after recrystallization from ethanol, afforded 7.4 g (79%) of a solid, mp 288–290°.

Anal. Calcd for $C_{17}H_{23}NO_2 \cdot HBr$: C, 57.63; H, 6.83; N, 3.95. Found: C, 57.52; H, 6.89; N, 3.94.

Method B.—A solution of 0.10 g of **12** in 15 ml of hydrobromic acid was refluxed for 6 hr. On standing, there was deposited 0.11 g of a crystalline solid, mp 288–290°. This sample was shown to be identical with that obtained in method A by the method of mixture melting point.

***cis-syn*-2,3,4,4a,5,6,8,9,13b,13c-Decahydro-11,12-dihydroxy-1*H*-dibenzo[*a*,*h*]quinolizine Hydrobromide (7).**—A solution of 7.0 g of **6** in 175 ml of hydrobromic acid was refluxed for 8 hr. On standing there was deposited a solid which on recrystallization from ethanol afforded 6.9 g (84%) of a solid, mp 329–331°.

Anal. Calcd for $C_{17}H_{23}N_2O_2 \cdot HBr$: C, 57.63; H, 6.83; N, 3.95. Found: C, 57.43; H, 6.76; N, 3.97.

1,2,3,4,4a,5,6,8,9,13c-Decahydro-11,12-dimethoxydibenzo[*a*,*h*]quinolizinium Perchlorate (13).—To a solution of 50 g of **8** in 1 l. of 5% acetic acid was added a solution of 530 g of mercuric acetate in 1.5 l. of 5% acetic acid. After the addition had been completed the solution was heated at 95° for 3 hr with stirring. The hot reaction mixture was saturated with hydrogen sulfide and filtered. Treatment of the filtrate with perchloric acid gave, after recrystallization from methanol, 44 g (66%) of a solid, mp 180–182°. Further recrystallization gave an analytical sample, mp 187–188°.

Anal. Calcd for $C_{19}H_{25}NO_2 \cdot HClO_4$: C, 57.07; H, 6.55; N, 3.50. Found: C, 56.83; H, 6.56; N, 3.78.

Hydrogenation of 1,2,3,4,4a,5,6,8,9,13c-Decahydro-11,12-dimethoxydibenzo[*a*,*h*]quinolizinium Perchlorate (13).—To a solution of 30 g of **13** in 60 ml of water and 800 ml of ethanol was added 3.0 g of platinium oxide and the mixture was hydrogenated at atmospheric pressure. Uptake ceased after the theoretical amount of hydrogen had been absorbed. The catalyst was removed by filtration. After removal of the solvent the residue was treated with 300 ml of 10% sodium hydroxide solution and 2.3 l. of ether. The ether layer was washed with water and dried over sodium sulfate and the solvent was removed. The residue was chromatographed on 600 g of alumina. Elution of the column with benzene gave 6.0 g (27%) of *cis-syn*-2,3,4,4a,5,6,8,9,13b,13c-decahydro-11,12-dimethoxy-1*H*-dibenzo[*a*,*h*]quinolizine (**6**), mp 120–122°.

Anal. Calcd for $C_{19}H_{27}NO_2$: C, 75.71; H, 9.03; N, 4.65. Found: C, 75.70; H, 9.01; N, 4.73.

Elution of the column with chloroform–methanol gave 5.4 g of material which contained mostly trans-anti-2,3,4,4a,5,6,8,9,13b,13c-decahydro-11,12-dimethoxy-1*H*-dibenzo[*a*,*h*]quinolizine (**8**) as shown by thin layer chromatography.

Preparation of the C-13b-*d* Derivatives of *cis-syn*- and *trans-anti*-2,3,4,4a,5,6,8,9,13b,13c-Decahydro-11,12-dimethoxy-1*H*-dibenzo[*a*,*h*]quinolizine.—To a solution of 4.9 g of **13** in 45 ml of deuterium oxide was added 1.8 g of sodium borodeuteride over a 10-min interval. The reaction mixture was extracted with methylene chloride. The methylene chloride layer was dried over sodium sulfate and the solvent was removed. The residue (4.9 g) was chromatographed on 160 g of alumina. Elution of the column with benzene gave 1.7 g of *cis-syn*-2,3,4,4a,5,6,8,9,13b,13c-decahydro-11,12-dimethoxy-1*H*-dibenzo[*a*,*h*]quinolizine-13b-*d*, mp 121–122°.

Anal. Calcd for $C_{19}DH_{26}NO_2$: C, 75.45; H, 9.33; N, 4.63. Found: C, 75.59; H, 9.37; N, 4.39.

Elution of the column with 1% methanol in ether gave 0.6 g which was rechromatographed on 40 g of alumina. Elution with methylene chloride gave 0.31 g which was subjected to preparative thin layer chromatography on silica gel. The plates were developed with ethyl acetate–benzene (1:1). The desired zone was removed from the plate and extracted with methylene chloride. The methylene chloride was removed and the residue dissolved in Skellysolve B. On standing there was deposited 0.06 g of a *trans-anti*-2,3,4,4a,5,6,8,9,13b,13c-decahydro-11,12-dimethoxy-1*H*-dibenzo[*a*,*h*]quinolizine-13b-*d*, mp 95–98°.

Registry No.—**1**, 31446-56-7; **2**, 31446-57-8; **3**, 31446-58-9; **4**, 31446-59-0; **5**, 31446-60-3; **6**, 31446-61-4; **7**, 31446-62-5; **8**, 31446-63-6; **9**, 31446-64-7; **10**, 31446-65-8; **11**, 31446-66-9; **12**, 31446-67-0; **13**, 31446-68-1; **13**-13b-*d* (cis-syn,) 31446-69-2; **13**-13b-*d* (trans-anti), 31446-70-5.

Preparation of Amidines from *gem*-Dichloroaziridines[1,2]

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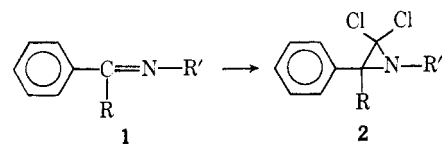
The first preparation of a *gem*-dichloroaziridine was reported by Fields and Sandri in 1959.[3] They synthesized 1,3-diphenyl-2,2-dichloroaziridine (**2a**) by the addition of dichlorocarbene, generated by the reaction of chloroform with sodium methoxide, to benzylidene-



1 **2**

aniline (**1a**). A number of other methods have been used to generate the dichlorocarbene in this reaction and the methods are summarized in Table I. The new

TABLE I

gem-DICHLOROAZIRIDINES[a]

Imine	R	R′	Aziridine	Yield, %	Method[b]	Ref
1a	Hydrogen	Phenyl	**2a**	55	A	3
				80	B	*c*
				61	C	*d*
				68, 91[e]	D	*f*
1b	Phenyl	Phenyl	**2b**	*g*	D	*h*
1c	Hydrogen	1-Naphthyl	**2c**	39	A	*i*
				44	B	*i*
1d	Phenyl	Benzyl	**2d**	65[i]	A	*i*
				7	B	*i*
1e	Ethyl	Phenyl	**2e**	56	A	*i*
				52	B	*i*
1f	Ethyl	1-Naphthyl	**2f**	68	A	*i*
				31	B	*i*

[a] This table also contains the other reported *gem*-dichloroaziridine systems. [b] The reaction of sodium methoxide with chloroform (A), ethyl trichloroacetate (B), hexachloroacetone (C), and the reaction of potassium *tert*-butoxide with chloroform (D). [c] J. A. Deyrup and R. B. Greenwald, *J. Amer. Chem. Soc.*, **87**, 4538 (1965). [d] P. K. Kadaba and J. O. Edwards, *J. Org. Chem.*, **25**, 1431 (1960). [e] Yields reported for R′ = *p*-chlorophenyl and *p*-methoxyphenyl, respectively. [f] A. G. Cook and E. K. Fields, *ibid.*, **27**, 3686 (1962). [g] Not reported. [h] J. A. Deyrup and R. B. Greenwald, *Tetrahedron Lett.*, 321 (1965). [i] This report. [j] This yield was obtained in one run; typical yields for this reaction were *ca.* 4%.

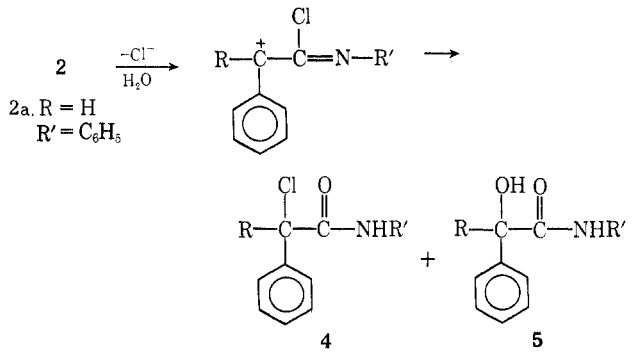
alkyl- and aryl-substituted *gem*-dichloroaziridines reported in Table I were prepared by two of these methods. Although the yields are comparable for the two methods, the aziridines were more readily purified from the reaction which employed chloroform as the carbene source.

Hydrolysis.—The hydrolysis of 1,3-diphenyl-2,2-dichloroaziridines (**2a**) has been reported to afford α-chloro-α-phenylacetamide (**4a**) in quantitative

(1) Presented in part at the 41st Meeting of the Colorado–Wyoming Academy of Science, Greeley, Colo., May 1,2, 1970.

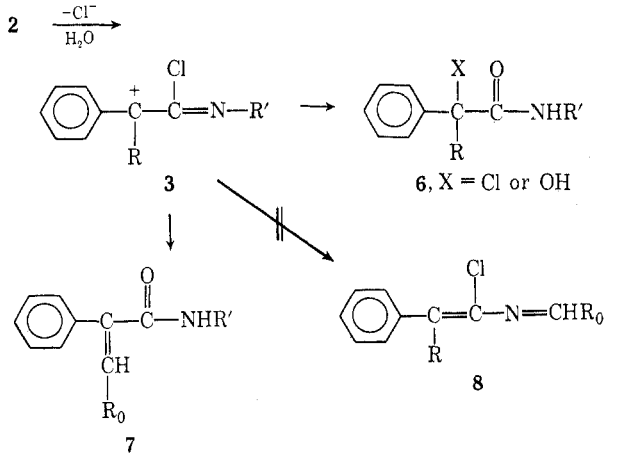
(2) We are plaesed to acknowledge the support of the Research Corporation by a Frederick Gardner Cottrell grant.

(3) E. K. Fields and S. M. Sandri, *Chem. Ind. (London)*, 1216 (1959).



yields, while the homogeneous hydrolysis affords a mixture of amides **4** and **5**. The mechanism of the ring-opening reaction has been studied in detail and cation **3** has been suggested as an intermediate.[4] Prior to this report only products of substitution of the intermediate cation **3** had been observed in the hydrolytic ring opening of known *gem*-dichloroaziridines. However, as shown in Scheme I, when alkyl groups are substituted on the aziridine the intermediate cation in the ring opening can also give rise to products by elimination pathways.

SCHEME I



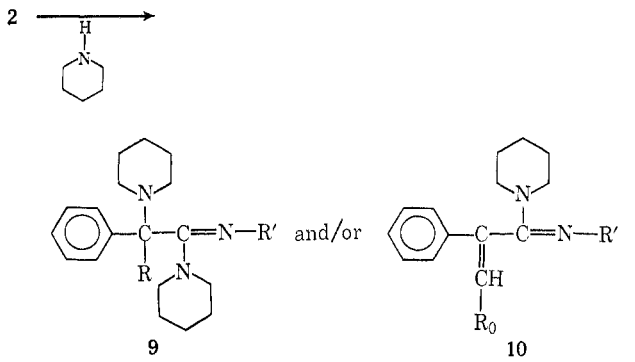
To test the plausibility of the elimination pathways, the hydrolysis of two alkyl-substituted *gem*-dichloroaziridines, **2d** and **2e**, was examined. The hydrolysis of 1,3-diphenyl-3-ethyl-2,2-dichloroaziridine (**2e**) gave the α,β-unsaturated amide **7** (R_0 = methyl) in 35% yield demonstrating the feasibility of elimination. Analysis of the mother liquors by nmr failed to detect any additional unsaturated amide. Hydrolysis of aziridine **1d** gave the α-hydroxyamide **6** (R = phenyl, R′ = benzyl, X = OH) in high yields. Products resulting from the hydrolysis of **8** were not observed.

Aminolysis.—The aminolysis of *gem*-dichloroaziridines provides a new, convenient synthesis of amidines.[5] The *gem*-dichloroaziridine is dissolved in the amine and the solution is slowly heated to and maintained at 100–130° for several hours. The amine hydrochloride which is formed in the reaction is removed from the cooled reaction mixture by filtration or by an aqueous work-up. The amidine is generally isolated by crystallization. The aryl-substituted *gem*-dichloroaziridines (**2a** and **2c**) afford α-aminoamidines (**9**) in reasonable yields. The 3-alkyl-substituted *gem*-dichloroaziridines afforded α,β-unsaturated amidines (**10**) as the predominant isolated product. The amidines which have been prepared by this new method are summarized in Table II.

TABLE II

AMIDINES PREPARED FROM *gem*-DICHLOROAZIRIDINES

Aziridine	Amine	Amidine	R	R′	R_0	Yield, %
2a	Piperidine	**9a**	H	C_6H_5		59
2a	Morpholine	**9b**	H	C_6H_5		36
2a	Pyrrolidine	**9c**	H	C_6H_5		72
2c	Piperidine	**9d**	H	1-Naphthyl		74
2e	Piperidine	**10a**		C_6H_5	CH_3	51
2f	Piperidine	**10b**		1-Naphthyl	CH_3	50



The amidines reported in Table II and the hydrolysis products, **6** and **7**, support the intermediacy of cation **3** in this type of ring-opening reaction. The potential of cation **3** to serve as a useful reaction intermediate in organic chemistry is being examined.

Experimental Section

All melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The nuclear magnetic resonance spectra were recorded on a Varian Associates A-60A spectrometer using tetramethylsilane as an internal standard. Infrared spectra were determined in potassium bromide on a Perkin-Elmer Model 137 spectrophotometer. The microanalyses were performed by Midwest Microlab, Ltd., Indianapolis, Ind., and Huffman Laboratories, Inc., Wheatridge, Colo.

N-1-(**1-Phenylpropylidene**)-**1-naphthylamine** (**1f**).—To a solution of 30 g (0.21 mol) of 1-naphthylamine and 28 g (0.21 mol) of propiophenone in 100 ml of dry toluene was added *p*-toluenesulfonic acid (*ca.* 0.1 g). The flask was connected to a water separator fitted with a condensor and drying tube and the solution was heated at the reflux temperature for 18 hr. The solvent was removed *in vacuo* from the cooled solution and crystallization of the residue from methanol afforded 33 g (61%) of the crude imine, mp 102–104°. Short-path distillation, flask temperature 220° (0.2 mm), followed by crystallization from hexane afforded an analytical sample of the light yellow imine: mp 103–104°; ir (KBr) 1625 cm^{-1} (C=N); nmr (CCl_4) δ 8.3–6.6 (m, 12, aromatic), 2.6 (broad q, 2, J = 7 Hz, CH_2CH_3), 1.0 (broad t, 3, J = 7 Hz, CH_2CH_3).

Anal. Calcd for $C_{19}H_{17}N$: C, 87.98; H, 6.62. Found: C, 87.73; H, 6.54.

General Synthesis of *gem*-Dichloroaziridines. Method A.—Chloroform (0.08 mol) was slowly added dropwise to a magnetically stirred mixture of sodium methoxide (0.08 mol), imine (0.02 mol), and purified hexane (10–20 ml). The mixture was stirred for several hours, hexane or ether was added (*ca.* 25 ml), and the solution was filtered.[6] The *gem*-dichloroaziridine was isolated from the filtrate by crystallization.

(4) R. E. Brooks, J. O. Edwards, G. Levey, and F. Smith, *Tetrahedron*, **22**, 1279 (1966).

(5) For a review of amidine chemistry see (a) L. Weintraub, S. R. Oles, and N. Kalish, *J. Org. Chem.*, **33**, 1679 (1968); R. I. Fryer, J. V. Earley, G. F. Field, W. Zally, and L. H. Sternbach, *ibid.*, **34**, 1143 (1969), and references cited therein; (b) R. L. Shriner and F. W. Newmann, *Chem. Rev.*, **35**, 351 (1944).

(6) (a) In those cases where the imine was slightly soluble in hexane, it was dissolved in a hexane–ether solution. (b) The mixture may be poured into water, extracted with ether, dried ($MgSO_4$), and filtered.

Method B.—The procedure was the same as method A except that during the dropwise addition of ethyl trichloroacetate the mixture was cooled in an ice bath. Using the above procedures the following *gem*-dichloroaziridines were prepared.

1-(1-Naphthyl)-3-phenyl-2,2-dichloroaziridine (2c).—Crystallization from ethyl acetate afforded the light yellow crystalline aziridine: mp 120–121°; nmr (CCl_4) δ 7.3 (m, 12, aromatic) and 3.75 (s, 1, aziridinyl H).

Anal. Calcd for $C_{18}H_{13}Cl_2N$: C, 68.80; H, 4.18; N, 4.56. Found: C, 68.75; H, 4.45; N, 4.47.

1-Benzyl-3,3-diphenyl-2,2-dichloroaziridine (2d).—Crystallization from hexane–ethyl acetate afforded the white crystalline aziridine: mp 136–137°; nmr ($DCCl_3$) δ 7.3 (m, 15, aromatic) and 3.97 (s, 2, CH_2).

Anal. Calcd for $C_{21}H_{17}Cl_2N$: C, 71.18; H, 4.85; N, 3.95. Found: C, 71.04; H, 4.91; N, 3.95.

1,3-Diphenyl-3-ethyl-2,2-dichloroaziridine (2e).—Crystallization from hexane afforded the white crystalline aziridine: mp 82–83°; nmr (CCl_4) δ 7.2 (m, 10, aromatic), 1.9 (m, 2, CH_2CH_3), and 1.07 (m, 3, CH_2CH_3).

Anal. Calcd for $C_{16}H_{15}Cl_2N$: C, 65.67; H, 5.18; N, 4.79. Found: C, 65.72; H, 5.18; N, 4.67.

1-(1-Naphthyl)-3-phenyl-3-ethyl-2,2-dichloroaziridine (2f).—Crystallization from hexane–ethyl acetate afforded the white crystalline aziridine: mp 90.5–92°; nmr (CCl_4) δ 7.4 (m, 12, aromatic), 2.1 (m, 2, CH_2), and 1.17 (t, 3, CH_3).

Anal. Calcd for $C_{20}H_{17}Cl_2N$: C, 70.17; H, 5.02; N, 4.09. Found: C, 69.94; H, 5.15; N, 4.17.

2-Phenyl-2-butenanilide.—A solution of 0.639 g (0.0022 mol) of 1,3-diphenyl-3-ethyl-2,2-dichloroaziridine (**1e**), water (5 ml), and tetrahydrofuran (15 ml) was heated at the reflux temperature overnight. The solution was poured into water, extracted with ether, dried ($MgSO_4$), and filtered. The solvent was removed *in vacuo* and the residue was crystallized from ethyl acetate–hexane to afford 0.180 g (35%) of the crude amide, mp 141–146°. Recrystallization afforded 0.148 g (29%) of the pure amide: mp 152–153°; ir (KBr) 1650 cm^{-1} (C=O); nmr ($DCCl_3$) δ 7.3 (m, 10, aromatic), 6.13 (q, 1, J = 7 Hz, C=CH), and 1.98 (d, 3, J = 7 Hz, =CHC**H**$_3$).

Anal. Calcd for $C_{16}H_{15}NO$: C, 80.97; H, 6.38. Found: C, 81.02; H, 6.15.

***N*-Benzylbenzilamide.**—A solution of 0.245 g (0.0067 mol) of 1-benzyl-3,3-diphenyl-2,2-dichloroaziridine (**2d**), *p*-dioxane (10 ml), and water (1 ml) was heated at the reflux temperature for 9 hr, poured into water, and extracted with ether. The combined ether extracts were dried ($MgSO_4$) and concentrated to afford a light yellow oil. Crystallization of the oil from ethyl acetate–hexane afforded 0.137 g (62%) of the amide, mp 99–100° (lit.[7] mp 99–100°). An additional 0.016 g (7%) of the crude amide was isolated: mp 97–99°; ir (KBr) 1650 cm^{-1} (C=O); nmr ($DCCl_3$) δ 7.3 (m, 16, aromatic and NH), 4.45 (d, 2, J = 6 Hz, CH_2NH), and 3.9 (s, 1, OH).

General Synthesis of Amidines from *gem*-Dichloroaziridines.—A solution of the *gem*-dichloroaziridine (0.02 mol) and the amine (5–10 ml) was slowly heated to and maintained at 100–130° for several hours. The amine hydrochloride was removed from the cooled solution by filtration.[8] The filtrate was concentrated *in vacuo* and crystallization of the residue afforded the crude amidines which were purified by crystallization.

1-[*N*,2-Diphenyl-2-(1-piperidino)acetimidoyl]piperidine (9a).—The amidine was isolated in 59% yield after a reaction period of 1.5 hr by crystallization from ethyl acetate, mp 104–105.5°. Recrystallization afforded an analytical sample: mp 105–106.5°; ir (KBr) 1625 cm^{-1} (C=N); nmr (CCl_4) δ 7.0 (m, 10, aromatic), 4.63 (s, 1, CH), 3.58 (m, 4, CH_2N), 2.53 (m, 4, CH_2N), and 1.35 (m, 12, CH_2).

Anal. Calcd for $C_{24}H_{31}N_3$: C, 79.72; H, 8.66. Found: C, 79.70; H, 8.65.

4-[*N*,2-Diphenyl-2-(4-morpholino)acetimidoyl]morpholine (9b).—The amidine was isolated in 36% yield after a reaction period of 3 hr by crystallization from ethyl acetate, mp 170–172°. Recrystallization afforded an analytical sample: mp 172–174°; ir (KBr) 1625 cm^{-1} (C=N); nmr ($DCCl_3$) δ 7.5–6.7 (m, 10, aromatic), 4.67 (s, 1, CH), 3.9–3.2 (m, 12, CH_2O and CH_2N), and 2.6 (m, 4, CH_2N).

Anal. Calcd for $C_{22}H_{27}N_3O_2$: C, 72.42; H, 7.42; N, 11.44. Found: C, 72.54; H, 7.34; N, 11.20.

1-[*N*,2-Diphenyl-2-(1-pyrrolidino)acetimidoyl]pyrrolidine (9c).—The amidine was isolated in 72% yield after a reaction period of 3 hr by crystallization from hexane, mp 118–121°. Recrystallization afforded an analytical sample: mp 120.5–122.5°; ir (KBr) 1600 cm^{-1} (C=N); nmr ($DCCl_3$) δ 6.90 (m, 10, aromatic), 4.52 (s, 1, CH), 4.0–2.1 (m, 8, CH_2N), and 1.75 (m, 8, CH_2).

Anal. Calcd for $C_{22}H_{27}N_3$: C, 79.24; H, 8.15. Found: C, 78.98; H, 8.41.

1-[*N*-(1-Naphthyl)-2-phenyl-2-(1-piperidino)acetimidoyl]piperidine (9d).—The amidine was isolated in 74% yield after a reaction period of 12 hr by crystallization from hexane: mp 144–145.5; ir (KBr) 1600 cm^{-1} (C=N); nmr (CCl_4) δ 8.0–6.5 (m, 12, aromatic), 4.68 (s, 1, CH), 3.7 (m, 4, CH_2N), 2.5 (m, 4, CH_2N), and 1.5 (m, 12, CH_2).

Anal. Calcd for $C_{28}H_{33}N_3$: C, 81.49; H, 8.08. Found: C, 81.31; H, 8.08.

1-[*N*-Phenyl-2-phenyl-2-butenimidoyl]piperidine (10a).—The amidine was isolated in 51% yield after a reaction period of 9 hr by crystallization from hexane, mp 82.5–85°. Recrystallization afforded an analytical sample: mp 86.5–87.5°; ir (KBr) 1600 cm^{-1} (C=N and C=C); nmr (CCl_4) δ 7.4–6.3 (m, 10, aromatic), 6.0 (q, 1, J = 7 Hz, CH=C), 3.5 (m, 4, CH_2N), and 1.60 (m, 9, CH_2 and CH_3).

Anal. Calcd for $C_{21}H_{24}N_2$: C, 82.84; H, 7.96. Found: C, 82.96; H, 7.88.

1-[*N*-(1-Naphthyl)-2-phenyl-2-butenimidoyl]piperidine (10b).—The amidine was isolated after a reaction period of 3 hr by crystallization from hexane in 50% yield, mp 113–116°. Crystallization afforded an analytical sample: mp 116.5–118°; ir (KBr) 1625 (C=N) and 1600 cm^{-1} (C=C); nmr (CCl_4) δ 8.1, 7.6–6.9 6.3 (m, 12, aromatic), 6.02 (q, 1, J = 7 Hz, =C**H**CH_3), 3.6 (m, 4, CH_2N), 1.68 (m, 6, CH_2), and 1.48 (d, 3, J = 7 Hz, $CHCH_3$).

Anal. Calcd for $C_{25}H_{26}N_2$: C, 84.69; H, 7.41. Found: C, 84.68; H, 7.56.

Registry No.—**1f**, 31528-94-6; **2c**, 31528-95-7; **2d**, 31528-96-8; **2e**, 31528-97-9; **2f**, 31528-98-0; **9a**, 31528-99-1; **9b**, 31529-00-7; **9c**, 31529-01-8; **9d**, 31529-02-9; **10a**, 31529-03-0; **10b**, 31529-04-1; 2-phenyl-2-butenanilide, 31529-05-2; *N*-benzylbenzilamide, 13415-45-7.

Acknowledgment.—The authors wish to thank Dr. W. E. Parham for his helpful comments prior to and during the course of this study and Drs. J. A. Beel and R. D. Bach for their support and encouragement.

(7) V. E. Johnsen, C. R. Jacobsen, R. A. LaForge, and C. Hanna, *J. Pharm. Sci.*, **51**, 799 (1962).

(8) The amine hydrochloride may be removed by pouring the solution into a mixture of 10% sodium hydroxide and ether and stirring until the solid material dissolves. The ether layer is separated and dried and the solvent removed *in vacuo* to afford the crude amidine.

Reaction of Acetone Azine and *p*-Toluenesulfonyl Azide

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Contribution No. 1637 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Received October 31, 1969

Acetone azine and *p*-toluenesulfonyl azide reacted to produce a compound which had the elements of both azine and azide minus nitrogen and a methyl group of the azine. The product has been assigned the structure of *N*-[1-(isopropylidenehydrazino)ethylidene]-*p*-toluenesulfonamide (**1**). The reaction occurred very slowly at reflux in tetrahydrofuran solution, and a 12%