at 24° with 1-iodobutane, only 15.7% (glc) of the new amine was obtained. Small impurities of *N*-(*n*-butyl)-*N*-methylaniline (6), *N*-(*n*-pentyl)-*N*-methylaniline (7), and *p*-(*n*-butyl)-*N*-(*n*-butyl)-*N*-methylaniline (11) were detected in the reaction mixture by glc: ir 3.44 s, 3.52 s, 3.60 m, 6.20 s, 6.61 s, 6.80 m, 7.45 m, 8.18 w, 8.41 w, 8.62 m, 8.85 w, 9.45 w, 10.57 w, and 12.42 μ m; pmr δ 0.92 (3 H), 1.61 (4 H), 2.48 (2 H), 2.80 (6 H), and 6.78 (4 H, A_2B_2, q).

Attempted Lateral Alkylation of 3.—(1) In two parallel experiments, **3** was prepared. In one the reaction mixture from the exchange and hydrolysis was analyzed (**4**, 53%; **7**, 6.2%; **8**, 12%); the other was treated with 25 mmol **2** and 51.5 mmol 1-iodobutane at −15° and the mixture stirred during 4 hr, allowing it to warm up to 15°. Glc analysis gave **4** (37.0%), **7** (6.05%), and **8** (11.0%). No lateral alkylation of **3** was achieved by the standard alkyllithium–alkyl iodide technique. (2) To **3** from 5 mmol of **1** and 22.5 mmol of **2** (24 hr, 25°) was added 5 ml of anhydrous ether and, at 0°, 12.5 mmol of 1-iodobutane. The temperature was allowed to go up to 20° during 3 hr. The quenched reaction mixture was analyzed (glc): **3** (40%), **7** (4.5%), and **8** (4.4%). No lateral alkylation was therefore achieved by the addition of 1-iodobutane.

Lateral Alkylation of *p*-Bromo-*N*,*N*-dimethylaniline (1). Lithium–Bromine Exchange of *p*-Bromo-*N*-(*n*-pentyl)-*N*-methylaniline (14) with *n*-Butyllithium (12).—*p*-Bromo-*N*,*N*-dimethylaniline (**1**) (5 mmol) and *n*-butyllithium (**2**) (20 mmol) were mixed at −10° and, as soon as a homogeneous solution formed, 1-iodobutane (10 mmol) was added. After stirring for 1 hr at −8°, the solution was gradually warmed up to 18° in 23 hr. The quenched reaction mixture contained (glc) **4** (23%), **7** (2.55%), **8** (1.2%), **1** (14.9%) and **14** (6%). The dry hexane mixture was then stirred 24 hr with excess *n*-butyllithium at room temperature and quenched as usual. Both brominated amines disappeared completely while the **7** to **8** ratio increased from 2.13 to 3.1.

***p*-Deuterio-*N*,*N*-dimethylaniline (5).**—This compound could be easily obtained by adding deuterium oxide to the exchange mixture and distilling the product:[20] ir 3.27 m, 3.33 m, 3.50 s, 3.60 s, 4.44 w, 4.84 w, 5.33 w, 5.70 w, 5.86 vw, 6.29 s, 6.70 s, 6.97 s, 7.45 s, 8.22 s, 8.42 s, 8.86 m, 9.45 s, 9.78 m, 10.23 s, 10.62 s, 11.61 w, 12.19 s, 13.37 w, 13.63 m, 13.94 m, and 14.52 μ w; pmr (neat) δ 2.65 (6 H, s), 6.85 (4.28 H, A_2B_2, q). This spectrum is in agreement with that reported in the literature.[5]

***o*-Deuterio-*N*,*N*-dimethylaniline.**—This compound, with possible traces[17] of *m*-deuterio substitution, and in admixture with *o*,*o*′-dideuterioaniline and unreacted *N*,*N*-dimethylaniline (**4**) may be obtained by repetitive metalation with refluxing *n*-butyllithium (**2**) followed by quenching with deuterium oxide. A sample in our hands contained (4 iterations) 18% unreacted material, 53% monodeuterioaniline and 29% dideuterioaniline, as was determined by mass spectrometry.

***N*,*N*,*N*′,*N*′-Tetramethyl-*p*-benzidine (9).**—This compound was prepared according to a method described in the literature,[21] by adding 20 mmol of potassium permanganate in 100 ml of 2 *N* sulfuric acid to a well-stirred solution of 0.1 mol of *N*,*N*-dimethylaniline in 60 ml of 2 *N* sulfuric acid at room temperature during 15 min. Work-up as indicated,[21] followed by treatment with base, extraction with ether–alcohol, evaporation of the solvent, and recrystallization from ethanol, gave slightly ochre needles: mp 194–198° (lit.[21] 198°); ir (KBr) 3.42 w, 6.17 s, 6.63 s, 6.92 m, 7.37 s, 8.13 m, 8.33 s, 8.50 m, 9.48 w, 10.54 w, and 12.36 μ s; pmr (CS_2–CCl_4) δ 6.77 (8 H, A_2B_2, q) and 2.94 (12 H, s); mass spectrum (vaporized from the solid inlet system at ~90°) mol wt, 240. The same compound was obtained in low yield from the interaction of *p*-benzidine with dimethyl sulfate (3 hr at 100°).

Registry No.—**1**, 586-77-6; **2**, 109-72-8; **4**, 121-69-7; **5**, 19125-73-6; **6**, 3416-49-7; **7**, 3299-39-6; **8**, 13330-29-5; **9**, 366-29-0; **11**, 25906-38-1; **12**, 25906-36-9; **14**, 25906-39-2; *o*-*d*-*N*,*N*-dimethylaniline, 24214-95-7.

Acknowledgments.—We wish to express our gratitude to Mrs. Armida B. Giumanini for recording the mass and pmr spectra and to Professor U. Pallotta of the Institute of Industrial Agriculture of this University for kindly allowing us to use some of his laboratory facilities.

(20) The isotopic purity of the separated dimethylaniline is ~80%. The deviation from the theoretical value may be due to some protolysis (see above) during the exchange reaction and, only partially, to the proton content of heavy water.

(21) R. Willstaetter and R. Pummerer, *Chem. Ber.*, **37**, 3733 (1904).

Schmidt Reaction of 2,4,6-Cyclooctatrien-1-one

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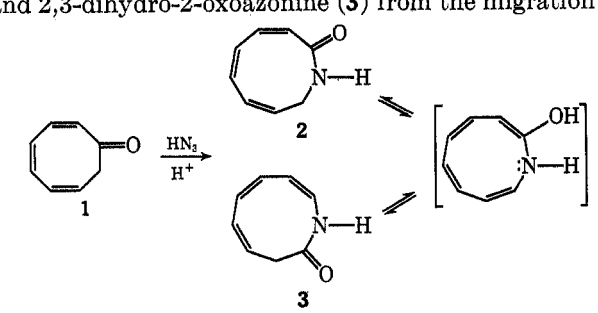
The Schmidt reaction of 2,4,6-cyclooctatrien-1-one in concentrated sulfuric acid produced 8,9-dihydrophthalimidine (**4**), which could have formed only from the migration of the methylene group. The other isomeric product, 3a,9a-dihydroindolone, which would have required the migration of the vinyl group, was not observed. On the other hand, the same reaction in trifluoroacetic acid produced 5*H*-tetrazolo[1,5-*a*]azonine (**5**) and its valence isomer 5a,9a-dihydro-5*H*-tetrazolo[5,1-*a*]isoindole (**6**) as the main products, with a small amount of **4**.

The Schmidt reaction of 2,4,6-cyclooctatrien-1-one (**1**) is expected to produce 2,9-dihydro-2-oxoazonine (**2**) and 2,3-dihydro-2-oxoazonine (**3**) from the migration of alkyl and vinyl groups, respectively. Both **2** and **3** are tautomers of 2-hydroxyazonine, a 10-π electron system which could show aromatic properties. Azonine and its analogs, oxonin and thionin, are of theoretical interest due to the possibility of their being 10-π aromatic systems isoelectronic with cyclooctatetraene dianion[1b] and cyclononatetraene anion,[2] both of which are 10-π aromatic systems. 4,5:6,7-Dibenzoxonin and 4,5:6,7-dibenzothionin have been prepared and shown to exist in nonaromatic buckled conformations.[3] The urethan



(1) (a) This is publication number 23-69 from Colorado State University. (b) T. J. Katz, *J. Amer. Chem. Soc.*, **82**, 3784 (1960).

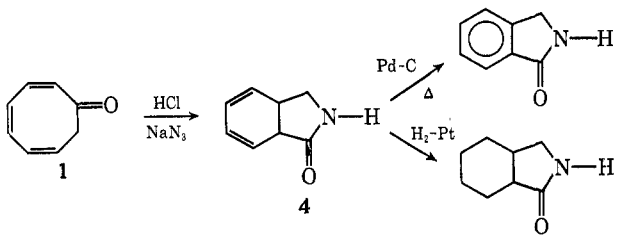
(2) (a) E. A. LaLancette and R. E. Benson, *ibid.*, **85**, 2853 (1963); **87**, 1941 (1965). (b) T. J. Katz and P. J. Garratt, *ibid.*, **85**, 2852 (1963); **86**, 5194 (1964).

(3) A. P. Bindra, J. A. Elix, P. J. Garratt, and R. H. Mitchell, *ibid.*, **90**, 7372 (1968).

of the parent azonine, namely *N*-carbethoxyazonine,[4b] and the parent oxonin[4a] have been recently prepared; neither compound shows aromatic stability.

Results

Reaction in Hydrochloric Acid.—The reaction of **1** with an equimolar quantity of sodium azide in concentrated HCl produced only 8,9-dihydrophthalimidine (**4**) in 66% yield, due to the migration of the methylene group. The other isomeric product, 3a,7a-dihydroindolone, which would result from the migration of the vinyl group, was not found. Also no evidence was found for the formation of either **2** or **3**. The structure of **4** was assigned on the basis of its spectral data (ir, uv, nmr, mass spectral) and its catalytic dehydrogenation to phthalimidine, a known compound. Furthermore, catalytic hydrogenation of **4** gave a product whose

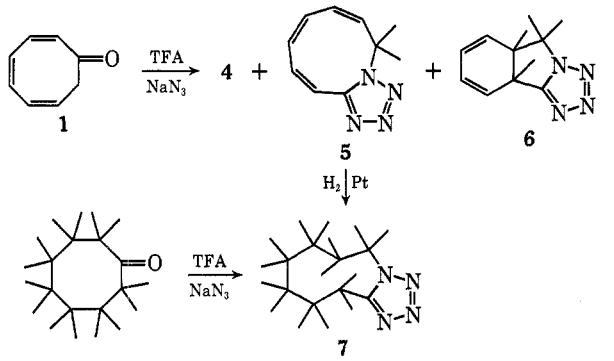


melting point agrees with the known *cis*-hexahydrophthalimidine, indicating that **4** probably has a cis-ring fused geometry.

Kroner[5] isolated **4** as a minor product from the Beckmann rearrangement of *anti*-2,4,6-cyclooctatrienone oxime benzenesulfonate (anti relative to CH_2).

Reaction in Sulfuric Acid.—The reaction of **1** with an equimolar quantity of sodium azide in concentrated sulfuric acid at 0° gave a 10% yield of **4** and recovered ketone **1**. Again, there was no evidence for **2**, **3**, or 3a,7a-dihydroindolone.

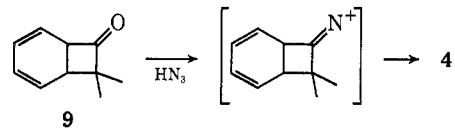
Reaction in Trifluoroacetic Acid (TFA).—Treatment of **1** with an excess of sodium azide in trifluoroacetic acid at 0° gave a small amount of **4**, unreacted ketone, and two new products, 5*H*-tetrazolo[1,5-*a*]azonine (**5**) and 5a,9a-dihydro-5*H*-tetrazolo[5,1-*a*]isoindole (**6**).



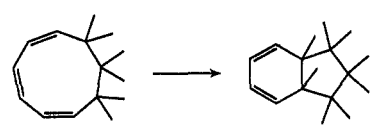
Compounds **5** and **6** were obtained in lower yields with more recovered ketone when an equimolar quantity of sodium azide was used. The structure of **5** is compatible with the spectral data. Its nmr spectrum showed a multiplet between δ 6.8 and 5.9 for the six olefinic protons and a doublet at δ 5.36 (J = 7.5 Hz) for the two methylene protons. Proof for the structure of **5** comes from quantitative hydrogenation to azacyclonona[1,2-*d*]tetrazole (**7**). This hydrogenation required 3 mol of hydrogen for each mole of **5**, ruling out a tricyclic structure with two double bonds such as an isomer of **6**. In addition, **7** was independently synthesized by the Schmidt reaction on cyclooctanone in TFA. The spectral properties (nmr, ir) of the tetrazole obtained from reduction of **5** were identical with those of the tetrazole obtained from the Schmidt reaction with cyclooctanone. The structure of **6** was assigned on the basis of the close resemblance of its nmr spectrum to that of **4** and the facile thermal conversion of **5** to **6**. Thus, heating a solution of **5** in diphenyl ether furnished cleanly and exclusively a crystalline product which has identical nmr and ir spectra with those of **6** obtained from the Schmidt reaction.

Discussion

The isolation of 8,9-dihydrophthalimidine (**4**) from the Schmidt reaction of **1** could be indicative of the formation of **2** as a reactive intermediate in this reaction. It is possible that **4** could also arise from treatment of bicyclo[4.2.0]octa-2,4-dien-7-one (**9**), the valence



bond isomer of **1** to Schmidt reaction conditions. Huisgen and coworkers[6] have reported that at 60° cyclooctatrienone (**1**) contains 6.6% of **9** at equilibrium. Although we do not know the equilibrium concentration of **9**, under our conditions it is undoubtedly sufficiently high to be the precursor of **4**. However, the isolation of **5** as a major product from the reaction in TFA is difficult to explain in terms of **9** as the starting component of the reaction sequence. The possibility that **5** would arise from an equilibrium between it and its valence isomer **6** is not ruled out, but it is very unlikely that **5** would be the major product of such an equilibrium in view of its facile and apparently complete isomerization to **6**. Comparison of such an equilibrium reaction to the equilibrium of *cis,cis,cis*-1,3,5-cyclononatriene (**10**) and *cis*-2,3,3a,7a-tetrahydroindene which contains less than 0.2% of the monocyclic isomer[7] indicates the validity of this assumption. On the other hand, our inability to isolate **2** casts doubt on its formation. Should **2** form, its isomerization to **4** would be analogous to the isomerization of **10**. This



latter reaction was observed by Glass, Watthey, and Winstein[7] to have an activation energy of 23.0 kcal/mol, sufficiently high to allow rather easy isolation of **10**. From a comparison of the models of **2** and **10** and

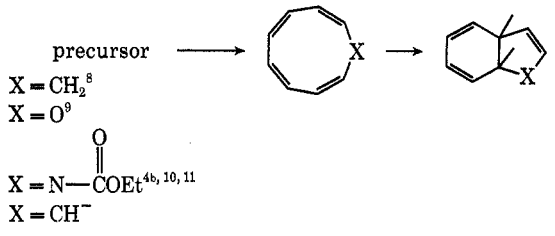
(4) (a) A. G. Anastassiou and R. P. Cellura, *Chem. Commun.*, 903 (1969); (b) A. G. Anastassiou and J. H. Gebrian, *J. Amer. Chem. Soc.*, **91**, 4011 (1969).

(5) M. Kroner, *Chem. Ber.*, **100**, 3162 (1967).

(6) R. Huisgen, G. Boche, A. Dahmen, and W. Hechtl, *Tetrahedron Lett.*, 5215 (1968).

(7) D. S. Glass, J. W. H. Watthey, and S. Winstein, *ibid.*, 377 (1965).

neglecting electronic contributions from the amide group, a fair approximation considering the high degree of puckering in the ring (the amide π system is orthogonal to the olefinic π systems), one would expect approximately the same resistance to ring closure in each case and therefore isolation of **2** should also be relatively easy. Our failure to isolate the monocyclic amide, **2**, would indicate that either it is not as stable towards transannular ring closing as might be thought or it is formed in a very small yield and is not an intermediate in the formation of **4**. Evidence bearing on this point is provided by the stabilities of known unsubstituted cyclononatetraene systems. Katz[2b] has reported that when water is added to cyclononatetraene anion, the resulting neutral compound rapidly goes through a transannular ring closing reaction to form 8,9-dihydroindene. The isolation of cyclononatetraene (X = CH_2) and its thermal isomerization to *cis*-8,9-

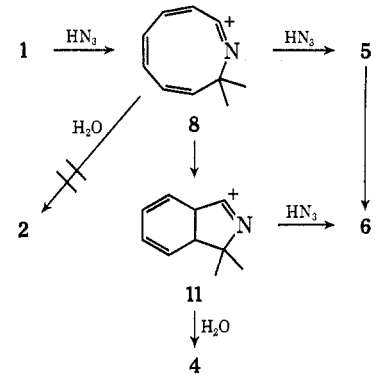


dihydroindene has been reported independently by Radlick[8a] and Masamune.[8b] Oxonin (X = O) was shown to undergo thermal rearrangement into *cis*-8,9-dihydrobenzofuran[9] in accordance with the conservation of orbital symmetry. Anastassiou[4b,10] has recently reported that *N*-carbethoxy-1-azacyclonona-2,4,6,8-tetraene (X = N-C(O)OEt) is not stable at room temperature but readily undergoes thermal isomerization to *N*-carbethoxy-*cis*-8,9-dihydroindole through transannular ring closing. The same result was obtained by other workers.[11] In fact, up to this date, the cyclononatetraene anion (X-CH$^-$) is the only species that is thermally stable at room temperature. Vogel[12] has suggested that this instability is the result of ring strain in the puckered tetraene due to the fourth double bond in the ring.

The instability of **8** is analogous to that observed for the above systems and suggests that **2** is not an intermediate in the formation of **4**, but rather that **4** arises from the reaction of water with 3a,7a-dihydroisoindolium ion (**11**), which is the ring closed isomer of **8**.

The ring strain in **8** can be relieved by either transannular ring closing or by reacting with a nucleophile capable of forming a double bond to carbon thus destroying the iminocarbonium ions which are causing the strain.

If ring closing is competitive with nucleophilic attacks, then it is not surprising that the relatively weak nucleophile, water, is unable to compete to form **2**, while the much better nucleophile, HN_3, competes readily and forms **5** as the major product. A scheme showing the relationship of the various products is shown below.



It is interesting to note that no evidence was found for vinyl migration although it occurs readily in the corresponding Beckmann rearrangement.[5,13] Apparently the products are controlled completely by migratory aptitude.

Experimental Section[14]

Cyclooctatetraene Oxide.—This compound was prepared by oxidation of cyclooctatetraene following the procedure of Cope and Tiffany.[15] The oxide was obtained in 27% yield as a light yellow liquid: bp 74–75° (12 mm); $n^{25}D$ 1.5389 [lit.[15] bp 74–75° (12 mm), $n^{25}D$ 1.5383].

2,4,6-Cyclooctatrien-1-one (**1**).—This ketone was prepared by the base-catalyzed ring opening reaction of cyclooctatetraene oxide according to the procedure of Cope and Tiffany.[15] The yellow ketone was obtained in 90% yield: bp 75–101° (13 mm); $n^{25}D$ 1.5749 [lit.[15] bp 75–105° (13 mm), $n^{25}D$ 1.5750]. Semicarbazone had mp 193–194° dec (lit.[15] mp 192–194° dec).

Schmidt Reaction of 2,4,6-Cyclooctatrien-1-one.—A solution of 2.3 g (19 mmol) of 2,4,6-cyclooctatrien-1-one (**1**) in 12 ml of concentrated hydrochloric acid was cooled in an ice bath while 1.87 g (28.7 mmol) of sodium azide was added slowly over a period of 1 hr. The solution darkened and a large quantity of gas evolved. After 4 hr at room temperature, during which the mixture was occasionaly stirred, significant gas evolution ceased. The reaction mixture was poured into 50 ml of cold water and exhaustively extracted with chloroform. The chloroform extracts were combined and washed with 25 ml of 10% sodium bicarbonate solution and two 50-ml portions of water. After drying over anhydrous potassium carbonate, the solvent was evaporated. There was obtained 1.7 g (66%) of the crude product as a brown solid. The nmr spectrum showed peaks attributable only to 8,9-dihydrophthalimide. It was purified by chromatographing on alumina (neutral activity grade I). Chloroform (fourteen 50-ml fractions) was collected from the column. The solvent was stripped from each fraction and the melting point of the residue was determined. The melting points ranged between 97 and 101°, thus indicating the similarities of the residues which were then combined in one fraction. Recrystallization from hexane provided an analytical sample of 8,9-dihydrophthalimidine (**4**) as colorless plates: mp 98.5–101°; uv λ_{max} (hexane) 258 mμ (ϵ 4.04 × 10^3), 266 (3.85 × 10^3), and 276 (shoulder, 2.25 × 10^3); ir (KBr) 3.1 (lactam NH), 5.93 and 6.02 (lactam C=O), 7.54, 7.97, 9.39, 13.98, and 14.66 μ; nmr ($CDCl_3$) δ 7.7 (s, 1 H), 5.86 (m, 4 H), 3.66 (m, 1 H), and 3.26 ppm (m, 3 H).

Schmidt Reaction of 2,4,6-Cyclooctatrien-1-one in Concentrated Sulfuric Acid.—To the dark mixture of 1.8 g (0.015 mol) of 2,4,6-cyclooctatrien-1-one (**1**) in 1.5 ml of concentrated sul-

(8) (a) P. Radlick and G. Alford, *J. Amer. Chem. Soc.*, **91**, 6529 (1969); (b) S. Masamune, P. M. Baker, and K. Hojo, *Chem. Commun.*, 1203 (1969).

(9) (a) A. G. Anastassiou and R. P. Cellura, *ibid.*, 1521 (1969); (b) J. M. Holouka, R. P. Grabbe, P. D. Gardner, C. B. Strow, M. L. Hill, and T. V. Van Auken, *ibid.*, 1522 (1969); (c) S. Masumune, S. Takada, and R. T. Seidner, *J. Amer. Chem. Soc.*, **91**, 7769 (1969).

(10) A. G. Anastassiou and J. H. Gebrian, *Chem. Eng. News*, **47**, 48 (1969).

(11) S. Masamune, K. Hojo, and S. Takada, *Chem. Commun.*, 1204 (1969).

(12) E. Vogel, *Angew. Chem.*, **74**, 838 (1962).

(13) A. H. Khuthier, Ph.D. Thesis, Colorado State University, Fort Collins, Colo., 1969.

(14) The following instruments were used in this work: ir, Perkin-Elmer Models 337 and 457; nmr, Varian A-60A; mass spectra, AEI Model MS-12 spectrometer; uv, Bausch and Lomb Spectronic 500. Microanalysis was performed by Galbraith Laboratories, Knoxville, Tenn. Quantitative hydrogenation was performed by Huffman Laboratories, Wheatridge, Colo.

(15) A. C. Cope and B. D. Tiffany, *J. Amer. Chem. Soc.*, **73**, 4158 (1951).

furic acid at 0° was added 0.98 g (0.015 mol) of sodium azide over a period of 0.5 hr. The brown thick paste was allowed to stand at room temperature for 3 hr with occasional stirring. The reaction mixture was poured into water containing some crushed ice. The brown oil that separated was extracted several times with chloroform. The chloroform extracts were washed with 10% sodium bicarbonate solution, followed by water, and dried over anhydrous potassium carbonate. Evaporation of the solvent produced a dark oil whose nmr spectrum showed unreacted ketone with a small amount of 8,9-dihydrophthalimidine (4). The mixture was placed onto alumina (neutral activity grade I) and the unreacted ketone was eluted with Skellysolve H. The lactam was collected with several fractions of chloroform which were combined and the solvent was evaporated. There was obtained 0.2 g (10%) of a yellow solid. Recrystallization from hexane produced an analytical sample of 8,9-dihydrophthalimidine (4) as colorless plates, mp 99–101°.

Schmidt Reaction of 2,4,6-Cyclooctatrien-1-one in Trifluoroacetic Acid.—To a mixture of 2.0 g (16.6 mmol) of 2,4,6-cyclooctatrien-1-one (1) in 10 ml of trifluoroacetic acid at 0° was added 2.7 g (42 mmol) of sodium azide over a period of 1 hr. The solution darkened a little and an exothermic reaction took place with evolution of a large quantity of gas. After 3 hr during which the mixture was occasionally stirred, 3 ml more of trifluoroacetic acid was added. The mixture was allowed to stand at room temperature for 3 hr more and then poured into 50 ml of cold water. The oil that separated was extracted with three 40-ml portions of chloroform. The chloroform extracts were combined and washed with 50 ml of 10% sodium bicarbonate solution and 50 ml of water. After drying over anhydrous sodium carbonate, the solvent was evaporated. The resulting dark oil was chromatographed on alumina (neutral activity grade I) with Skellysolve H containing an increasing proportion of chloroform. Elution with pure Skellysolve H produced 0.13 g of unreacted ketone. Skellysolve H–chloroform (10:1) fractions yielded 0.51 g of a colorless crystalline product which was identified as 5*H*-tetrazolo-[1,5-*a*]azonine (5). Recrystallization of this material from benzene–hexane produced an analytical sample of 5 as colorless sharp needles: mp 85–86°; uv λ_{max} (MeOH) 215 mμ (ϵ 9.0 × 10^3), 252 (2.68 × 10^3); ir (KBr) 6.1, 6.67, 7.3, 8.0, 9.13, 9.48, 11.6, 12.37, 13.47, and 15.29 μ; nmr ($CDCl_3$) δ 6.8–5.9 (m, 6 H), 5.36 (d, 2 H, J = 7.5 Hz); mass spectrum m/e (rel intensity) 160 (2) 131 (9), 103 (17), 78 (100), 77 (35), 52 (46).

Anal. Calcd for $C_8H_8N_4$: C, 60.00; H, 5.00; N, 35.00. Found: C, 60.18; H, 4.95; N, 35.10.

Skellysolve H–chloroform (10:2) gave a second product (0.17 g) as light yellow crystals which was identified as 5a,9a-dihydro-5*H*-tetrazolo[5,1-*a*]isoindole (6). Recrystallization from benzene–hexane provided an analytical sample of 6 as colorless needles: mp 100–100.5°; uv λ_{max} (MeOH) 205 mμ (ϵ 2.44 × 10^3), 255 (4.4 × 10^3), 246 (shoulder), 264 (4.05 × 10^3), 275 (shoulder); ir (KBr) 6.6, 6.76, 7.6, 8.7, 9.2 (w), 9.3, 10.4, 11.76, 13.3, 14.0, and 14.3 μ; nmr ($CDCl_3$) δ 5.96 (m, 4 H), 4.66 (m, 1 H), 4.2 (m, 3 H); mass spectrum m/e (rel intensity) 160 (2), 105 (9), 78 (100), 77 (16), 52 (22).

Anal. Calcd for $C_8H_8N_4$: C, 60.00; H, 5.00; N, 35.00. Found: C, 59.88; H, 5.23; N, 34.86.

Later Skellysolve H–chloroform (1:1) elutions gave 0.1 g of colorless solid which was identified as 8,9-dihydrophthalimidine (4).

Reduction of 8,9-Dihydrophthalimidine (4).—A solution of 0.172 g (1.27 mmol) of 4 in 5 ml of *p*-dioxane containing a catalytic amount of platinum black was subjected to hydrogenation at 90° and 30 psi for 12 hr. After removal of the catalyst and solvent, 0.2 g of the crude product was obtained as a yellow solid. It was purified by sublimination at 70–80° and 0.3 mm followed by two recrystallizations from hexane. The product, *cis*-hexahydrophthalimidine, was obtained as colorless crystals: mp 95.5–97° (lit.[16] mp 98°); ir (KBr) 3.1 (lactam NH), 5.95 (lactam C=O), 6.92, 7.03, 7.7, 9.88, and 13.3 μ; nmr ($CDCl_3$) δ 7.1 (s, 1 H), 3.43 (m, 1 H), 3.0 (m, 1 H), 2.43 (m, 2 H), 2.06–1.0 ppm (m, 8 H).

Schmitd Reaction of Cyclooctanone in Trifluoroacetic Acid.—To a mixture of 4.2 g (0.033 mol) of cyclooctanone in 10 ml of trifluoroacetic acid at 0° was added 6.5 g (0.1 mol) of sodium azide over a period of 1 hr. After 4 hr 5 ml more of trifluoroacetic acid was added. A large quantity of nitrogen gas was evolved. The reaction mixture was allowed to stand overnight at room temperature with occasional stirring, then was poured into 50 ml of water. The oil that separated was extracted with four 30-ml portions of chloroform. The chloroform extracts were combined and washed with a 10% solution of sodium carbonate followed by water. Evaporation of the solvent, after drying over anhydrous potassium carbonate, yielded 5 g of a colorless oil which was shown by nmr to contain a mixture of products. The desired tetrazole was separated, as a colorless oil, either by chromatographing on alumina (neutral activity grade I) with Skellysolve H–chloroform (10:1) as the eluent or by distillation under reduced pressure: bp 144° (0.1 mm) [lit.[17] 145–146° (0.1 mm)]; ir (neat) 3.4, 3.5, 6.6, 6.8, 6.9, 7.0, 8.06, 8.9, 9.16, 9.48, 9.85, 10.1, 12.3, and 13.2 μ; nmr (CCl_4) δ 4.55 (t, 2 H, J = 6 Hz), 3.06 (t, 2 H, J = 6 Hz), 1.93 (m), and 1.38 ppm (m). The last two poorly resolved multiplets integrate for 10 H.

Reduction of 5*H*-Tetrazolo[1,5-*a*]azonine (5).—A solution of 50 mg of 5 in 10 ml of glacial acetic acid containing a catalytic amount of Adams catalyst was subjected to hydrogenation of 30 psi and room temperature for 20 hr. After removal of the catalyst the reaction mixture was poured into 40 ml of water. The oil that separated was extracted with four 30-ml portions of chloroform. The chloroform extracts were combined and washed with 30 ml of 10% solution of sodium carbonate followed by 30 ml of water. Evaporation of the solvent, after drying over anhydrous potassium carbonate, produced 45 mg (87%) of the product as a colorless oil. The nmr and ir spectra of this material were identical with those of the tetrazole prepared by the Schmidt reaction of cyclooctanone: ir (neat) 3.4, 3.5, 6.6, 6.8, 6.9, 7.0, 8.06, 8.9, 9.16, 9.48, 9.85, 10.1, 12.3, and 13.2 μ; nmr (CCl_4) δ 4.5 (t, 2 H, J = 6 Hz), 3.05 (t, 2 H, J = 6 Hz), 1.93 (m), and 1.38 ppm (m). The last two poorly resolved multiplets integrate for 10 H.

Dehydrogenation of 8,9-Dihydrophthalimidine (4).—A mixture of 110 mg of 8,9-dihydrophthalimidine (4) (obtained from the Schmidt reaction of 2,4,6-cyclooctatrien-1-one in concentrated HCl) and a small amount of 10% palladium-on-carbon catalyst in 5 ml of toluene was refluxed for 2 hr. Removal of the catalyst and solvent produced 100 mg (92%) of colorless crystals. Recrystallization from benzene yielded analytical sample of phthalimidine as fine white felted needles: mp 152–152.5° (lit.[18] 152.5–152.8°); uv λ_{max} (methanol) 227 mμ (ϵ 1.0 × 10^4), 263 (shoulder), 271 (1.75 × 10^3), and 278 (1.7 × 10^3); ir (KBr) 3.1 (lactam NH), 6.0 (lactam C=O), 6.8, 6.9, 7.6, 8.8, 10.6, and 13.75 μ; nmr ($CDCl_3$) δ 7.6 (s, 1 H), 7.1 (m, 1 H), 6.7 (m, 3 H), and 3.5 ppm (s, 2 H).

Registry No.—1, 4011-22-7; 4, 16327-30-3; 5, 276-65-3; 6, 25902-76-5; 7, 7140-70-7.

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