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.

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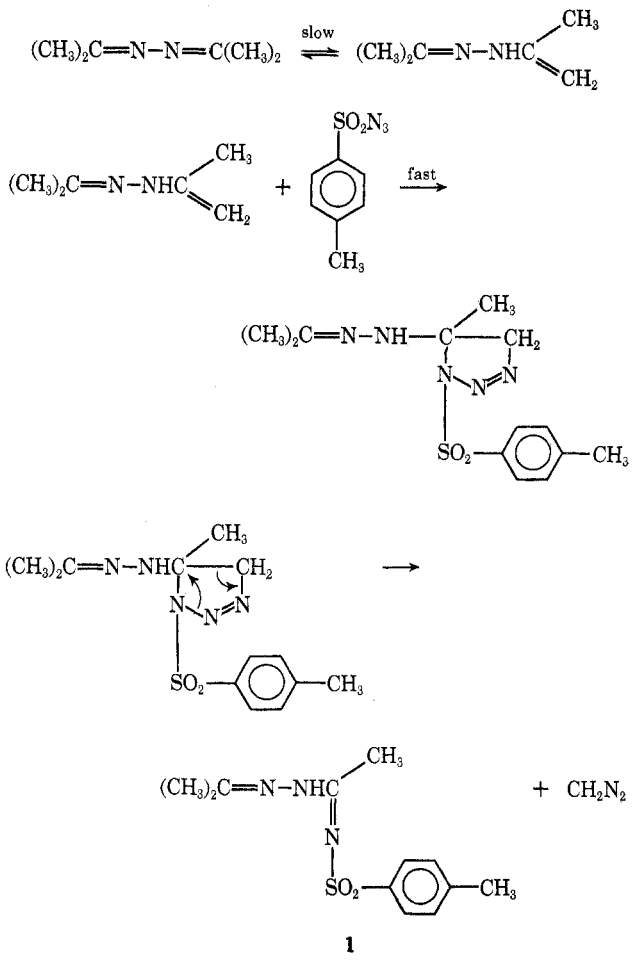
Acetone azine and *p*-toluenesulfonyl azide reacted to produce a compound which had the elements of both azine and azide minus nitrogen and a methyl group of the azine. The product has been assigned the structure of *N*-[1-(isopropylidenehydrazino)ethylidene]-*p*-toluenesulfonamide (**1**). The reaction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

yield of **1** was obtained after 7 days. The reaction occurred at approximately the same rate at which deuterium (from D_2O) was incorporated into the azine. The structure of **1** was confirmed by the nmr spectrum which showed the absorptions of four different methyl groups, the infrared spectrum which showed the absorption of the NH group, and the ultraviolet absorption spectrum.

Scheme I is suggested for the reaction. The slow incorporation of deuterium into acetone azine is

SCHEME I



1

in agreement with the postulated equilibrium between the azine and the substituted hydrazone. The hydrazone would be expected to undergo rapid deuterium exchange and thus provide a means for the entrance of deuterium into the azine. The azide should add rapidly to the enamine derivative to give the triazoline.[1,2] Analogous fragmentations of triazolines to diazo compounds have been observed previously.[1-3] Diazomethane was not isolated from the reaction but suggestive evidence for its formation was obtained by the isolation of methyl *p*-nitrobenzoate from the reaction of acetone azine, *p*-toluenesulfonyl azide, and *p*-nitrobenzoic acid.

Experimental Section

***N*-[1-(Isopropylidenehydrazino)ethylidene]-*p*-toluenesulfonamide (1).**—A solution of 12 g of acetone azine and 20 g of *p*-toluenesulfonyl azide in 50 ml of tetrahydrofuran was heated at reflux for 7 days. Gas was slowly evolved. The mixture was cooled and the solvent was removed under reduced pressure. The residue was stirred with methanol and filtered to give white, crystalline **1**, 3.19 g (12%), mp 154–156.5°. Recrystallization from methanol gave material which melted at 158–159°: uv λ_{max}^{EtOH} 264 mμ (ε 23,400), 224 (13,100); nmr ($CDCl_3$) δ 1.98 (3), 2.05 (3), 2.22 (3), 2.42 (3), 7.58 (4).

Anal. Calcd for $C_{12}H_{17}O_2N_3S$: C, 53.91; H, 6.41; N, 15.72; S, 11.99; mol wt, 267. Found: C, 53.62, 53.75; H, 6.38, 6.48; N, 15.57, 15.45; S, 11.90, 11.80; mol wt (mass spectrum), 267.

From the original methanol filtrate there was obtained in successive crops a total of 6.18 g (36%) of *p*-toluenesulfonamide, mp 125–126° from benzene.

Acetone Azine in Deuterium Oxide.—A solution of acetone azine in deuterium oxide was heated at 65°. After 4 days the intensity ratio of the two azine methyl groups to the exchange peak of H_2O in D_2O in the nuclear magnetic resonance spectrum was 6.3, indicating exchange of 14% of the original methyl hydrogens for deuterium. After 9 days the ratio was 4.6 (18% exchange) and after 16 days the ratio was 3.2 (24% exchange).

Registry No.—**1**, 31600-81-4; acetone azine, 627-70-3; *p*-toluenesulfonyl azide, 941-55-9.

Acknowledgment.—We wish to thank Dr. Howard E. Simmons for helpful discussions

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On the Structure of the Diels–Alder Adduct of Ditropyl and Dimethyl Acetylenedicarboxylate

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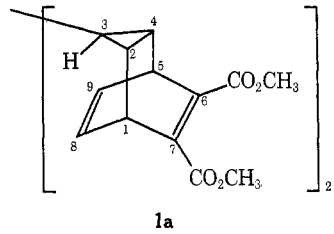
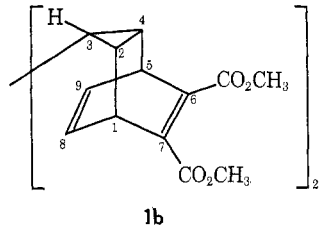
Recently we assigned structure I to the Diels–Alder adduct of ditropyl and 2 mol of dimethyl acetylenedicarboxylate,[1] by employing both nmr evidence and reactivity arguments. However, the configuration at



1a



1b

C-3 (and C-3′) could not be unequivocally established. Thus, the nmr signal at τ 9.08 which we confidently assign to the hydrogen at C-3 (and C-3′) moves upfield to τ 9.49 when all of the double bonds are hydrogenated. Since, in the most likely anti-3-exo arrangement[2] Ia,

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