

Spectroscopic Studies. Fluorescence spectra of nitrogen-purged samples were recorded on a Perkin-Elmer MPF-44A spectrofluorimeter. The TR³ measurements were carried out with the apparatus described in ref 32. The beams of a pulsed nitrogen laser and of an excimer laser pumped dye laser (3 mJ at 480 nm, 20 ns) were focused into the cell through quartz windows. The scattered light was collected under 90° and spectrally dispersed in a double grating spectrograph (5-cm⁻¹ resolution; bandpass 550 cm⁻¹ at 480 nm). After amplification in a gated image intensifier the Raman spectra were recorded by an optical multichannel analyzer and stored in a minicomputer for further data handling. Improvement in signal to noise ratio is achieved by sampling over 500 excite-probe cycles. Complete RR spectra (400–2500 cm⁻¹) were composed of four spectrally overlapping sequences with a fixed number of pump-probe cycles and subsequent computer calculation. The excitation spectrum was measured with a fixed delay time between photolysis and probe laser pulse as the dependence of TR³ band intensities upon the excitation wavelength. The TR³ band intensities were normalized to the simultaneously measured solvent band intensities of the same spectral window. This procedure cancels the variation of the probe laser intensity with different laser dyes and also the wavelength dependent absorption

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of the excitation laser intensity in the sample.¹⁹ The measurements of the kinetic behavior of the transient species were carried out with fixed probe laser wavelength by observing the normalized TR³ band intensities as a function of the delay time between the photolysis and the probe laser pulse.

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Registry No. *trans*-Stilbene-ethyl-diisopropylamine, 88131-18-4; *trans*-stilbene-triethylamine, 88131-19-5; *trans*-stilbene-1,4-diazabicyclo[2.2.2]octane, 88131-20-8; ethyl-diisopropylamine, 7087-68-5; triethylamine, 121-44-8; trimethylamine, 75-50-3; 1-azabicyclo[2.2.2]octane, 100-76-5; tetraethyl-1,2-ethanediamine, 150-77-6; 1,4-diazabicyclo[2.2.2]octane, 280-57-9; *trans*-stilbene, 103-30-0; *trans*-stilbene radical anion, 34473-61-5; ethyl-diisopropylamine radical cation, 88131-21-9; triethylamine radical cation, 36752-99-5; 1,4-diazabicyclo[2.2.2]octane radical cation, 54159-20-5.

Photoinitiated Autocatalytic Chain Decomposition of Phenyl Azide

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Abstract: Quantum yields of disappearance of phenyl azide (ϕ -PhN₃) were determined for 10⁻⁵–10⁻¹ M acetonitrile solutions at room temperature by monitoring changes in its electronic absorption spectra. For dilute solutions, ϕ -PhN₃ = 0.5; however, at higher concentrations ϕ -PhN₃ values greatly exceed unit efficiency and indicate a chain decomposition mechanism. At ca. 2 × 10⁻¹ M, ϕ -PhN₃ ≈ 3000! A plot of [ϕ -PhN₃] vs. log [PhN₃] appears exponential and since a plot of the chain length, n , vs. [PhN₃] is linear ($r^2 = 0.972$), when n is calculated from an exponential function, the experimental results provide evidence for a branching chain reaction also known as an autocatalytic (spontaneously explosive) reaction. The branching chain mechanism is thought to result from reaction of a phenyl nitrene intermediate with a ground-state phenyl azide molecule to form two phenyl nitrenes. A 1,4-tetraazadiene or triaza species may also participate in the chain reaction.

The use of organic azides as photoaffinity labels, as photopolymerization initiators, as starting materials in the synthesis of nitrogen heterocycles, and in the preparation of photoresists has prompted considerable interest in their photochemical properties.¹ The chemistry of phenyl azide (PhN₃) is particularly interesting. Upon irradiation in organic matrices at 77 K, molecular nitrogen is lost and phenyl nitrene is formed²⁻⁵ with a temperature-independent quantum yield, determined by monitoring the production of molecular nitrogen (ϕ -N₂), somewhat higher in nonpolar (ϕ -N₂ = 0.52)⁶ than in polar solvents (ϕ -N₂ = 0.43).^{4,7} ESR studies have shown that the triplet state is the ground state of phenyl nitrene.⁸⁻¹⁰

In neutral solvents, azobenzene¹¹ and an intractable polymeric material^{12,13} are the major photoproducts. Azobenzene is formed exclusively as the *E* isomer in deaerated solvents;¹⁴ however, in oxygen-saturated solutions nitrosobenzene is the primary photoproduct.¹⁴ Azepines and anilines are produced upon irradiation of PhN₃ in solutions containing ammonia, organic amines, or other nucleophilic reagents.^{12,15} The pathway by which azepines are formed is a subject of controversy since phenyl nitrene is thought to undergo intramolecular rearrangement to form 7-azabicyclo[4.1.0]hepta-2,4,6-triene^{12,16,17} or 1-aza-1,2,4,6-cycloheptatetraene.^{18,19}

Our investigation²⁰ of the photochemical properties of PhN₃ has led to discovery of a photoinitiated autocatalytic chain de-

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composition (PACD) reaction. Upon 254-nm irradiation in either 3-methylpentane or the polar solvent acetonitrile, quantum yields of disappearance (ϕ -PhN₃), determined by monitoring changes in its electronic absorption spectra, were found to be highly dependent upon concentration ([PhN₃]) whereby increasing [PhN₃] resulted in notably higher ϕ -PhN₃ values. In deaerated acetonitrile, ϕ -PhN₃ values *greatly exceeding unit efficiency* were determined at [PhN₃] > ca. 3×10^{-3} M.²⁰ (*E*)-Azobenzene was the only product.¹⁴ At [PhN₃] $\leq 3 \times 10^{-3}$ M, dissolved oxygen effectively quenched the chain decomposition by reacting with phenyl nitrene to form nitrosobenzene.¹⁴ In order to have a better understanding of the photoinitiated autocatalytic chain decomposition (PACD) reaction of PhN₃, we have made a detailed investigation of its solution photochemistry by extending our determination of ϕ -PhN₃ to concentrations ranging from 10^{-5} to 10^{-1} M.

Experimental Section

Materials. Phenyl azide was prepared according to the procedure of Lindsay and Allen²¹ by reacting the hydrochloride salt of phenylhydrazine (Eastman) with sodium nitrite (Baker), purified by column chromatography or by vacuum distillation, and characterized by IR, NMR, UV-vis, and MS methods. 3-Methylpentane (Phillips Petroleum) was purchased as 99.4% and distilled over Dri-Na (Baker) prior to use. Acetonitrile (spectrograde, Burdick and Jackson) and prepurified nitrogen and oxygen gases (West Penn Laco) were used as received. All other chemicals were purchased as reagent grade from either Baker, Eastman, or Fisher and were used without further purification.

Instrumentation. Electronic absorption spectra were recorded on either a Perkin-Elmer Model 330 or a Perkin-Elmer Model 575 UV-vis spectrophotometer at room temperature in matched quartz cuvettes (Precision Cells) with pure solvent as the reference. Vibrational absorption spectra were recorded on a Perkin-Elmer Model 580 IR spectrophotometer interfaced to an Interdata 6/16 computer. ¹H nuclear magnetic resonance spectra were recorded on a Hitachi Perkin-Elmer R-24B 60 MHz spectrometer and ¹³C and ¹⁵N NMR spectra recorded on a Bruker WM 300-MHz spectrometer. Mass spectra were recorded on a Varian MAT 112 spectrometer (70 eV) equipped with an SS200 data system and a Varian 1400 gas chromatograph (10% SP 2100 stainless steel column, 6 ft \times 1/8 in.). High-pressure liquid chromatographic (LC) analyses were performed using a Waters ALC/GPC 204 LC equipped with a Spectra-Physics minigrator. A Waters μ -Porasil column (12 \times 1/4 in.), 2% anhydrous ether in hexane, 1–2 mL/min, and 254- or 280-nm absorbance detection were used. Irradiations were accomplished using a Canrad-Hanovia 1000-W Hg-Xe lamp and Bausch & Lomb high-intensity monochromator or 450-W Hg arc.

Photochemistry. Quantum yields of disappearance (ϕ -PhN₃) were determined for 10^{-1} M acetonitrile solutions that were prepared directly and for 10^{-2} – 10^{-5} M solutions prepared by volumetric dilution of aliquots of the 10^{-1} M solution. The photochemical reaction was monitored by recording electronic absorption spectra of each solution prior to and after each irradiation. Absorbances of solutions of 10^{-4} and 10^{-5} were measured directly and those of higher concentration after volumetric dilution. ϕ -PhN₃ was calculated from

$$\phi\text{-PhN}_3 = \frac{N \times C \times V \times \Delta}{I \times F \times t} \quad (1)$$

where N = Avogadro's number in molecules $\text{mg}^{-1} \text{mol}^{-1}$, C = concentration in mmol mL^{-1} , V = volume of irradiated solution in mL, Δ = fraction of molecules decomposed = $(A_0 - A_t)/A_0$ where A_0 = absorbance at time = 0 and A_t = absorbance at time = t , I = light intensity measured by irradiating a 0.006 M solution of potassium ferrioxalate,²² F = $1 - 10^{-4\phi}$ = the fraction of light absorbed at the irradiating wavelength, and t = irradiation time in seconds. For ϕ -PhN₃ determinations, the fraction of molecules converted was generally less than 3% so that absorption of light by the photoproduct, (*E*)-azobenzene, was negligible. ϕ -PhN₃ was measured while an isobestic point was maintained. Actinometry was performed prior to and after sample irradiations in matching cuvettes.

Unless otherwise stated, samples were deaerated by bubbling with purified nitrogen gas for 3 min at 0 °C and were oxygen-saturated by bubbling with purified oxygen gas for 3 min at 0 °C.

All sample preparations and purifications and photochemical experimentation were performed under red illumination.

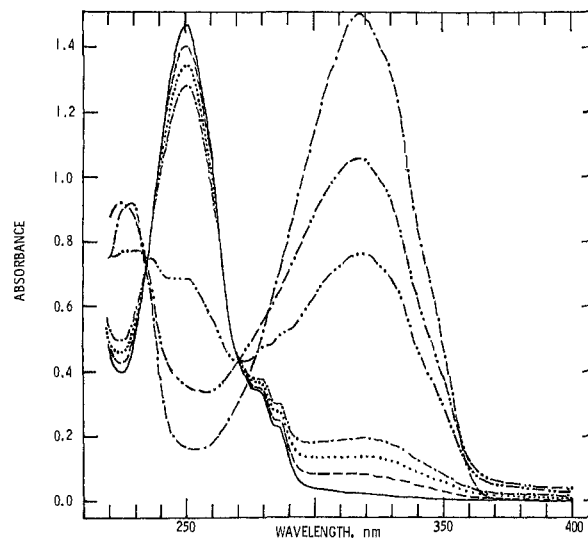


Figure 1. Room temperature electronic absorption spectra of a 1.48×10^{-4} M solution of phenyl azide in nitrogen-saturated acetonitrile prior to (—) and after irradiation with 254-nm light for a total of 30 (---), 60 (···), 90 (-·-·-), 720 (- - - -), and 2340 s (- - - - -). Absorption spectrum of a 6.48×10^{-5} M solution of (*E*)-azobenzene in acetonitrile (- - - -).

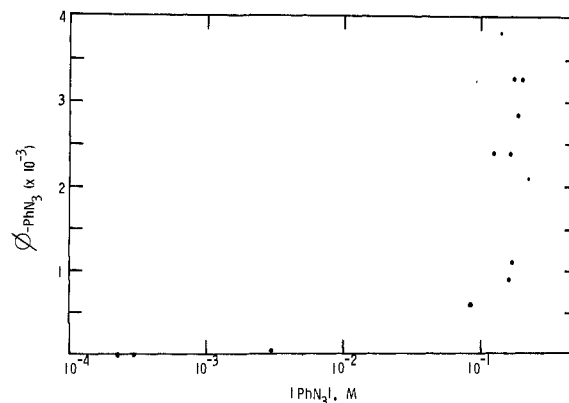


Figure 2. Plot of ϕ -PhN₃ vs. $\log [\text{PhN}_3]$ for data shown in Table I. Data for $[\text{PhN}_3] = 2.30 \times 10^{-5}$ M are not shown.

Results and Discussion

Room temperature irradiation of 10^{-4} – 10^{-5} M phenyl azide (PhN₃) in deaerated acetonitrile with 254-nm light results in a decrease in intensity of its 250-nm band maximum ($\epsilon = 1.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and concomitant increase in intensity in the 270–360-nm region. Continued irradiation establishes the presence of an isobestic point at 271 nm (Figure 1), which can be maintained for PhN₃ conversions up to ca. 40%. The two-component system is verified by high-pressure LC analyses, which revealed that the percentage of PhN₃ decreased linearly with irradiation time while that of (*E*)-azobenzene increased linearly. At $[\text{PhN}_3] = 2.3 \times 10^{-5}$ M, ϕ -PhN₃ = 0.5, a value in excellent agreement with those of Reiser and co-workers.^{4,6,7} (*Z*)-Azobenzene is formed upon continued irradiation of the photolysis solution but is a primary photoproduct of (*E*)-azobenzene^{23–31} and not of PhN₃.¹⁴

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Table I. Quantum Yields of Disappearance of Phenyl Azide upon 254-nm Irradiation

concn, M ^a	ϕ -PhN ₃ ^b	<i>n</i>
2.18 × 10 ⁻¹	2.64 × 10 ³	12.4
1.95 × 10 ⁻¹	3.78 × 10 ³	12.9
1.84 × 10 ⁻¹	3.34 × 10 ³	12.7
1.74 × 10 ⁻¹	3.78 × 10 ³	12.9
1.69 × 10 ⁻¹	1.62 × 10 ³	11.7
1.64 × 10 ⁻¹	2.89 × 10 ³	12.5
1.58 × 10 ⁻¹	1.42 × 10 ³	11.5
1.37 × 10 ⁻¹	4.33 × 10 ³	13.1
1.25 × 10 ⁻¹	2.92 × 10 ³	12.5
8.68 × 10 ⁻²	6.03 × 10 ²	10.2
3.00 × 10 ⁻²	3.00 × 10 ²	9.2
3.00 × 10 ⁻³	5.25 × 10 ¹	6.7
3.00 × 10 ⁻⁴	3.49	2.8
2.30 × 10 ⁻⁴	2.11	2.1
2.30 × 10 ⁻⁴	1.83	1.9
2.30 × 10 ⁻⁴	1.57	1.7
2.30 × 10 ⁻⁵	0.56	
2.30 × 10 ⁻⁵	0.47	
2.30 × 10 ⁻⁵	0.46	

^a Acetonitrile solutions at room temperature. Solutions of 3.0 × 10⁻² M and lower concentrations were deaerated by bubbling with nitrogen gas. ^b ϕ -PhN₃ ± 10%.

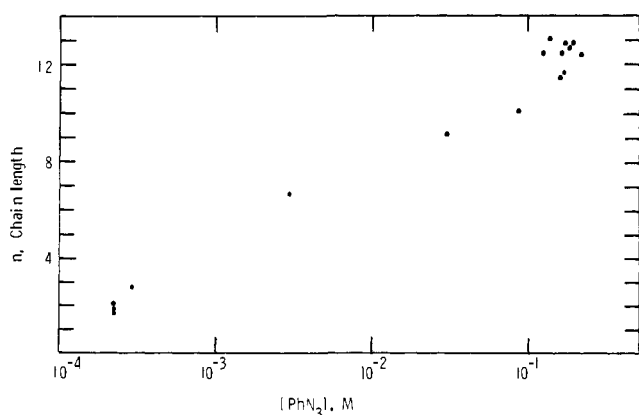


Figure 3. Plot of chain length *n* vs. log [PhN₃] for data shown in Table I. Data obtained for [PhN₃] = 2.30 × 10⁻⁵ M are not shown.

An intractable polymeric material is also formed;^{12,13} however, it is not an eluent under our high-pressure LC experimental conditions.³²

Upon irradiation of 10⁻³–10⁻² M PhN₃ in deaerated acetonitrile or 10⁻¹ M PhN₃ in aerated acetonitrile, similar absorption spectral changes are recorded but after volumetric dilution. Namely, the 250-nm band maximum continually decreased in intensity with increasing irradiation time and an absorbance in the 270–360-nm region continually increased in intensity. (*E*)-Azobenzene is the only photoproduct. However, ϕ -PhN₃ values determined for these solutions greatly exceeded unit efficiency, indicating a chain decomposition reaction.

With increasing [PhN₃], ϕ -PhN₃ clearly increased (Table I). A plot of ϕ -PhN₃ vs. log [PhN₃] is not linear but appeared to follow an exponential pattern (Figure 2). The plot of the chain

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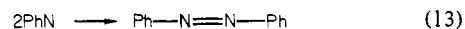
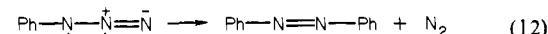
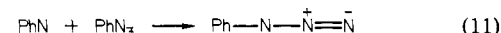
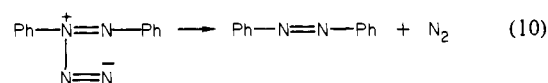
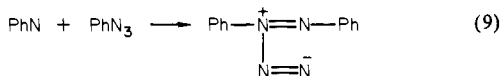
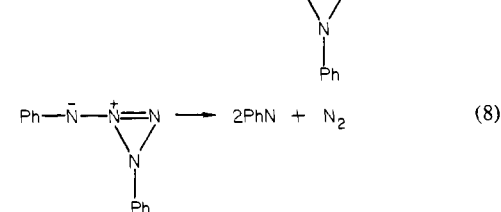
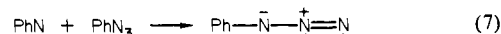
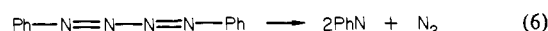
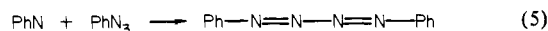
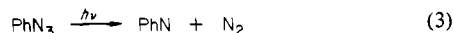
(32) Approximately 15% by weight of the irradiated sample is material that could be collected by filtration. An empirical formula of C₇H₆N is determined from a phenyl azide sample irradiated in vacuum-degassed (five freeze-pump-thaw cycles) acetonitrile. N-H and aromatic C-H stretching vibrations are present in the IR spectrum. No aliphatic C-H absorptions are observed. Upon irradiation in air, polymeric materials having the empirical formula C₆H₆NO and C₆H₅NO were obtained. Materials were not soluble in organic solvents or concentrated inorganic acids; thus, molecular weight determinations were not possible. No polymeric material was observed upon 313-nm irradiation of phenyl azide in the presence of the triplet sensitizer acetophenone. Azobenzene was the only photoproduct. The polymeric material is thought to result from singlet phenyl nitrene attack of a C-H bond of the aromatic ring of a phenyl azide molecule,¹³ a suggestion consistent with our observations.

length (*n*) vs. log [PhN₃] is linear (*r*² = 0.972),³³ Figure 3, calculating *n* from the expression for an exponential function,³⁴ eq 2

$$\phi\text{-PhN}_3/\phi^0\text{-PhN}_3 = 2^n \quad (2)$$

where ϕ^0 -PhN₃ is approximated by using the ϕ -PhN₃ value obtained for very dilute solutions (Table I) or the ϕ -N₂ value obtained for frozen organic matrices of PhN₃ at 77 K.^{4,6,7}

That plots of ϕ -PhN₃ vs. log [PhN₃] appear exponential is expected if a mechanism of disappearance of PhN₃ exists other than photodecomposition (eq 3). Reaction of a phenyl nitrene intermediate with a ground-state phenyl azide occurs;³⁵ however, it is not known if the reaction affords two phenyl nitrenes directly (eq 4) or some other intermediate. A 1,4-diphenyltetrazadiene,^{11,36} which then decomposes into two phenyl nitrenes (eq 5 and 6), may be formed via nitrene attack at N₃. Nitrene insertion at N₂ and N₃ may afford a triaza species, which may decompose into two phenyl nitrenes (eq 7 and 8). Alternatively, attack at N₁ or N₁ and N₂ might afford a 1,2-diphenyltetrazadiene (eq 9) and triaza species (eq 11), respectively, intermediates which probably decompose to azobenzene and nitrogen (eq 10 and 12). Azobenzene may also be formed via dimerization of two phenyl nitrenes (eq 13), a reaction that occurs for dilute PhN₃ solutions.¹⁴ Reactions 4, 5 and 6, and 7 and 8 serve as chain propagation steps, while reactions 9 and 10, 11 and 12, and 13 are chain termination steps.



Experimental evidence for the existence of a 1,4-diphenyltetrazadiene is derived from the reaction of organometallics with aryl azides to afford stable cobalt,³⁷ nickel, and platinum³⁸ com-

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plexes of 1,4-diaryltetraazadiene. Also, gas-phase mass spectroscopic studies of the reaction of phenyl nitrene anion radical with phenyl azide³⁹ suggest the formation of the anion radical of 1,4-diphenyltetraazadiene. Experimental evidence for formation of a cyclic triaza species is derived from the photochemical cyclization of an azimine to a triaziridine⁴⁰ and from the reaction of ¹⁵N-enriched hydrazine with nitrous acid, which may have formed a cyclic azide intermediate.⁴¹ Nanosecond transient absorption spectral studies of PhN₃⁴² provide evidence of the intermediacy of phenyl nitrene. Other species were not observed on a time scale as short as 15 ns.

Reaction 4, or the set of reactions 5 and 6 or 7 and 8, may result in the formation of *two* phenyl nitrene intermediates from bimolecular reaction of one phenyl nitrene and one phenyl azide molecule. The net reaction of any set is not only a chain reaction but also specifically a branching chain reaction, known as an autocatalytic or spontaneously explosive reaction.⁴³ Such reactions occur in the vapor phase and theoretical descriptions have been developed based upon thermal initiation of the chain reaction;^{43,44} however, they are not useful to our solution studies. Explosions of metallic azide crystals have been reported;⁴⁵⁻⁴⁸ however,

branching chain reactions (or explosions) were not reported to occur in solution. Nevertheless, the relationship between ϕ -PhN₃ and *n* with [PhN₃] provides experimental evidence for occurrence of a *branching chain reaction in solution*.

The photochemical initiation of chain reactions is well documented.⁴⁹ The photochemical initiation of the branching chain reaction of phenyl azide that we have just examined occurs with an efficiency of 0.5 (Table I). The chain length, *n*, is therefore calculated by using this experimental value and *assuming* that reaction 4, and/or reactions 5 and 6 and 7 and 8, occurs with unit efficiency. Were the reaction of phenyl nitrene and phenyl azide to be less than unit efficient, then the calculated values of *n* presented in Table I are necessarily underestimated.

Conclusion

A chain decomposition reaction of phenyl azide can be initiated photochemically. Upon irradiation of phenyl azide in solution, molecular nitrogen is evolved and phenyl nitrene is formed. In dilute solutions of [PhN₃] $\sim 10^{-5}$ M, ϕ -PhN₃ = 0.5. Dimerization of two phenyl nitrenes¹⁴ then leads to (*E*)-azobenzene formation. At higher concentrations of phenyl azide, phenyl nitrene can react with a phenyl azide molecule to net *two* phenyl nitrene intermediates. This reaction is repeated, affording *four* phenyl nitrenes, and is manifested as ϕ -PhN₃ values that greatly exceed unit efficiency. ϕ -PhN₃ depends exponentially upon the concentration of phenyl azide, a result indicative of a branching chain or autocatalytic reaction. The results provide experimental data for the occurrence of a molecular explosion in solution.

Acknowledgment. We are indebted to the National Science Foundation for support of this research via a grant to the Center for the Joining of Materials (DMR 76-81561).

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Synthesis of (\pm)-11-Ketoprogesterone, a Precursor to the Corticosteroids. An Improved Method for the Introduction of the Carbon 19 Methyl Group into A-Ring Aromatic Steroids[†]

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Abstract: A new approach to corticosteroids is presented that realizes 11-ketoprogesterone. The C₈-C₁₄ stereochemistry of the steroid is established by a Cope rearrangement that allows for the stereocontrolled formation of the C and D rings by acid-catalyzed cyclizations. The formation of an 11 β -hydroxyl group permits the stereocontrolled introduction of the C₁₉-methyl group under Simmons-Smith-Sawada conditions having the C₃ ketone protected as a ketal.

We have previously described a formal total synthesis of estrone employing the (trimethylsilyl)cyanohydrin Cope rearrangement.¹ We report in this paper mechanistic aspects of the acid-mediated ring-forming reaction, the applicability of a methyl acetylene

terminator to these cyclizations, and an improved method for introduction of the C₁₉-methyl substituent into A-ring aromatic steroids. These studies have culminated in a synthesis of (\pm)-

[†]Dedicated to Professor William S. Johnson on the occasion of his seventieth birthday.

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