Compound	ν (C=O) cm⁻¹ in Carbon Tetrachloride	ν (C=O) cm⁻¹ in Acetonitrile	ν (C=O) cm⁻¹ in Deuteriochloroform
2E	1670 (vs)	1670 (vs)	1664 (vs)
2Z	1670 (m) and 1696 (vs)	1688 (vs)	1685 (vs)
3E	1672 (vs)	1669 (vs)	1666 (vs)
3Z	1665 (m) and 1695 (vs)	1686 (vs)	1686 (vs)
4E	1667 (vs)	1667 (vs)	1665 (vs)
4Z	1676 (m) and 1690 (vs)	1682 (vs)	1680 (vs)
5E	1665 (vs)	1667 (vs)	1662 (vs)
5Z	1666 (m) and 1691 (vs)	1682 (vs)	1680 (vs)

isomers it appears that there are two conformers present in carbon tetrachloride solution, one of which enjoys pseudoconjugation (i.e., cisoid), and one which does not (i.e., gauche). The origin of the anomalous bands can be attributed to restricted rotation of the carbonyl moiety.

As recently shown in these laboratories, solvent polarity appears also to effect the relative populations of the two conformers (see again, Table II). This is borne out by the fact that the (Z)-(cis) isomer shows what would appear to be only one carbonyl stretch in the more polar solvents, deuteriochloroform and acetonitrile. This single carbonyl stretch appears at high frequency only and is attributed to the fact that the gauche conformer is of far greater abundance in these solvents, i.e., all of these carbonyl stretches occur in the $1680\text{-}1688\text{ cm}^{-1}$ region. This seems reasonable since it is the gauche conformer which is of greater polarity owing to its lack of three-ring carbonyl hyperconjugation. Therefore, while one could possibly invoke Fermi resonance (17) as a plausible explanation based only on the data from the carbon tetrachloride studies, this new evidence in polar solvent makes the Fermi resonance argument quite dubious. However, low temperature studies in carbon tetrachloride would provide further insight as to the relative stabilities of the gauche and cisoid conformers.

Acknowledgement.

EXPERIMENTAL

Infrared spectra were measured in either reagent grade carbon tetrachloride, chloroform-d or acetonitrile with a Perkin-Elmer Model 621 grating spectrophotometers. The ^{1}H nmr were determined with a Varian A-60 high resolution spectrometer. Melting points were determined with an electrically heated melt-temp apparatus and are uncorrected. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Illinois, and Chemalytics, Inc., Tempe, Arizona.

(E)-(trans) and (Z)-(cis)-1-(2-endo-Norbornyl)-2-phenyl-3-benzoyl-aziridines, (2E) and (2Z).

Following a procedure analogous to Tarburton, Chung and Cromwell (18) α,β-dibromochalcone (19) was reacted with endo-2-aminonorbornane; however, as only the hydrochloride of endo-2-aminonorbornane is available from Aldrich, a procedure to effectively neutralize this salt and then dry its free base had to be established. Although sodium bicarbonate was unsuccessfully tried, it was found that 12.5 g. (84.7 mmoles) of endo-2-aminonorbornane hydrochloride could best be neutralized by the addition of sodium hydroxide pellets to a 15 ml. aqueous solution containing the salt, the pH was brought to a caustic level (ca. 11) and the free base rose out of solution whereupon the amine was removed from the water layer and was dried with molecular sieves 4A. The endo-2-aminonorbornane was tared and found to weigh 9.41 g. (neutralization was quantitative). (Note: To avoid formation of an amine sulfate, dry with molecular sieves and not magnesium sulfate!).

Following the above procedure 9.06 g. (81.5 mmoles) of endo-2-aminonorbornane dissolved in 10.0 ml. of dry benzene was added dropwise to a stirring suspension of 10.0 g. (27.2 mmoles) of α,β-dibromochalcone in 50 ml. of dry benzene over a 15 minute period. The mixture was chilled to 15° and stirred for one hour. The mixture was then stirred in the dark at 25° for one day and afterwards 8.50 g. (81.6% yield) of endo-2-amino-norbornane hydrobromide (dec. ~258°) was recovered after washing with ether. (This salt had been removed from the benzene layer by filtration). After reducing the total benzene volume to ca. ~20 ml., 20 ml. of petroleum ether (b.p. 60-69°) was added and the mixture was stored in the freezer for 48 hours. Filtration and recrystallization from petroleum ether (b.p. 60-69°) afforded 3.20 g. (37.1% yield) of white fluffy crystals identified as 2Z, m.p. 108-110°; ir (carbon tetrachloride): ν C=O 1670 and 1696 cm^{-1}; ^{1}H nmr (carbon tetrachloride): δ = 7.10-7.94 (m, 10H, aromatic), 3.07 (d, J = 3.9 Hz, 1H, C$_3$-H), 3.00 (d, J = 3.9 Hz, 1H, C$_2$-H), 2.25 (m, 1H, N-CH or norbornyl C$_2$-H), 1.20-2.34 (m, 10H, norbornyl).

Anal. Calcd. for C$_{22}$H$_{23}$NO: C, 83.24; H, 7.30; N, 4.41. Found: C, 82.95; H, 7.31; N, 4.41.

The benzene-petroleum ether (b.p. 60-69°) filtrate from 2Z was then condensed down to an oil and was stored in the freezer for one week. Recrystallization twice from methanol and once from absolute ethanol afforded 0.50 g. (5.8% yield) of square white crystals identified as 2E, m.p. 60-65°; ir (carbon tetrachloride): ν C=O 1670 cm^{-1}; ^{1}H nmr (carbon tetrachloride): δ = 7.10-8.17 (m, 10H, aromatic), 3.55 (d, J = 4.3 Hz, 1H, C$_3$-H), 3.50 (d, J = 4.3 Hz, 1H, C$_2$-H), 3.03 (m, 1H, N-CH or norbornyl C$_2$-H), 0.85-2.5 (m, 10H, norbornyl).

Anal. Calcd. for C$_{22}$H$_{23}$NO: C, 83.24; H, 7.30; N, 4.41. Found: C, 83.19; H, 7.46; N, 4.29.

(E)-(trans) and (Z)-(cis)-1-(2-exo-Norbornyl)-2-phenyl-3-benzoyl-aziridines (3E) and (3Z).

Following a procedure analogous to Tarburton, Chung and Cromwell (18) 9.06 g. (81.5 mmoles) of exo-2-aminonorbornane (Aldrich) dissolved in 10.0 ml. of dry benzene was added dropwise to a stirring suspension of 10.0 g. (27.2 mmoles) of α,β-dibromo-chalcone (19) in 50 ml. of dry benzene over a 15 minute period. The mixture was chilled to 15° for one hour and stirred in the dark for 24 hours and afterwards 9.21 g. (88.4% yield) of exo-2-aminonorbornane hydrobromide (dec. ~285°) was recovered after washing with ether. After reducing the volume of benzene to 20 ml., 20 ml. of petroleum ether (b.p. 60-69°) was added and the mixture was stored in the freezer for 24 hours. Filtration and recrystallization twice from petroleum ether (b.p. 60-69°) afforded 2.81 g. (32.6% yield) of white fluffy crystals identified as 3Z, m.p. 100.5-102°; ir (carbon tetrachloride): ν C=O 1665 and 1695 cm^{-1}; ^{1}H nmr (carbon tetrachloride): δ = 6.92-7.94 (m, 10H, aromatic), 3.06 (d, J = 2.5 Hz, 1H, C$_3$-H), 3.02 (d, J = 2.5 Hz, 1H, C$_2$-H), 2.33 (m, 1H, N-CH or norbornyl C$_2$-H), 0.99-2.44 (m, 10H, norbornyl).

Anal. Calcd. for C$_{22}$H$_{23}$NO: C, 83.24; H, 7.30; N, 4.41. Found: C, 83.12; H, 7.45; N, 4.36.

The benzene-petroleum ether (b.p. 60-69°) filtrate from the (Z)-(cis) isomer 3Z was then evaporated down to an oil with a rotatory evaporator at room temperature, the residue mixed with 40 ml. of petroleum ether (b.p. 60-69°) and stored in the freezer for four days. Square white crystals formed on the side of the flask and were collected by filtration. Recrystallization from methanol gave 2.13 g. (24.7% yield) of white square crystals identified as 3Z, m.p. 93.5-95°; ir (carbon tetrachloride) ν C=O 1672 cm^{-1}; ^{1}H nmr (carbon tetrachloride): δ = 6.90-8.16 (m, 10H, aromatic), 3.51 (d, J = 8.3 Hz, 1H, C$_3$-H), 3.37 (d, J = 8.3 Hz, 1H, C$_2$-H), 2.75 (m, 1H, N-CH or norbornyl C$_2$-H), 0.92-2.94

(m, 10H, norbornyl).

Anal. Calcd. for $C_{22}H_{23}NO$: C, 83.24; H, 7.30; N, 4.41. Found: C, 83.12; H, 7.45; N, 4.36.

(*E*)-(*trans*) and (*Z*)-(*cis*)-1-Ethyl-2-phenyl-3-(*p*-phenylbenzoyl)aziridines, (*4E*) and (*4Z*).

Following the procedure of Graff and Cromwell (20) α,β-dibromo-4′-phenylchalcone was prepared and then 10.0 g. (22.5 mmoles) was suspended in 50 ml. of dry benzene and reacted with 3.03 g. (67.5 mmoles) of ethylamine in 20 ml. of dry benzene at 0°. The reaction mixture was stirred for one hour at *ca.*~10° and then stirred in the dark overnight at room temperature. The next day an orange-red solution with a rather rank odor was filtered to remove ethylamine hydrobromide which was washed with ether to give 5.01 g. (99.4% yield) of the salt. Upon removal of the salt by filtration and subsequent condensing of the benzene layer to a small volume, 25 ml. of petroleum ether (b.p. 30-60°) was added to afford 2.5 g. (34.1% yield) of a compound identified as *4Z*, m.p. 115.5-117°; ir (carbon tetrachloride): ν C=O 1672 and 1690 cm⁻¹; ¹H nmr (deuteriochloroform): δ = 7.05-8.25 (m, 14H, aromatic), 3.23 (d, 1H, C₃-H), 3.03 (d, 1H, C₂-H), 2.13-2.96 (m, 2H, N-CH₂), 1.27 (t, 3H, CH₃).

Anal. Calcd. for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28. Found: C, 84.37; H, 6.52; N, 4.33.

After several weeks of storing in the freezer some more crystals were recovered; however, they seemed to liquefy at room temperature. Hence, the resultant oil was dissolved in a minimum amount of absolute ethanol and subsequently some light yellow crystals precipitated out of the mother liquor. These buff-colored crystals were recrystallized a second time from absolute ethanol and were collected and dried in the usual fashion and found to weight 1.84 g. (25.1% yield). They were then identified as *4E*, m.p. 60.5-63°; ir (carbon tetrachloride): ν C=O 1667 cm⁻¹; ¹H nmr (deuteriochloroform): δ = 7.05-8.23 (m, 14H, aromatic), 3.59 (d, 1H, C₃-H), 3.49 (d, 1H, C₂-H), 2.15-2.40 (m, 2H, N-CH₂), 0.88-1.47 (t, 3H, CH₃).

Anal. Calcd. for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28. Found: C, 84.14; H, 6.38; N, 4.08.

(*E*)-(*trans*) and (*Z*)-(*cis*)-1-Isopropyl-2-phenyl-3-(*p*-phenylbenzoyl)-aziridines (*5E*) and (*5Z*).

Following the procedure of Graff and Cromwell (20) α,β-dibromo-4′-phenylchalcone was prepared and then 10.0 g. (22.5 mmoles) was suspended in 50 ml. of dry benzene and reacted with 3.98 g (67.5 mmoles) of isopropyl amine in 20 ml. of dry benzene at 15°. The reaction mixture was stirred at this temperature for one hour and then in the dark overnight at room temperature.

The next day an orange colored solution was filtered to remove isopropylamine hydrobromide which was washed with ether to afford 5.80 g. (92.3% yield) of the salt. Then the benzene solution was condensed down to a small volume and 25 ml. of petroleum ether (b.p. 30-60°) was added. This solution was stored in the freezer for 1-2 hours. Some yellow colored crystals were recovered and recrystallized from petroleum ether (b.p. 30-60°) to afford 2.5 g. (32.7% yield) of a compound identified as *5Z*, m.p. 119-121°; ir (carbon tetrachloride): ν C=O 1666 and 1691 cm⁻¹; ¹H nmr (deuteriochloroform): δ = 6.95-8.05 (m, 14H, aromatic), 3.28 (d, 1H, C₃-H), 3.13 (d, 1H, C₂-H), 1.85 (m, 1H, N-CH), 1.26 (d, 6H, two CH₃).

Anal. Calcd. for $C_{24}H_{23}NO$: C, 82.95; H, 6.68; N, 4.03. Found: C, 82.89; H, 6.63; N, 3.93.

The mother liquor was then condensed down to an oil and 25 ml. of *n*-hexane was added. This mixture was stored in the freezer overnight. Upon recovery and two recrystallizations from methanol, 1.16 g. (15.2% yield) of tan colored plate-like crystals

were recovered and identified as *5E*, m.p. 79.5-81°; ir (carbon tetrachloride): ν C=O 1665 cm⁻¹; ¹H nmr (deuteriochloroform): δ = 7.15-8.25 (m, 14H, aromatic), 3.66 (d, 1H, C₃-H), 3.59 (d, 1H, C₂-H), 1.90 (m, 1H, N-CH), 0.84-1.40 (d, 6H, two CH₃).

Anal. Calcd. for $C_{24}H_{23}NO$: C, 82.95; H, 6.68; N, 4.03. Found: C, 82.46; H, 6.39; N, 3.53.

(*E*)-(*trans*) and (*Z*)-(*cis*)-1-Neopentyl-2-phenyl-3-benzoylaziridines, (*6E*) and (*6Z*).

Following a procedure analogous to that of Tarburton, Chung, and Cromwell (18) 7.10 g. (81.5 mmoles) of neopentylamine (available from Aldrich, Alfred Bader Rare Chemicals) dissolved in 10.0 ml. of dry benzene was added dropwise to a stirring suspension of 10.0 g. (27.2 mmoles) of α,β-dibromochalcone (19) in 50 ml. of dry benzene over a 15 minute period. The mixture was kept at 15° for one hour and stirred in the dark for 24 hours. Afterwards 8.03 g. (88.0% yeild) of neopentylamine hydrobromide (dec. 274-276°) was recovered after the salt had been washed with ether. After reducing the volume of the benzene to 20 ml., 25 ml. of petroleum ether (b.p. 38-47°) was added and the mixture was stored in the freezer for 24 hours. Filtration and recrystallization twice from petroleum ether (b.p. 38-47°) afforded 1.25 g. (16.3% yield) of snow-white fluffy crystals identified as *6Z*, 78-80°; ir (carbon tetrachloride): ν C=O 1691 cm⁻¹; ¹H nmr (deuteriochloroform): δ = 7.07-7.98 (m, 10H, aromatic), 3.18 (d, 1H, C₃-H), 3.13 (d, 1H, C₂-H), 2.10-2.80 (d, 2H, N-CH₂), 1.05 (s, 9H, three CH₃).

Anal. Calcd. for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.57; H, 8.05; N, 4.72.

The benzene-petroleum ether (b.p. 38-47°) filtrate from the *cis* isomer *6Z* was then evaporated down to an oil with a rotatory evaporator at *ca.* 25° under reduced pressure; the residue mixed with 40 ml. of petroleum ether (b.p. 38-47°) and stored in the freezer for one week. Square off-white crystals formed on the side of the flask and were collected by filtration. Recrystallization from methanol gave 2.45 g. (32.0% yield) of *6E*, m.p. 58-59°; ir (carbon tetrachloride): ν C=O 1680 cm⁻¹; ¹H nmr (deuteriochloroform): δ 7.16-8.14 (m, 10H, aromatic), 3.51 (d, 1H, C₃-H), 3.39 (d, 1H, C₂-H), 2.57 (s, 2H, N-CH₂), 0.95 (s, 9H, three CH₃).

Anal. Calcd. for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.41; H, 7.89; N, 4.76.

(*E*)-(*trans*) and (*Z*)-(*cis*)-1-Benzhydryl-2-phenyl-3-benzoylaziridines, (*7E*) and (*7Z*).

Following a procedure analogues to that of Tarburton, Chung, and Cromwell (18) 14.9 g. (81.5 mmoles) of aminodiphenyl-methane (benzhydrylamine) dissolved in 20.0 ml. of dry benzene was added dropwise to a stirring suspension of 10.0 g. (27.2 mmoles) of α,β-dibromochalcone (19) in 50 ml. of benzene over a 15 minute period. The mixture was kept at 15° for one hour and stirred in the dark for 216 hours. Afterwards 7.30 g. (73.2% yield) of benzhydrylamine hydrobromide (dec. 230-235°) was recovered after the salt had been washed with ether. The benzene volume was then reduced and 25 ml. of petroleum ether (b.p. 38-47°) was added. An additional 1.60 g. (16.0% yield, total yield = 89.2%) of benzhydrylamine hydrobromide was recovered by the following procedure: the mother liquor was stored in the freezer and a large precipitate formed. The precipitate was then placed in 100 ml. of methanol and heated on a steam bath. More hydrobromide salt (1.60 g.) was then removed by filtration. Work-up of the benzene-petroleum ether's (b.p. 38-47°) second precipitate afforded very impure crystals thereby necessitating their recrystallization from methanol to afford two batches of crystals. The first batch of snow-white crystals was identified as pure *7Z* in 5.2% yield (0.45 g.), m.p. 150-152°; ir (carbon tetra-

chloride): ν C=O 1666 and 1690 cm^{-1}; ^{1}H nmr (deuterio-chloroform): δ = 7.00-7.97 (m, 20H, aromatic), 4.10 (s, 1H, N-CH), 3.45 (d, 2H, C$_2$-H and C$_3$-H).

Anal. Calcd. for C$_{28}$H$_{23}$NO: C, 86.34; H, 5.95; N, 3.60. Found: C, 86.36; H, 6.06; N, 3.55.

The second batch of white crystals had a broad melting point (122-129°) and were identified as a *cis/trans* mixture of **7E** and **7Z** isolated in 9.5% yield (1.01 g.) (21): ir (carbon tetrachloride): ν C=O 1666 and 1690 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 7.00-7.97 (m, 20H, aromatic), 5.11 (m, 1H of **7E** N-CH), 4.10 (m, 1H of **7Z** N-CH), 3.81 (d, 1H of **7E** C$_3$-H), 3.71 (d, 1H of **7E** C$_2$-H), 3.45 (d, 2H of **7Z** C$_3$-H and C$_2$-H).

Anal. Calcd. for C$_{28}$H$_{23}$NO: C, 86.34; H, 5.96; N, 3.60. Found: C, 86.04; H, 6.05; N, 3.63.

(E)-(trans) and *(Z)-(cis)*-1-Cyclohexyl-2-methyl-3-benzoylaziridines, (**8E**) and (**8Z**).

Following a procedure analogous to that of Cromwell and Mohrbacher (22) 4.0 g. (13.3 mmoles) of α,β-dibromocrotono-phenone (23) in 25 ml. of dry benzene was cooled to 15°, and over a 30 minute period 3.95 g. (39.9 mmoles) of cyclohexyl-amine was added. The mixture was then stirred in the dark for 24 hours. The next day 4.45 g. (24.7 mmoles) of the cyclohexyl-amine hydrobromide (dec. 201-204°) was recovered in 92.8% yield after it had been washed with ether. The reaction mixture was then condensed down to a volume of approximately 20 ml. and 25 ml. of petroleum ether (b.p. 38-47°) was added. This mixture was stored in the freezer for several days with no apparent crystal formation. Five days later, some white needle-like crystals were observed. They were collected, dried and recrystallized. These crystals were then tared to afford 0.82 g. of the *cis* isomer **8Z** in 25.3% yield, m.p. 64-65°; ir (carbon tetrachloride): ν C=O 1666 and 1692 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 7.40-8.17 (m, 5H, aromatic), 3.0 (d, 1H, C$_3$$H$), 2.9 (d, 1H, C$_2$$H$), 2.05 (m, 1H, N-C$H$), 0.97-2.00 (m, 10H, cyclohexyl).

Anal. Calcd. for C$_{16}$H$_{21}$NO: C, 78.96; H, 8.70; N, 5.76. Found: C, 79.18; H, 8.75; N, 5.82.

Two weeks later 0.40 g. more of the *cis* isomer **8Z** was recovered for a total yield of 37.7%. Then the mother liquor was condensed down to an oil which was revealed by ^{1}H nmr to be a 3:1 mixture of *trans* **8E**/*cis* **8Z**. As all attempts to obtain crystals failed the ^{1}H nmr was assumed to be analogous to **8Z** except that for the *trans* isomer the ^{1}H nmr (deuteriochloroform): gave δ = 3.25 (d, C$_2$-H and C$_3$-H, 2H) and ir (carbon tetrachloride): ν C=O 1668 cm^{-1}. (Here compound **8E** was assumed to have formed in 4.6% yield (24).)

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(1) N. H. Cromwell, R. D. Babson, and C. E. Harries, *J. Am. Chem. Soc.*, **65**, 312 (1943).

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(3) N. H. Cromwell and J. Caughlin, *ibid.*, **67**, 2235 (1945).

(4) N. H. Cromwell, N. G. Barker, R. A. Wankel, P. J. Vanderhorst, F. W. Olson and J. H. Anglin, Jr., *ibid.*, **73**, 1044 (1951); N. H. Cromwell, J. H. Anglin, Jr., F. W. Olson and N. G. Barker, *ibid.*, **73**, 2803 (1951).

(5) P. Tarburton, P. B. Woller, R. C. Badger, E. Doomes, and N. H. Cromwell, *J. Heterocyclic Chem.*, **14**, 459 (1977) and references cited therein.

(6) N. H. Cromwell, D. J. Cram, and C. E. Harries, *Org.*

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(7) However, owing to the fact that the first mole of amine is recovered as its hydrobromide salt and the dibromo chalcone is much easier to handle (it is a nice, white solid) the former synthetic route has been selected.

(8) N. H. Cromwell, G. V. Hudson, R. A. Wankel, and P. J. Vanderhorst, *J. Am. Chem. Soc.*, **75**, 5384 (1953).

(9) Although tried repeatedly, the reaction with α-bromo or α,β-dibromochalcone with *t*-butylamine failed to give aziridine. For details on the general procedure employed see Experimental in reference (5). For example, the reaction of 3 moles of *t*-butyl-amine with α,β-dibromo-4-nitrochalcone gave β-*t*-butylamino-4-nitrochalcone (**1**) in good yield: m.p. 140.5°; ir (carbon tetra-chloride): ν N-H 3400 and ν C=O 1603 cm^{-1}; ^{1}H nmr (carbon tetrachloride): δ = 11.84 (s, 1H, N-H), 7.34-8.51 (m, 9H, aromatic), 5.63 (s, 1H, α-proton), 1.25 (s, 9H, C(CH_3)$_3$).

Anal. Calcd. for C$_{19}$H$_{20}$N$_2$O$_3$: C, 70.35; H, 6.22; N, 8.64. Found: C, 70.26; H, 6.29; N, 8.62.

However, no aziridinyl ketone was formed in this reaction and may be attributed to the steric demand of the *t*-butyl group.

(10) P. Tarburton, C. A. Kingsbury, A. E. Sopchik, and N. H. Cromwell, *J. Org. Chem.*, submitted.

(11) The C$_1$-N-C$_2$ angle was calculated by molecular orbital theory to be 92° (for details see M. A. Graff and N. H. Cromwell, *J. Org. Chem.*, **17**, 414 (1951) and references cited therein.)

(12) While the *N*-*t*-butylaziridine is available by another synthetic route (13), it can only be suggested that the reason this aziridine will not form has to do with a steric factor in the final Walden inversion. Further, the fact that one of the methyl groups points over the three-ring (14) would lead to product instability.

(13) A. Padwa and W. Eisenhardt, *J. Am. Chem. Soc.*, **90**, 2442 (1968).

(14) The fact that the methyl group lies over the plane of the three-ring was rationalized on the basis of a 5-7 ppm upfield steric compression shift observed for the ring protons in (*Z*)-(*cis*)-*t*-butyl-2-phenyl-3-benzoylaziridine as revealed in reference (10).

(15) N. H. Cromwell, R. E. Bambury and J. L. Adelfang, *J. Am. Chem. Soc.*, **82**, 4241 (1960) and references cited therein.

(16) The steric requirements for maximum three-ring carbonyl hyperconjugation have been assessed to be that the *p*-orbitals of the attached groups must be free to orient themselves so that their axes approach a parallel relation to the plane of the three-ring and a near symmetrical relationship with respect to the bent bonds; for further details see references (15) and (11) for details.

(17) For a discussion of Fermi Resonance see R. M. Silverstein, G. C. Bassler, and T. C. Morrill, "Spectrometric Identification of Organic Compounds", 3rd Ed., John Wiley and Sons, Inc., New York, N.Y., 1974, pp. 77-78.

(18) P. Tarburton, A. Chung, R. C. Badger, and N. H. Cromwell, *J. Heterocyclic Chem.*, **13**, 295 (1976).

(19) Prepared following the procedure of C. F. H. Allen, R. D. Abell and J. B. Normington, *Org. Synth.*, Coll. Vol. I, p. 200.

(20) See reference in footnote (11) for details.

(21) Repeated attempts to separate this *ca.* 1:1 isomeric mixture have been unsuccessful.

(22) N. H. Cromwell and R. J. Mohrbacher, *J. Am. Chem. Soc.*, **75**, 6252 (1953).

(23) This known dibromo compound, α,β-dibromocrotono-phenone, was prepared from crotonophenone (Eastman Kodak) in 67.1% yield. For the procedure, see: C. Dufraisse and M. Demontrignier, *Bull. Soc. Chim. France*, **41**, 843 (1927).

(24) An elemental analysis on the phenyl carbinol derivative of a liquid mixture of **8E** and **8Z** has already been performed; for details, see J. D. Sculley and N. H. Cromwell, *J. Org. Chem.*, **16**, 94 (1950).