Anal. Calcd for $C_{49}H_{34}$: C, 94.5; H, 5.5. Found: C, 93.1; H, 5.4.

Secondly, *exo*-1,2,3,4,5-pentaphenylphenanthro[9,10-*f*]tricyclo-[3.2.1^{1,5}.0^{2,4}]oct-6-en-8-one (**29**) crystallized as colorless needles: mp 270°; ν_{max} (KBr) 1776 cm^{-1}.

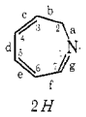
Anal. Calcd for $C_{50}H_{34}O$: C, 92.3; H, 5.3. Found: C, 91.1; H, 5.2.

Registry No.—**1a,** 479,33-4; **1b,** 26307-17-5; **1c,** 51932-77-5; **2a,** 7654-06-0; **2b,** 16205-14-4; **2c,** 16483-98-0; **2d,** 52124-00-2; **2e,** 18709-44-9; **2f,** 32687-32-4; **3a,** 33070-61-0; **3b,** 33070-63-2; **3c,** 33070-66-5; **3d,** 52124-01-3; **3e,** 33654-83-0; **3f,** 33070-60-9; **3g,** 33070-62-1; **3h,** 33070-65-4; **3i,** 52124-02-4; **3j** picrate, 51932-79-7; **3k,** 52124-03-5; **4a,** 52124-04-6; **5b,** 52124-05-7; **10,** 18709-43-8; **11,** 33654-82-9; **12,** 33654-81-8; **16,** 23414-46-2; **17,** 5660-91-3; **18a,** 39934-14-0; **18b,** 39934-15-1; **18c,** 39934-16-2; **19a,** 39934-03-7; **19b,** 39934-04-8; **19c,** 52124-06-8; **19d,** 52124-07-9; **20a,** 52124-08-0; **20b,** 52124-09-1; **20c,** 52124-10-4; **20d,** 52124-11-5; **22,** 16510-49-9; **23,** 52124-12-6; **25,** 52154-42-4; **26,** 52124-13-7; **27,** 52124-14-8; **28,** 52154-43-5; **29,** 52124-15-9; **30,** 39934-07-1; **31,** 33535-80-7; **32a,** 52124-16-0; **32b,** 52124-17-1; **32c,** 52124-18-2; **32f,** 52124-19-3; **33a,** 52124-20-6; **33b,** 52124-21-7; **33c,** 52124-22-8; **33f,** 52124-23-9.

References and Notes

(1) Cycloadditions. XVII. For the previous paper in the series see ref 9b.
(2) For preliminary communications see (a) D. J. Anderson and A. Hassner, *J. Amer. Chem. Soc.*, **93,** 4339 (1971); (b) A. Hassner and D. J. Anderson, *ibid.*, **94,** 8255 (1972).
(3) (a) A. Hassner and F. W. Fowler, *J. Amer. Chem. Soc.*, **90,** 2869 (1968); (b) for a review on azirines, see F. W. Fowler in "Advances in Heterocyclic Chemistry," Vol. 13, A. R. Katritzky and A. J. Boulton, Ed., Academic Press, New York, N. Y., 1971, p 45.
(4) A. Hassner, A. S. Miller, and M. J. Haddadin, *Tetrahedron Lett.*, 1353 (1972).
(5) F. P. Woerner, H. Reimlinger, and R. Merenyi, *Chem. Ber.*, **104,** 2786 (1971).
(6) V. Nair, *Tetrahedron Lett.*, 4831 (1971).
(7) V. Nair, *J. Org. Chem.*, **37,** 802 (1972).
(8) H. Hemetsberger and D. Knittel, *Monatsh. Chem.*, **103,** 205 (1972).
(9) (a) V. Nair, *J. Org. Chem.*, **37,** 2508 (1972); (b) A. Hassner and D. J. Anderson, *ibid.*, **39,** 2031 (1974).
(10) V. Nair, *J. Org. Chem.*, **33,** 2121 (1968).
(11) A. Padwa, S. Clough, M. Dhara, J. Smolanoff, and S. I. Wetmore, *J. Amer. Chem. Soc.*, **94,** 1395 (1972).
(12) A. Padwa, J. Smolanoff, and S. I. Wetmore, *J. Chem. Soc., Chem. Commun.*: (a) 404 (1972); (b) 1116 (1972).
(13) N. Gakis, M. Maerky, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55,** 748 (1972).
(14) A. Padwa and J. Smolanoff, *J. Amer. Chem. Soc.*, **93,** 549 (1971).
(15) A. Padwa, D. Dean, and J. Smolanoff, *Tetrahedron Lett.*, 4087 (1972).
(16) H. Giezendanner, M. Maerky, B. Jackson, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55,** 745 (1972).
(17) For a review on azepines see L. A. Paquette in "Nonbenzenoid Aromatics," Vol. I, J. P. Snyder, Ed., Academic Press, New York, N. Y., 1969, p 249.
(18) R. J. Sundberg, S. R. Suter, and M. Brenner, *J. Amer. Chem. Soc.*, **94,** 513 (1972).
(19) M. Anderson and A. W. Johnson, *J. Chem. Soc. C*, 2411 (1965).
(20) W. Dittmar, J. Sauer, and A. Steigel, *Tetrahedron Lett.*, 5171 (1969).
(21) E. Cartensen-Oeser, *Chem. Ber.*, **105,** 982 (1972).
(22) A. Steigel, J. Sauer, D. A. Kleier, and G. Binsch, *J. Amer. Chem. Soc.*, **94,** 2770 (1972).
(23) M. J. S. Dewar and N. Trinajstic, *Tetrahedron*, **26,** 4269 (1970).
(24) S. Sternhell, *Quart. Rev.*, **23,** 236 (1969).
(25) M. D. Mehta, D. Miller, and E. F. Mooney, *J. Chem. Soc.*, 6695 (1965).
(26) F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, **89,** 2077 (1967).
(27) A. Hassner and F. W. Fowler *J. Amer. Chem. Soc.*, **90,** 2869 (1968).
(28) This is in contrast to the reaction of azirine with cyclopropenones, A. Hassner and A. Kascheres, *J. Org. Chem.*, **37,** 2328 (1972), where the C–N bond of the azirine is broken.
(29) Although 3,3-dimethylcyclopropene failed to react with cyclopentadiene [G. L. Closs, L. E. Closs, and W. A. Boll, *J. Amer. Chem. Soc.*, **86,** 3796 (963)], it did react with 3,6-diphenyl-5-tetrazine.[22]
(30) The sluggishness of 3-carbomethoxycyclopropenes in Diels–Alder additions has already been noted: (a) M. A. Battiste, *Tetrahedron Lett.*, 3795 (1964); (b) M. A. Battiste and T. J. Barton, *ibid.*, 1227 (1967).
(31) S. C. Clarke and B. L. Johnson, *Tetrahedron*, **27,** 3557 (1971).
(32) W. Dilthey, I. ter Horst, and W. Schommer, *J. Prakt. Chem.*, **143** 189 (1935).
(33) The reaction of **16** with azirines was somewhat sluggish in refluxing toluene probably due to the slow dissociation of the dimer at this temperature.
(34) M. A. Battiste, *J. Amer. Chem. Soc.*, **85,** 2175 (1963).
(35) B. Halton, M. A. Battiste, R. Rehberg, C. L. Deyrup, and M. E. Brennan, *J. Amer. Chem. Soc.*, **89,** 5964 (1967).
(36) E. L. Allred and A. L. Johnson, *J. Amer. Chem. Soc.*, **93,** 1300 (1971), and references therein.
(37) Varian Index No. 318.
(38) H. Newman and R. B. Angier, *Tetrahedron*, **26,** 825 (1970).
(39) L. A. Paquette, *J. Amer. Chem. Soc.*, **86,** 4096 (1964).
(40) T. J. van Bergen and R. M. Kellogg, *J. Org. Chem.*, **36,** 978 (1971).
(41) A. Mannschreck, G. Rissmann, F. Vogtle, and D. Wild, *Chem. Ber.*, **100,** 335 (1967).
(42) All melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer 457 spectrophotometer as KBr pellets Nmr spectra were recorded with a Varian A-60A spectrometer using tetramethylsilane as an internal standard and $CDCl_3$ as a solvent. The elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.
(43) Since the numbering of the azepine system is not completely systematic,[17] the lettering system adopted in this paper follows the numbers

3H



2H

Reactions of 3*H*-Azepines Derived from Cyclopentadienones and 1-Azirines[1]

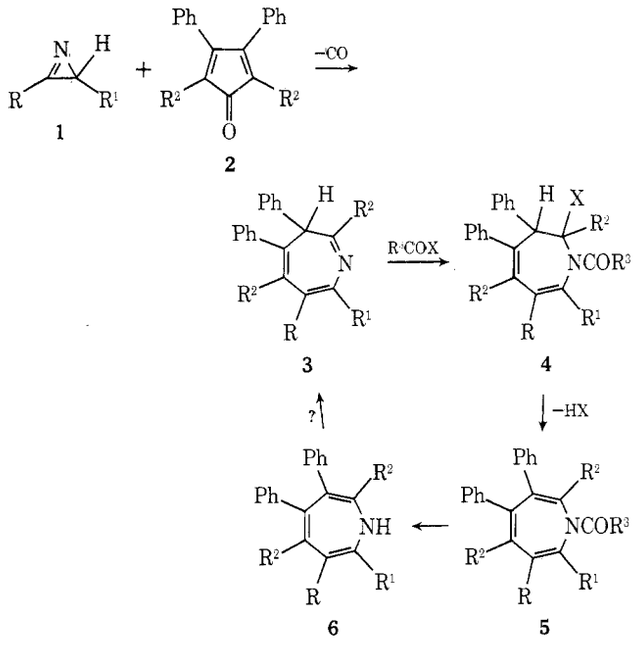
David J. Anderson, Alfred Hassner,* and David Y. Tang

Chemistry Department, University of Colorado, Boulder, Colorado 80302

Received March 26, 1974

Reactions of 3*H*-azepines **3,** available from cycloaddition of 1-azirines with cyclopentadienones, were examined with a view to producing 1*H*-azepine derivatives. Treatment of **3** with benzoyl chloride resulted in 2-alkylidine-*N*-benzoyl- 2,3-dihydro-1-azepines (**7**), which failed to isomerize to the antiaromatic system **5.** Photolysis of **7** led to 1,3 (N to C) benzoyl transfer. Attempted base-catalyzed deuterium exchange underlined the difficulty of isolating an 8-π-electron system. Acid isomerization of 7-unsubstituted azepines **3a–c** produced substituted anilines, presumably *via* unstable 1-azepines, while the 7-methyl substrate **19** afforded cyclohexadienone products.

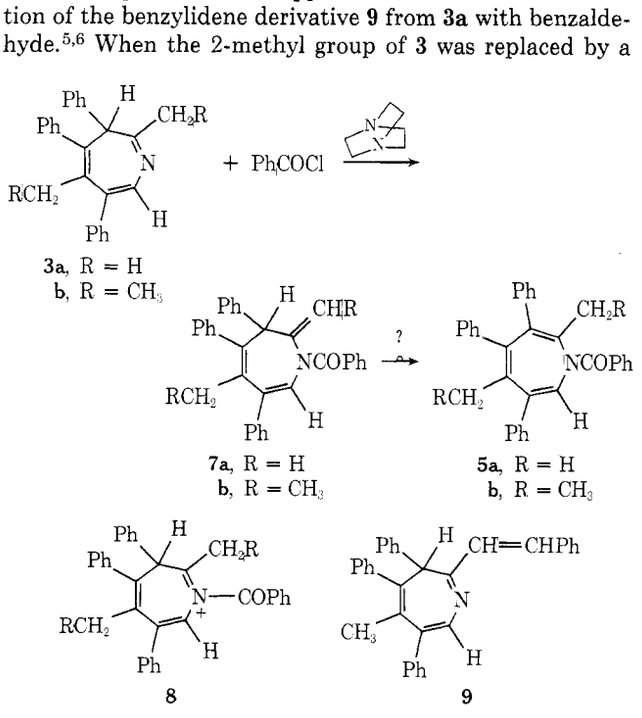
Recently we have developed[1,2] a procedure for the preparation of 3*H*-azepines **3** by cycloaddition of 1-azirines **1** with cyclopentadienones **2.** Such compounds might provide an entry into the interesting 8-π-electron system,[3] the 1*H*-azepine **5** or **6.** For instance, addition of acid chlorides to the imine double bond of **3** may lead directly or *via* **4** to the N-substituted 1*H*-azepine **5.** Removal of RCO from **5** could give the elusive N-unsubstituted 1*H*-azepine **6,** which in our case should be stabilized by the multiple substitution on the ring carbons. Alternatively, **6** might just revert to **3,** since it has been shown that the 3*H*-azepine is in general the thermodynamically more stable isomer.



Results and Discussion

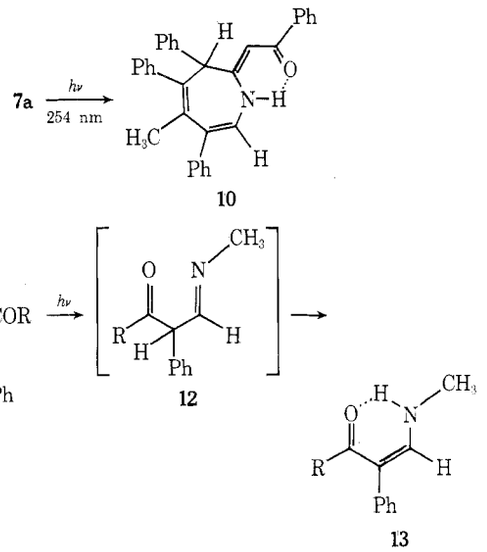
Addition of benzoyl chloride to the azepine **3a** in benzene proceeded fairly rapidly to give a new product. The formation of this product was enhanced by the presence of 1,4-diazabicyclo[2.2.2]octane (Dabco) in the solution. Mass spectral and elemental analyses showed it to be an HCl elimination product of an azepine–benzoyl chloride adduct. Infrared showed an amide absorption at 1640 cm^{-1} while nmr demonstrated the loss of one methyl group with the concurrent appearance of a methylene (=CH_2) group at *ca.* 5.0 ppm. These data suggested the *exo*-methylene structure **7a.** The ethylidene derivative **7b** likewise showed nmr absorptions consistent with its structure.

The reaction may involve formation of intermediate **8,** or benzoylation of the enamine tautomer of the imine **3.** Evidence supporting this pathway was found in the easy exchange of the protons of the 2-methyl group in **3a** with D_2O in analogy with the D exchange reported for **19.**[5] The acidity of these protons is also apparent from the ease of formation of the benzylidene derivative **9** from **3a** with benzaldehyde.[5,6] When the 2-methyl group of **3** was replaced by a phenyl group as in **3c,** there was no reaction with benzoyl chloride even under forcing conditions.

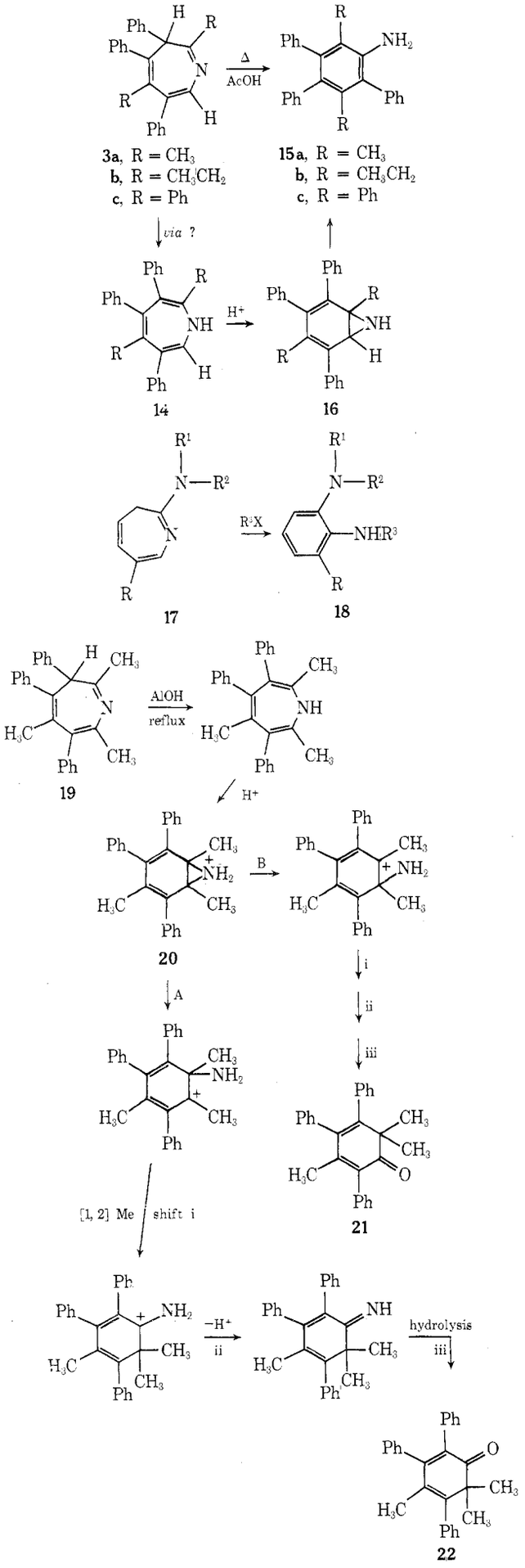


Several attempts were made to isomerize the *exo*-methylene azepine **7a** to the conjugated 1*H* isomer **5a.** With various bases, either no reaction took place (weak bases) or simple debenzoylation took place (strong bases, *e.g.,* KO-*t*-Bu) to regenerate **3a.** No exchange of the benzylic 3 proton in **3a** was observed even in the presence of potassium *tert*-butoxide in *t*-BuOD, in spite of the fact that the 2-methyl protons readily exchanged.[7] This differential behavior of the endocyclic *vs.* the exocyclic protons α to the C=N in **3** and the failure to achieve isomerization to **5** may be indicative of the low stability inherent in the anti aromatic 8-π-electron 1*H*-azepines.

Attempted photochemical transformation of **7a** to **5** resulted only in a benzoyl transfer to give the amino ketone **10.** The strong H bonding of the NH to the C=O was evident by the low-field (τ − 3.05) appearance of the NH. Additional structure proof came from the fact that the NH and the vinylic azepine ring proton were coupled (J = 5 Hz). This coupling disappeared on exchange with D_2O. This type of transformation, which corresponds to a nonaromatic photo-Fries rearrangement,[8a] has also been observed in the photolysis of **11** to **13,** presumably *via* **12.** The proposed mechanism may involve a radical pair.[8b]

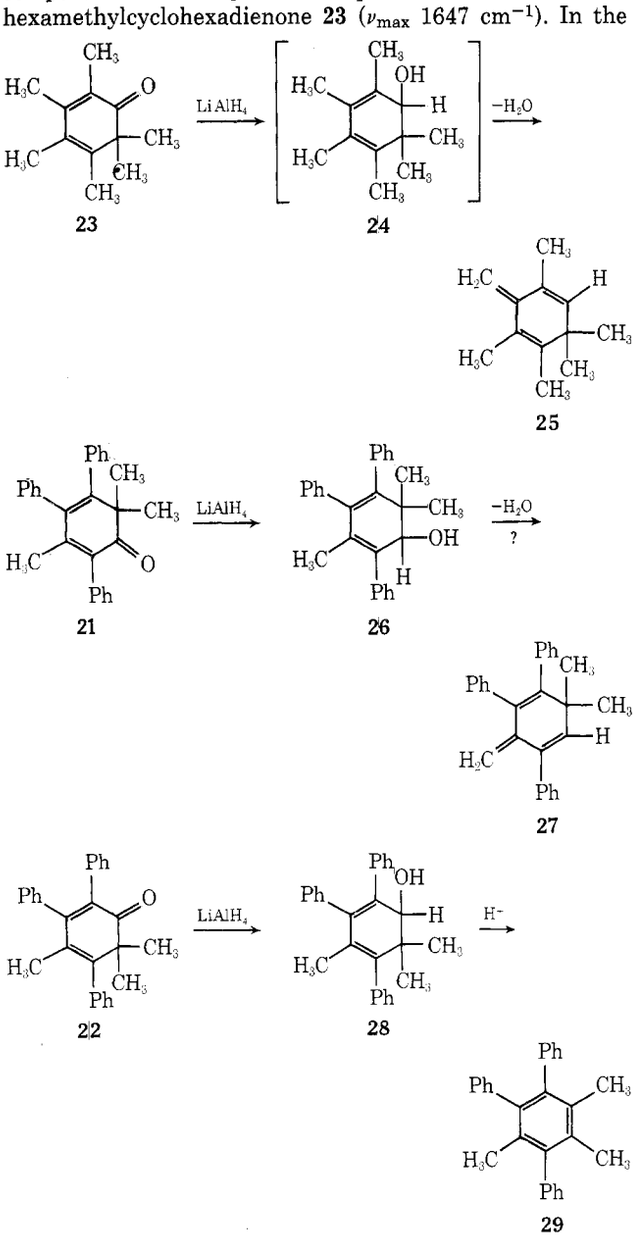


When acetic acid was used as an isomerization catalyst on **7a,** minute quantities of aniline derivatives were detected together with much polymeric and resinous material. Investigation of the reaction of 3*H*-azepine **3a** with glacial acetic acid revealed that a very clean and efficient isomerization to **15a** took place within 2 hr at reflux temperature. No side products were detected. The presence of an $-NH_2$ group in **15a** was clear from both the nmr and ir spectra. An equally facile reaction was observed with the diethyl-3*H*-azepine **3b.** The isomerization of the pentaphenyl-3*H*-azepine **3c** required a reflux time of 4 days to achieve complete conversion to pentaphenylaniline **15c.** The reaction may be interpreted as involving isomerization of the 3*H*-azepine to its 1*H* isomer **14,** which then undergoes ring contraction[9] to the azanorcaradiene **16** in acid, to give finally the aniline **15.** N-Substituted 1*H*-azepines have been found[10] to rearrange to anilines in the presence of acid. Not too dissimilar ring contractions have been reported[11] for other 3*H*-azepines (*i.e.,* **17** → **18**). The important criterion for our observed 3*H*-azepine → aniline conversions was the presence of the ring proton at the 7 position of the azepine nucleus. When this was replaced by a CH_3 group as in **19,** the reaction took a different course inasmuch as the mix-



ture became dark brown and very complex (by tlc). However one homogeneous product was isolated (mp 198°) possessing the following spectral properties: mol wt 364, empirical formula $C_{27}H_{24}O$ (364) by elemental analysis, ν_{max} 1656 cm^{-1}. The nmr spectrum was quite unusual, since besides 15 aromatic protons, there was a nine-proton singlet at τ 8.66 in $CDCl_3$. The nine-proton signal appeared as a narrowly spaced doublet in C_6D_6, but addition of Eu(fod)$_3$ caused the doublet to separate into a three-proton singlet and a six-proton singlet. The six-proton singlet experienced the greatest downfield shift upon addition of increasing amounts of Eu(fod)$_3$. The ir absorption at 1656 cm^{-1} is consistent with an $\alpha,\beta,\gamma,\delta$-unsaturated carbonyl, and the nmr suggested a *gem*-dimethyl group in closer proximity to the carbonyl than the other lone methyl group [Eu(fod)$_3$ shifts].

Consideration of a possible mechanistic pathway and of the spectral data suggests structures **21** or **22.** Formation of the protonated azanorcaradiene **20** may be postulated in analogy to **3** → **14** → **16** → **15. 20** can then open by either pathway A or pathway B, both of which involve a [1,2]-methyl shift followed by deprotonation and hydrolysis. In order to distinguish between regioisomers **21** and **22** we compared the $LiAlH_4$ reduction product with that[12] from hexamethylcyclohexadienone **23** (ν_{max} 1647 cm^{-1}). In the



latter the intermediate allylic alcohol was exceedingly unstable and readily underwent a 1,4-elimination of H_2O to give the hydrocarbon **25**. We could reasonably expect that if our isolated ketone had structure **21**, than a similar reduction might lead to the hydrocarbon **27** *via* the allylic alcohol **26**. On the other hand reduction of **22** should lead to the alcohol **28** with little tendency to eliminate H_2O.

Reduction with $LiAlH_4$ of the dienone, followed by an acidic work-up, gave an alcohol stable to dilute HCl and assigned structure **28**. This was further confirmed by the dehydration–rearrangement of **28** to **29** in acetic acid–sulfuric acid. As expected, the methyl protons between the two phenyl groups are shielded (τ 8.28)[13] compared with the other two methyl groups (τ 7.98). Consequently we have assigned the cyclohexadienone structure **22** to the product isolated from 3*H*-azepine **19** and acetic acid. It is possible that **21** may also be present in the reaction mixture but that, owing to the complex nature of the reaction, it was not isolated.

Experimental Section

Reaction of 2,5-Dimethyl-3,4,6-triphenyl-3*H*-azepine (3a) with Benzoyl Chloride in the Presence of Dabco. The azepine[2] (5.0 g, 14.3 mmol) was dissolved in benzene (50 ml) and Dabco (1.65 g, 14.7 mmol) was added. The mixture was stirred at 25° and benzoyl chloride (2.5 g, 17.7 mmol) dissolved in benzene (10 ml) was added dropwise. The mixture was stirred overnight and then poured into water (400 ml). The organic layer was separated and dried ($MgSO_4$). Removal of the solvent gave a pale yellow solid. Recrystallization from hexane gave pale yellow plates (5.4 g, 83%) of 1-benzoyl-1*H*-5-methyl-2-methylene-3,4,6-tripheny l-3*H*-azepine (**7a**): mp 160°; nmr ($CDCl_3$) τ 8.38 (s, CH_3), 5.06 (br s, =CH**H**), 4.97 (br s, =C**H**H), 4.76 (s, CH), 3.73 (s, =CH), 3.10–2.30 (m, 20 H); ν_{max} (KBr) 1690, 1640, 1597, 1325, 1250, 870, and 695 cm^{-1}; mass spectrum *m/e* 453, 377, 362, 349, 348, 334, 308, 258, 257, 215, 105, 91, 78, 77.

Anal. Calcd for $C_{33}H_{21}NO$: C, 87.4; H, 6.0. Found: C, 87.5; H, 6.1.

Reaction of Phenylazirine with 2,5-Diethyl-3,4-diphenylcyclopenta-2,4-dienone. α-Styryl azide (1.45 g, 10 mmol) was heated under reflux in toluene (25 ml) for 2 hr. The dienone (2.3 g, 8 mmol) was then added and the mixture was refluxed for 17 hr. Removal of the solvent gave a reddish oil. Purification was achieved by chromatography over alumina to afford **2,5-diethyl-3,4,6-triphenyl-3*H*-azepine (3b)** as a colorless oil (3.0 g, 99%): nmr ($CDCl_3$) τ 9.28 (t, J = 7.5 Hz, 3 H), 8.05–7.25 (m, 4 H), 4.70 (s, 1 H), 3.00–2.40 (m, 16 H) (possible 1 H singlet at τ 2.85). The picrate was obtained as yellow microneedles from ethanol, mp 169°.

Anal. Calcd for $C_{34}H_{30}N_4O_7$: C, 67.3; H, 5.0; N, 9.2. Found: C, 67.3; H, 5.0; N, 9.2.

Reaction of the Diethyl-3*H*-azepine 3b with Benzoyl Chloride in the Presence of Dabco. The azepine (400 mg, 1.06 mmol) was dissolved in benzene (25 ml) and Dabco (120 mg, 1.07 mmol) was added. Benzoyl chloride (160 mg, 1.14 mmol) was added and the mixture was heated under reflux for 6 hr. After cooling, the mixture was poured into water (50 ml) and the bright yellow benzene layer was separated and dried ($MgSO_4$). Removal of the solvent gave a yellow-brown oil (450 mg) which crystallized on prolonged trituration. Recrystallization from hexane gave 1-benzoyl-1*H*-2-ethylidene-5-ethyl-3,4,6-triphenyl-3*H*-azepine (**7b**) as bright yellow crystals: mp 68°; nmr ($CDCl_3$) τ 9.25 (t, J = 7.5 Hz, CH_3CH_2), 8.47 (d, J = 7.25 Hz, CH_3CH), 8.22–7.62 (m, CH_3CH_2), 4.63 (br s, CH), 4.32 (q, J = 7.25 Hz, $CHCH_3$), 3.56 (s, =CH), 3.10–2.20 (m, 20 H); ν_{max} (KBr) 1682, 1594, 1276, 1245, 895, and 707 cm^{-1}.

Anal. Calcd for $C_{35}H_{31}NO$: C, 87.3; H, 6.5; N, 2.9. Found: C, 87.4; H, 6.6; N, 3.0.

Photolysis of the *exo*-Methylene Azepine 7a. The azepine (500 mg, 1.1 mmol) was dissolved with difficulty in dioxane (50 ml) in a quartz vessel and irradiated at 254 nm in a Rayonet reactor. After 60 hr the solvent was removed to give a brown oil. Chromatography (neutral Al_2O_3) with graduate elution from hexane to methylene chloride afforded the major fraction in the more polar fractions. Recrystallization from chloroform–hexane gave dark yellow crystals (145 mg, 29%) of the amino ketone **10**: mp 201–205°; nmr ($CDCl_3$) τ 8.35 (s, 3 H), 5.17 (br s, 1 H), 4.14 (s, 1 H), 3.73 (d, J = 5 Hz, 1 H), 3.10–2.40 (m, 18 H), 2.20–1.95 (m, 2 H), −3.05 (v br d, J = 5 Hz, 1 H) (addition of D_2O caused the τ −3.05 signal to disappear and the doublet at τ 3.73 to collapse to a singlet); ν_{max} (KBr) 1560 (vs), 1423, 1395, 1374, 760, and 709 cm^{-1}; mass spectrum *m/e* 453, 436, 376, 348, 337, 308, 270, 215.

Anal. Calcd for $C_{33}H_{27}NO$: C, 87.4; H, 6.0. Found: C, 87.4; H, 6.0.

Reaction of 2,5-Dimethyl-3,4,6-triphenyl-3*H*-azepine (3a) with Acetic Acid. The azepine (200 mg, 0.575 mmol) was heated under reflux in glacial acetic acid (5 ml) for 2 hr. Removal of the solvent gave a buff-colored solid (140 mg, 70%). Recrystallization from ethanol gave pale yellow plates of **2,5-dimethyl-3,4,6-triphenylaniline (15a)**: mp 241°; nmr ($CDCl_3$) τ 8.26 (s, 3 H), 8.07 (s, 3 H), 6.12 (br s, 2 H, NH_2), 3.20–2.80 (m, 10 H), 2.70–2.40 (m, 5 H); ν_{max} (KBr) 3460, 3380, 1607, 750, and 701 cm^{-1}; mass spectrum *m/e* 349 (100%), 333, 261, 215.

Anal. Calcd for $C_{26}H_{23}N$: C, 89.5; H, 6.6. Found: C, 89.2; H, 6.5.

Reaction of 2,5-Diethyl-3,4,6-triphenyl-3*H*-azepine (3b) with Acetic Acid. The azepine (450 mg, 1.19 mmol) was heated under reflux in glacial acetic acid (5 ml) for 2.5 hr. Removal of the solvent and passage of the residue in ether through a short, dry packed column of Merck alumina gave an orange oil which rapidly solidified. Recrystallization from chloroform–ethanol gave pale orange flakes of **2,5-diethyl-3,4,6-triphenylaniline (15b)**: mp 191°; nmr ($CDCl_3$) τ 9.35 (t, J = 7.5 Hz, 3 H), 8.97 (t, J = 7.5 Hz, 3 H), 7.80 (q, J = 7.5 Hz, 2 H), 7.64 (q, J = 7.5 Hz, 2 H), 6.50 (br s, 2 H, NH_2), 2.90 (s, 5 H), 2.88 (s, 5 H), 2.50 (s, 5 H); ν_{max} (KBr) 3465, 3380, 1602, 1421, 754, and 710 cm^{-1}.

Anal. Calcd for $C_{28}H_{27}N$: C, 89.1; H, 7.2. Found: C, 88.9; H, 7.3.

Reaction of 2,3,4,5,6-Pentaphenyl-3*H*-azepine (14) with Acetic Acid. The azepine[2] (226 mg, 0.48 mmol) and acetic acid (8 ml) were heated under reflux for 4 days, after which time solid began to precipitate out of solution. Removal of the solvent and washing of the residue with ether gave a pinkish solid (168 mg, 75%) which was recrystallized from chloroform–ethanol to give colorless crystals of **pentaphenylaniline (15c)**: mp 263–265°; nmr ($CDCl_3$) τ 6.85–6.30 (br, 2 H, NH_2), 3.22 (s, 5 H), 3.17 (s, 10 H), 2.82 (s, 10 H); ν_{max} (KBr) 3465, 3375, 1598, 1410, 750, and 704 cm^{-1}; mass spectrum *m/e* 473, 395, and 378.

Anal. Calcd for $C_{36}H_{27}N$: C, 91.3; H, 5.75. Found: C, 91.3; H, 5.85.

Reaction of 2,5,7-Trimethyl-3,4,6-triphenyl-3*H*-azepine (19) with Acetic Acid. The azepine[2] (3.63 g, 10 mmol) was heated under reflux in glacial acetic acid (30 ml) for 4 hr, during which time the mixture turned dark brown. Removal of the solvent gave a brown oil which was dissolved in chloroform (150 ml) and washed with Na_2CO_3 solution. After drying ($MgSO_4$), the solvent was removed to give a brown, frothy oil (3.6 g). Trituration with ether–pentane gave a yellow solid (1.1 g). Chromatography (Al_2O_3) of the residue did not yield any homogenous fractions. Two recrystallizations of the solid gave very fine, pale yellow needles (436 mg, 12%) of **4,6,6-trimethyl-2,3,5-triphenylcyclohexa-2,4-dienone (22)**: mp 198°; nmr ($CDCl_3$) τ 8.66 (s, 9 H), 3.10–2.50 (m, 15 H); ν_{max} (KBr) 1656, 1335, 1127, 750, 741, and 700 cm^{-1}; mass spectrum *m/e* 364, 349, 336, 321, 306, 291, 243, 229, and 228.

Anal. Calcd for $C_{27}H_{24}O$: C, 89.0; H, 6.6. Found: C, 89.2; H, 6.5.

Reduction of the Cyclohexadienone 22 with $LiAlH_4$. The dienone (200 mg, 0.55 mmol) in anhydrous ether (10 ml) was treated with $LiAlH_4$ (25 mg, 0.66 mmol). The mixture was stirred at 25° for 2 hr and then dilute HCl (15 ml) was added dropwise. Extraction of the organic layer and drying over $MgSO_4$ gave a colorless foam after removal of the solvent. The foam crystallized on trituration with pentane to give a colorless solid (147 mg, 73%). Recrystallization from hexane gave colorless crystals of **4,6,6-trimethyl-2,3,5-triphenylcyclohexa-2,4-dienol(28)**: mp 137°; nmr ($CDCl_3$) τ 9.00 (s, 3 H), 8.70 (s, 6 H), 7.98 (br s, OH), 6.00 (s, 1 H), 3.00–2.50 (m, 15 H); ν_{max} (KBr) 3550, 3450, 767, and 709 cm^{-1}.

Anal. Calcd for $C_{27}H_{26}O$: C, 88.5; H, 7.15. Found: C, 88.4; H, 6.9.

Rearrangement of 28 to 29. To 2 ml of glacial acetic acid was added 21 mg of **28** and 1 drop of concentrated sulfuric acid. The mixture was stirred for 24 hr at room temperature, 10 ml of $CHCl_3$ was added, and the mixture was neutralized to pH 8 with 10% K_2CO_3. The organic layer was dried (Na_2SO_4), the solvent was evaporated to dryness, and the residue (18 mg) was recrystallized from $CHCl_3$–pentane to afford 13.5 mg (66%) of **28** as a white solid, mp 224–226° (lit. mp 223°).[13]

Deuterium Exchange Studies. A solution of **3a** or **3b** (100 mg) in 1 ml of $CDCl_3$ was shaken with 2 drops of D_2O (99.8% d_2) at room temperature and let stand for 1 hr. Nmr indicated a 70% diminution of the CH_3 (or CH_2, respectively) absorption at τ 7.7 with no change in the intensity of the singlet near τ 4.7. Similar re-

sults were found in the presence of potassium tert-butoxide in *tert*-butyl alcohol or if **3a** was stirred in dioxane–D_2O (30:1) at 82° for 24 hr.

Acknowledgment. Support of this work by PHS Grant CA-04474 of the National Cancer Institute is gratefully acknowledged.

Registry No.—1 (R = Ph; R^1 = H), 7654-06-0; **2b**, 51932-77-5; **3a**, 33070-60-9; **3b**, 51932-78-6; **3b** picrate, 51932-79-7; **7a**, 51932-80-0; **7b**, 51932-81-1; **10**, 51932-82-2; **14**, 33070-61-0; **15a**, 51932-83-3; **15b**, 51932-84-4; **15c**, 51932-85-5; **19**, 33070-62-1; **22**, 51932-86-6; **28**, 51932-87-7; benzoyl chloride, 98-88-4; acetic acid, 64-19-7.

References and Notes

(1) Cycloadditions. XVIII. For previous paper in the series see A. Hassner and D. J. Anderson, *J. Org. Chem.*, **39**, 3070 (1974).
(2) D. J. Anderson and A. Hassner, *J. Amer. Chem. Soc.*, **93**, 4339 (1971); A. Hassner and D. J. Anderson, *ibid.*, **94**, 8255 (1972).
(3) L. A. Paquette, *Angew. Chem., Int. Ed. Engl.*, **10**, 11 (1971).
(4) G. Schaden, *Chem. Ber.*, **106**, 2084 (1973); R. J. Sundberg, S. R. Suter, and M. Breamer, *J. Amer. Chem. Soc.*, **94**, 513 (1972).
(5) V. Nair, *J. Org. Chem.*, **37**, 802 (1972).
(6) T. J. van Bergen and R. M. Kellogg, *J. Org. Chem.*, **36**, 978 (1971).
(7) At 80° **19** was found (ref 5) to undergo D exchange not only at the C-2 methyl but also at the C-7 methyl function. We found that heating of **3a** at 80° in dioxane–D_2O for 24 hr showed exchange of the C-2 methyl hydrogens but not of the C-7 proton.
(8) (a) D. Bellus, *Advan. Photochem.*, **8**, 109 (1971); (b) R. W. Hoffman and K. R. Eicken, *Chem. Ber.*, **102**, 2987 (1969).
(9) W. D. Stohrer and R. Hoffmann, *Angew Chem., Int. Ed. Engl.*, **11**, 825 (1972).
(10) L. A. Paquette, D. E. Kuhla, and J. H. Barrett, *J. Org. Chem.*, **34**, 2879 (1969).
(11) (a) W. von E. Doering and R. A. Odum, *Tetrahedron Lett.*, 81 (1966); (b) F. R. Atherton and R. W. Lambert, *J. Chem. Soc., Perkin Trans. 1*, 1079 (1973); (c) R. K. Smalley, W. A. Strachan, and H. Suschitzky, *Tetrahedron Lett.*, 825 (1974).
(12) A. J. Waring and H. Hart, *J. Amer. Chem. Soc.*, **86**, 1454 (1964).
(13) H. Dietle and P. M. Maitlis, *Chem. Commun.*, 481 (1968). The originally reported value of τ 7.23 for one of the methyl groups in **29** has been corrected to 8.33 (in CH_2Cl_2): H. Dietle, H. Reinbeiruer, J. Moffat, and P. M. Maitlis, *J. Amer. Chem. Soc.*, **92**, 2276 (1970).

Formation of 5-Aryl-5,6-dihydro-4*H*-1,2,4-thiadiazine 1,1-Dioxides and *N*-*trans*-Styrylamidines by Base Treatment of *N*-(*trans*-Styrylsulfonyl) amidines[1]

W. L. Matier* and W. T. Comer

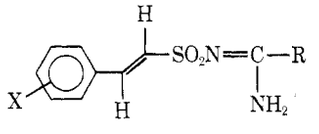
Department of Chemical Research, Mead Johnson Research Center, Evansville, Indiana 47721

Received June 3, 1974

Treatment of *N*-(*trans*-styrylsulfonyl)amidines (**1**) with base affords 5-aryl-5,6-dihydro-4*H*-1,2,4-thiadiazine 1,1-dioxides (**2**) and/or *N*-(*trans*-styryl)amidines (**3**). Formation of **3** is favored by electron-withdrawing substituents in the styryl aromatic ring and by polar reaction solvents. Possible mechanisms for the formation of **2** and **3** are discussed. With electron-rich aromatic rings, intramolecular Michael addition occurs predominantly at the carbon atom β to the sulfonyl group to afford the expected product **2**. However, with electron-withdrawing substituents in the aromatic ring, we propose that addition occurs α to the sulfonyl group to afford an unstable thiadiazoline intermediate, which gives **3** by loss of SO_2. This rearrangement of **1** to **3** is analogous to a Smiles rearrangement in which intramolecular nucleophilic attack occurs on a vinylic rather than an aromatic carbon.

We recently reported the synthesis of 5-aryl-4*H*-1,2,4-thiadiazine 1,1-dioxides by base-catalyzed, intramolecular cyclization of *N*-(α-bromostyrylsulfonyl)amidines.[2] As an approach to the synthesis of 5-aryl-5,6-dihydro-4*H*-1,2,4-thiadiazine 1,1-dioxides (**2**), we treated *N*-(*trans*-styrylsulfonyl)amidines (**1**) with base and obtained dihydrothiadiazines **2** and/or *N*-(*trans*-styryl)amidines **3**. This paper examines some of the parameters which determine the types

Table I
***N*-(*trans*-Styrylsulfonyl)amidines (1)[a]**



Compd	X	R	Mp, °C	Crystn solvent	Yield, %	Formula
1a	H	Me	134.5–137	*i*-PrOAc	76	$C_{10}H_{12}N_2O_2S$
1b	H	Ph	192.5–194.5	Me_2CO	90	$C_{15}H_{14}N_2O_2S$
1c	4-Cl	Me	166.5–169.5	EtOAc	93	$C_{10}H_{11}ClN_2O_2S$
1d	3,4-Cl_2	Me	197.5–198.5	Me_2CO–*i*-Pr_2O	83	$C_{10}H_{10}Cl_2N_2O_2S$
1e	3,4-Cl_2	Ph	147–150	MeOH	88	$C_{15}H_{12}Cl_2N_2O_2S$
1f	3,4-Cl_2	$PhCH_2$	159–161	*i*-PrOH	81	$C_{16}H_{14}Cl_2N_2O_2S$
1g	4-NO_2	Me	203–203.5	MeCN	92	$C_{10}H_{11}N_3O_4S$
1h	4-NO_2	Ph	171–173	*i*-PrOH	87	$C_{15}H_{13}N_3O_4S$
1i	2-NO_2	Me	175–178	Me_2CO–*i*-Pr_2O	85	$C_{10}H_{11}N_3O_4S$

[a] Satisfactory analytical data (±0.3% for C, H, N) were reported for compounds **1a–i**, **2a–f**, and **3a–j**: Ed.