small, rapid initial absorbance change with the rate proportional to $[CN^-]$ preceding the process associated with the large absorbance change which is easy to measure. We tried to see if the situation could be improved by using a different wavelength to follow the reaction but without success.

In the case of the reaction of **5** with cyanide the situation is no better because here the total overall absorbance change associated with the transformation of **5** to the final reaction products is so small as to make any reliable kinetic studies impossible, given the special type of mixing that has to be employed in stopped-flow kinetic work with sulfinyl sulfones.

Acknowledgment. This research was supported in its initial stages by the National Science Foundation (Grant MPS 75-19408) and during its later stages by the Robert A. Welch Foundation (Grant D-650).

Registry No.—**1**, 25331-82-2; **2**, 63059-28-9; **3**, 64728-07-0; **4**, 40227-43-8; **5**, 57821-65-5; **6**, 62609-77-2; **7**, 64754-26-3; **8**, 64754-27-4; **9**, 64754-28-5; **10**, 64754-29-6; **16**, 64754-25-2; sulfite, 14265-45-3; cyanide, 57-12-5.

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(5) Since cyanide and sulfite are present in large excess over **4**, the reactions can be treated for kinetic purposes as reversible reactions obeying first-order kinetics in both the forward and reverse directions. For this type of kinetic situation

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

the experimental first-order rate constant is equal to $(k_1 + k_{-1})$.[6]

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(10) A value of 5×10^{-5} s^{-1} for k_r in eq 5 would mean that K_{eq} for the **6** + CN$^-$ ⇄ **15** equilibrium was only 600 times larger than K_{eq} for the **4** + CN$^-$ ⇄ **10** equilibrium. However, there are good reasons to believe it should actually be at least 100 times larger than this and that k_r for **15** is therefore in actuality much smaller than 5×10^{-5} s^{-1}. Specifically, other studies[11] have suggested that the equilibrium constant for a ring-opening reaction involving a cyclic α-disulfone will normally be much larger than for the same reaction and the analogous cyclic sulfinyl sulfone. Since results to be discussed in the next section indicate that K_{eq} for a reaction involving **2** is 5×10^4 times larger than K_{eq} for the same reaction involving **1**, one would certainly expect K_{eq} for the **6** + CN$^-$ ⇄ **15** equilibrium to be at least 10^4 larger than K_{eq} for the **4** + CN$^-$ ⇄ **10** equilibrium, and therefore that k_r for **15** must be much smaller than 5×10^{-5} s^{-1}.

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Diaziridinones (2,3-Diazacyclopropanones). Structure (X Ray).[1a] Thermal Decomposition via a Nitrenoid Fragment[1b]

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The structure of a diazacyclopropanone, bis(p-bromo-α,α-dimethylbenzyl)diaziridinone (**3**), has been determined by x-ray analysis. The substituents attached to the nitrogen atoms are 56° above and below the plane defined by the ring atoms; the bond lengths in the ring are 1.60 (N–N) and 1.325 Å (N–CO). Thermal decomposition of the diaziridinone affords the following (in moles of product per mole of reactant): p-bromo-α,α-dimethylbenzyl isocyanate (**9**) (0.35), p-bromo-N-(1-methylethylidene)benzenamine (**10**) (0.24), N-(1-p-bromophenylethylidene)methanamine (**11**) (<0.01), p-bromo-α-methylstyrene (**12**) (0.15), and p-bromocumene (**13**) (0.01). The major path of decomposition is fragmentation to the isocyanate **9** and a nitrenoid species which rearranges (aryl migration) to imine **10**.

Diaziridinones (2,3-diazacyclopropanones) pose several problems of interest in structure and reactivity.[2] NMR and IR data for N,N'-di-*tert*-alkyldiaziridinones are suggestive of the nonplanar trans structure **1**.[2a] Physical data and reactions of a bicyclic diaziridinone **2** are in accord with structure **2**, although the NMR shows a single methyl signal (and a single methylene signal) even down to −150 °C.[2c]

Here we report the structure of the diaziridinone **3**, determined by x-ray analysis, and a study of the thermal decomposition of this diaziridinone.

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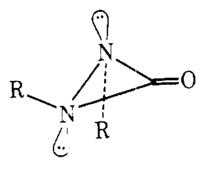
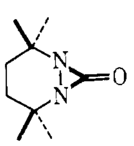


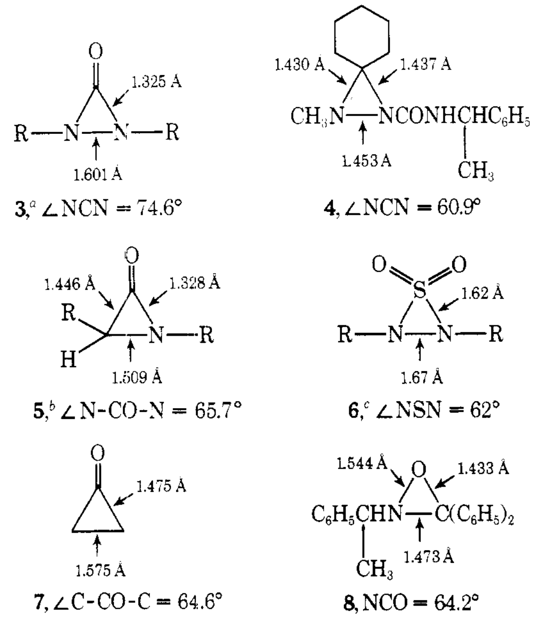
1



2

Structure of the Diaziridinone 3. The diaziridinone was prepared from the corresponding urea.[2a] The structure (Figure 1; see the Experimental Section for details on the x-ray analysis)[3] is seen to be the transoid arrangement of structure 1. The substituent atoms, C-2 of Figure 1, are 56° above and below the plane defined by the ring atoms. Comparisons of the ring bond lengths of **3** with related small-ring systems **4**,[4a] **5**,[4b] **6**,[4c,d] **7**,[4e] and **8**[4b] are summarized in Chart I. The N-N bond length in the diaziridinone **3** (and in the thiadiaziridine 1,1-dioxide **6**)[4d] is considerably longer than the N-N bond in acyclic systems (e.g., the N-N bond length in F_2N-NF_2[5a] is 1.47 Å; in H_2N-NH_2,[5a] 1.45 Å; in OCH-NH-NH-CHO,[5b] 1.39 Å) or six-membered ring systems (the N-N bond length in 3,4-dimethyl-3,4-diazabicyclo[4.4.0]decane is 1.486 Å; in 2,3-dimethyl-2,3-diazatricyclo[8.4.0.0^{4,9}]tetradec-9-ene, 1.450 Å).[6a,b] The N-CO bond in **3**, 1.325 Å, is close to the value for N-CO, 1.33 Å,[5c] in typical planar amide systems and considerably shorter than the value for N-Csp^2 in 2,4,6-trimethylnitrobenzene, 1.48 Å,[6c] or the average value for N-Csp^3, 1.47 Å.[5c] However, the C=O bond length in **3** is 1.20 Å, the same (within experimental error) as the C=O length in the cyclopropanone **7**,[4e] 1.19 Å, and in the aziridinone **5**,[4b] 1.20 Å; these values are closer to those for typical ketone C=O lengths, 1.215 Å,[5d] than for amide C=O lengths, 1.235 Å.[5d] In summary, the diaziridinone N-N bond is unusually long and the N-CO bonds are unusually short. The geometry for **3** established in this study and the IR carbonyl absorptions of diaziridinones (1855–1880 cm^{-1} vs. 1837–1850 cm^{-1} for aziridinones and 1813–1840 cm^{-1} for cyclopropanones)[2] are not in accord with amide resonance stabilization in diaziridinones. The relative reactivity toward nucleophiles of diaziridinones and cyclopropanones[2b] remains something of a puzzle; the lower reactivity of diaziridinones may be associated, in part, with the larger internal carbonyl angle (see Chart I), with repulsion between a nitrogen lone pair and an attacking nucleophile, and with amide resonance (reduced, but presumably not absent, in **3**).

Chart I



[a] R = p-$BrC_6H_4C(CH_3)_2$-. [b] R = 1-Adamantyl. [c] R = $(CH_3)_3CCH_2C(CH_3)_2$-.

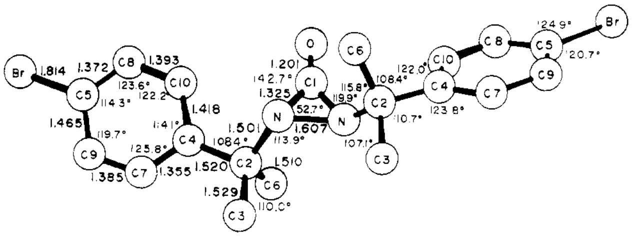
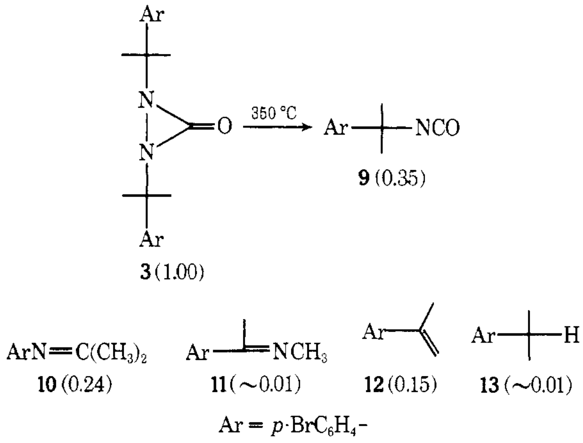


Figure 1.

Chart II

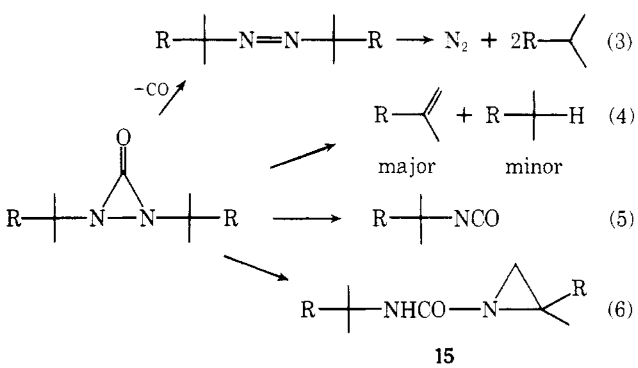


Thermal Decomposition of the Diaziridinone 3. At temperatures above 200 °C, compound **3** decomposes. Because of the sensitivity of some of the products to moisture, the study was carried out directly on GC columns, with decomposition in the injection port (glass liner). The results are summarized in Chart II. The values in parentheses are moles of product per mole of reactant. Yields of products **9**, **10**, and **12** account for 50% of the diaziridinone. Raising the injection port from 350 to 425 °C increased the amount of styrene **12** without decreasing **9** and **10** (Table I), implying a second path for formation of **12** (e.g., eq 2).

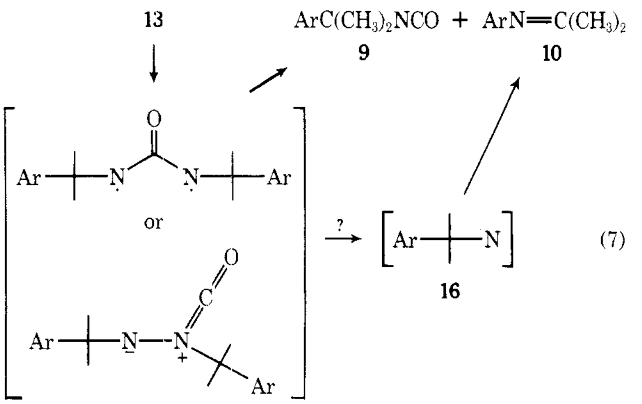
$$3 \xrightarrow{350\,^\circ\mathrm{C}} 9, 10, 12 \qquad (1)$$

$$3 \searrow [14] \xrightarrow{>350\,^\circ\mathrm{C}} 12, 13 \qquad (2)$$

Previous studies on diaziridinones have provided evidence for several modes of decomposition (eq 3–6).[2,7]



The principal contribution of the present thermal study is the evidence for involvement of a nitrenoid species, leading to the imine **10** (Chart II). The large amounts of isocyanate **9** and imine **10** are most simply ascribed to formation of both by a common path, e.g., eq 7. In a search for evidence on ni-



(7)

trene **16**, the corresponding azide, **17a**, was prepared. Decomposition of a series of azides of type **17** has been described,[8] affording mixtures of the two possible imines, **10** and **11** (eq 8). Compound **17a** was decomposed under the conditions of decomposition of diaziridinone **3**. Both imines were obtained. In contrast to **3**, the ratio of **10**/**11** from **17a** was quite dependent on the GC column temperature. Alternate injection of **17a** and **3** on a Carbowax column at 225 °C afforded these results.

$$\underset{\mathbf{17}}{\mathrm{Ar}+\mathrm{N_3}} \rightarrow \underset{\mathbf{10}}{\mathrm{ArN{=}C(CH_3)_2}} + \underset{\mathbf{11}}{\mathrm{ArC(CH_3){=}NCH_3}} \qquad (8)$$

$$\cdot\ \mathbf{17a},\ \mathrm{Ar} = p-\mathrm{BrC_6H_4}$$

substrate $\xrightarrow[\Delta]{}$ 10/11	
azide 17a	~2:1
diaziridinone 3	~50:1

Clearly, under these conditions, decomposition of **17a** and **3** is not proceeding by a common intermediate.[9] Decomposition of **17** (Ar = C_6H_5) affords the two possible imines: from thermal decomposition, **10′**/**11′** = 2:1; from photochemical decomposition, **10′**/**11′** = 1:2.[8]

Also of interest is the possibility of conversion of **3** to *p*-bromocumyl radicals, N_2 and CO, either stepwise (eq 3) or synchronously. Di-*tert*-butyldiaziridinone undergoes some decarbonylation, affording di-*tert*-butyldiazene.[7] Decarbonylation of **3** would be followed instantly by decomposition of the resulting diazene (azo) compound and is the probable origin, via radical–radical disproportionation, of the small amount, 1%, of cumene **13** (and an equal amount of styrene **12**). Overall, styrene **12** is formed in large excess over the cumene **13** (see Chart II), suggestive of direct formation of most of **12** by the cyclic six-center decomposition of **3**. Some *p*-bromocumyl radicals may transfer a hydrogen atom to diaziridinone **3**, initiating a radical chain process known to convert diaziridinones to aziridine rearrangement products, **15**[2a] (eq 6), and to ureas. In all likelihood some **15** is produced from **3**, and the increase in styrene **12** at higher decomposition temperature (Table I) is ascribed to the breakdown of **15** (eq 2, **14** = **15**).

In summary, a primary mode of decomposition of the diaziridinone **3** is breaking of ring bonds and fragmentation to the isocyanate **9**. Aryl migration is the principal reaction path in the nitrenoid fragment, affording imine **10**.

Experimental Section

***p*-Bromo-α-methylstyrene:** mp 14–15 °C (lit.[10] 11 °C); NMR (CCl_4) 2.10 (s, 3 H), 5.0 (m, 1 H), 5.27 (s, 1 H), 7.23 (q, 4 H).

***N*-(*p*-Bromo-α,α-dimethylbenzyl)formamide** was prepared by a Ritter reaction.[11] To a cooled mixture of acetic acid (5 mL) and 96% sodium cyanide (6 g) at 0 °C was added a cooled solution of sulfuric acid (25 g) and glacial acetic acid (5 mL). The mixture was allowed to come to room temperature as *p*-bromo-α,α-dimethylbenzyl alcohol (10 g)[12] was added, maintaining the temperature between 25 and 30 °C. The reaction mixture was stirred for 12 h at room temperature, neutralized (aqueous K_2CO_3), and extracted with ether, and the ethereal layer was washed, dried, and evaporated. The product was recrystallized from pentane to give *N*-(*p*-bromo-α,α-dimethylbenzyl)formamide: 9.0 g (79%); mp 106–107 °C; NMR (CCl_4) 1.6 (s, 6 H), 7.0–7.5 (m, 4 H), 7.6–8.2 (1 H); IR 1690 cm^{-1}. Anal. Calcd for $C_{10}H_{12}NOBr$: C, 49.60; H, 4.96; N, 5.78; Br, 33.05. Found: C, 49.51; H, 4.97; N, 5.56; Br, 33.26.

Table I. Decomposition of the Diaziridinone 3

Injection port temp, °C	Products (mol/mol of 3)			
	9	**10**	**12**	**13**
300	0.35	0.25	0.15	0.01
350	0.35	0.25	0.15	0.01
375	0.35	0.25	0.16	0.02
400	0.35	0.25	0.25	(0.08)
425	0.35	0.25	0.27	(0.15)

***p*-Bromo-α,α-dimethylbenzylamine.** The formamide (12 g, 0.05 mol) was heated at relfux for 5 h in 120 mL of 20% sodium hydroxide solution and then steam distilled. The distillate was extracted several times with ether, and the ethereal portion was washed with water and dried over potassium carbonate. The ether was removed on a steam bath, and the crude product was distilled [142–144 °C (10 mm)], giving the amine as a colorless liquid: 8.55 g (81%); $n^{25}{}_D$ 1.5547; NMR (CCl_4) 1.4 (s, 6 H), 7.5 (s, 4 H) [lit.[13] bp 122–124 °C (8 mm)]. Anal. Calcd for $C_9H_{12}NBr$: C, 50.45; H, 5.61; N, 6.54. Found: C, 50.57; H. 5.67; N, 6.40.

1,3-Bis(*p*-bromo-α,α-dimethylbenzyl)urea. The *p*-bromo-α,α-dimethylbenzylamine (1.55 g, 0.00724 mol) was heated with urea (0.403 g, 0.00672 mol) for 15 h at 140–150 °C. The product was recrystallized from acetone to give the dialkylurea as white needles: 0.92 g (56%); mp 236–237 °C; IR ($CHCl_3$) 1660 cm^{-1}; UV (in acetonitrile) 275 nm (ε 417), 267 (647), 260 (585). Anal. Calcd for $C_{19}H_{22}N_2OBr_2$: C, 50.20; H, 4.84; N, 6.17; Br, 35.20. Found: C, 50.34; H, 5.03; N, 6.23; Br, 34.78.

Bis(*p*-bromo-α,α-dimethylbenzyl)diaziridinone was prepared from the corresponding urea (mp 236–237 °C) by the method of Greene et al.[2a] (method B), using *tert*-butyl alcohol as solvent. The crude product, a yellow oily solid, was recrystallized from pentane, giving the diaziridinone as white plates: mp 76–77 °C; 63% yield; IR (CCl_4) intense doublet at 1885, 1850, sharp band at 1585 cm^{-1}; NMR (CCl_4) 1.47 (s, 12 H), 7.25 (q, 8 H, J = 9 Hz); UV (in acetonitrile) 274 nm (ε 383), 263 (689), 257 (746). Anal. Calcd for $C_{19}H_{20}N_2OBr_2$: C, 50.46; H, 4.45; N, 6.19; Br, 35.34. Found: C, 50.58; H, 4.47; N, 6.49; Br, 35.37.

***N*-(1-*p*-Bromophenylethylidene)methanamine (imine 11)** was prepared by the method of Kyba.[14] A mixture of *p*-bromoacetophenone, methylamine, and molecular sieves in ether was heated at 100 °C in an autoclave for 55 h. Distillation of the reaction mixture afforded the imine: mp 67–70 °C; IR ($CHCl_3$) 2960 (s), 1640 (s, sh), 1590 (s, sh), 1485 (s, sh), 1085 (s, sh), 1010 (s, sh); NMR ($CDCl_3$) 2.17 (s, 3 H), 3.30 (s, 3 H), 7.50 (q, 4 H, J = 9 Hz).

***p*-Bromo-*N*-(1-methylethylidene)benzenamine (imine 10)** was prepared in 43% yield: bp 57–58 °C (0.04–0.05 mmHg) [lit.[15] bp 98–102 °C (5 mmHg)]; IR ($CHCl_3$) 2960 (m), 1660 (s, sh), 1480 (s, sh), 1065 (m, sh), 1000 (m, sh), 840 (s); NMR ($CDCl_3$) 1.72 (s, 3 H), 2.10 (s, 3 H), 6.53 (d, 2 H), 7.35 (d, 2 H).

***p*-Bromo-α,α-dimethylbenzyl Isocyanate (9).** Phosgene gas was bubbled through 35 mL of toluene for 10 min and the solution brought to reflux. A solution of 2.14 g (0.01 mol) of the amine in 10 mL of toluene was added dropwise and with stirring to the refluxing toluene solution over a period of 1.5 h. A continuous stream of phosgene gas was maintained throughout the addition and 10 min thereafter. The reaction mixture was refluxed vigorously for 2 h. The toluene was removed by distillation and the residue was fractionally distilled, giving 1.65 g (69%) of the isocyanate: bp 144–164 °C (10 mmHg); IR ($CHCl_3$) 2970 (w), 2270 (s), 1100 (m, sh), 1010 (m, sh); NMR ($CDCl_3$) 1.67 (s, 6 H), 7.33 (q, 4 H, J = 9 Hz).

***p*-Bromocumene** was prepared by the method of Bruce and Todd[16] by the action of isopropyl chloride on a suspension of aluminum chloride in bromobenzene. A mixture of products was obtained from which a sample of the pure para isomer was isolated by gas chromatography on a 6-ft column of 15% SE-30 on Chromosorb W (80–100 mesh): IR (CCl_4) 2960 (s), 1490 (s), 1460 (s), 1400 (m, sh), 1080 (s), 1010 (s); NMR 1.20 (d, 6 H, J = 7 Hz), 2.80 (septet, 1 H, J = 7 Hz), 7.13 (q, 4 H, J = 9 Hz).

***p*-Bromo-α,α-dimethylbenzyl azide** was prepared by the method of Saunders and Caress[8] and purified by chromatography on alumina:

IR (CCl_4) 3320 (w, br), 2980 (m), 2450 (w, br), 2090 (s), 1490 (m), 1400 (m, sh), 1370 (m, sh), 1150 (m), 1100 (m, sh), 1010 (m, sh); NMR (neat) 1.47 (s, 6 H), 7.23 (q, 4 H, J = 9 Hz).

Thermal Decompositions. A. Diaziridinone. The diaziridinone (in concentrated cyclohexane solution) and the azide were decomposed by injection into a gas chromatograph with the injection port at 350 °C. Peaks were identified by collection and spectral comparison (IR and NMR) with authentic samples. The imines, styrene **12**, and the cumene were also checked by coinjection of authentic samples with the diaziridinone. Two 6 ft × 0.25 in. aluminum columns were used: one of 15% (w/w) silicone oil SE-30 and one of 15% (w/w) Carbowax 20M, both on a 80–100 mesh Chromosorb W diatomite support. Pyrex glass liners were used in the injection port. Yield and product ratio data were obtained using hydrocarbon standards (undecane, tridecane, and pentadecane). The order of elution and relative retention times on SE-30 were $C_{11}H_{24}$ (0.45), *p*-bromocumene (0.73), *p*-bromo-*α*-methylstyrene (0.87), $C_{13}H_{28}$ (1.00), unknown (E2) (1.1), *p*-bromo-*N*-(1-methylethylidene)benzenamine (imine **10**) (1.45), *p*-bromo-*α*,*α*-dimethylbenzyl isocyanate (1.98), and $C_{15}H_{32}$ (2.38). *N*-(1-*p*-Bromophenylethylidene)methanamine (imine **11**) has the same retention time as the isocyanate; collection of the isocyanate peak from decomposition of a sample of the diaziridinone and examination by IR and NMR showed no evidence for imine **11**. On the Carbowax column, the order of elution of the products is the same; the isocyanate, however, is not eluted. A peak of the same retention time as imine **11** is observed, corresponding to <0.5% yield. The results are summarized in Chart II and Table I.

B. Azide. Thermal decomposition of *p*-bromo-*α*,*α*-dimethylbenzyl azide and product analysis were carried out as described above. The major products are the styrene, imine **10**, and imine **11**. On the SE-30 column, imine **11** and the azide have the same retention time; on the Carbowax column, imine **10** and the azide have the same retention time. The ratio of imine **10** to imine **11** is dependent on column temperature, associated, in part, with some variability in the extent of decomposition of the azide. Analysis was best carried out on the Carbowax column with the injection port at 350 °C and the column at 225 °C.

Crystal data for 3: $C_{18}H_{20}Br_2N_2O$; mp 76–77 °C; orthorhombic; space group $p2_12_12$; a = 7.79 (4), b = 17.70 (7), c = 6.86 (2) Å. By assuming two molecules per unit cell (thus explicitly forcing the molecule, itself, to have a twofold rotation axis), a reasonable density of 1.586 g/cm^3 was calculated. Least-squares lattice constants were determined from 20 measurements of the copper $K\alpha_1 - K\alpha_2$ doublet at values of 2θ greater than 65° under fine conditions (1° takeoff angle and 0.05° slit). The measurements were taken on a G.E. XRD-5 diffractometer. Subsequently, three-dimensional intensity data were collected on a G.E. XRD-490 automated diffractometer system using the stationary-counter, stationary-crystal method, balanced Ni and Co Ross filters; and Cu $K\alpha$ radiation. A total of 1130 reflections were measured to a 2θ limit of 140°. Of these, 717 reflections were considered statistically significant and only these reflections were used in the structure determination. The structure was solved by the standard heavy atom method and refined by block-diagonal least-squares techniques to a final $R = \Sigma\|kF_o| - |F_c\|/\Sigma|kF_o|$ of 0.06, and a weighted $R_2 = \Sigma[w\|kF_o| - |F_c\|^2/\Sigma w|kF_o|^2]^{1/2}$ of 0.069. The shift errors in the last cycle of refinements were all less than 0.002. The positions of the phenyl hydrogen atoms were calculated based upon a reasonable chemical model (CH = 1.0 Å; CHC = 120°) and then included in the final cycles of least-squares refinement as fixed contributors. A final difference Fourier map was essentially featureless, with only the ripples about the bromine heavy-atom positions exceeding 0.4 e/Å^3. (See paragraph regarding supplementary material.)

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Registry No.—**3**, 64586-25-0; **9**, 64586-20-5; **10**, 40938-44-1; **11**, 64586-22-7; *p*-bromo-*α*-methylstyrene, 6888-79-5; *N*-(*p*-bromo-*α*,*α*-dimethylbenzyl)formamide, 64586-24-9; *p*-bromo-*α*,*α*-dimethylbenzyl alcohol, 2077-19-2; sodium cyanide, 143-33-9; *p*-bromo-*α*,*α*-dimethylbenzylamine, 17797-12-5; 1,3-bis(*p*-bromo-*α*,*α*-dimethylbenzyl)urea, 64586-23-8; urea, 57-13-6; *p*-bromoacetophenone, 99-90-1; methylamine, 74-89-5; phosgene, 75-44-5; *p*-bromocumene, 586-61-8; *p*-bromo-*α*,*α*-dimethylbenzyl azide, 64586-21-6.

Supplementary Material Available: A list of atomic coordinate positions and anisotropic thermal parameters for the nonhydrogens and the calculated positions for the hydrogen atoms (2 pages). Ordering information is given on any current masthead page.

References and Notes

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