β-(2,4,6-Cycloheptatrien-1-yl)ethylcarbene. The Synthesis of 9-Substituted Bicyclo[4.2.1]nona-2,4,7-trienes and 9-Substituted Barbaralanes[1]

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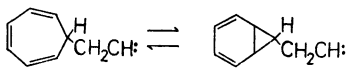
The thermal decomposition of sodium salt of (2,4,6-cycloheptatrien-1-yl)acetaldehydes tosylhydrazone (**4**, **6**, and **8**) afforded 9-substituted bicyclo[4.2.1]nona-2,4,7-triene (**9**, **11**, and **14**) and 9-substituted barbaralane (**10**, **12**, and **15**). In the case of **8**, products containing two nitrogen atoms (**17** and **18**) were isolated. The structure and the photochemical reaction of **17** provided strong support for the intermediacy of the tetracyclo[4.3.0.$0^{2,9}$.$0^{5,7}$]-nona-3-ene (**37**) derivative for the formation of the bicyclo[4.2.1]nona-2,4,7-triene derivatives. The difference in energy surface between C_9H_{10} and $C_{10}H_{10}$ hydrocarbons was discussed.

The intramolecular addition of carbene to an isolated double bond has been a useful tool in synthesizing strained compounds. Recently, the application of this reaction to compounds with conjugated double bonds has received considerable attention. However, these reactions tend to afford complicated products, because an originally-formed strained intermediate easily rearranges into more stable compounds under these reaction conditions. For example Jones[2] and Masamune[3] investigated the thermal and photochemical decomposition of bicyclo[6.1.0]nona-2,4,6-triene-9-carboxaldehyde tosylhydrazone and reported the formation of seven and six products respectively. Similarly, the thermal decomposition of bicyclo[5.1.0]octa-2,4-diene-8-carboxaldehyde tosylhydrazone afforded four products.[2,4] We chose to study the reaction of β-(2,4,6-cycloheptatrien-1-yl)ethylcarbene (**1**) in order to see how the terminal carbene reacts intramoleculary to a conjugated triene or to a conjugated diene of the norcaradiene valence isomer (**2**). It also seemed of

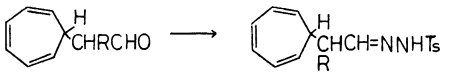


(**1**) (**2**)

interest to investigate the thermal stability of the expected highly strained intermediates.

Results

When sodium salt of (2,4,6-cycloheptatrien-1-yl)-acetaldehyde tosylhydrazone (**4**) was heated in dry dioxane at 90—95°C, two kinds of C_9H_{10} hydrocarbon were obtained. The major liquid product (yield=16%) (M=118) was identified as bicyclo[4.2.1]nona-2,4,7-triene (**9**) by a comparison of its NMR and IR spectra with those of an authentic sample.[5] The catalytic reduction of **9** in ether afforded a known bicyclo[4.2.1]nonane (mp 95°C).[6]



(**3**): R=H (**4**): R=H
(**5**): R=CH_3 (**6**): R=CH_3
(**7**): R=Ph (**8**): R=Ph

The minor crystalline compound (**10**; yield=4%) shows a very characteristic NMR spectrum containing four symmetrical groups of peaks with relative intensities of 2:4:2:2 (Table 1). This spectrum is in good agreement with that of tricyclo[3.3.1.$0^{2,8}$]nona-3,6-diene (barbaralane).[7,8] A comparison of the NMR data with those of known bridged homocycloheptatrienes shown in Table 1 indicate that H_a-absorption tends to shift to a lower field, while H_b and H_c tend to shift to a higher field, with an increase in the number of the bridged methylene. One of the reasons for this phenomenon may be a change in the anisotropic

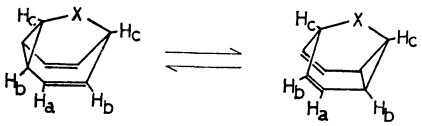


TABLE 1. NMR SPECTRA OF BARBARALANE DERIVATIVES (τ).

	H_a	H_b	H_c	X	
Semibullvalene[10]	4.92	5.83	7.03		
10	4.45	6.10	7.72	$-(CH_2)-$	8.98
Dihydrobullvalene[11]	4.37	6.32	8.1	$-(CH_2)_2-$	8.1
12	4.46	6.13	7.98	$C\underline{H}CH_3$	8.78
15	4.34	6.00	7.58	$C\underline{H}Ph$	7.58

1) Preliminary reported: H. Tsuruta, K. Kurabayashi, and T. Mukai, *Tetrahedron Lett.*, **1967**, 3775; *J. Amer. Chem. Soc.*, **90**, 7167 (1968). Organic Thermal Reaction, XIV. Part XIII: H. Tsuruta, T. Sugiyama, and T. Mukai, *Chem. Lett.*, **1972**, 185.

2) a) M. Jones, Jr. and L. T. Scott, *J. Amer. Chem. Soc.*, **89**, 150 (1967). b) M. Jones, Jr., S. D. Reich, L. T. Scott, and L. E. Sullivan, *Angew. Chem. Internat. Edit.*, **7**, 644 (1968). c) M. Jones, Jr., S. D. Reich, and L. T. Scott, *J. Amer. Chem. Soc.*, **92**, 3118 (1970).

3) a) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *ibid.*, **89**, 4804 (1967). b) S. Masamune, *Angew. Chem. Internat. Edit.*, **7**, 645 (1968).

4) M. Jones, Jr. and S. D. Reich, *J. Amer. Chem. Soc.*, **89**, 3935 (1967).

5) L. G. Cannell, *Tetrahedron Lett.*, **1967**, 5967. We thank Dr. Cannell for providing us a copy of the IR spectrum of **9**.

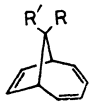
6) G. Sartori, U. Turba, A. Varvassori, and M. Riva, *ibid.*, **1966**, 4777.

7) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders. *Tetrahedron*, **23**, 3943 (1967).

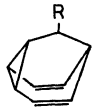
8) U. Biethan, H. Klusacek, and H. Musso, *Angew. Chem. Internat. Edit.*, **6**, 176 (1967); H. Musso, *ibid.*, **7**, 306 (1968).

effect[9] of the three-membered ring.

The heating of the sodium salt of α-(2,4,6-cycloheptatriene-1-yl)propionaldehyde tosylhydrazone (**6**) in dry dioxane at 75°C afforded two hydrocarbons. The major oil (yield=22%) was shown to be a mixture of **11a** and **11b** in a 2: 1 ratio, based on the area of the methylproton signal at τ 9.10 and 9.33 and of isolated olefinic-proton peaks at 4.85 and 4.97. Although the separation of the mixture was difficult, a reduced product which was obtained after the uptake of three equivalents of hydrogen could be separated into two sorts of $C_{10}H_{18}$. However, it remains uncertain which is the predominant product between **11a** and **11b**. The structure of the minor component (yield=5%) is consistent with 9-methylbarbaralane (**12**) judging from the NMR spectrum (Table 1).

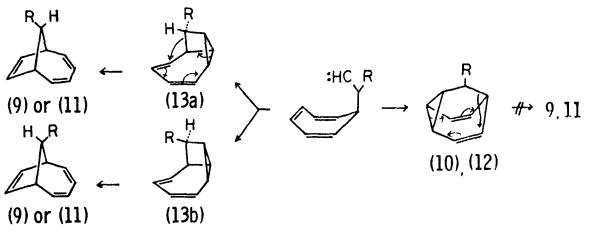


(**9**): R=R′=H
(**11a**): R=H, R′=CH_3
(**11b**): R=CH_3, R′=H



(**10**): R=H
(**12**): R=CH_3

The formation of barbaralane derivatives can be explained in terms of the intramolecular addition of the carbene to the C_4–C_5 bond in the cycloheptatriene nucleus, whereas that of bicyclo[4.2.1]nona-2,4,7-triene is rather surprising. One possible path is as follows. A highly-strained intermediate (**13**), formed by the addition of the carbene to the C_2–C_3 olefinic bond, rearranges to **9** and/or **11** by way of bond cleavage and migration, as is depicted in Scheme 1. As an alternative path, the rearrangement in barbaralane derivatives (**10** and **12**) shown by the arrow is pertinent, but the control experiment eliminated this possibility. The attempted thermolysis of barbaralane **10** under the same conditions as in the decomposition of **4** resulted in the complete recovery of **10**. Assuming the strained compound **13** to be an intermediate, the formation of *syn*- and *anti*-9-methyl bicyclo[4.2.1]nona-2,4,7-triene is understandable, because a small substituent such as hydrogen or methyl will not cause any significant difference in nonbonding interaction between **13a** and **13b**. However, when the substituent, R, is larger than hydrogen or methyl, the ratio of *syn*- and *anti*-**11** will change considerably because the nonbonding



Scheme 1.

interaction of R with the rest of the molecule is heavier in **13b** than in **13a**. The phenyl derivative (R=Ph) was chosen for study next in order to confirm this point.

The thermolysis of the sodium salt of α-phenyl-α-(2,4,6-cycloheptatrien-1-yl)acetaldehyde tosylhydrazone (**8**) was carried out similarly; a three hydrocarbons (**14**, **15**, and **16**) in addition to two nitrogen-containing products (**17** and **18**) were thus formed. The structural elucidation of the main hydrocarbon (**14**, yield=33%) is based on a comparison of the spectral data with that of **9**. The geometry of the phenyl group at the C_9-position was determined in the following way. In the NMR spectrum of **14**, the signal ascribed to C_9-hydrogen appears as a singlet at τ 7.18, suggesting that the bond angle between the bridgehead proton and the C_9-proton is nearly 90°. An inspection of the model of **14** shows that the bond angles between *syn*-H_9 and H_1 and between *anti*-H_9 and H_1 are 90 and 30° respectively. The value calculated on the basis of the Karplus equation ($J_{syn\text{-}H_9,H_1}\approx 0$, $J_{anti\text{-}H_9,H_1}=6.0$ Hz) is in good agreement with the observed value for **14**, in which the phenyl group is located at the *anti*-position relative to the conjugated diene. Contrary to the case of methyl derivatives, it should be noted that only one stereoisomer **14** was selectively formed; this is in accord with the mechanistic discussion described in Scheme 1.

The NMR spectrum of (**15**, yield=3%) involves three groups of peaks, as is shown in Table 1, in addition to the peaks due to phenyl protons. Thus, compound **15** was identified as 9-phenylbarbaralane. The methin proton signal at the C_9-position bearing the phenyl group shifts downfield to overlap with the two protons at C_1 and C_5. The third crystalline hydrocarbon (**16**, yield=2%) was an aromatic compound; its structure was established to be 2-phenylindene by a comparison of its spectra and melting point with those of an authentic specimen.[12]

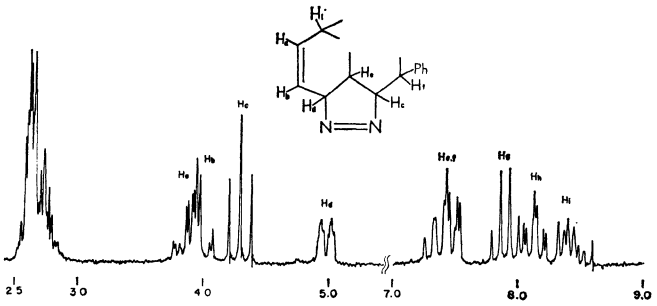


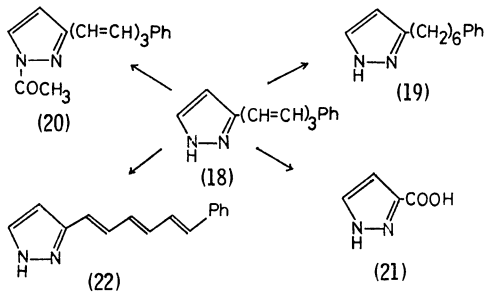
Fig. 1. NMR Spectrum of **17** in $CDCl_3$ (100 MHz).

Compound **17**, with a formula of $C_{15}H_{14}N_2$ (M=222), has no bands ascribable to NH and NH_2 groups in the IR spectrum, but the absorption band at 1534 cm^{-1} as well as the UV maximum (340 nm, ε 240) suggested the presence of an azo function. The NMR spectrum exhibits complex peaks (Fig. 1). All nine protons except the phenyl protons are in different circumstances; each proton is named alphabetically from downfield to upfield. It seems reasonable to assign H_c and H_d to

9) K. Tori and K. Kitahonoki, *J. Amer. Chem. Soc.*, **87**, 386 (1965).
10) H. E. Zimmerman and G. L. Grunewald, *ibid.*, **88**, 183 (1966).
11) R. Merényi, J. F. M. Oth, and G. Schröder, *Chem. Ber.*, **97**, 3150 (1964).
12) N. Campbell and E. Ciganek, *J. Chem. Soc.*, **1956**, 3834.

the protons adjacent to an azo group. Generally, under these circumstamces the methin proton appears in a fairly low field.[13-15] A decoupling experiment clarified the relationship between all the protons and led to the partial structure shown in Fig. 1. Irradiation on H_d affected the signals of three protons, H_a, H_b, and H_e. The signals due to H_a and H_b changed into a quartet (J=10.5, 4.5 Hz) and a doublet (J=10.5 Hz) respectively, while H_e, overlapped with H_f, turned into an apparent quartet (J=8.7, 7.0 Hz). Synchronous irradiation on both H_c and H_d made H_e a doublet (J=7.0 Hz), and H_f an apparent split doublet (J=2.0 Hz). Additional simultaneous irradiation on both H_e and H_f altered H_c to a sharp singlet and H_d to a finely-split singlet. Finally, H_i changed into a triplet upon irradiation on H_a. Three opened bonds of the partial structure in Fig. 1 are joined to build a three-membered ring and 7-phenyl-9,10-diazatetracyclo-[6.2.1.$0^{4,6}$.$0^{5,11}$]undeca-2,9-diene is assigned for **17**. The coupling constant (4.5 Hz) between H_a and H_i seems compatible with the reported values which were observed between a three-membered ring proton and an olefinic proton in bicyclo[4.2.1]heptene[16] and tricyclo[2.2.2.$0^{2,7}$]octene.[17] The chemical shifts and coupling constants of **17** are summarized in the Experimental section. Additional support for the structure was obtained from the photochemical behavior of **17** and from a mechanistic consideration of the reaction path which will be discussed later.

A nitrogen-containing product (**18**, yield=25%) (M=222) has the same formula as **17**. The NMR spectrum shows a very complicated multiplet between τ 2.4 and 3.9 containing two sets of doublets at 2.46 and 3.59 (J=2.0 Hz). The catalytic reduction of **18** over 10% Pd-C in ethanol afforded an oily product **19** after the uptake of three equivalents of hydrogen. In the NMR spectrum of **19**, the AB doublet still remains at τ 2.63 and 4.07 (J=2.0 Hz), whereas the complex signals of olefinic protons disappear and instead new two signals due to methylenic protons appear at τ 7.42 (4H, broad quartet) and 8.61 (multiplet, 8H). The signals at τ 7.42 can be ascribed to the methylene protons adjacent to the aromatic ring. The IR spectrum of **18** showed a strong hydrogen-bonded NH absorption at 3175—2883 cm^{-1}. In the NMR spectrum of monoacetate **20**, the AB doublet was observed at τ 3.53 and 1.83 (J=2.9 Hz), suggesting that the original peaks at τ 2.46 in **18** suffered from shielding by the acetyl group and shifted downfield such as to τ 1.83, whereas the other peaks remained unchanged in nearly the same field.[18] Another piece of evidence that **18** is a 3-substituted pyrazole derivative was given by oxidation with potassium permanganate, in which case pyrazole-3-carboxylic acid (**21**) was obtained.[19] When a solution of **18** in benzene containing iodine was heated under reflux, an isomer (**22**) was formed. In the IR spectrum of **22**, a strong peak appeared at 1005 cm^{-1} (*trans*-CH=CH), while the originally-observed peak at 746 cm^{-1} (*cis*-CH=CH) disappeared. Furthermore, the UV spectrum of **22** is very similar to that of *trans*, *trans*, *trans*-1,6-diphenyl-1,3,5-hexatriene,[20] suggesting the presence of the same triene system. On the basis of these data, compound **18** was identified as 1-phenyl-6-(3-pyrazolyl)-1,3,5-hexatriene, in which at least one double bond has a *cis*-configuration.



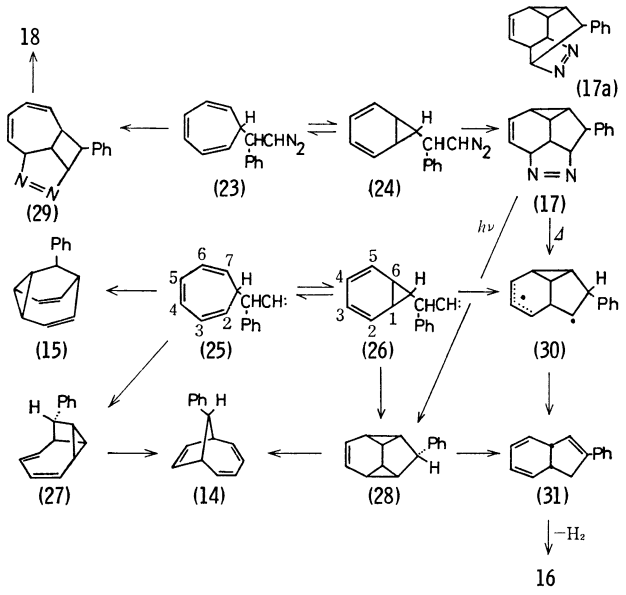
Discussion

A possible mechanistic pathway for the formation of all the products from the thermal decomposition of **8** is depicted in Scheme 2. Of the two nitrogen-containing products, the tetracyclic compound **17** is obviously produced from the norcaradiene valence isomer **24** by the 1,3-dipolar addition of a diazomethane counterpart to one of the double bonds. Another possible structure **17a** was ruled out on the basis of the decoupling experiment in the NMR spectrum. The formation of the pyrazole derivative **18** can be explained by assuming an intermediate of a tetracyclic azo compound **29**, which is derived by the 1,3-dipolar addition of a diazomethane counterpart to the C_2–C_3 bond in **23**, followed by the cleavage of the four-membered ring of **29** and by subsequent aromatization. The driving force for this reaction may be ascribed to release from the strain as well as to the stabilization arising from the formation of the full conjugated compound linked by two aromatic groups.

On the other hand, two pathways are possible for the formation of **14**. The divalent carbon in **25** may be added to the C_2–C_3 bond, giving a highly-strained intermediate **27**, which may then be immediately relieved from the strain in the manner described in Scheme 1 to afford **14**. An alternative route is that the carbene center in the norcaradiene isomer **26** is added to the C_2–C_3 bond[21,22] to form a tetracyclic intermediate **28**, which then easily gives rise to **14** by

13) R. M. Moriarty, *J. Org. Chem.*, **28**, 2385 (1963).
14) M. Schwarz, A. Besold, and E. R. Nelson, *ibid.*, **30**, 2425 (1965).
15) S. G. Cohen and R. Zand, *J. Amer. Chem. Soc.*, **84**, 586 (1962).
16) J. J. Sims, *ibid.*, **87**, 3511 (1965).
17) C. F. Huebner, E. Donoghue, L. Dorfman, F. A. Stuber, N. Danieli, and E. Wenkert, *Tetrahedron Lett.*, **1966**, 1185.
18) H. Dorn and H. Dilcher, *Ann. Chem.*, **707**, 141 (1967).
19) H. v. Pechmann and E. Burkard, *Chem. Ber.*, **33**, 3595 (1900).
20) K. Lunde and L. Zechmeister, *J. Amer. Chem. Soc.*, **76**. 2308 (1954).
21) M. J. Goldstein and B. G. Odell, *ibid.*, **89**, 6356 (1967).
22) J. Daub and P. von R. Schleyer, *Angew. Chem. Internat. Edit.*, **7**, 468 (1968).

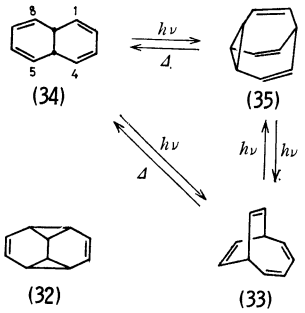
the retro-Diels-Alder reaction.[23,24] In both routes the stereochemistry of the phenyl group in **14** can be satisfactorily explained by assuming that the phenyl group is on the less-crowded side to avoid a nonbonding repulsion. The fact that **14** was produced in a 43% yield by the irradiation of **17** with Pyrex-filtered light strongly supports the latter pathway (**26**→**28**→**14**).



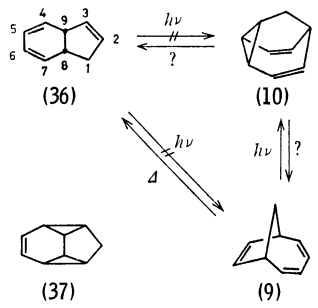
Scheme 2.

At this stage, it is of interest to compare the energy surface of C_9H_{10} hydrocarbons with that of $C_{10}H_{10}$ hydrocarbons. A part of the chemistry of the $C_{10}H_{10}$ hydrocarbons,[25] which have been extensively studied, is displayed in Scheme 3. The corresponding chemistry of the C_9H_{10} hydrocarbons, which are derived from the $C_{10}H_{10}$ hydrocarbons in Scheme 3 by the replacement of the etheno group with a methylene bridge, is depicted in Scheme 4.

A few years ago, Cannell[5] studied the photoreaction of **9** in acetone, in which case a $(2+2)\pi$ cyclization of the conjugated diene moiety took place to give *exo*-(**38**) and *endo*-tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene (**39**). The repetition of the photolysis of **9** using a low-pressure



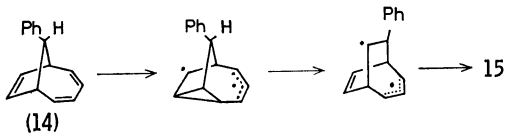
Scheme 3.



Scheme 4.

lamp without any sensitizer in dioxane resulted in the formation of four kinds of photoproducts and the recovery of a small amount of **9**. Although we confirmed two of the products to be **38** and **39** on the basis of their reported NMR spectra,[5] neither vpc nor NMR peaks due to **10** could be detected in the photoproducts.

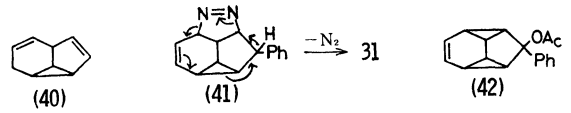
The sensitized photoreaction of this system provided different results. When the photolysis of **14** was carried out in benzene using benzophenone as a sensitizer, **15** was formed as a single product. This transformation is in sharp contrast to the direct irradiation described above and may be characterized in terms of a di-π-methane cyclization, as is shown below. This reaction corresponds to the photoreaction of bicyclo[4.2.2]deca-2,4,7,9-tetraene (**33**) to bullvalene (**35**), as is shown in Scheme 3.[26]



The thermal transformation of **9** to *cis*-8,9-dihydroindene (**36**) was recently found by Berson *et al.*[27] This is formally similar to the thermal conversion of **33** into 9,10-dihydronaphtalene (**34**), but the mechanism is different. The intermediate from **33** to **34** was proved to be tetracyclo[4.4.2.$0^{2,10}$.$0^{5,7}$]deca-3,8-diene (**32**) on the basis of a deuterium-labeling experiment,[28] while the conversion of **9** into **36** proceeds through an unsymmetric tricyclic intermediate (**40**). If a step-by-step mechanism is involved in the transformation of **33** to **34**, the cleavage of a three-memberd ring of **32** will afford a stable diallylradical, which will then force the subsequent fission of another three-membered ring and will be stabilized by the formation of two sets of conjugated diene **34**. On the other hand, the tetracyclic compound **28**, which is formed *via* the intramolecular Diels-Alder cyclization of **14**, can not afford such a stable radical; instead, it may give a rather unstable homoallyl or 1,3-diradical **30**. Moreover, it must be accompanied by a hydrogen shift to form a *cis*-8,9-dihydroindene derivative. Thus, **28**, even if formed, tends to return to **14** or, at a high temperatures,

23) S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *J. Amer. Chem. Soc.*, **90**, 5286 (1968).
24) L. A. Paquette, R. E. Wingard, Jr., and R. H. Meisinger, *ibid.*, **93**, 1047 (1971).
25) T. L. Burkoth and E. E. van Tamelen, "Nonbenzenoid Aromatics" Ed. by J. P. Snyder, Academic Press (1969), Vol. 1, p. 115.
26) S. Masamune, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *J. Amer. Chem. Soc.*, **90**, 2727 (1968).
27) J. A. Berson, R. R. Boettcher, and J. J. Vollmer, *ibid.*, **93**, 1540 (1971).
28) a) M. Jones, Jr. and G. Fairless, *Tetrahedron Lett.*, **1968**, 4881. b) R. T. Seidner, N. Nakatsuka, and S. Masamune, *Canad. J. Chem.*, **48**, 187 (1970).

to follow the homodienyl hydrogen migration path to give dihydroindene (**31**).[27] The formation of **31** through a diradical, followed by a 1,2-hydrogen migration, or through a concerted 1,9-hydrogen shift ($_{\pi}2_s+_{\sigma}2_s+_{\sigma}2_s+_{\sigma}2_s+_{\sigma}2_s$), as is shown in **41**, was illustrated in the thermolysis of the diazo compound **17**. The refluxing of **17** in diglyme in air gave **16** in a 49% yield. The yield of **16**, however, dropped to 5% when the thermolysis was carried out in a nitrogen atmosphere, and instead 2-phenyl-8,9-dihydroindene **31** (mp 56—58°C) was formed in a 51% yield. The structure identity of **31** was based on the NMR spectrum, consisting of four groups of peaks at τ 2.72 (m, 5H), 4.00 (m, 1H), 4.36 (m, 4H), and 6.0—7.7 (m, 4H), and on its rapid interconversion into 2-phenylindene when left standing in air. Because of the existence of a thermally-labile diazo group, the heating of **17** easily releases nitrogen to give an energy-



(40) (41) (42)

rich diradical intermediate **30**, which then affords **31** by 1,2-hydrogen migration (Scheme 2). The possibility that **31** was formed by the thermal rearrangement of initially-formed nonatriene **14**[27] could be precluded by control experiments. The nonatriene **14** was very stable and was recovered not only under the pyrolytic condition of **17** in refluxing diglyme, with or without an oxidizing reagent, but also upon pyrolysis in a flow system by passing it through a column containing glass helics preheated at 400°C. However, when **28** has a leaving group such as the acetyl group at the C_8-position such as **42**, the thermal conversion into 2-phenylindene becomes facile.[29]

The irradiation of **36** was performed by Vogel *et al.*[30] and by Schwartz,[31] in each case, *trans*-8,9-dihydroindene was obtained as the main product. This *trans*-formation was explained in terms of a disrotatory ring closure of the intermediate, *cis, cis, trans, cis*- or *cis, cis, cis, trans*-cyclononatetraene, formed from the dihydroindene **36** by a conrotatory ring opening. Neither **9** nor **10** was found in the photolysate. The bond formation between C_1 and C_8 and between C_4 and C_5 in **34** leads to tetracyclodecadiene **32** and takes place without a hydrogen shift (Scheme 3), whereas the hydrogen shift from the methylene group is essential to derive a tetracyclic intermediate such as **37** from **36** (Scheme 4). Therefore, in the photoreaction of **36**, a fission at the C_8–C_9 bond or $(2+2)\pi$ cycloaddition in the diene moiety is preferable to the cyclization leading to **37**. However, if *cis*-8,9-dihydroindene is highly substituted and if the ring opening to the corresponding cyclononatetraene causes steric hindrance, the bonding not only between C_3 and C_4, but also between other positions, becomes possible, depending on the nature of the sbustituents.[32] In these cases, no barbaralane or bicyclo[4.2.1]nona-2,4,7-triene derivatives were characterized. Although the photochemical and thermal reaction of **10** have not been well documented, Daub and Schleyer reported the acetone-sensitized conversion of tricyclo[3.2.2.$0^{2,4}$]nona-6,8-diene into **10**[22] and described that **10** is not stable under photolytic conditions.

In any event, these results add some information on the difference between the energy surfaces of C_9H_{10} and $C_{10}H_{10}$ hydrocarbons. Studies of the thermal and photochemical behavior of C_9H_{10} groups, especially that of barbaralane, are now in progress in this laboratory.

Experimental

All the melting points and boiling points are uncorrected. Vpc was carried out on Hitachi K-53 (analytical), Hitachi KGL-2B, and Willkins (A-700) (preparative) instruments. The IR and NMR spectra were taken on Shimadzu IR-27 and Varian 60A or 100A spectrometers respectively. The mass and UV spectra were recorded on Hitachi RUM-6D and Hitachi EPS-3 spectrometers respectively.

Preparation of (2,4,6-Cycloheptatrien-1-yl)acetaldehyde Tosylhydrazone (4). To a solution of tosylhydrazide (17.3 g, 0.93 mol) dissolved in a 3:1 mixture of ethanol and water, (**3**) (12.5 g, 0.93 mol) was added, drop-by-drop at room temperature, to produce white crystals (27.4 g, 98%). White needles from ethanol; bp 130°C (d).

Found: C, 63.61; H, 5.96; N, 9.05%. Calcd for $C_{16}H_{18}N_2O_2S$: C, 63.56; H, 6.00; N, 9.27%. IR (KBr): 3226, 1597, 1361, 1326, 1163, 747, 714 cm^{-1}. NMR ($CDCl_3$): τ 2.18 (m, 2H), 2.72 (m, 3H), 3.40 (m, 2H), 3.90 (m, 2H), 5.03 (m, 2H), 7.49 (m, 2H), 7.61 (s, 3H), 8.17 (m, 1H).

Thermal Decomposition of 4. Formation of Bicyclo[4.2.1]-nona-2,4,7-triene (9) and Tricyclo[3.3.1.$0^{2,8}$]nona-3,6-diene (10) (barbaralane). A suspension of 47% sodium hydride (5.1 g, 0.1 mol) in dry dioxane (5 m*l*) was added to a solution of **4** (20 g, 0.66 mol) in dioxane (130 m*l*). The suspension of the sodium salt was then heated at 90—95°C under a stream of nitrogen. The evolution of nitrogen ceased after one hour and left crystals of sodium *p*-toluenesulfinate (11 g). The filtrate was diluted with petroleum ether (bp 40—60°C) and washed well to remove the dioxane. The organic layer was extracted with a 40% aqueous silver nitrate solution, which was then decomposed by 28% aqueous ammonia (*ca.* 100 m*l*). It was extracted with petroleum ether, washed with water, dried (Na_2SO_4), and evaporated to give yellowish-orange oil (5 g), which was subsequently passed through a column containing alumina (B.G.l). Elution with petroleum ether (bp 40—60°C) afforded a colorless oil (1.0 g, 20%) which consisted of two components in a ratio of 4:1 and which was separated on a preparative vpc column (3 m × 1/4″ 10% Carbowax at 120°C). The oily product corresponding to the shorter retention time and to the main component was **9**.

Found: C, 91.34; H, 8.78%. Calcd for C_9H_{10}: C, 91.47; H, 8.53%. IR (neat): 3021, 1642, 732, 679 cm^{-1}. UV (cyclohexane nm ε) 259 (2710), 268 (2460), 278 (1360). NMR (CCl_4): τ 4.12 (m, 4H), 4.87 (m, 2H), 6.92 (bd, J=

29) T. S. Cantrell and H. Schechter, *J. Amer. Chem. Soc.*, **89**, 5868 (1967); A. S. Kende and T. L. Bogard, *Tetrahedron Lett.*, **1967**, 3383.

30) E. Vogel, W. Grimme, and E. Dinne, *ibid.*, **1965**, 391.

31) J. Schwartz, *Chem. Commun.*, **1969**, 833.

32) W. Eberbach and H. Prinzbach, *Helv. Chim. Acta*, **50**, 2490 (1967); R. Kitzing and H. Prinzbach, *ibid.*, **53**, 158 (1970), and references cited therein.

11.3 Hz, 1H), 8.07 (t×d, J=11.3, 6.2 Hz, 1H), 8.71 (d, J=11.3 Hz, 1H).

The second product was established to be **10**; mp 39—40°C.

Found: C, 91.08; H, 8.48%. Calcd for C_9H_{10}: C, 91.47; H, 8.53%. IR (CCl_4): 3030, 2915, 1678, 1616, 1381 cm^{-1}.

A solution of **10** (10 mg) in dioxane was heated under reflux and monitored by vpc. No other peaks except **10** appeared after heating for 116 min.

Catalytic Reduction of ***9***. A solution of **9** (118 mg, 1 mmol) dissolved in ether (10 m*l*) was catalytically reduced over an Adams catalyst (10 mg) at the temperature of ice water. It consumed three equivalents of hydrogen (72.3 m*l*, calcd 67.2 m*l*) after 138 min. The filtration of the catalyst and the evaporation of the ether left 117 mg of crystals; mp 90—93°C. Sublimation afforded bicyclo[4.2.1]nonane; mp 94—95°C.

Found: C, 86.96; H, 13.00%. Calcd for C_9H_{16}; C, 87.02; H, 12.98%. NMR (CCl_4): τ 7.8—9.3 (m).

*Preparation of α-(2,4,6-Cycloheptatrien-1-yl)propionaldehyde Tosylhydrazone (****6****).* Morphorinoenamine of propionaldehyde (27 g, 0.212 mol) was added, drop by drop and at room temperature, to a solution of tropyliumfluoroborate (41.5 g, 0.233 mol) in water (500 m*l*). The solution was stirred for two hours and then extracted with ether. The extracts were washed with water, dried (Na_2SO_4), and evaporated to leave 24.7 g (78.5%) of **5**: bp 86—87°C/0.8 mmHg.

Found: C, 80.94; H, 8.27%. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16%. IR (neat): 3012, 2817, 1724, 746, 709 cm^{-1}. NMR (CCl_4): τ 0.36 (d, J=2.0 Hz, 1H), 3.37 (m, 2H), 3.80 (m, 2H), 4.80 (m, 2H), 7.33 (d×q×d, J=7.5, 7.0, 2.0 Hz, 1H), 8.08 (m, 1H), 8.85 (d, J=7.0 Hz, 3H).

Into a solution of tosylhydrazide (11.2 g, 0.06 mol) in a mixture of ethanol and water (3:2) (260 m*l*), **5** (7.7 g, 0.052 mol) was stirred at room temperature. The filtration of the deposited white crystals yielded 15.5 g (94%) of the deposited white crystals yielded 15.5 g (94%) of the tosylhydrozone **6**. Needles from ethanol; mp 129—130°C.

Found: C, 64.56; H, 6.50; N, 8.89%. Calcd for $C_{17}H_{20}N_2O_2S$: C, 64.54; H, 6.37; N, 8.86%. IR (KBr): 3226, 1600, 1362, 1325, 1167, 751, 710 cm^{-1}. NMR ($CDCl_3$): τ 1.88 (bs, 1H), 2.14 (m, 2H), 2.68 (m, 2H), 2.87 (d, J=6.4 Hz, 1H), 3.38 (m, 2H), 3.92 (m, 2H), 4.98 (m, 2H), 7.33 (m, 1H), 7.57 (s, 3H), 8.50 (m, 1H), 8.89 (d, J=7 Hz, 3H).

Thermal Decomposition of ***6****. Formation of 9-Methylbicyclo[4.2.1]nona-2,4,7-triene (****11****) and 9-Methyltricyclo[3.3.1.0^{2,8}]nona-3,6-diene (****12****).* Sodium salt, prepared from 10 g of **6**, in dioxane (120 m*l*) was subjected to decomposition at 75—80°C. A subsequent workup similar to the decomposition of **4**, without extraction with a silver nitrate solution, produced 5 g of a crude oil, which was then passed through a column of alumina. Elution with petroleum ether (bp 40—60°C) yielded 1.35 g (27%) of a colorless oil, which was a mixture of **11** and **12** in a ratio of 9:2 (based on the area of the vpc peak). Preparative vpc (10 mm×1 m 20% DOP at 70°C) separated **11** (shorter retention time) and **12**. NMR of **11** (CCl_4): τ 4.10 (m, 8H), 4.85 and 4.97 (m, combined area 4H), 7.0—7.5 (4H), 7.6—8.5 (4H), 9.10 and 9.33 (d, J= 7.0 Hz, combined area 6H).

A solution of **11** (205 mg, 1.5 mmol) in ether (5 m*l*) was hydrogenated over 10% prereduced Pd-C (25 mg) at the temperature of ice-water. It absorbed three equivalents of hydrogen (104.8 m*l*, calcd 104.2 m*l*) after 170 min. The catalyst was removed, and the filtrate was evaporated to give 210 mg of a colorless oil, which was separated by preparative vpc (10 mm×1 m 20% DOP at 80°C). A colorless oil was eluted first.

Found: C, 87.09; H, 13.03%. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12%. NMR (CCl_4): τ 7.8—8.9 (m, 15H), 9.12 (d, J=7.0 Hz, 3H). Then were eluted colorless, sublimable needles; mp 117—118°C.

Found: C, 86.79; H, 12.83%. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12%. NMR (CCl_4): τ 7.7—8.6 (m, 15H), 8.95 (d, J=7.0 Hz, 3H).

*Preparation of α-Phenyl-α-(2,4,6-cycloheptatrien-1-yl)acetaldehyde Tosylhydrazone (****8****).* β-Ethoxystyrene (3.07 g, 0.021 mol) was dropped into a solution of tropyliumfluoroborate (7.3 g, 0.040 mol) in water (90 m*l*) at room temperature and stirred overnight. The separated oil was extracted with ether, and the extract was washed with water, dried (Na_2SO_4), and evaporated to give an orange oil. Distillation (bp 134—135°C/1.5 mmHg) yielded 4.1 g (95%) of the acetaldehyde **7**, which crystallized on standing. Colorless crystals from *n*-hexane; mp 55—57°C.

Found: C, 85.37; H, 6.78%. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71%. IR (neat): 3021, 2817, 1724, 760, 747, 701 cm^{-1}. NMR (CCl_4): τ 0.5 (d, J=2.6 Hz, 1H). 2.84 (m, 5H), 3.43 (m, 2H), 3.95 (m, 2H), 4.92 (m, 2H), 6.23 (d×d, J=11.0, 2.6 Hz, 1H), 7.47 (m, 1H).

To a solution of tosylhydrazide (10.2 g, 0.055 mole) dissolved in a mixture of ethanol and water (8:13) (210 m*l*), **7** (10 g, 0.048 mol) in ethanol (20 m*l*) was added, drop by drop and at room temperature, to form white crystals. Filtration afforded 15.5 g (87%) of **8**; mp 163—165°C. Needles from ethanol; mp 165.5—166°C.

Found: C, 69.69; H, 6.09; N, 7.58%. Calcd for $C_{22}H_{22}N_2O_2S$: C, 69.82; H, 5.86; N, 7.40%. IR (KBr): 3226, 1597, 1364, 1325, 1167, 747, 705 cm^{-1}. NMR ($CDCl_3$): τ 1.88 (bs, 1H), 2.20 (m, 2H), 2.80 (m, 8H), 3.36 (m, 2H), 3.87 (m, 2H), 5.01 (m, 2H), 6.24 (d×d, J=11.5, 7.0 Hz, 1H), 7.58 (s, 3H), 7.86 (m, 1H).

Thermal Decomposition of ***8****. Formation of* ***14****,* ***15****,* ***16****,* ***17****, and* ***18****.* A suspended sodium salt, prepared from 10 g of **8**, in dioxane (130 m*l*) was heated at 80—83°C and then treated as in the work-up described in connection with the formation of **11** and **12**. A crude red oil (4.7 g) was then separated using alumina-column chromatography. The product eluted first with petroleum ether (bp 40—60°C) was a colorless oil (1.7 g, 36%) whose vpc (20% DC-11 at 200°C) showed that it was a mixture of **14** and **15** in a ratio of 11:1. The petroleum ether solution of the mixture, upon cooling at −60°C, left erystals (mp 36—38°C), which, on sublimation, afforded **14** as colorless prisms; mp 39—41°C.

Found: C, 93.02; H, 7.38%. Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26%. IR (neat): 3030, 2933, 1605, 982, 794, 725, 699 cm^{-1}. UV (cyclohexane nm ε) 255 (2200) (sh), 261 (2480) (sh), 264 (2190). 271.5 (2370), 283 (1490) (sh), NMR (CCl_4): τ 2.93 (s, 5H), 3.65—4.35 (m, 4H), 4.83 (m, 2H), 6.90 (d, J=6.5 Hz, 2H), 7.18 (s, 1H).

The petroleum ether–benzene (2:1) mixture eluted yellow crystals (mp 150—156°C) (116 mg), which were subsequently recrystallized from ethanol to give **16** (95 mg, 2%) as colorless scales; mp 165—166°C.

Subsequent elution with ether afforded **17**; mp 91—93°C (410 mg). Colorless needles from cyclohexane–ethanol (10:1) (330 mg, 7%); mp 93—94°C.

Found: C, 80.84; H, 6.48; N, 12.66%. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60%. IR (KBr): 3040, 2907, 1642, 1600, 1534, 1490, 1449, 930, 750, 725, 696 cm^{-1}. UV (MeOH nm ε) 260 (1080, sh), 269 (660, sh), 340 (240). NMR ($CDCl_3$) H_1 (split doublet, τ 4.97), H_2 (quartet, 4.01), H_3 (split quartet, 3.84), H_4 (octet, 8.42), H_5 (triplet of doublet, 7.90), H_6 (split quartet, 8.13), H_7 (split doublet, 7.48), H_8 (triplet, 4.29) and H_{11} (octet, 7.37); $J_{1,2}$=2.8, $J_{1,3}$=2.0,

$J_{1,11}=8.0$, $J_{2,3}=10.5$, $J_{3,4}=4.5$, $J_{4,5}=7.5$, $J_{4,6}=8.0$, $J_{5,6}=7.0$, $J_{5,11}=7.0$, $J_{6,7}=2.0$ and $J_{7,8}=J_{8,11}=8.7$ Hz.

Finally, an ether–ethanol mixture (9:1) eluted **18**; mp 125—130°C (1.3 g). Colorless needles from benzene; mp 133—134°C (1.18 g 25%).

Found: C, 81.25; H, 6.53; N, 12.52%. Calcd for $C_{15}H_{14}N_2$, C, 81.05; H, 6,35; N, 12.60%. IR (KBr): 3175—2888; 987, 746 cm^{-1}. UV (MeOH nm ε) 260 (7080), 340 (46710).

Reactions of 1-Phenyl-6-(3-pyrazolyl)-1,3,5-hexatriene ***18****. Acetate.* Acetylation was accomplished on the treatment of **18** with acetylchloride in pyridine. Pale yellow small scales from ethanol; mp 137—138°C (80%).

Found: C, 77.33; H, 6.31; N, 10.33%. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60%. IR (KBr): 3040, 1736, 986, 787, 751, 691 cm^{-1}. UV (MeOH nm ε) 235 (7150), 348 (63250), 364 (48870) (sh).

Catalytic Reduction. A solution of **18** (504 mg, 2.3 mmol) in ethanol (50 m*l*) was reduced over prereduced 10% Pd-C (50 mg). After the uptake of three equivalents of hydrogen (160 m*l*, calcd 152 m*l*), the filtration of the catalyst, followed by the evaporation of the filtrate, yielded a pale yellow oil (516 mg); bp 175—178°C/3 mmHg.

Found: C, 78.36; H, 8.81, N, 11.88%. Calcd for $C_{15}H_{20}N_2$: C, 78.90; H, 8.83, N, 12.27%. IR (neat): 3195, 3096, 2907, 2841, 1458, 936, 749, 700 cm^{-1}.

Oxidation with Potassium Permanganate. A solution of **18** (333 mg, 1.5 mmol) dissolved in acetone (50 m*l*) and water (200 m*l*) was refluxed for eight hours with potassium permanganate (10.7 g, 0.068 mol). The excess potassium permangnate was then decomposed by the addition of methanol and the manganese dioxide deposited was washed with hot water. The combined filtrate was concentrated to *ca.* 50 m*l*, neutralized with 6N HCl, and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated to yield benzoic acid (84 mg, 63%). The acidic filtrate, from which the benzoic acid had been removed, was continuously extracted with ether, which was then evaporated to afford pyrazole-3-carboxylic acid (mp 208°C) (d) (96 mg, 78%). Colorless needles from water; mp 213°C; identified by a comparison of the IR spectra and by a mixed-melting-point determination with an authentic sample.[19]

IR (KBr): 3534, 3322, 3145, 1712, 1445, 770 cm^{-1}. NMR (D_2O): τ 2.13 (d, $J=2.5$ Hz, 1H), 3.03 (d, $J=2.5$ Hz, 1H).

Isomerization. A solution of **18** (222 mg, 1 mmol) in benzene (6 m*l*) was refluxed for five hours in the presence of iodine (22 mg). On cooling, yellow crystals (mp 186—191°C) (205 mg, 92%) were filtered. Pale yellow scales from benzene, mp 201—203°C.

Found: C, 80.60, H, 6.54; N, 12.27%. Calcd for $C_{15}H_{14}N_2$: C, 91.05; H, 6.35; N, 12.60%. IR (KBr): 3236, 3049, 2976, 1495, 1005, 933, 770, 751, 691 cm^{-1}. UV (MeOH nm ε) 240 (9550), 344 (74300), 361 (56500). NMR (DMSO-d_6): τ 2.38—3.98 (m).

Reactions of ***17****. Thermolysis. a)* An anhydrous diglyme (1 m*l*) solution of **17** (50 mg) was refluxed for six hours *in air*. The subsequent addition of ether, which has been washed with water and dried (Na_2SO_4), followed by the removal of the solvent, gave 46 mg of yellow crystals. The crude crystals were purified by alumina-column chromatography. Petroleum ether (bp 40—60°C)-benzene (2:1) eluted colorless **16**, mp 165—166°C (21 mg, 49%). *b)* The above reaction was carried out *in a nitrogen atmosphere* using 226 mg of **17** in diglyme (2 m*l*); it yielded a pale yellow oil (117 mg) which was then passed through a column of alumina. Colorless crystals (mp 49—55°C) (100 mg, 51%) were eluted with petroleum ether. Colorless needles from ethanol, mp 56—58°C; those needles were converted into **16** on standing in air and were assigned to **31**. IR (KBr): 3021, 2841, 1493, 1443, 754, 718, 686 cm^{-1}.

Petroleum ether–benzene (9:1) eluted colorless crystals (30 mg) (mp 161—164°C), which were recrystallized from ethanol to yield 10 mg (5%) of **16**. Finally we eluted 38 mg of colorless crystals; mp 173—182°C. Colorless needles from benzene; mp 185—186°C (29 mg, 15%); their structure was not identified.

Found: C, 92.32; H, 7.42%. Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26%. IR (KBr): 3021, 2882, 1597, 1493, 1443, 866, 753, 726, 687 cm^{-1}.

Photolysis. A solution of **17** (130 mg) dissolved in dioxane was irradiated for one hour through a Pyrex filter using a Toshiba H 400-p high-pressure lamp. The photolysate was diluted with ether, and then washed with water, dried (Na_2SO_4), and evaporated to yield a pale yellow oil (96 mg). Alumina-column chromatographic separation afforded 44 mg (43%) of **14** on elution with petroleum ether and 10 mg of **17** on elution with benzene ether (9:1).

Photolysis of ***9****.* A solution of **9** (3.5 g, 29.7 mmol) dissolved in anhydrous dioxane and placed in a quartz cell was irradiated for 72 hr using a 6 W low-presssure lamp (Ushio-UM6). Dilution with water was followed by the addition of petroleum ether (bp 40—60°C). The organic layer was washed well with water to remove the dioxane and then dried over Na_2SO_4. The evaporation of the solvent left a pale yellow oil (2.9 g), whose vpc (3 mm×1 m 5% DOP at 120°C) showed five peaks with a ratio of 4: 7.5: 5:1: 11.5 in the order of the retention time; it was submitted to preparative vpc (10 mm×3 m PEG 4000 at 100°C). The oil eluted first (area 4) involved five groups of peaks at τ 3.81 (s, 2H), 3.95 (bs, 2H), 7.66 (bs, 4H), 8.47 (bd, $J=8.5$ Hz, 1H), and 8.75 (bs, 1H), and was proved to **38** on the basis of the reported data.[5] Secondly, a colorless oil was obtained. Its NMR spectrum contained six groups of peaks, at τ 4.15 (s, 2H), 4.25 (t, $J=2.0$ Hz, 2H), 7.05 (bd, $J=3.8$ Hz, 2H), 7.43 (m, 2H), 8.13 (bd, $J=8.5$ Hz, 1H) and 8.50 (bd, $J=8.5$ Hz, 1H); it was identified as **39**. Besides **38**, **39**, and **9** (area 1), two kinds of oily products (area 5 and 11.5) were obtained, but their structures were not characterized.

Sensitized Photolysis of ***14****. Formation of 9-Phenylbarbaralane* ***15****.* A solution of **14** (58 mg, 0.3 mmol) and benzophenone (309 mg, 1.7 mmol) dissolved in benzene (5 m*l*) was irradiated through a Pyrex filter using Rayonet MGR-black light. The progress of the reaction was monitored on vpc (3 mm×1 m 5% SE-30 at 170°C), and the peak due to **14** disappeared after 5 hr of irradiation. The benzene was removed and the residue was subjected to preparative tlc separation and developed by a mixture of *n*-hexane–benzene (1:2) to afford **15** (27 mg) from $R_f=0.91$. IR (neat): 3030, 2940, 2875, 1618, 1602, 1492, 1450, 794, 735, and 694 cm^{-1}.