A Walk Rearrangement of a Diazanorcaradiene. Mechanistic and Exploratory Organic Photochemistry. LXXVIII¹

Howard E. Zimmerman* and Wolfgang Eberbach

Contribution from the Chemistry Department of the University of Wisconsin, Madison, Wisconsin 53706. Received November 17, 1972

Abstract: The present study reports the existence of a photochemical heterocyclic walk process in which an isopropylidene moiety moves around the π system of 2,5-diphenylpyridazine. In this reaction, 4,4-dimethyl-3,7-diphenyl-1,2-diazepine is formed from 7,7-dimethyl-2,5-diphenyl-3,4-diazanorcaradiene on direct photolysis. Evidence was obtained that the reaction originates from the first excited singlet, that this singlet is $\pi - \pi^*$, and that the triplet excited state is unreactive. The quantum yield was determined as 0.0021. Despite the low efficiency, the reaction proved especially free of by-product and synthetically useful. Consideration of rate data excluded an alternative mechanism involving expulsion of isopropylidene followed by recombination. A second photochemical process was uncovered when shorter wavelength light was employed, this being an electrocyclic closure of 4,4-dimethyl-3,7-diphenyl-1,2-diazepine to afford 4,4-dimethyl-3,7-diphenyl-1,2-diazabicyclo[3.2.0]hepta-2,6diene. Both this latter reaction and the photolysis leading to the diazepine could be shown to arise as true electronically excited state processes rather than from vibrationally excited species; this evidence derived from comparison of the photochemistry with the thermal behavior of the compounds. The interconversions studied were also of interest since thermally the processes proceeded in the reverse direction than photochemically.

 \mathbf{A}^n especially intriguing transformation is the walk rearrangement.² This is typified in the case of thermal processes by the elegant scrambling reaction described by Berson³ in which the isopropylidene moiety of the norcaradiene valence tautomer of several trimethylcycloheptatrienes was shown to move about the periphery of the six ring.



In photochemistry there is an even more limited number of walk rearrangements. One dramatic case⁴ is the transformation of the bicyclic diene 3 to afford the homofulvene 4 by a mechanism in which the iso-

$$\begin{array}{c} \downarrow \\ \downarrow \\ 3 \end{array} \xrightarrow{h_{V}} \end{array} \qquad \begin{array}{c} \downarrow \\ \downarrow \\ 4 \end{array} \qquad (2)$$

propylidene group slithers along the π system.

The present research was part of our continuing investigation of such walk rearrangements. 7,7-Dimethyl-2,5-diphenyl-3,4-diazanorcaradiene (5) was selected for study.

Synthetic Aspects. The desired diazanorcaradiene 5 was synthesized as outlined in Chart I. This preparation began with the reaction of diphenylsulfonium isopropylide with diethyl maleate to give the stereoisomeric diethyl 3,3-dimethylcyclopropane-1,2-dicarboxylates (6a and 6b); the cis product predominated

Chart I. Preparation of 7,7-Dimethyl-2,5-diphenyl-3,4-diazanorcaradiene (5)



in a 5:1 ratio.⁵ Saponification and reaction of the corresponding cis diacid 7b with phenyllithium afforded cis-1,2-dibenzoyl-3,3-dimethylcyclopropane (8).6 This, in turn, was treated with hydrazine to give the desired 7,7-dimethyl-2,5-diphenyl-3,4-diazanorcaradiene (5).

Exploratory Photochemical Results and Product Structure Elucidation. Photolysis of the diazanorcaradiene 5 with a Pyrex filter and a 450-W immersion lamp led to a slow but very clean formation of a single primary product. The reaction could be brought to the point where essentially all starting material was consumed. The primary product melted at 88° and was a pale yellow solid. Additionally, ca. 5% of a secondary product, mp 151°, resulted when complete conversion was attempted.

High resolution mass spectral analysis of the 88° primary photochemical product indicated that this was an isomer of the diazanorcaradiene reactant 5. The ultraviolet spectrum with its maximum at 284 nm (13,500) offered weakly suggestive information that the photoproduct might contain the moiety PhC=N-N=

⁽¹⁾ For paper LXVII, note H. E. Zimmerman and J. A. Pincock, J. Amer. Chem. Soc., 95, 3246 (1973).

⁽²⁾ A number of thermal and photochemical rearrangements have now been termed walk processes. A walk process is best defined as one in which a three-ring carbon moves along the surface of a π system

one in which a three-ring carbon moves along the surface of a π system and in which generally both bonds are conjugated with the π system. (3) (a) J. A. Berson and M. R. Willcott, J. Amer. Chem. Soc., 88, 2494 (1966); (b) J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Willcott, *ibid.*, 89, 4076 (1967). (4) H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schröder, J. Amer. Chem. Soc., 93, 3662 (1971); 92, 3474 (1970).

⁽⁵⁾ The general procedure described for the preparation of methyl chrysanthemate by E. J. Corey and M. Jautelat, J. Amer. Chem. Soc., 89, 3912 (1967), was employed. The methyl ester corresponding to 6 was reported, without details, to be accessible.

⁽⁶⁾ This compound has been isolated from the degradation of 7,7-dimethyl-2,5-diphenylnorcaradiene by L. A. Paquette and L. M. Leichter, J. Amer. Chem. Soc., 93, 5128 (1971).

CPh; cf. the 270-nm (20,900) absorption⁷ of propiophenone azine. More helpful, the nmr spectrum revealed the presence of two adjacent vinyl hydrogens in the form of an AB quartet (J = 10.0 Hz, $\tau 3.76$ and 4.01). Even more significant was the appearance of two broad methyl signals in the nmr, these centered at $\tau 8.78$ and 9.10. At 73° the signals merged and gave a modestly sharp six-hydrogen singlet; and at 0° the two peaks became relatively sharp again but remained separate. Thus, evidence was available that the 88° photoproduct had two methyl groups which rapidly equilibrated at the higher temperatures but remained in different environments at lower temperatures.

The juxtaposition of the three moieties



leads directly to tentative structure **9** for the 88° photoproduct. The nonequivalence of the two methyl groups observed in the nmr can be understood on the basis of the boat-form conformation (note **9a**). In fact, the temperature dependence observed finds literature parallel in the case of 2-carbomethoxy-6,7-diphenyl-4*H*-azepine (**10**).⁸



That this assignment was indeed correct was established by catalytic reduction of photoproduct 9 followed by acidic hydrolysis of the dihydro-photoproduct 11 to afford 2,2-dimethyl-1,5-diphenyl-1,5-pentanedione (12) as outlined in Chart II. This same diketone

Chart II. Degradation and Structure Proof of Photoproduct 9



(*i.e.*, **12**) was prepared for comparison by reaction of 2,2-dimethylglutaric acid with phenyllithium. Additionally, treatment of the diketone with hydrazine led to the dihydro-photoproduct **11**.

With the structure of the 88° product established as 4,4-dimethyl-3,7-diphenyl-1,2-diazepine (9), attention was focussed on the secondary photoproduct melting at 151°. The nmr revealed a single vinyl peak at τ 4.00 coupled with a τ 5.38 hydrogen. The coupling (J = 1.2 Hz) was small as might be expected for 1,7-related hydrogens of a [3.2.0] bicyclic ring system. Such a skeleton was suggested also by the expectation of a simple electrocyclic ring closure common to tropylidene photochemistry.⁹ Electrocyclic closure of the primary photoproduct 9 affords structure 13 as one of the two *a priori* such products. This structure not

(9) For a review, cf. L. B. Jones and V. K. Jones, Fortschr. Chem. Forsch., 13, 307 (1969). only is in accord with the nmr evidence cited above but also with the presence of two unsplit and nonequivalent methyl absorptions at τ 8.50 and 8.55. Supporting such an assignment was the thermal reversion of the 151° product to the diazepine 9 on heating to 195° (vide infra).

Thus, the photochemistry of diazanorcaradiene 5 can be outlined as in eq 3.



Thermal and Acid-Catalyzed Rearrangements. Originally it was thought that the thermal and acidcatalyzed behavior of the heterocyclic compounds would provide useful structure elucidation information. This turned out to be only partially correct. Nevertheless, the transformations of these compounds proved most interesting, especially in view of the rearrangements observed.

Thus, as delineated in Chart III at 195° the diazepine

Chart III. Thermal and Acid-Catalyzed Behavior



9 was found to be converted into the diazanorcaradiene 5. The latter, in turn, thermally rearranged to afford 4-isopropyl-3,6-diphenylpyridazine (14). Although pyrolysis of diazepine 9 gave both 5 and 14, inspection of the composition of the pyrolysate as a function of time suggested that the pyridazine was not formed directly from diazepine, but this is not a certainty. Finally, at the same temperature the diaza[3.2.0]bicyclic compound 13 was found to afford the diazepine 9; however, in this case the reaction was sufficiently rapid that diazepine 9 could be determined to be the primary product of pyrolysis. In this case, subsequent formation of norcaradiene 5 and thence pyridazine 14 was comparatively slow.

Turning attention now to the acid-catalyzed runs, we note (see Chart III) that both the diazepine 9 and the diazanorcaradiene 5 on treatment with hydrochloric acid afforded pyridazine 14. While one might be tempted to use the acid-catalyzed reaction of diazanorcaradiene 5 as part of the structure elucidation in order to define the basic molecular skeleton, the fact that the same product results from diazepine 9 reveals this not to be totally safe.

Quantum Yield and Multiplicity Studies. Results. Two questions remained. First, it was important to determine just how efficient the heterocyclic walk process was. Secondly, it was of real interest to determine the multiplicity of the reacting excited state. Thus far, excited state walk processes have involved singlets.⁴

The quantum yields were determined on our Black

⁽⁷⁾ E. R. Blout, V. Eager, and M. Gofstein, J. Amer. Chem. Soc., 68, 1983 (1946).

⁽⁸⁾ A. Steigel, J. Sauer, D. A. Kleier, and G. Binsch, J. Amer. Chem. Soc., 94, 2770 (1972).
(9) For a review, cf. L. B. Jones and V. K. Jones, Fortschr. Chem.

Box apparatus¹⁰ using ferrioxalate actinometry.¹¹ The results of these runs are summarized in Table I and detailed in the Experimental Section.

	Starting		Ouantum yields	
Runª	material	Sensitizer ⁹	9.	13/
16	5	None	0.00204	
2 ^b	5	None	0.00212	
3°	5	Michler's ketone	0.000088	
4°	5	Michler's ketone	0.000079	
5ª	9	None		0.00259
	9	None		0.00267

Table I. Quantum Yield Determinations

^a Photolysis in methanol. ^b Filter transmission 290-370 nm. ^c Filter transmission 375-455 nm. ^d Filter transmission 250-305 nm. ^e In millimoles of 4,4-dimethyl-3,7-diphenyl-1,2-diazepine (9) per mEinstein of light captured. ^f In millimoles of 4,4-dimethyl-3,7-diphenyl-1,2-diazabicyclo[3.2.0]hepta-2,6-diene (13) per mEinstein of light captured. ^g Ca. 99% of light absorbed by sensitizer.

Comparison of the sensitized irradiations of the diazanorcaradiene 5 with the direct photolyses revealed that the sensitized runs were at most 4% as efficient. Even this 4% may result from direct light absorption by reactant 5, since this per cent does not differ greatly from the 1% direct light absorption anticipated on the basis of relative absorbancies of reactant *vs.* sensitizer.

One might concern himself about the possibility of the relative energies of sensitizer and reactant being unfavorable for transfer. However, experiments using 0.113 M biacetyl in methanol and 0.00118 M diazanorcaradiene and 400-nm excitation of the biacetyl led to biacetyl emission in which the normal 510-nm biacetyl phosphorescence was very close to totally missing while the 460-nm fluorescence persisted. Thus the diazanorcaradiene 5 proves to have a low enough energy triplet to be capable of quenching the 55 kcal/mol biacetyl triplet. With 55 kcal/mol then set as an upper limit for the triplet energy of 5, the 62 kcal/mol triplet energy of the Michler ketone sensitizer used must then be more than adequate to generate the triplet of diazanorcaradiene 5; and we must conclude that this is an unreactive triplet.

Supporting this conclusion were experiments in which photolyses were run in neat acetone ($E_T = 80 \text{ kcal/mol}^{12}$) and compared with comparable runs in methanol. The acetone runs afforded product with only 30% of the efficiency found in methanol. Even the 30% seems likely to derive from incomplete light capture by the acetone (note Experimental Section for details).

Interpretative Discussion of the Photochemical Results. Most important of all is the actual observation of the walk rearrangement which was the initial goal of the present research. This constitutes the first example of such a photochemical rearrangement of a heterocyclic system.¹³ In this connection, however, one does

(10) H. E. Zimmerman, Mol. Photochem., 3, 281 (1971).

(11) C. G. Hatchard and C. A. Parker, Proc. Roy. Soc., Ser. B, 140,

470 (1953). (12) R. F. Borkman and D. R. Kearns, J. Chem. Phys., 44, 945 (1966)

(13) During the course of this research there has been a report⁶ of a carbocyclic rearrangement analogous to the present heterocyclic process. However, this was run qualitatively in an nmr tube and no have to concern himself that an alternative dissociation-recombination mechanism, one in which dimethylcarbene and 2,5-diphenylpyridazine are formed and recombine, is not operative.

This conclusion is clear from consideration of the competitive reactivity of the dimethylcarbene toward intramolecular rearrangement to give propylene vs. bimolecular attack on the diphenylpyridazine to give a diazanorcaradiene (e.g., 16). Thus, dimethylcarbene



rearranges intramolecularly exceedingly rapidly to propylene as evidenced by the fact that photochemical generation of dimethylcarbene from dimethyldiazirine in neat cyclohexene gives only propylene and no addition product.¹⁷ Although the rate of rearrangement of dimethylcarbene itself is not known, the closely related rate of rearrangement of ethylidene to ethylene has been reported¹⁸ as $k = 1.4 \times 10^9 \text{ sec}^{-1}$; such intramolecular rearrangement is in competition with the bimolecular recombination of dimethylcarbene with the diphenylpyridazine. In the present studies, the diphenyldiazanorcaradiene 5 was utilized at a concentration of ca. 0.001 M. Even assuming that all of this dissociated at once, the concentration of diphenylpyridazine 15 then can only reach 0.001 M. This leads to a pseudo-unimolecular rate of $k_{\text{recom}} = 0.001 k_{\text{diff}} =$ $0.001 \times 10^9 = 10^6 \text{ sec}^{-1}$ if we assume diffusion control in which every encounter of carbene and pyridazine leads to reaction. Thus, being unreasonably conservative at every point, we arrive at a rate which is $\frac{1}{1000}$ th of the rate of the intramolecular rearrangement.

With the photochemical walk mechanism established, it is of interest to note that it is the singlet excited state which exhibits this reactivity and that the triplet does not give the rearrangement. While it is much too early to generalize with any certainty, we do note that in the two previous examples⁴ of a photochemical walk reaction it was the singlet which underwent the rearrangement.

Knowing that the rearrangement is a singlet process, we can inquire if the reaction proceeds via a $\pi-\pi^*$ or an $n-\pi^*$ excited state; both are *a priori* possibilities in view of the availability of the unshared nitrogen electron

information on efficiency, multiplicity, or intramolecularity is reported. There are some further examples which might formally proceed *via* photochemical walk processes; however, in each case the results have been or may be interpreted by alternative mechanisms.¹⁴

(14) (a) E. Ciganek, J. Amer. Chem. Soc., 89, 1458 (1967). In this case evidence for dissociation-recombination involving dicyanocarbene in the rearrangement of a dicyanotropylidene was advanced. (b) D. M. Madigan and J. S. Swenton, *ibid.*, 92, 7513 (1970). (c) T. Toda, M. Nitta, and T. Mukai, *Tetrahedron Lett.*, 4401 (1969). In this case a slither mechanism^{4,15} was proposed, and an alternative phenyl migration via a di- π -methane process¹⁶ was argued against. However, in this instance isolation of the product of three-ring fission to give a carbene suggests a dissociation-recombination mechanism.

(15) H. E. Zimmerman, D. Döpp, and P. S. Huyffer, J. Amer. Chem. Soc., 88, 5352 (1966); H. E. Zimmerman and D. S. Crumrine, *ibid.*, 90, 5612 (1968); H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *ibid.*, 91, 434 (1969).

(16) H. E. Zimmerman and G. L. Grunewald, J. Amer. Chem. Soc.,
88, 183 (1966), cf. ref 4; H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. S. Sherwin, *ibid.*, 89, 3932 (1967); H. E. Zimmerman and P. S. Mariano, *ibid.*, 91, 1718 (1969).
(17) H. M. Frey and I. D. R. Stevens, J. Chem. Soc., 3514 (1963).

(17) H. M. Frey and I. D. R. Stevens, J. Chem. Soc., 3514 (1963).
(18) H. M. Frey, Progress in Reaction Kinetics," G. Porter, Ed., Macmillan, New York, N. Y., 1964, p 158. pairs. The lack of solvent effect (note Experimental Section) on the energy of excitation forming S_1 reveals that this excited species cannot be $n-\pi^*$. In such an event one would have selective ground-state stabilization by hydrogen bonding in polar solvents, and the excitation energy would increase with an absorption shift to shorter wavelengths. A $\pi-\pi^*$ S_1 could well be relatively independent of such hydrogen bonding, and the evidence thus supports a $\pi-\pi^*$ assignment. While characterizing S_1 as $\pi-\pi^*$ does not prove that an upper singlet (e.g., an $n-\pi^*$ one) is not reacting, the simplest interpretation has the lowest excited state rearranging.

Where there is both thermal- and photochemistry observed for a molecule it is of interest to compare these. Thus, one can inquire if the photochemistry and thermal chemistry are parallel and if the photochemistry derives from a thermal transformation of hot ground-state species formed by conversion of electronic excitation into vibrational excitation. Presently, it is noted that 4-isopropyl-3,6-diphenylpyridazine (14) is a primary product of the thermolysis of the diazanorcaradiene 5; yet this pyridazine is not observed in any of the photochemical experiments. We can take this pyridazine formation as characteristic of the behavior of vibrationally excited diazanorcaradiene 5 and hence exclude intervention of vibrationally excited species in the photochemistry of 5.

In the case of the behavior of diazepine 9, formation of diazanorcaradiene 5 is most characteristic of the vibrationally excited species, but this is absent from the photochemistry of 9. Again, vibrationally hot molecules of reactant can be excluded in the photochemistry.

These conclusions are in agreement with our earlier commentary¹⁹ in which we noted that only where an exceedingly low thermal activation barrier is present can thermal reaction of a vibrationally hot ground-state species compete with cooling by solvent.

Finally, in connection with the photochemical walk process, it is interesting to consider the molecular electronics of the process. Ordinarily this would involve a mere discussion of the symmetry of the highest occupied and lowest vacant MO's of different moieties of the molecule since symmetry is not maintained along the reaction coordinate. One could apply the Möbius-Hückel method²⁰ (vide infra) but presently an even more detailed analysis is possible. This utilizes the recent method of MO Following²² which allows orbital following even when symmetry is absent.

(19) H. E. Zimmerman and J. W. Wilson, J. Amer. Chem. Soc., 86, 4036 (1964).

(20) (a) H. E. Zimmerman, J. Amer. Chem. Soc., 88, 1564 (1966);
(b) Accounts Chem. Res., 4, 272 (1971); note ref 21.

(21) (a) The approach by M. J. S. Dewar, Tetrahedron, Suppl., 8, 75 (1966), based on perturbation treatment of Hückel MO's is very similar in conclusion to the Möbius-Hückel approach:²⁰ the main difference is in terming our "Möbius" systems as "anti-Hückel." (b) Inconsistent with earlier publications, Dewar in a recent review^{21c} has misunderstood and misquoted our definition of Möbius and then criticized the misquoted viewpoint. Actually, in contrast to Dewar's statement,^{21c} a Möbius system as defined by us may be either aromatic or antiaromatic depending on the number of electrons, 4N or 4N + 2, respectively. The earlier criticism that our Möbius-Hückel treatment is weakened by its being derived from Hückel theory is not really serious since the method is primarily of qualitative rather than quantitative value. However, the same weakness is even more inherent in the Dewar method which is just an approximation to Hückel theory. (c) M. J. S. Dewar, Angew. Chem., Int. Ed. Engl., 10, 761 (1971).

(22) (a) H. E. Zimmerman, Accounts Chem. Res., 5, 393 (1972);
(b) H. E. Zimmerman and L. R. Sousa, J. Amer. Chem. Soc., 94, 834 (1972).



σ 1 2	1-2	1-2+3-4	<u>-1-6</u> -016
[¥] 4	3-4+5-6	-1-4+5-6	-2+3-4+5
Ψз	3-4-5+6	-1+2+3-4-5+6	- 2+ 3+ 4-5 - ⁴ 3
Ψ ₂	••	-1-2+3+4-5-6	Ψ2
- ¥1	***-5-6	-1+4+5+6	2+3-4-5
σ 12	€€	1+2+3+4	-1+6 °16

Basis Orbital Conversion:

Figure 1. MO Following for the rearrangement of 5 to 9 with inversion (Möbius). The electronic configuration is indicated by \bullet for the ground state and by | for the excited state.

Thus the correlation diagram in Figure 1 can be constructed for the slither stereochemistry;^{4,15} we note that this is equivalent to the formulation of the reaction as a 1,5-suprafacial rearrangement²³ with inversion of the migrating carbon (note 17a and 17b). The counter-



part stereochemistry is illustrated in structure 18



which represents the alternative pivot mechanism.¹⁵ This corresponds to a 1,5-suprafacial sigmatropic²³ rearrangement with retention of configuration of the migrating group.

If we first focus attention on the half-migrated species 17 and 18, we note that representation 17b is a Möbius system (*i.e.*, one or an odd number of sign inversions). With its six delocalized electrons, this would correspond to a forbidden, or antiaromatic transition state in a ground-state process if one uses this Möbius-Hückel treatment first described by us some seven years ago.²⁰ The excited state process is, however, predicted to be allowed.²⁰

The reverse is predicted in the case of 18 which is a Hückel system (0 or an even number of sign inversions) and the thermal rearrangement *via* 18 is allowed through an aromatic transition state. Conversely, the photochemical process is forbidden.

MO Following²² is really an extension in the present case of the Möbius-Hückel approach which does allow drawing of the correlation diagrams for cyclic transition states of the present variety (note Figures 1 and 2). MO Following, however, inspects the form of the MO's

(23) R. B. Woodward and R. Hoffmann, Angew. Chem., Int. Ed. Engl., 8, 781 (1969).

Zimmerman, Eberbach | Walk Rearrangement of a Diazanorcaradiene

3974

Sasis Orbital Conversion:



Figure 2. MO Following for the rearrangement of 5 to 9 with retention (Hückel). The electronic configuration is indicated by \bullet for the ground state and by | for the excited state.

at half-reaction and provides justification for the correlations drawn in Figures 1 and 2.²⁴

The fascinating result is that only for the walk process with inversion of configuration will the photochemical rearrangement be allowed. This follows from the observation that in Figure 1 (*i.e.*, the Möbius electronics) an adiabatic transformation affords an excited product with the same configuration as the reactant excited state while in Figure 2 (*i.e.*, with Hückel electronics) the product of an adiabatic conversion is doubly excited compared to the singly excited state reacting. The overall result is in agreement with the conclusion of Mukai^{14e} based on perturbation considerations.

Interpretative Discussion of the Thermal and Acid-Catalyzed Rearrangements. A point of considerable interest is that MO Following suggests that the thermal rearrangement of the diazepine 9 to give the diazanorcaradiene 5 should proceed by a somewhat similar walk process but instead with retention of configuration of the migrating group. Thus the retention mechanism utilizes a Hückel transition state and Figure 2 applies. Here no occupied, bonding MO's become antibonding and the reaction is allowed. In Figure 1, corresponding to the slither (*i.e.*, inversion) stereochemistry, occupied bonding MO's become antibonding and the reaction is forbidden. This is in agreement with the conclusions of Berson, et al.,3 in connection with the carbocyclic analog and more recently by Paquette⁶ using a perturbation treatment.

Still remaining are the mechanisms of the acidcatalyzed reactions. These most reasonably involve in each case protonation of a ring nitrogen of the norcaradiene valence tautomer of reactant followed by three-ring opening. This is illustrated below.



Conclusion

It is seen that the walk rearrangement is more general than previously thought and may well eventually become as ubiquitous as the di- π -transformation.

Experimental Section²⁵

Diphenylethylsulfonium Fluoroborate.²⁶ To 103.0 g (0.54 mol) of triethyloxonium fluoroborate²⁷ in 200 ml of dichloromethane under nitrogen, 100.0 g (0.54 mol) of diphenyl sulfide was added. After the mixture was stirred 7 days, 50 ml of anhydrous ether was added and the resulting crystals were filtered. Recrystallization from dichloromethane and ether afforded 149.0 g (89%) of diphenyl-ethylsulfonium fluoroborate, mp 74° (lit.²⁸ 74–76°).

cis-3,3-Dimethylcyclopropane-1,2-dicarboxylic Acid. The general method of Corey⁵ was used. A solution of 60.0 g (0.20 mol) of diphenylethylsulfonium fluoroborate and 17.0 g (0.20 mol) of dichloromethane in 1000 ml of dry dimethoxyethane was cooled to -70° and treated with 0.22 mol of a cold solution of lithium diisopropylamide (prepared by the addition of 98 ml of 2.3 M n-butyllithium in hexane to 22.4 g of diisopropylamine in 100 ml of dry dimethoxyethane at -70°). After 30 min, 28.4 g (0.20 mol) of methyl iodide was added and the reaction mixture was stirred at -70° for 2 hr, after which time 0.22 mol more of lithium diisopropylamide was added at -70° . After 1 hr at this temperature, diethyl maleate (34.4 g, 0.20 mol) was slowly introduced. The reaction mixture was maintained at -70° for 2.5 hr, at -70 to -50° for 4 hr, and then allowed to warm over 30 min to 0°. After addition of 1200 ml of n-hexane, the mixture was washed with 200 ml of 2 N HCl and 1500 ml of water and then dried over MgSO₄. Distillation afforded 24.6 g of a fraction, bp 61-66° (0.1 mm), which was shown to be cis- and trans-diethyl 3,3-dimethylcyclopropane-1,2-dicarboxylate (ratio ca. 5:1, by nmr), only slightly contaminated with traces of diethyl maleate and diphenyl sulfide.

The mixture of the *cis*- and *trans*-diethyl 3,3-dimethylcyclopropane-1,2-dicarboxylates (15.0 g, 70 mmol) in 20 ml of methanol was added to a solution of 39 g of potassium hydroxide in 60 ml of water and 150 ml of methanol at 0°. After the mixture was stirred for 15 hr at room temperature, the methanol was removed *in vacuo*. Ether extraction of the aqueous phase gave only traces of unhydrolyzed ester. The solution was acidified with 5 N HCl and ether extracted affording 10.5 g of a crystalline mixture which contained 75-80% of the cis acid. Repeated recrystallization from water gave 5.4 g (58%) of pure *cis*-3,3-dimethylcyclopropane-1,2dicarboxylic acid, mp 176° (lit.²⁹ 176°).

The nmr (DMSO- d_6) consisted of τ 0–1.3 (br, 2 H, COOH), 8.15 (s, 2 H, CH), 8.68 (s, 3 H, CH₃), 8.85 (s, 3 H, CH₃).

Anal. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 53.34; H, 6.42.

cis-1,2-Dibenzoyl-3,3-dimethylcyclopropane. To a stirred solution of 3.75 g (23.7 mmol) of cis-3,3-dimethylcyclopropane-1,2-dicarboxylic acid in 150 ml of tetrahydrofuran was added 150 ml of freshly prepared 0.76 M phenyllithium in ether at 0°. The mixture was stirred 4 hr at room temperature and then poured into icewater and ether extracted; the extracts were washed with water,

- (28) V. Franzen, H. J. Schmidt, and C. Mertz, Chem. Ber., 94, 2942 (1961).
- (29) W. H. Perkin and J. F. Thorpe, J. Chem. Soc., 75, 48 (1899).

⁽²⁴⁾ The half-reacted MO's for the Hückel mechanism are merely the normalized sum and difference $(C^+ = (1/\sqrt{2})(C_a + C_b), C^- = (1/\sqrt{2})(C_a - C_b))$ of the MO's $(C_a = (\sqrt{2/N}) \cos (2k + 1)\pi r/N$ and $C_b = (\sqrt{2/N}) \sin (2k + 1)\pi r/N)$ as usually written; small terms are left out. In the case of the Möbius system, the half-reacted MO's again must conform to the geometry of the reacting system and rather than being the coefficients given by us previously, they are the sum and difference orbitals (*i.e.*, presently more useful linear combinations). Additionally, it is to be noted that the correlation diagrams are for the isoconjugate hydrocarbons; this is reasonable since the unshared pairs are not involved in the reaction and because the correlation diagram will be changed only quantitatively but not qualitatively by electronegative nitrogen atoms.

⁽²⁵⁾ All melting points were taken on a hot-stage apparatus calibrated with known compounds.

⁽²⁶⁾ This preparation has been reported without details by Corey and Jautelat.^{δ}

⁽²⁷⁾ H. Meerwein, Org. Syn., 46, 113 (1966).

dried over MgSO₄ and concentrated to *ca.* 20 ml. After 15 hr at 0°, 1.92 g of crude product crystallized. Recrystallization from ethanol gave 1.58 g (24%) of pure *cis*-1,2-dibenzoyl-3,3-dimethyl-cyclopropane: mp 142° (lit.³⁰ 136–137°); ir (CHCl₃) 3.1, 3.37, 5.98, 6.27, 6.32, 6.90, 7.10, 7.35, 8.05–8.35, 8.50, 8.98, 9.62, 9.98, 10.06, 10.51, 11.59, 14.30, 14.58, 15.10 μ ; nmr (CDCl₃) τ 1.9–2.2 (m, 4 H, Ar), 2.4–2.8 (m, 6 H, Ar), 7.22 (s, 2 H, CH), 8.50 (s, 3 H, CH₃), 8.60 (s, 3 H, CH₃).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 82.03; H, 6.51.

7,7-Dimethyl-2,5-diphenyl-3,4-diazanorcaradiene. A solution of 1.10 g (4.0 mmol) of *cis*-1,2-dibenzoyl-3,3-dimethylcyclopropane and 2.0 ml of hydrazine hydrate (99–100%) in 400 ml of methanol was stirred for 2 days. The yellow reaction mixture was diluted with 400 ml of water and *n*-hexane-ether extracted. The extracts were dried over MgSO₄ and concentrated affording 1.03 g (95%) of 7,7-dimethyl-2,5-diphenyl-3,4-diazanorcaradiene which was recrystallized from *n*-hexane giving yellow needles: mp 156–157°; ir (CCl₄) 3.25, 3.29, 3.37, 6.49, 6.68, 6.91, 7.19, 8.00, 8.49, 8.97, 9.30, 9.69, 9.86, 14.05, 14.50, 15.65 μ ; uv λ_{max}^{Euch} 321 nm (ϵ 15,800), 259 (12,000); uv unchanged in isopentane; nmr (CDCl₃) τ 1.8–2.2 (m, 4 H, Ar), 2.4–2.8 (m, 6 H, Ar), 7.56 (s, 2 H, CH), 8.38 (s, 3 H, CH₈), 9.32 (s, 3 H, CH₃).

Anal. Calcd for $C_{19}H_{18}N_2$: C, 83.18; H, 6.61; N, 10.21. Found: C, 83.02; H, 6.51; N, 10.10. Photolysis of 7,7-Dimethyl-2,5-diphenyl-3,4-diazanorcaradiene.

(a) With Corex Glass as Filter. A solution of 548 mg (2.0 mmol) of the norcardiene in 500 ml of methanol was photolyzed for 6 hr using a 450-W Hanovia medium-pressure mercury lamp with a 1-mm Corex glass filter. The reaction mixture was purged with nitrogen before and during the irradiation. Removal of the solvent gave a yellow oil which was chromatographed on a 70 \times 3 cm alumina column (80-200 mesh, Fisher) slurry packed in 2% ether in nhexane. Elution with n-hexane-ether (1:1) in 80-ml fractions gave: fractions 1-9, nil; 10-14, 89 mg of 4,4-dimethyl-3,7-diphenyl-1,2-diazabicyclo[3.2.0]hepta-2,6-diene; 15-17, 114 mg of a mixture of the bicyclic photoproduct and 4,4-dimethyl-3,7-diphenyl-1,2diazepine (ratio ca. 1:5); 18-25, 234 mg of the diazepine. Further elution with 300 ml of ethyl acetate afforded 47 mg of a mixture of starting material (ca. 30%), an unidentified product (ca. 20%) [nmr signals, without arom, at τ 4.04 (d, J = 2.4 Hz), 4.42 (d, J = 2.4 Hz), 8.55 (s), 8.58 (s) with the relative areas ca. 1:1:3:3], and further unidentified material. The mass balance of identified material was 447 mg (82%). Pure samples of the diazepine, mp 88°, and the bicycloheptadiene, mp 151°, were obtained by recrystallization of the fractions 10-14 and 18-25, respectively.

Spectral data of 4,4-dimethyl-3,7-diphenyl-1,2-diazabicyclo-[3.2.0]hepta-2,6-diene were: ir (CCl₄) 3.26, 3.37, 3.41, 3.48, 6.73, 6.86, 6.92, 7.23, 7.33, 7.60, 7.70, 7.91, 8.27, 8.51, 9.28, 9.44, 10.32, 11.00, 14.49 μ ; uv $\lambda_{\max}^{\text{EtoH}}$ 254 nm (ϵ 13,600); nmr (CCl₄) τ 2.2–2.55 (m, 4 H, Ar), 2.55–2.9 (m, 6 H, Ar), 4.00 (d, 1 H, vinyl, J = 1.2 Hz), 5.37 (d, 1 H, CH, J = 1.2 Hz), 8.50 (s, 3 H, CH₃), 8.55 (s, 3 H, CH₃). *Anal.* Calcd for C₁₉H₁₈N₂: C, 83.18; H, 6.61; N, 10.21. Found: C, 83.20; H, 6.64; N, 10.21.

Spectral data of 4,4-dimethyl-3,7-diphenyl-1,2-diazepine were: ir (CCl₄) 3.26, 3.29, 3.36, 3.40, 3.46, 6.22, 6.71, 6.81, 6.93, 7.10, 7.22, 7.85, 8.32, 9.40, 9.98, 10.10, 10.41, 11.15, 14.26, 14.43 μ ; uv λ_{max}^{EtoH} 284 nm (ϵ 13,500); nmr (CCl₄) τ 2.0–2.35 (m, 2 H, Ar), 2.4– 2.9 (m, 8 H, Ar), 3.76 (d, 1 H, A part of AB spectrum, J = 10.0 Hz), 4.01 (d, 1 H, B part of AB spectrum, J = 10.0 Hz), 4.01 (d, 1 H, B part of AB spectrum, J = 10.0 Hz), 4.01 (d, 1 H, B part of AB spectrum, J = 10.0 Hz), 4.01 (d, 1 H, B part of AB spectrum, J = 10.0 Hz), 4.01 (d, 1 H, B part of AB spectrum, J = 10.0 Hz), 8.78 and 9.10 (two broad overlapping peaks, half-width *ca*. 8 Hz, 6 H, CH₃); at 0° the CH₃ signals were singlets at τ 8.73 and 9.13; at 73° only one signal at τ 8.92 was observed; the other signals were not affected by the temperature change.

Anal. Calcd for $C_{19}H_{18}N_2$: C, 83.18; H, 6.61; N, 10.21 Found: C, 83.40; H, 6.70; N, 10.07.

(b) With Pyrex Glass as Filter. The solution of 700 mg (2.56 mmol) of diazanorcaradiene in 650 ml of methanol was photolyzed for 12 hr under the conditions described above, except a Pyrex glass filter was used. Chromatography of the irradiated material gave a 72-mg fraction of a 3:1 mixture of the diazepine and diazabicycloheptadiene, a 526-mg fraction of diazepine, and a 56-mg fraction of diazanorcaradiene. The mass balance of the three recovered compounds was 654 mg (93%) and the conversion to photoproducts was 598 mg (85%).

(c) Comparison of Product Distribution after Direct and Acetone Sensitized Photolysis. Solutions of 100 mg (0.365 mmol) of

diazanorcaradiene in 250 ml of methanol and 250 ml of acetone, respectively, were irradiated for 90 min with a Hanovia lamp using a Pyrex glass filter. Chromatography of the mixture photolyzed in methanol gave 2 mg (2%) of the diazabicycloheptadiene, 77 mg (77%) of the diazepine, and 16 mg (16%) of starting material. Chromatography of the mixture photolyzed in acetone gave 1 mg (1%) of the diazbicycloheptadiene, 23 mg (23%) of the diazepine, and 65 mg (65%) of starting material.

For the sensitized run, the percentage of light absorbed by acetone was estimated to be approximately 96% at 280 nm, 93% at 290 nm, 87% at 300 nm, 80% at 310 nm, 60% at 320 nm, and 30% at 340 nm.

4-Isopropyl-3,6-diphenylpyridazine. 7,7-Dimethyl-2,5-diphenyl-3,4-diazanorcaradiene (100 mg, 0.365 mmol) was heated in 8.0 ml of acetic acid and 4.0 ml of concentrated HCl for 1.5 hr at 100°. The reaction mixture was poured into water, neutralized with NaOH, ether extracted, dried over MgSO₄, and concentrated to afford 100 mg of a colorless oil which slowly crystallized. Recrystallization from *n*-hexane afforded 81 mg of pure 4-isopropyl-3,6-diphenylpyridazine: mp 110°; ir (CHCl₃) 3.27, 3.36, 3.48, 6.32, 6.95, 7.14, 9.80, 11.06, 14.45, 15.15 μ ; uv λ_{max}^{EtOH} 258 nm (ϵ 24,000); nmr (CDCl₃) τ 1.7-2.0 (m, 2 H, Ar), 2.21 (s, 1 H, Ar), 2.3-2.7 (m, 8 H, Ar), 6.77 (sep, 1 H, CH, J = 7.2 Hz), 8.74 (d, 6 H, CH₃, J = 7.2 Hz).

Anal. Calcd for $C_{19}H_{18}N_2$: C, 83.18; H, 6.61; N, 10.21. Found: C, 83.02; H, 6.69; N, 9.95.

5,6-Dihydro-4,4-dimethyl-3,7-diphenyl-1,2-diazepine. From Hydrogenation of Photoproduct. 4,4-Dimethyl-3,7-diphenyl-1,2-diazepine (150 mg, 0.55 mmol) in 50 ml of ethanol was hydrogenated at atmospheric pressure using 60 mg of 5% Pd/CaCO₃. After the uptake of 1 equiv of hydrogen (12.2 ml, 6 min), the catalyst was filtered and the solvent removed in vacuo affording a colorless oil which was chromatographed on a 30 \times 1 cm alumina column (80-200 mesh, Fisher) slurry packed in 1:1 ether-n-hexane. Elution with ether in 10-ml fractions gave: fractions 1 and 2, nil; 3, 15 mg of the tetrahydrodiazepine (vide infra); 4 and 5, 48 mg of a 1:1 mixture of the di- and tetrahydrodiazepines; 6-12, 77 mg of the dihydrodiazepine; 13-16, 8 mg of the diazepine. Recrystallization of fractions 6-12 from n-pentane gave pure dihydrodiazepine; the crystals showed no sharp melting point but melted partially at 86° and were completely molten at 106°. On cooling and remelting the material gave a mp of 96-106° with no change in the nmr spectrum.

The spectral data were: ir (CCl₄) 3.25, 3.30, 3.36, 3.41, 6.42, 6.70, 6.92, 7.19, 7.38, 7.68, 8.48, 9.50, 9.96, 10.31, 11.04, 14.25, 14.49, 15.06 μ ; uv $\lambda_{max}^{\rm leoH}$ 286 nm (ϵ 11,730), 244 (13,680); nmr (CCl₄) τ 2.1–2.9 (m, 10 H, Ar), 7.10–7.45 and 7.55–7.90 (AA'BB', 4 H, CH₂), 8.90 (s, 6 H, CH₂).

Anal. Calcd for $C_{19}H_{20}N_2$: C, 82.57; H, 7.29; N, 10.14. Found: C, 82.49; H, 7.27; N, 10.22.

1,5,6,7-Tetrahydro-4,4-dimethyl-3,7-diphenyl-1,2-diazepine. An 80-mg (0.29 mmol) portion of 4,4-dimethyl-3,7-diphenyl-1,2-diazepine in 50 ml of ethanol was hydrogenated at atmospheric pressure using 90 mg of 5% Pd/CaCO₂. After the uptake of 2 equiv of hydrogen (13.1 ml, 15 min), the catalyst was filtered and the solvent removed *in vacuo* affording a pale yellow oil which was chromatographed on a 30 × 1 cm alumina column (80–200 mesh, Fisher) slurry packed in ether-*n*-hexane (1:1). Elution with ether gave a colorless oil which crystallized on standing. Recrystallization from *n*-pentane afforded 69 mg (85%) of pure tetrahydrodiazepine: mp 64°; ir (CCl₄) 2.99, 3.26, 3.29, 3.40, 3.48, 3.51, 6.26, 6.70, 6.90, 7.21, 7.35, 7.57, 8.99, 9.45 (br), 9.75, 9.85, 10.00, 10.25, 10.81, 11.70, 14.34, 14.89 μ ; uv λ_{max}^{EtOH} 264 nm (ϵ 3910); nmr (CCl₄) τ 2.5–3.0 (m, 10 H, Ar), 4.60 (br, 1 H, NH), 6.21 (approx d of d, 1 H, J = 10 Hz, J = 4 Hz, ArCH₃).

Anal. Calcd for $C_{10}H_{22}N_{c}$: C, 81.97; H, 7.97; N, 10.06. Found: C, 82.05; H, 7.98; N, 10.03.

2,2-Dimethyl-1,5-diphenyl-1,5-pentanedione. To a solution of 8.00 g (50.0 mmol) of 2,2-dimethylglutaric acid,³¹ mp 84-85°, in 500 ml of tetrahydrofuran was added 240 ml of a freshly prepared 1.25 M solution of phenyllithium in ether, at 0° under nitrogen. The mixture was stirred 15 hr and refluxed 3 hr and was then poured into ice-water. Ether extraction gave a yellow brown oil which was chromatographed on a 60×2.5 cm silica gel (60-200 mesh) column slurry-packed in *n*-hexane. Elution with 5% ether in *n*-hexane gave 4.60 g (33%) of 2,2-dimethyl-1,5-diphenyl-1,5-pentanedione as a colorless oil: ir (CCl₄) 3.26, 3.36, 5.92, 5.98, 6.28,

⁽³⁰⁾ Paquette and Leichter⁶ obtained this compound from another route.

⁽³¹⁾ H. Rupe and C. Liechtenhan, Chem. Ber., 41, 1278 (1908).

6.91, 7.20, 7.33, 7.77, 7.95, 8.25, 8.50, 10.00, 10.44, 14.05, 14.55 μ ; nmr (CCl₄) τ 2.0–2.45 (m, 4 H, Ar), 2.45–2.9 (m, 6 H, Ar), 7.0–7.4 and 7.6–8.0 (AA'BB', 4 H, CH₂), 8.65 (s, 6 H, CH₃).

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.38; H, 7.24.

Independent Synthesis of 5,6-Dihydro-4,4-dimethyl-3,7-diphenyl-1.2-diazepine. To a solution of 700 mg (2.5 mmol) of 2,2-dimethyl-1,5-diphenyl-1,5-pentadione in 1400 ml of ethanol and 150 ml of acetic acid, 1.1 ml of hydrazine hydrate (99-100%) was added. After 11 hr the reaction mixture was diluted with 500 ml of water and n-hexane extracted. The extracts were washed with water, dried over MgSO4, and concentrated affording 262 mg of a yellow oil which was dissolved in 5 ml of ether. After the mixture stood at 0° for 4 hr, 37 mg of a crystalline product³² was isolated. The filtrate was concentrated and the residue chromatographed on a 30×1 cm alumina column (80-200 mesh, Fisher) slurry packed on ether-*n*-hexane (1:1). Elution with 20% hexane in ether in 20-ml fractions gave: fraction 1, nil; 2-4, 74 mg of nonidentified products; 5-13, 92 mg (13%) of the 5,6-dihydrodiazepine; further elution with 120 ml of ether-ethyl acetate (1:1) gave 49 mg of nonidentified products.

Recrystallization of fractions 5–13 from *n*-pentane afforded a crystalline compound which was identical with the dihydro photoproduct (*vide supra*).

Hydrolysis of 5,6-Dihydro-4,4-dimethyl-3,7-diphenyl-1,2-diazepine. A sample of the 5,6-dihydrodiazepine (40 mg), derived from photoproduct, was heated in 8.0 ml of 5 N HCl at $80-90^{\circ}$ for 40 min. To the clear solution 10 ml of water was added and the mixture then *n*-hexane extracted, affording after the usual work-up 38 mg of a colorless oil which was identical with the 2,2-dimethyl-1,5-diphenyl-1,5-pentadione obtained by the direct synthesis.

The same result was obtained on hydrolysis of the independently synthesized 5,6-dihydro-4,4-dimethyl-3,7-diphenyl-1,2-diazepine.

Quantum Yields for the Rearrangements of 7,7-Dimethyl-2,5diphenyl-3,4-diazanorcaradiene and 4,4-Dimethyl-3,7-diphenyl-1,2diazepine. The quantum yield irradiations were performed on the Black Box apparatus described previously.¹⁰ Light output was monitored by ferrioxalate actinometry¹¹ and the light absorbed in the reaction cell was determined by the splitting ratio technique previously described.¹⁰ The bandpass was controlled by one of the filter solutions: filter A, 0.50 *M* NiSO₄· 6H₂O in 5% H₂SO₄, 0.44 *M* CoSO₄· 7H₂O in 5% of H₂SO₄, 1.33 × 10⁻² *M* SnCl₂· 2H₂O in 10% HCl; transmission, 0% at 290 nm, 43% at 322 nm, 0% at 370 nm; filter B, 0.5 *M* CuSO₄ in 5% H₂SO₄, 0.35 *M* CoSO₄· 7H₂O in 5% H₂SO₄, 0.15 *M* NaVO₃ in 0.1 *M* NaOH; transmission, 0% at 375 nm, 32% at 403 nm, 0% at 455 nm; filter C, 1.0 *M* NiSO₄· $6H_2O$ in 5% H_2SO_4 , 1.0 *M* CoSO₄·7 H_2O , 5 × 10⁻⁴ *M* BiCl₈ in in 10% HCl; transmission, 0% at 250 nm, 30% at 283 nm, 0% at 305 nm.

The quantum yields for product formation were determined by vpc analysis using a 1/8 in. \times 50 in. 2% SE 54 on Chromosorb W (60-80 mesh) column at 143° and 20 ml/min flow rate. Triphenylethylene was used as an internal standard. Retention times were: triphenylethylene, 5 min; 4,4-dimethyl-3,7-diphenyl-1,2-diazabicyclo[3.2.0]hepta-2,6-diene, 11 min; 4,4-dimethyl-3,7-diphenyl-1,2-diazepine, 17 min. The flame ionization detector of the Varian Aerograph Model 2100 gas chromatograph was calibrated for the relative response of the photoproducts and the standard. Before the photolyzed mixture of the norcaradiene was analyzed, the starting material was separated by chromatography on an alumina column (80-200 mesh, Fisher) slurry packed in *n*-hexane-ether (2:1). Elution with ether gave the diazepine which after concentration was analyzed as described; the norcaradiene was obtained by further elution with ethyl acetate.

Summary of Quantum Yield Results. Data are listed as follows: filter, solvent and volume, starting material (mmol), sensitizer (if any), light absorbed, photoproducts (mmol), quantum yield, per cent conversion.

Run I-1: filter A, 750 ml of methanol, diazanorcaradiene (0.948 mmol), 11.95 mEinsteins, diazepine (0.0244 mmol), $\Phi = 0.00204$, 2.6%.

Run I-2: filter A, 750 ml of methanol, diazanorcaradiene (0.896 mmol), 14.98 mEinsteins, diazepine (0.0317 mmol), $\Phi = 0.00212$, 3.5%.

Run II-1: filter B, 750 ml of methanol, diazanorcaradiene (0.2 mmol), Michler's ketone (2.0 mmol), 23.63 mEinsteins, diazepine (0.0021 mmol), $\Phi = 0.000088$, 1.05%.

Run II-2: filter B, 750 ml of methanol, diazanorcaradiene (0.18 mmcl), Michler's ketone (1.8 mmol), 20.08 mEinsteins, diazepine (0.0016 mmol), $\Phi = 0.000079, 0.9\%$.

Run III-1: filter C, 750 ml of methanol, diazepine (0.111 mmol), 3.81 mEinsteins, diazabicycloheptadiene (0.00989 mmol), $\Phi = 0.00259, 8.9\%$.

Run III-2: filter C, 750 ml of methanol, diazepine (0.0518 mmol), 0.49 mEinstein, diazabicycloheptadiene (0.00131 mmol), $\Phi = 0.00267, 2.5\%$.

Pyrolysis of 7,7-Dimethyl-2,5-diphenyl-3,4-diazanorcaradiene (5), 4,4-Dimethyl-3,7-diphenyl-1,2-diazepine (9), and 4,4-Dimethyl-3,7diphenyl-1,2-diazabicyclo[3.2.0]hepta-2,6-diene (13). The pyrolyses of 5, 9, and 13 were carried out in diphenyl ether at 195° and were monitored by nmr spectroscopy. The approximate product distribution after 140 min was as follows: starting material 5, 45% of 5, 55% of 14; starting material 9, 41% of 5, 32% of 9, 27% of 14; starting material 13, 5% of 5, 65% of 9, 30% of 13.

Acknowledgment. W. E. acknowledges a Deutsche Forschungsgemeinschaft fellowship with pleasure. Also, support of this research by National Institutes of Health Grant GM-07487 and by the U. S. Army Research Office (Durham) is gratefully acknowledged.

⁽³²⁾ This compound, mp 250–252°, was a 2:2 condensation product of the diketone and hydrazine; both mass spectrum and elemental analysis correspond to the formula $C_{38}H_{40}N_{4.}$ The nmr data (CDCl₃) were: 2.5–3.0 (m, 20 H, Ar), 6.7–7.1 and 7.8–8.3 (AA'BB' spectrum, 8 H, CH₂), 8.76 (s, 12 H, CH₃). The dimer can be obtained in almost quantitative yield if the reaction of 2,2-dimethyl-1,5-diphenyl-1,5pentanedione with hydrazine is carried out in acetic acid.