Synthesis and Thermal Rearrangement of Tricyclo[3.2.0.$0^{2,4}$]hept-6-enes. An Analysis of Structural Requirements for Effective Intramolecular Trapping of a 1,3-Diradical by a Remote Cyclobutene Ring[1-3]

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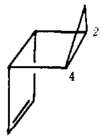
Abstract: *anti*-Tricyclo[3.2.0.$0^{2,4}$]hept-6-enes were prepared by Diels–Alder addition of cyclobutadiene to isopyrazoles and photochemical extrusion of nitrogen from the resulting endo adducts. Pyrolysis of the 3,3-dimethyl-2,4-diphenyl derivative **6** (and also its azo precursor **5**) at 100–135° led exclusively to quadricyclane **7**. At higher temperatures (175°), **7** was converted into norbornadiene **8** which underwent further isomerization at 200° to tropilidene **9** and then norcaradiene **10**. Photoisomerization of **10** regenerated **9**. In contrast, phenyltrimethyl substitution as in **15** and **16** resulted in the operation of several competing radical reactions. Quadricyclane **17** and norbornadiene **18** were isolated in a combined yield of 25%. Bicyclo[3.2.0]heptadiene **19** (15%) and cycloheptatriene **20** (53%) were also produced. In the tetramethyl examples **26** and **27**, thermolysis afforded only bicyclo[3.2.0]heptadiene **28** and tropilidene **29**. Structural assignments in all cases were based upon spectral data and chemical transformations. The mechanistic considerations relating to quadricyclane formation, as well as to the conversions to bicycloheptadienes and tropilidenes, are discussed in terms of transient 1,3-diradicals and their intramolecular capture.

1,3-Diradicals have traditionally been postulated as reactive intermediates in numerous chemical reactions. Presently, interest in such species has intensified to the point where some knowledge of their physical and chemical properties is now being gained. For example, the current studies of Berson[5] and Bergman[6] have served to dissect the relative rates of bond rotation and ring closure involved in the thermal scission and reconstitution of cyclopropyl bonds. Recent attention has likewise been focused on the kinetics of the thermal equilibration of bicyclo[2.1.0]pentanes.[7,8] The elegant studies of Arnold, Evnin, and their coworkers have led to the direct observation ($T < 77°$K) of triplet 1,3-diradicals from the photoinduced decomposition of azo compounds.[9] Equally instructive have been the investigations concerned with the use of azo compound fragmentation reactions to evaluate conformational changes at radical centers, intramolecular σ-bond rotations, and inversions of electron spin.[10]

Chemically speaking, 1,3-diradicals prefer to react intramolecularly to the exclusion of other possible processes. The radical recombination phenomenon is not only the most widely observed, but the most useful since it provides a source of many highly strained compounds. Hydrogen-transfer reactions sometimes occur competitively. This paper reports efforts to trap 1,3-diradicals by intramolecular insertion into a remotely positioned olefinic center. Prior to this work, little attention had been given to this possible reaction type. The only attempt in this direction appears to be a report describing the trapping of 1,3-diradicals (from 3*H*-indazoles) on an *intermolecular* basis with olefins such as isobutylene.[11]

The tricyclo[3.2.0.$0^{2,4}$]hept-6-ene ring system (**1**) was selected as the object of this study because of the presence within the structure of a bicyclo[2.1.0]pentane moiety, the central bond of which is recognized to be subject to facile thermal homolysis.[7,12] Furthermore, the cyclobutene double bond in **1**, although not in direct conjugation with the incipient odd-electron centers, lies within adequate bonding distance to these atoms. It was recognized that should the anticipated trapping reaction be successful, quadricyclane derivatives could be produced. Because the total strain energy in the quadricyclane ring system **2** is extremely high (95 kcal/mol[13]), the driving force behind the conversion of **1** to **2** can be expected to be derived chiefly from the appreciable strain energy of **1**. The transformation has indeed been realized;[2] as shall be seen, however, quadricyclane formation is dependent upon the nature of the substitution at positions 2 and 4 in **1**.



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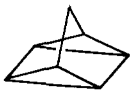

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[1] Partial support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is acknowledged with gratitude.

[2] A preliminary report of this work has appeared: L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, **92**, 1765 (1970).

[3] In our communication,[2] the title compounds were named tricyclo[4.1.0.$0^{2,5}$]hept-3-enes; they have now been renamed to follow the nomenclature suggested by J. Meinwald and J. K. Crandall, *ibid.*, **88**, 1292 (1966).

[4] National Institutes of Health Predoctoral Fellow, 1969–present.

[5] J. A. Berson and J. M. Balquist, *J. Amer. Chem. Soc.*, 90, 7343 (1968).

[6] W. L. Carter and R. G. Bergman, *ibid.*, 90, 7344 (1968); R. G. Bergmann and W. L. Carter, *ibid.*, **91**, 7411 (1969).

[7] M. J. Jorgenson, T. J. Clark, and J. Corn, *ibid.*, **90**, 7020 (1968).

[8] J. MacKenzie, W. P. Lay, J. R. Telford, and D. L. Williams-Smith, *Chem. Commun.*, 761 (1969).

[9] (a) D. R. Arnold, A. B. Evnin, and P. H. Kasai, *J. Amer. Chem. Soc.*, **91**, 784 (1969); (b) A. B. Evnin, D. R. Arnold, L. A. Karnischky, and E. Strom, *ibid.*, **92**, 6218 (1970).

[10] For a summary of leading references, consult: (a) W. R. Roth and K. Enderer, *Justus Liebigs Ann. Chem.*, 730, 82 (1969); (b) E. L. Allred and R. L. Smith, *J. Amer. Chem. Soc.*, **91**, 6766 (1969).

[11] G. L. Closs and L. R. Kaplan, *ibid.*, **91**, 2168 (1969).

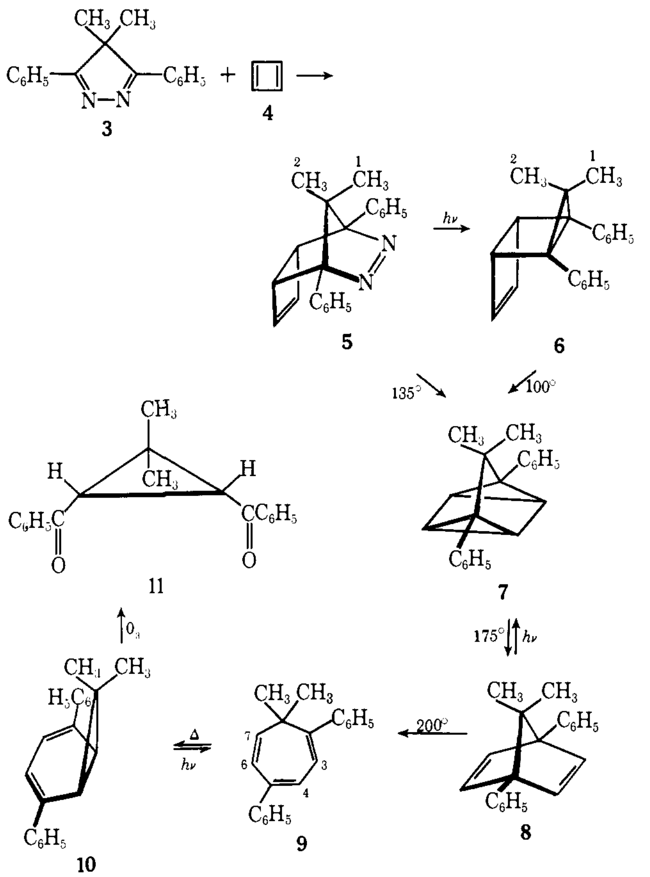
[12] For a review, see K. B. Wiberg, *Advan. Alicycl. Chem.*, **2**, 185 (1968).

[13] R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, 90, 4315 (1968).

Results

The Dimethyldiphenyl Case. Of the several possible (in theory) methods to gain synthetic entry of tricyclo-[3.2.0.0^{2,4}]hept-6-enes, the route involving cycloaddition of cyclobutadiene to an isopyrazole followed by photochemical extrusion of nitrogen from the resulting azo adduct was considered most feasible. Although its full potential remains to be exploited, this sequence holds unquestionable promise because it provides substantial opportunity for substituent control (*vide infra*). In the present example, tricyclic azo compound **5** was obtained in 68% yield on exposure of isopyrazole **3** to cyclobutadiene (**4**), generated *in situ* by ceric ion oxidation of cyclobutadieneiron tricarbonyl (Scheme I).

Scheme I



The ultraviolet spectrum of **5** in ethanol displays weak maxima at 343 (ϵ 64) and 353 nm (64) as expected for the azo chromophore. Its nmr spectrum (in $CDCl_3$) reveals three-proton singlets at δ 0.28 and 1.04 (1- and 2-CH_3, respectively), two-proton singlets at 3.88 (allyl) and 6.05 (olefinic), and a multiplet (10 H) in the aromatic region (7.32–7.80). The endo stereochemistry of **5** and the spatial relationships of the two methyl groups were established experimentally by application of nuclear Overhauser effects.[14] Thus, of the two methyl groups, that labeled 1-CH_3 is sufficiently distant from the allylic and olefinic hydrogens that it should not contribute to the relaxation of either proton type. In line with this consideration and an awareness that 1-CH_3 should experience substantial shielding because of its close proximity to the azo group, double irradiation of the δ 0.28 singlet did not result in any significant intensity change of the remaining signals. Saturation of the δ 1.04 absorption, however, reproducibly gave evidence of a 10% intensity enhancement in the 3.88 peak. Accordingly, the 2-CH_3 group and the allylic hydrogens must be proximal, an observation which requires the spatial relationship embodied uniquely in the endo isomer.

Irradiation of **5** in ether solution with a 200-W Hanovia lamp (Pyrex optics) for 3 hr gave rise to **6** in quantitative yield. The structural assignment follows chiefly from the nmr spectrum which shows (in $CDCl_3$) two methyl singlets at δ 0.88 and 1.44, doublets ($|J| = 1.5$ Hz) at 3.36 (allylic) and 6.41 (olefinic), and a ten-proton aryl multiplet centered at 7.22. The anti stereochemistry of **6** was likewise established by an NOE experiment which revealed a 7% intensity enhancement in the 3.36 absorption upon saturation of the 1.44 methyl singlet. The relatively small NOE effects in both **5** and **6** are likely attributable to the mutual relaxation of the two allylic hydrogens such that outside protons contribute less by comparison. The ^{13}C magnetic resonance spectrum of **6** has also been determined (see Experimental Section).

Clearly, nitrogen elimination from **5** has proceeded with retention of configuration. In an attempt to gain evidence on the possible intermediacy of the structurally related syn isomer,[15] a degassed methylene chloride solution of **5** contained in a sealed Pyrex nmr tube was photolyzed at −70°. The progress of the reaction was followed by periodic nmr analysis at −60°. Under these conditions, the decomposition of **5** was found to be kinetically first order and to afford only **6**. A concerted (${}_\sigma 2_s + {}_\sigma 2_s$-double retention) process involving synchronous tricycloheptene formation and nitrogen departure would lead to such a stereochemical outcome. On the other hand, a stepwise mechanism necessitating the intervention of a planar or rapidly interconverting pyramidal 1,3-diradical intermediate would appear to be precluded since no **7** was produced (see below).[16] Evidently, the present example affords no syn crossover product (as do a number of somewhat related structures[10]) because of the excessive strain inherent in this isomer, a situation which could serve to promote still further the exclusivety of the concerted mechanism.

The thermolysis of **6** in tetrachloroethylene solution at 100° could be conveniently monitored by nmr spectroscopy. After approximately 4 hr, quantitative conversion to quadricyclane **7** was observed. Evaporation of the solvent and recrystallization of the residue from ethanol gave **7** in 60% isolated yield. This hydrocarbon exhibits moderate ultraviolet absorption (in isooctane) at 234 nm (ϵ 8900) and three singlet nmr absorptions (in $CDCl_3$) at δ 1.03 (6, methyls), 2.02 (4, cyclopropyls), and 7.29 (10, aryls). Thermal decomposition of **5** at 135° in $Cl_2C{=}CCl_2$ solution likewise gave rise exclusively to **7**. When the thermolysis of this azo compound at different temperatures was monitored by nmr spectroscopy, it was noted that nitrogen evolution and quadricyclane production were slow below 125°. At

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(14) For a recent review, see G. Moreau, *Bull. Soc. Chim. Fr.*, 1770 (1969).

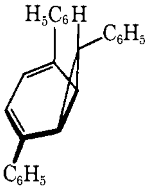
(15) The syn isomer, if formed at all, was expected to exhibit an ephemeral existence at room temperature due to exceptionally rapid stereomutation *via* central bond scission.[7,8]

(16) Of course, it remains conceivable that the relative efficiencies of the various possible photochemical steps leading from **5** may be ordered such as not to favor intramolecular trapping as in the thermal reaction.

135°, however, the conversion was complete after 1.5 hr.

Assignment of the quadricyclane structure to **7** follows from its ultraviolet absorption[17] and the highly symmetrical nature of its nmr spectrum. In particular, the absence of olefinic protons demands that the molecule be tetracyclic. Chemical substantiation of the quadricyclane formulation was derived by thermal rearrangement of **7** in $Cl_2C{=}CCl_2$ solution at 175°. At this temperature, **7** was converted cleanly to the norbornadiene **8**. Both the uv and nmr spectra of **8** reflect the generation of two nonconjugated olefinic linkages in a highly symmetrical setting (see Experimental Section). Not unexpectedly,[18] irradiation of **8** in hexane solution through quartz optics resulted in reconversion to **7**.

At this point, we were prompted by the somewhat unusual substitution pattern in **8** to examine its thermochemical behavior. Previous studies of norbornadiene[19] and benzonorbornadiene pyrolyses[20] have revealed a marked propensity for skeletal rearrangement to cycloheptatrienes and benzocycloheptatrienes, respectively. These structural changes, in actuality a combination of a 1,3-sigmatropic shift of the bridge carbon atom and subsequent valence isomerization of the resulting norcaradiene, are of considerable current interest. When **8** was heated in an evacuated tube at 200° for 1–2 hr, two isomeric hydrocarbons (**9** and **10**) were produced. Continued pyrolysis (to 4 hr) gave rise to **10** which was easily isolated as a yellow crystalline substance. Its ultraviolet spectrum in isooctane [maxima at 242 (ϵ 17,600) and 357 nm (14,000)] was particularly informative, suggesting the presence of a diphenylnorcaradiene chromophore. The almost identical electron spectrum of **12**[21] provided supportive evidence for the indicated structure. Also, the presence in the nmr spectrum of **10** of two olefinic protons (broadened singlet at δ 6.55) and two low-field cyclopropyl hydrogens (broadened singlet at 2.38) is consistent with the norcaradiene formulation and inconsistent with the isomeric cycloheptatriene structure. In ultimate confirmation of the assignment, ozonolysis of **10** led to *cis*-1,2-dibenzoyl-3,3-dimethylcyclopropane (**11**).



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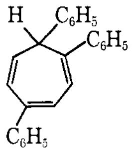

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Isolation of the kinetically favored pyrolysis product **9** proved difficult, particularly since conditions were not found which would cause this isomer to predominate over **8** and **10**. The discovery that photolysis of **10** affords **9** together with a small amount of *p*-terphenyl[23] did, however, permit its characterization. Significantly, the ultraviolet spectrum [$\lambda_{\max}^{\text{isooctane}}$ 238 (ϵ 20,800) and 303 nm (11,100)] was closely similar to that of **13**.[24] Additionally, because the four vinyl protons in **9** appear at widely separated chemical-shift positions, application of the double resonance technique permitted detailed analysis of the existing spin–spin interactions: $|J_{2,3}| = 7.5$ Hz, $|J_{3,5}| = 1.7$ Hz, $|J_{3,6}| = 0.7$ Hz, $|J_{2,5}| = 0.5$ Hz, and $|J_{5,6}| = 11.0$ Hz.

That **10** prefers the norcaradiene tautomeric form while **9** prefers the cycloheptatriene structure is clearly evident. Commentary on the factors controlling the direction of the various equilibria is deferred to the Discussion.

Phenyltrimethyl Substitution. Diels–Alder addition of cyclobutadiene (**4**) to 3-phenyl-4,5,5-trimethylisopyrazole (**14**), again strictly controlled by secondary orbital factors,[26] afforded only **15**. Facile conversion to **16** was achieved by photolysis of **15** in ether solution (Scheme II). Controlled pyrolysis of azo compound **15** in $CDCl_3$ at 152° (sealed tube) for 2 hr proceeded at a satisfactory rate to give five hydrocarbons with no evidence of unreacted starting material. A minor product was **16** (9%) which was seen to rearrange to the four isomeric structures **17**–**20** if pyrolysis was prolonged. Approximately one-fourth of the mixture consisted of quadricyclane **17** (16%) and norbornadiene **18** (7%). The remaining constituents were bicyclo[3.2.0]heptadiene **19** (15%) and tropilidene **20** (53%). The product distribution was determined by careful quantitative integration of nmr spectra; the mass balance in terms of these five products was essentially quantitative. As noted above, **16** was equally labile to heat, affording (154°, 2 hr) **17**–**20** in about the same ratio (18:9:18:46%) together with 9% of unchanged tricycloheptene.

The assignments of structure to the new substances rest on spectroscopic criteria and appropriate chemical transformations. Although **17** and **18** were not readily separated by vpc, their combined nmr spectrum (in $CDCl_3$) is in excellent agreement with the proposed assignments. The quadricyclane **17** shows the expected pairs of nonequivalent cyclopropyl protons as triplets ($|J| = 1.7$ Hz) centered at δ 1.55 and 1.80. The remaining portion of the spectrum consists of singlets at 0.98 for the bridgehead methyl group and 0.85 for the gem dimethyl substituents at C_7, together with aromatic absorption (singlet at 7.18). In the case of **18**, the requisite magnetic nonequivalence of the olefinic protons is

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(17) The ultraviolet spectrum of phenylcyclopropane serves as a rough analogy: M. T. Rogers, *J. Amer. Chem. Soc.*, **69**, 2544 (1947).

(18) See, for example: (a) S. J. Cristol and R. L. Snell, *ibid.*, **80**, 1950 (1958); (b) W. G. Dauben and R.L. Cargill, *Tetrahedron*, **15**, 197 (1961); (c) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Amer. Chem. Soc.*, **83**, 4674 (1961); (d) P. G. Gassman, D. H. Aue, and D. S. Patton, *ibid.*, **90**, 7271 (1968); (e) J. R. Edman, *ibid.*, **91**, 7103 (1969), and pertinent references cited in these papers.

(19) (a) M. G. Woods, *J. Org. Chem.*, **23**, 110 (1958); (b) W. M. Halper, G. Gaertner, E. W. Swift, and G. E. Pollard, *Ind. Eng. Chem.*, **50**, 1131 (1958); (c) J. H. Birely and J. P. Chesick, *J. Phys. Chem.*, **66**, 568 (1962); (d) W. G. Herndon and L. L. Lowry, *ibid.*, **68**, 2016 (1964); (e) W. C. Herndon and L. L. Lowry, *J. Amer. Chem. Soc.*, **86**, 1922 (1964); (f) R. K. Lustgarten and H. G. Richey, Jr., *Tetrahedron Lett.*, 4655 (1966); (g) M. R. Wilcott, III, and C. J. Boriack, *J. Amer. Chem. Soc.*, **90**, 3287 (1968).

(20) (a) R. K. Hill and R. M. Carlson, *J. Org. Chem.*, **30**, 2414 (1965); (b) S. J. Cristol and R. Caple, *ibid.*, **31**, 585 (1966); (c) M. Pomerantz and G. W. Gruber, *ibid.*, **33**, 4501 (1968).

(21) $\lambda_{\max}^{\text{cyclohexane}}$ 245 (ϵ 28,800) and 364 nm (10,700); see ref 22.

(22) T. Mukai, H. Kubota, and T. Toda, *Tetrahedron Lett.*, 3581 (1967).

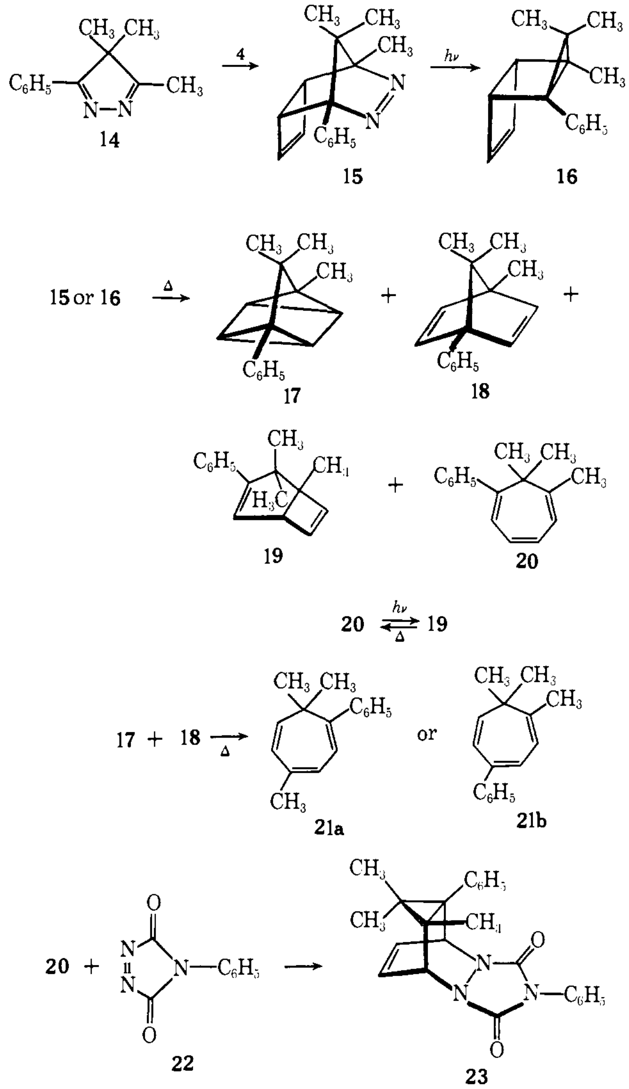
(23) The formation of *p*-terphenyl could plausibly occur by the expulsion of dimethylcarbene from the excited state of **10**. No attempts have been made in this study either to trap the reactive fragment or to establish conclusively its generation under these conditions.

(24) $\lambda_{\max}^{CH_3OH}$ 244 (ϵ 20,000) and 325 nm (15,100); see ref 25.

(25) T. Toda, M. Nitta, and T. Mukai, *Tetrahedron Lett.*, 4401 (1969).

(26) Such effects are recognized to be particularly influential when cyclobutadiene (4) is forced to function as the diene component: L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, **88**, 623 (1966); L. A. Paquette and J. A. Schwartz, *ibid.*, **92**, 3215 (1970). Apparently, the strong preference for endo stereochemistry also operates when 4 plays the dienophilic role in such (4 + 2) cycloadditions.

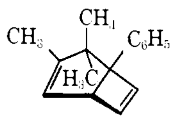
Scheme II



revealed by two sets of doublets ($|J| = 5.5$ Hz) at δ 6.58 and 6.84; like **17**, the norbornadiene shows methyl absorption at 1.28 (3 H) and 0.88 (6 H) and the aryl resonance (5 H) at 7.33.[27] Thermal rearrangement of this mixture at more elevated temperatures (175°) was found to give rise to a new tropilidine (**21**). Although isomer **21b** is preferred on mechanistic grounds (preference given to generation of transient benzylic radical formation), the available evidence did not adequately remove **21a** from consideration.

Elucidation of the structural features particular to **19** and **20** was greatly assisted by the finding that these substances could be readily interconverted. At elevated temperatures, for example, **19** was cleanly transformed into **20**; conversely, photolysis of **20** gave rise in unexceptional fashion to **19**.[28] Although the spectral characteristics of **20** establish its monocyclic nature (see Experimental Section), the exact position of attachment of the sp^2-bound methyl and phenyl groups remained to be confirmed. To this end, **20** was treated with *N*-phenyltriazolinedione (**22**) and the thermally labile adduct **23** was isolated. The observation that **23** possesses no cyclopropyl protons, but only olefinic and >C*H*N< nmr absorptions, requires that **20** be necessarily formulated as a 1,6,7,7-tetrasubstituted cycloheptatriene.

The formation of **19** from **20** is evidently a highly stereoselective electrocyclic reaction not directly involving the styrene chromophore. The direction of the photochemical bond-forming process is clearly indicated by the nmr spectrum of **19** which displays not only absorptions characteristic of *three* sp^3-bound methyl groups, but also three vinyl protons and a hydrogen attached to a doubly allylic carbon atom. Its ultraviolet spectrum (in isooctane) showed no maximum, but rather a shoulder at 236 nm (ϵ 5100) on the tail of end absorption. The overwhelming selectivity noted in the disrotatory cyclization which produces **19** may be steric in nature,[28b,c,29] but more likely finds its origin in electronic factors arising from charge polarization in the excited singlet state.[28d] The presence in **19** of the styrene functionality which further enhances its stability relative to **24** must also be important.



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The Tetramethyl Example. Phenyltrimethyl substitution is seen to result in the operation of several competing radical reactions with quadricyclane formation being less favored (*ca.* 25%) than in the case of **5** and **6**. This observation suggested that replacement of the remaining phenyl group by methyl should decrease further the capability of the 1,3-diradical for formation of a tetracyclic structure. In actuality, thermal decomposition of azo compound **26** (200°, 4 hr, neat) or of tricycloheptene **27** (144°, 12 hr, $CDCl_3$) led only to mixtures of bicycloheptadiene **28** and tropilidine **29** (Scheme III); no evidence for quadricyclane intervention was obtained.

For **28**, the absence of ultraviolet absorption and the appearance in the nmr spectrum of three vinyl protons, a bridgehead hydrogen, one sp^2-bound methyl group, and three high-field methyl singlets suggested that this product was a bicyclo[3.2.0]heptadiene. This conclusion was confirmed by further thermal rearrangement of **28** to 1,6,7,7-tetramethylcycloheptatriene (**29**) whose structure follows unequivocally from spectral data (see Experimental Section) and reaction with **22** to give adduct **30**. Further, photolysis of **29** in $CDCl_3$ through Pyrex resulted in ready isomerization[28] back to **28**.

Discussion

Quadricyclane Formation. The thermal rearrangement of **6** to **7** is the formal result of a ($_{\sigma}2_s$ + $_{\pi}2_s$) cycloaddition; consequently, a concerted rebonding process is intrinsically orbital-symmetry forbidden.[30] Rather, the C_2–C_4 bond almost certainly suffers homolytic rupture with formation of 1,3-diradical **31**. Although intermediate **31** is pictured as a planar species with sp^2 hy-

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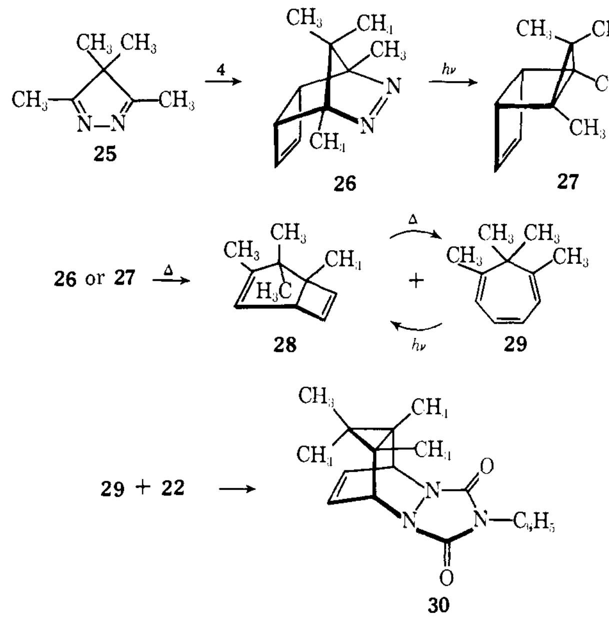
(27) Compare the nmr spectrum of bornadiene: $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 6.55 (dd, $|J| = 3.0$ and 1.6 Hz, 2, vinyl), 6.27 (dd, $|J| = 3.0$ and ~1 Hz, 2, vinyl), 3.01 (m, 1, bridgehead proton), 1.20 (s, 3, bridgehead methyl), and 1.03 (s, 6, C_7–methyls). We thank Professor M. R. Wilcott for a copy of this spectrum.

(28) For other examples of similar cycloheptatriene–bicyclo[3.2.0]heptadiene interconversions, see: (a) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961); (b) L. B. Jones and V. K. Jones, *J. Amer. Chem. Soc.*, **89**, 1880 (1967); **90**, 1540 (1968); (c) L. B. Jones and V. K. Jones, *Fortschr. Chem. Forsch.*, **13**, 307 (1969); (d) A. R. Brember, A. A. Gorman, R. L. Leyland, and J. B. Sheridan, *Tetrahedron Lett.*, 2511 (1970).

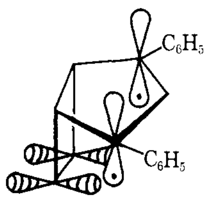
(29) L. B. Jones and V. K. Jones, *J. Org. Chem.*, **34**, 1298 (1969).

(30) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

Scheme III



bridization at the radical centers, the precise geometry of **31** is of course not known.[31] The data require only that the orbitals associated initially with the C_2–C_1 bond be intercepted by the cyclobutene π system with *retention* of configuration. Since azo compound **5** behaves analogously, it would appear that the same intermediate is involved in the thermal reaction which converts it to **7**. Unfortunately, because the decomposition of **5** requires temperatures ($\sim$135°) in excess of those required for the **6** → **7** rearrangement, no firm conclusion regarding the possible intervention of **6** can be drawn at this time. One might argue that, if the $({}_{\sigma}2_s + {}_{\sigma}2_s + {}_{\pi}2_s)$ transposition required to pass directly from **5** to **7** were concerted, a more ready fragmentation would be encountered. This line of reasoning must be tempered, however, by the realization that the cost of symmetry forbiddenness is necessarily a function of the reaction under study. Accordingly, a firm answer must await synthesis of the exo isomer of **5** and a comparison of the two rates of decomposition.



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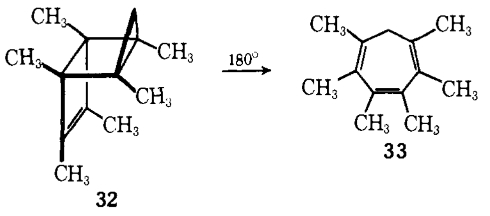
In **5** and **6**, intramolecular trapping of the diradical occurs to the virtual exclusion of other possible reactions. When the substitution pattern is altered from dimethyldiphenyl to phenyltrimethyl as in **15** and **16**, the capability for quadricyclane formation is substantially reduced (to *ca.* 25%). In the tetramethyl examples **26** and **27**, as well as **32**,[32,33] no analogous cycloaddition is seen. Inherent in these observations is the realization that the presence of at least one phenyl substituent at a radical center is necessary to ensure some measurable degree of radical capture by the cyclobutene ring. This phenomenon must be related, at least in part, to the added relative stabilization available to a benzylic radical which, in turn, serves to facilitate bond breaking in the rate-determining step.[34] In the absence of phenyl substitution, quadricyclane formation clearly loses its efficiency relative to alternative competing reactions (see below). The factor or combination of factors chiefly responsible for alteration of the mechanistic pathway remains to be elucidated.[35]



Conversion to Bicyclo[3.2.0]heptadienes and Tropilidenes. In mechanistic detail, the carbon skeletal rearrangement attending the formation of bicycloheptadienes **19** and **28** from their respective tricycloheptene and azo precursors also appears unprecedented. Two possible pathways deserve mention. One process necessitates that the 1,3-diradical intermediate (perhaps pyramidally hybridized at the radical centers bearing methyl groups[10b]) undergo antarafacial rupture of the "internal" cyclobutene σ bond with concomitant conro-

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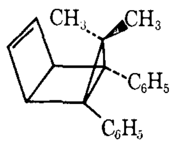
(31) It is to be noted, however, that sp^2 hybridization would accord maximum stabilization to the odd electrons at C_2 and C_4.

(32) E. Müller and H. Kessler, *Tetrahedron Lett.*, 3037 (1968), and personal communication.

(33) L. Leichter, unpublished observations. In this instance, the complexity of the nmr spectra and the insurgence of competitive [1,5]-sigmatropic hydrogen shifts render it difficult to exclude completely the possibility of quadricyclane formation.

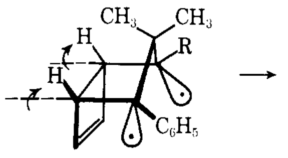
(34) (a) R. J. Crawford and A. Mishra, *Can. J. Chem.*, 47, 1515 (1969); (b) R. J. Crawford, R. Moore, and A. Mishra, *ibid.*, 46, 3305 (1968); (c) R. J. Crawford and B. H. Al-Sader, *ibid.*, 46, 3301 (1968), and earlier papers by the Crawford group.

(35) In a recent review (P. G. Gassman, *Accounts Chem. Res.*, 4, 128 (1971)), the intramolecular cycloaddition of the central bond of the bicyclo[2.1.0]pentane moiety in **6** to the cyclobutene double bond was stated "to be little more than another example of the well-established addition of carbon–carbon multiple bonds to bent σ bonds." To bypass the fundamental (at least to that author) objection that attack occurs directly on the top side of the bicyclo[2.1.0]pentane flap, the proposal was advanced that rapid flap inversion of **6** to syn isomer i precedes bonding "*via* expected attack. . .on the backside of the bicyclo[2.1.0]pentane flap." Furthermore, since the intermediacy of a diradical intermediate had to be necessarily disclaimed, the author was forced to hypothesize inversion *via* a planar intermediate in which the bridgehead carbons of the bicyclopentane moiety maintain their tetravalent character. Not unexpectedly, no supportive evidence was provided for these claims. We are of the opinion that this hypothesis has been contrived in an effort to encompass the present experimental observations into a stereotyped mechanistic framework which, although applicable to simple bicyclopentanes, need not be relevant to more complex derivatives of this ring system. We presently wish to call attention to the fact that, in contradiction to Gassman's unfounded claims, only diradical intermediate 31 appears to satisfy three relevant criteria. Firstly, syn isomer is prohibitively strained; not surprisingly, therefore, our search for this entity (see text) was not fruitful. More importantly, Gassman's proposal requires that the sp^2-hybridized cyclobutene carbon atoms move inward toward the inside of the bicyclopentane flap, a motion which is certain to cause additional steep increases in repulsive nonbonded interactions. We consider this to be energetically unrealistic. In contrast, the ring opening of **6** to diradical 31 does not engender added strain. Secondly, the stereoelectronic requirements for quadricyclane ring formation must be given adequate consideration. The ${}_{\sigma}2_s + {}_{\pi}2_s$ cycloaddition is required to proceed stepwise since it is a symmetry-forbidden thermal process. Accordingly, 1,3-diradical iv must intervene during the conversion of **6** to **7**. To arrive at iv, a



i

tatory motion (*cf.* **34**) to provide a mono-*trans*-cycloheptatriene (**35**). On the other hand, the internal cyclobutene bond could rupture in advance of, or concomitantly with, the cyclopropyl bond. The substantial strain in **35** would promote relatively rapid passage to bicycloheptadiene **36** under the reaction conditions.[36] It is to be noted that disrotatory opening of the same bond leads directly to the observed tropilidene products. Since the bicyclo[3.2.0]heptadienes **19** and **28** are converted only very slowly to cycloheptatrienes **20** and **29**, respectively, under the reaction conditions necessary for tricycloheptene rearrangement, the dienes do not serve as precursors to the trienes. Rather, the reactions are kinetically controlled and the two pathways must be competitive. This would require that conrotatory (and presumably symmetry controlled) ring opening be approximately 15–40% (depending on structure) less efficient than nonconcerted disrotatory opening.[37] Such an eventuality seems rather unlikely.



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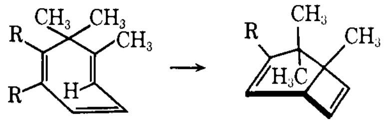
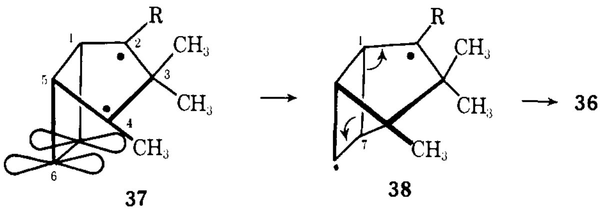


35 **36**

Alternatively, the conversion to bicycloheptadienes can occur by means of a formal homo-1,3-sigmatropic carbon rearrangement.[38] Because it is difficult to conceive of a process in which the C_1–C_7 bond of **37** undergoes total cleavage before appreciable C_4–C_7 bridging occurs, the favored approach to the transition state is considered to involve a torsional motion in which compression of the C_5–C_1–C_7 bond angle leads to effective overlap of the p orbital at C_7 with the free-radical center at C_4. Subsequent homolysis of the C_1–C_7 bond in **38** serves to complete the transposition to **36**. Some degree of credence is lent to this possibility by the observation that the photochemical rearrangement of certain bicyclo[3.2.0]heptadienes to quadricyclanes may involve similar utilization of a cyclobutene double bond.[39a] A polar counterpart is perhaps also operative in the unbuffered acetolysis of the bicyclo[4.2.0]oct-7-en-2-ol brosylates.[39b] In any event, this mechanistic possibility bears many similarities to the reaction which results in quadricyclane formation where the possible first step is bonding of C_7 to C_2 instead of to C_4. In **37**, the energy required to twist this intermediate in order that C_7 approach C_4 can hypothetically be counterbalanced at the transition state by an awareness in the reacting system at that stage (product development control) that the bicycloheptadiene to be formed is significantly less strained than the related quadricyclane.



37 **38**

In principle, a distinction between the two proposed pathways is available, since a skeletal rearrangement is uniquely associated with the latter case. The preparation of a suitable mono- or dideuterated tricycloheptene would provide the requisite test of these alternatives. However, this goal has yet to be achieved at the practical level.

The Norcaradiene–Cycloheptatriene Equilibria. Cycloheptatriene and the great majority of its derivatives do not contain detectable amounts of their norcaradiene valence tautomers at equilibrium.[40,41] Although the interconversion is symmetry allowed, an equilibrium constant favoring the norcaradiene form has been noted most frequently when the substituents at C_7 are strongly electron withdrawing[41,42] or incorporate external π systems geometrically disposed with the correct symmetry for orbital interaction.[43] A theoretical basis for these observations has recently been advanced.[44] Substituents on the cycloheptatriene have

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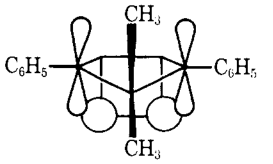
single bond between one bridgehead carbon of the bicyclopentane moiety and the proximate olefinic center must be generated. In diradical intermediate ii (= 31), the p orbitals are seen to be orthogonally aligned in such a fashion that overlap is maximized. In contrast, intramolecular cycloaddition from syn isomer i requires approach of a cyclobutene p orbital to the back lobe of the bent bond which lies substantially out of plane (*cf.* iii). Because this fancied intermediate is necessarily highly rigid, the electrons in this instance can partake only of marginal overlap at the transition state. The repercussions of such an unfavorable stereoalignment require no further elaboration. Lastly, the demonstrated need for at least one phenyl substituent at C_2 or C_4 in **1** is most consistent with the concept that facile rupture of the C_2–C_4 bond is a necessary prelude to quadricyclane formation (consult also the report by D. T. Longone and D. M. Stenhouwer, *Tetrahedron Lett.*, 1017 (1970)). In contrast, the attack of olefins on bent σ bonds has not been shown to exhibit a dependence on substitution at the bridgehead sites.



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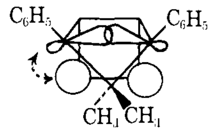

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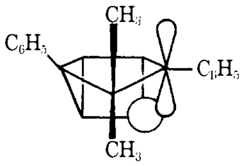

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(36) For examples of thermally induced *cis,trans*-1,3-cycloheptadiene cyclizations, see: (a) K. B. Wiberg and G. Szeimies, *ibid.*, 1235 (1968); (b) L. A. Paquette, G. R. Allen, Jr., and R. P. Henzel, *J. Amer. Chem. Soc.*, **92**, 7002 (1970).

(37) Within the present context, the direct $(_\sigma 2_s + {}_\sigma 2_a)$ conversion of tricycloheptenes to mono-*trans*-cycloheptatrienes can also be considered a possibility. However, since approximately the same product ratios arise from tricycloheptene and azo precursors (which do not enjoy such a concerted mechanistic option), the operation of this process would appear to be discountable.

(38) For a discussion of 1,3-sigmatropic carbon rearrangements, consult J. A. Berson, *Accounts Chem. Res.*, 1, 152 (1968).

(39) (a) A. A. Gorman and J. B. Sheridan, *Tetrahedron Lett.*, 2569 (1970); G. Linstrumelle, *ibid.*, 85 (1970); (b) B. A. Hess, Jr., *J. Amer. Chem. Soc.* 91, 5657 (1969).

(40) This subject has been recently reviewed: G. Maier, *Angew. Chem.*, 79, 446 (1967).

(41) The formal existence of such an equilibrium has been demonstrated: E. Ciganek, *J. Amer. Chem. Soc.*, **87**, 1149 (1965). See also H. J. Reich, E. Ciganek, and J. D. Roberts, *ibid.*, **92**, 5166 (1970).

(42) E. Ciganek, *ibid.*, **87**, 652 (1965); **89**, 1454 (1967).

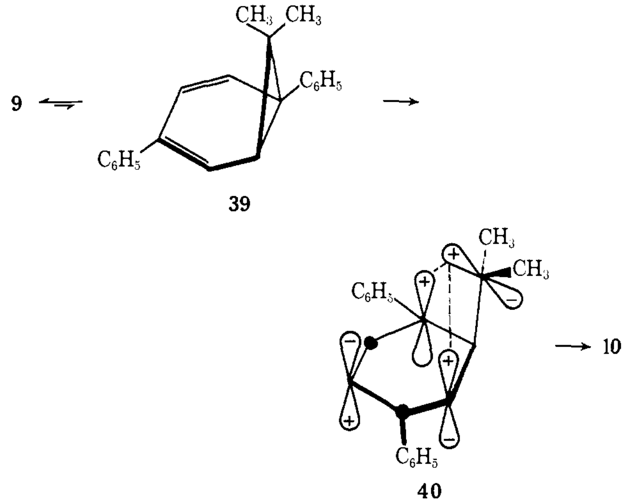
(43) D. Schönleber, *Angew. Chem.*, **81**, 83 (1969); M. Jones, Jr., *ibid.*, **81**, 83 (1969).

(44) R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970).

also been recognized to effect the position of equilibrium,[22,25,40,45] but much less is known about these influences.

Tropilidenes **9**, **13**, **20**, and **21**, when compared to norcaradienes **10** and **12**, provide some revealing information about substituent effects. Thus, the indiscriminate placement of one, two, or even three[22,25] aryl substituents on the cycloheptatriene ring does not shift the equilibrium toward the bicyclic form. However, when two phenyl groups are positioned at C_2 and C_5 as in **10** and **12**, stable norcaradienes are obtained. This strong bias very likely finds its origin in the extended conjugation now connecting the two aromatic centers, which stabilizing influence is not available to the monocyclic forms. This effect can be expected to be weakened significantly as the aryl groups are replaced by alkyl residues.

Lastly, the demonstrated interconversion of **9** and **10** is deserving of comment. As in the previous examples studied by Berson,[38,46] the basic assumption is that the thermally induced skeletal rearrangement of **9** to **10** occurs *via* the corresponding norcaradiene (estimated endothermicity about 11 kcal/mol[47]). A 1,5-sigmatropic carbon rearrangement of the gem dimethyl group (consequently, no stereochemical information derivable in this case) then leads to **10**. The driving force behind the directionally biased migration depicted in **40** is presumably the development of extended conjugation associated with the 1,4-diphenylbutadiene moiety. The interesting photo-1,5-sigmatropic carbon rearrangement of norcaradiene **10** back to **9**, although precedented,[25] particularly in benzonorcaradiene derivatives,[48] represents the first example of a "closed loop reaction sequence" within this series.



Experimental Section

General. Melting points are corrected. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Ultraviolet spectra were recorded with a Cary-14 spectrometer, while nmr spectra were taken with Varian A-60A and HA-100 instruments. The NOE experiments were carried out by Dr. Paul Demarco, Eli Lilly and Co., Indianapolis, Ind. The ^{13}C nmr spectrum was obtained through the courtesy of Professor Ernest Wenkert, Indiana University.

***endo*-7,8-Diaza-9,9-dimethyl-1,6-diphenyltricyclo[4.2.1.0^{2,5}]nona-3,7-diene (5).** To a cold (0°) magnetically stirred solution of 3,5-diphenyl-4,4-dimethylisopyrazole[9b] (**3**, 2.48 g, 0.01 mol) and cyclobutadieneiron tricarbonyl[49] (**4**, 1.92 g, 0.01 mol) in 125 ml of acetone under nitrogen was added 27.4 g (0.05 mol) of ceric ammonium nitrate in portions during 30 min. The resultant slurry was poured into anhydrous ether and the precipitated cerium salts were removed by filtration. The filtrates from two identical runs were evaporated and the combined crude product was chromatographed on silica gel. Elution with ether–hexane (1:9) and recrystallization from hexane gave 4.09 g (68%) of **5** as white crystals: mp 153–154° dec; ir ($CHCl_3$) 2924, 1605, 1495, 1464, 1443, 1389, 1372, 1290, 1030, and 998 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 343 (ϵ 64) and 353 nm (64); $\delta_{TMS}^{CDCl_3}$ 7.32–7.80 (m, 10, aryl), 6.05 (s, 2, olefinic), 3.88 (s, 2, allyl), 1.04 and 0.28 (s, 3 each, methyls).

Anal. Calcd for $C_{21}H_{20}N_2$: C, 83.96; H, 6.71. Found: C, 83.94; H, 6.78.

Photolysis of 5. A solution of 100 mg (0.33 mmol) of **5** in 2 ml of ether contained in a test tube was irradiated with a 200-W Hanovia lamp (Pyrex filter) housed in the usual cooling jacket. The progress of the reaction, followed by thin-layer chromatography, was deduced to be complete in 3 hr. Solvent removal afforded 90 mg (100%) of pure **6**: mp 65–67.0°; ir ($CHCl_3$) 1603, 1488, 1439, 1144, 1093, 1060, 812, 762, 747, 697, and 674 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.22 (m, 10, aryl), 6.41 (d, $|J|$ = 1.5 Hz, 2, olefinic), 3.36 (d, $|J|$ = 1.5 Hz, 2, allyl), 1.44 and 0.88 (s, 3 each, methyls). The ^{13}C nmr chemical shifts are in parts per million from external CS_2 based on internal CCl_4 (96.5): C_3, 158.0; C_4, 139.2; C_5, 144.5; C_6, 50.9; 1-CH_3, 169.7; 2-CH_3, 176.7; aryl carbon attached directly to tricycloheptene nucleus, 54.2; ortho C, 63.5; meta C, 65.3; para C, 66.9.

Anal. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.58; H, 7.65.

Low-Temperature Photolysis of 5. Into an nmr tube were placed 30.2 mg (0.10 mmol) of **5**, methylene chloride, and tetramethylsilane. After degassing, the tube was sealed. The irradiation was carried out by immersing the sealed nmr tube in a Pyrex dewar flask containing Dry Ice–isopropyl alcohol. The tube was positioned near a wall of the vessel for convenient exposure to the 200-W lamp. Low-temperature nmr spectra (−60°) were recorded at various intervals of time: 0.5 hr, *ca.* 25% conversion to **6**; 1.0 hr, *ca.* 50%; 1.75 hr, *ca.* 80%; 2.0 hr, *ca.* 100%. No other products were seen to develop.

Thermal Rearrangement of 6. A solution of 56 mg (0.21 mmol) of **6** in tetrachloroethylene (containing a small amount of TMS) was placed in an nmr tube and sealed *in vacuo* at −70°. Nmr spectra were recorded after the entire tube had been immersed in a preheated furnace for varying periods of time. After 4 hr at 100°, **6** was found to be transformed completely to quadricyclane **7**. The tube was opened and the product (34 mg, 60%) was isolated as long white needles, mp 136.5–138.5°, after recrystallization from ethanol: ir ($CHCl_3$) 1600, 1486, 1458, 1441, 1357, 919, 881, 847, and 814 cm^{-1}; $\lambda_{max}^{isooctane}$ 234 nm (ϵ 8900); $\delta_{TMS}^{CDCl_3}$ 7.29 (br s, 10, aryl), 2.02 (s, 4, cyclopropyl), and 1.03 (s, 6, methyls).

Anal. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.52; H, 7.47.

Thermolysis of 5. A solution of 201 mg (0.67 mmol) of **5** in 1 ml of tetrachloroethylene was sealed into an evacuated 12-mm Pyrex tube at −196°. The sealed tube was then placed in a mineral oil bath which had been preheated to 135°. After 1.5 hr, the tube was cooled, opened, and rinsed of its contents. Solvent removal at reduced pressure followed by two recrystallizations from ethanol gave 94 mg (46.5%) of quadricyclane **7**, mp 136.5–138.5°, which was identical with the material isolated above.

For the purpose of comparing the thermal behavior of **5** and **6**, *ca.* 50 mg of each substance in deuteriochloroform solution was sealed into evacuated nmr tubes. These tubes were placed adjacent to each other in the furnace and heated at 99° for 1 hr. The azo compound gave no evidence of conversion to **7**, whereas the tricycloheptene had undergone 37% conversion to this product.

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(45) M. Jones, Jr., *J. Org. Chem.*, **33**, 2538 (1968).

(46) J. A. Berson and M. R. Wilcott, III, *J. Amer. Chem. Soc.*, **87**, 2751, 2752 (1965); **88**, 2494 (1966); *Rec. Chem. Progr.*, **27**, 139 (1966); J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Wilcott, III, *J. Amer. Chem. Soc.*, **89**, 4076 (1967).

(47) M. R. Wilcott, III, Ph.D. Dissertation, Yale University, 1963.

(48) E. Ciganek, *J. Amer. Chem. Soc.*, **89**, 1458 (1967); J. S. Swenton and A. J. Krubsack, *ibid.*, **91**, 786 (1969); D. M. Madigan and J. S. Swenton, *ibid.*, **92**, 7513 (1970).

(49) L. A. Paquette and L. D. Wise, *ibid.*, **89**, 6659 (1967); L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965).

7,7-Dimethyl-1,4-diphenylnorbornadiene (8). Initial studies were performed with a 60-mg sample of **5** in tetrachloroethylene solution sealed in an evacuated nmr tube. After heating at 135° for up to several hours, only the presence of quadricyclane **7** was detected. Subsequent heating of the tube at 175° for 3.5 hr revealed essentially complete conversion to **8**. When the experiment was continued at 200° (~30 hr), **8** was seen to rearrange to **9** and then **10**.

In a typical preparative scale experiment, 201 mg (0.67 mmol) of **5** in 1.8 ml of tetrachloroethylene sealed in an evacuated length of 12-mm Pyrex tubing was heated at 175° for 5 hr. After cooling, the solvent was removed under reduced pressure and the residual solid was recrystallized twice from ethanol to afford 102 mg (50%) of **8** as white crystals: mp 188–190°; ir (neat) ($CHCl_3$) 1603, 1493, 1439, 1377, 1361, 1321, 1004, 972, and 911 cm^{-1}; $\lambda_{max}^{isooctane}$ 253 (ϵ 670), 258 (695), and 266 nm (485); $\delta_{TMS}^{CDCl_3}$ 7.40 (br s, 10, aryl), 7.07 (s, 4, olefinic), and 0.83 (s, 6, methyls).

Anal. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.30; H, 7.56.

Photolysis of 8. A solution of 50 mg (0.184 mmol) of **8** in 15 ml of hexane was irradiated with a 200-W Hanovia lamp using quartz optics. After a 1-hr period of irradiation, 33% conversion to **7** had been achieved (nmr analysis). Because continued irradiation resulted in gradual polymer formation, the 1-hr reaction time was considered optimal. The product was identical with quadricyclane **7**.

7,7-Dimethyl-2,5-diphenylnorcaradiene (10). As noted above, pilot nmr studies revealed that heating of **8** for several hours at 200° led *via* **9** to **10**. Preparative scale isolation of **10** was achieved by heating 102 mg (0.33 mmol) of **5** in an evacuated tube at 200° for 4 hr. The residue was recrystallized from ethanol to furnish 33 mg (33%) of **10** as bright yellow crystals: mp 159–161°; ir ($CHCl_3$) 1587, 1481, 1437, 1377, 1364, 894, and 692 cm^{-1}; $\lambda_{max}^{isooctane}$ 242 (ϵ 17,600) and 357 nm (14,000); $\delta_{TMS}^{CDCl_3}$ 7.20–7.80 (m, 10, aryl), 6.55 (br s, 2, olefinic), 2.38 (br s, 2, cyclopropyl), and 1.12 (s, 6, methyls).

Anal. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.68; H, 7.37.

Ozonolysis of 10. A solution of 100 mg (0.31 mmol) of **10** in 30 ml of absolute methanol was ozonized at −70° using 12.4 mequiv of ozone. To the resulting solution was then added a mixture of 2 ml of absolute methanol, 0.1 ml of glacial acetic acid, and 0.2 g of sodium iodide. Stirring for 4 hr was followed by dilution with 100 ml of water. Sodium bisulfite was added until the iodine color disappeared and then sodium carbonate was introduced to render the solution alkaline. Extraction with ether (three 125-ml portions) and drying of the combined extracts gave after evaporation a mixture of white crystals in a yellowish oil. Chromatography on silica gel and recrystallization from carbon tetrachloride afforded 28 mg (33%) of **11** as white crystals: mp 136–137°; ir ($CHCl_3$) 1672 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 247 (ϵ 24,200) and 275 sh nm (4300); $\delta_{TMS}^{CDCl_3}$ 7.38–8.08 (m, 10, aryl), 2.80 (s, 2, cyclopropyl), 1.50 and 1.40 (s, 3 each, methyls).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.93; H, 6.48.

Photolysis of 10. Into an nmr tube were placed 64 mg (0.25 mmol) of **10** and 0.5 ml of deuteriochloroform–tetramethylsilane. The solution was irradiated for various brief periods of time with a 200-W Hanovia lamp (Pyrex optics) until the nmr showed that **10** was no longer present (*ca.* 45 min). The nmr spectrum of the major product was identical with that observed earlier for the first-formed thermal rearrangement product of **8**.

Attempts to obtain **9** sufficiently pure for elemental analysis were not successful: $\lambda_{max}^{isooctane}$ 238 (ϵ 20,800) and 303 nm (11,100); $\delta_{TMS}^{CDCl_3}$ 7.12–7.63 (m, 10, aryl), 6.83 (dd, $|J_{3,5}|$ = 1.7 Hz, $|J_{2,3}|$ = 7.5 Hz, $|J_{3,6}|$ = 0.7 Hz, 1, H_3), 6.40 (dd, $|J_{2,5}|$ = 0.5 Hz, $|J_{5,6}|$ = 11.0 Hz, 1, H_5), 6.20 (d, $|J_{2,3}|$ = 7.5 Hz, 1, H_2), 5.37 (d, $|J_{5,6}|$ = 11.0 Hz, 1, H_6), and 1.03 (s, 6, methyls), with most of the absorptions showing long-range coupling.

A small amount of *p*-terphenyl, mp 210–212° (lit.[50] mp 213°), was also isolated from the photolysate. The uv,[51a] nmr,[51b] and ir spectra[51c] were identical with those of an authentic sample.

endo-**7,8-Diaza-1-phenyl-6,9,9-trimethyltricyclo[4.2.1.0^{2,5}]nona-3,7-diene (15).** Treatment of a cold (0°) solution of 1.86 g (0.01 mol) of 3-phenyl-4,5,5-trimethylisopyrazole (**14**)[9b] and 1.92 g (0.01 mol) of cyclobutadieneiron tricarbonyl (**4**)[49] in 125 ml of acetone with 27.4 g (0.05 mol) of ceric ammonium nitrate in portions during 30 min gave rise, after the previously described work-up (two identical runs combined at this point), chromatography on silica gel, and recrystallization from ethanol, to 1.30 g (27.3%) of **15** as white crystals: mp 103–105°; ir ($CHCl_3$) 3874, 1603, 1493, 1468, 1447, 1389, 1370, 1284, 1091, and 989 cm^{-1}; $\lambda_{max}^{isooctane}$ 324 sh (ϵ 31), 347 sh (100), and 356 nm (154); $\delta_{TMS}^{CDCl_3}$ 7.35–7.83 (m, 5, aryl), 6.07 (m, 2, olefinic), 3.68 (d, $|J|$ = 3.5 Hz, 1, allyl), 3.08 (d, $|J|$ = 3.5 Hz, 1, allyl), 1.67 (s, 3, bridgehead methyl), 0.93 and 0.42 (s, 3 each, methyls the latter of which is positioned above the azo linkage).

Anal. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61. Found: C, 80.48; H, 7.60.

anti-**2-Phenyl-3,3,4-trimethyltricyclo[3.2.0.0^{2,4}]hept-6-ene (16).** A solution of 200 mg (0.85 mmol) of **15** in 3 ml of ether contained in a test tube was irradiated with a 200-W Hanovia lamp source (Pyrex filter). After 2.5 hr, thin-layer chromatography showed the absence of starting material. Solvent removal under reduced pressure gave a quantitative yield of **16**. Molecular distillation afforded 150 mg of a colorless liquid: bp 44° (0.1 mm); ir (neat) 2865, 1608, 1493, 1445, 1295, 810, 776, 756, and 700 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.17 (br s, 5, aryl), 6.57 (m, 1, olefinic), 6.27 (m, 1, olefinic), 3.17 (m, 1, allyl), 2.97 (m, 1, allyl), 1.30 (s, 3, bridgehead methyl), 1.23 and 0.78 (s, 3 each, methyls).

Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.24; H, 8.52.

Pyrolysis of 15. Pilot nmr experiments revealed the following information: 105°, 1 hr, no decomposition; 132°, 1 hr, partial conversion to **16** under way; 158°, 1 hr, no **15**, some **16**, and four new products; 162°, 20 hr, only the new products (times are cumulative). For preparative purposes, a solution of 238 mg (1.0 mmol) of **15** in 1 ml of tetrachloroethylene was heated at 175° for 18 hr (evacuated tube) and the product mixture was subjected to vpc (125°, 5% XF-1150 on Chromosorb G). The first peak (14%) proved to be an inseparable 1:1 mixture of quadricyclane **17** and norbornadiene **18**. For **17**, $\delta_{TMS}^{CDCl_3}$ 7.18 (s, 5, aryl), 1.80 and 1.55 (t, $|J|$ = 1.7 Hz, 2 each, cyclopropyls), 0.98 and 0.85 (s, 3 each, methyls). For **18**, $\delta_{TMS}^{CDCl_3}$ 7.33 (m, 5, aryl), 6.84 and 6.58 (d, $|J|$ = 5.5 Hz, 2 each, olefinic), 12.8 (s, 3, bridgehead methyl), and 0.88 (s 6, methyls).

The second component (69%) was found to be **20**; ir (neat) 2825, 1603, 1445, 1420, 1350, 1335, 1328, 830, 762, 735, and 693 cm^{-1}; $\lambda_{max}^{isooctane}$ 225 sh (ϵ 10,800) and 283 nm (5600); $\delta_{TMS}^{CDCl_3}$ 7.00–7.33 (m, 5, aryl) 6.42–6.58 (m, 2, olefinic), 6.05–6.37 (m, 2, olfienic), 1.02 (s with additional small long-range coupling, 1,1-methyl), and 0.97 (s, 6, 7-methyls).

Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.24; H, 8.69.

The third component (17%) was **21**: ir (neat) 2950, 1600, 1493, 1471, 1443, 819, 775, 747, 703, and 694 cm^{-1}; $\lambda_{max}^{isooctane}$ 237 (ϵ 16,600) and 300 nm (5600); $\delta_{TMS}^{CDCl_3}$ 7.20–7.55 (m, 5, aryl), 673 (br d, $|J|$ = 7.0 Hz, 1, olefinic), 6.35 (br d, $|J|$ = 10.0 Hz, 1, olefinic), 6.7 (br d, $|J|$ = 7.0 Hz, 1, olefinic), 5.28 (d, $|J|$ = 10.0 Hz, 1, olefinic), 1.97 (br s, methyl), and 1.05 (s, 6, 7-methyls).

Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.25 H, 8.55.

This cycloheptatriene does not react with *N*-phenyltriazolinedione under the conditions used herein.

A shorter term pyrolysis (2 hr) of **15** (250 mg, 1.05 mmol) at a lower temperature (152°) and vpc separation of the products gave the following results. The first fraction consisted of **16** (9.9 mg, 9.1%). The second fraction (37.4 mg, 38%) was a mixture of quadricyclane **17** (16%), norbornadiene **18** (7%), and bicyclo[3.2.0]heptadiene **19** (15%). Although reproducible integrations of adequately separated peaks could be attained on small-sized injections of this mixture into the gas chromatograph, attempts to isolate pure samples were not successful. The third fraction (52.4 mg, 53%) was **20**.

Photoisomerization of 20. A solution of 48.6 mg (0.23 mmol) of **20** in $CDCl_3$–TMS contained in an evacuated nmr tube was irradiated (200-W Hanovia lamp) until the nmr spectrum revealed the total disappearance of starting material (12 hr). The lone volatile product was purified by vpc (101°, 5% XF-1150 on Chromosorb G); there was obtained 16.3 mg (33%) of **19**, identical with the pyrolysis product of the same structure; ir (neat) 3012, 2950, 1603, 1493, 1471, 1453, 1439, 1379, 1366, 1357, 1285, 894, 856, 840, 765, 747, and 698 cm^{-1}; $\lambda_{max}^{isooctane}$ 236 sh nm (ϵ 5100); $\delta_{TMS}^{CDCl_3}$ 7.27 (s, 5, aryl), 6.52 (d, $|J|$ = 2.5 Hz, 1, vinyl), 6.23 (dd,

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(50) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," Wiley, New York, N. Y., 1964.

(51) (a) $\lambda_{max}^{CHCl_3}$ 279 nm (ϵ 27,800); see A. E. Gillam and D. H. Hey, *J. Chem. Soc.*, 1170 (1939); (b) "High-Resolution NMR Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., 1963, no. 671; (c) Sadtler Standard Infrared Spectra, no. 8568.

$|J| = 2.5$ and 1.0 Hz, 1, vinyl), 5.80 (d, $|J| = 2.5$ Hz, 1, vinyl), 3.20 (m, 1, allyl), 1.36, 1.08, and 1.07 (s, 3 each, methyls).

Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.48; H, 8.58.

Thermal Rearrangement of 19. A solution of **19** in $CDCl_3$–TMS sealed in an evacuated nmr tube was heated at various temperatures with the following results: 100°, 1 hr, no reaction; 140°, 1 hr, no reaction; 150°, 1.5 hr, no reaction; 160°, 1 hr, no reaction; 170°, 1 hr, approximately 50% conversion to **20**.

In addition, heating a sample of **20** under similar conditions at 172° for 60 hr resulted in no reaction.

Thermal Rearrangement of 16. A solution of **16** (25 mg) in $CDCl_3$–TMS in an evacuated nmr tube was heated at 154° for 2 hr. Quantitative integration of nmr spectra gave the following product composition: **17** (18%), **18** (9%), and **20** (46%).

Cycloaddiion of 20 and *N*-Phenyltriazolinedione (22). A solution of 26.9 mg (0.128 mmol) of **20** and 22.8 mg (0.13 mmol) of **22** in 15 ml of acetone was stirred overnight at room temperature. Evaporation of the solvent and silica gel chromatography (elution with chloroform) gave **23** in high yield (45 mg). This adduct proved to be unstable upon heating or upon standing in solution, being subject to facile retro (4 + 2) cycloaddition. The nmr spectrum showed no cyclopropyl protons: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.45 (br s, 5, aryl), 7.55 (br s, 5, aryl), 6.43 (m, 2, olefinic), 5.02 (m, 2, bridgehead), 1.44, 1.38, and 0.81 (s, 3 each, methyls).

***endo*-7,8-Diaza-1,6,9,9-tetramethyltricyclo[4.2.1.0^{2,5}]nona-3,7-diene (26).** Portionwise treatment of a cold (0°) solution of 1.24 g (0.01 mol) of *freshly prepared* 3,4,4,5-tetramethylisopyrazole (**25**)[9b] and 1.92 g (0.01 mol) of cyclobutadieneiron tricarbonyl (**4**)[49] in 125 ml of acetone with ceric ammonium nitrate was terminated when further addition caused no additional evolution of carbon monoxide. Approximately 20 g of ceric salt was required and the duration of addition was 30 min. The resultant slurry was poured into 400 ml of ether, filtered to remove precipitated salts, washed with water (three 250-ml portions), dried, filtered, and evaporated to give a mixture of crystals in a red oil. Preparative scale vpc purification (130°, 10% SE-30 on Chromosorb W) afforded 519 mg (29.4%) of **26** as white crystals: mp 57.5–58.5°; ir ($CHCl_3$) 1466, 1439, 1387, 1372, 1277, 957, 901, and 851 cm^{-1}; $\lambda_{\max}^{\mathrm{isooctane}}$ 348 sh (ϵ 138) and 356 nm (230); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.05 (s, 2, olefinic), 2.90 (s, 2, allyl), 1.58 (s, 6, bridgehead methyls), 0.82, and 0.54 (s, 3 each, bridge methyls).

Anal. Calcd for $C_{11}H_{16}N_2$: C, 74.95; H, 9.15. Found: C, 74.83; H, 9.04.

***anti*-2,3,3,4-Tetramethyltricyclo[3.2.0.0^{2,4}]hept-6-ene (27).** A solution of 75 mg (0.426 mmol) of **26** in 2 ml of pentane contained in a test tube was irradiated with a 200-W Hanovia lamp (Pyrex optics). The progress of the reaction was monitored by vpc and shown to be complete after 1.5 hr. Isolation by preparative scale vpc (95°, 10% SE-30 on Chromosorb G) furnished 25 mg (33%) of **27** as a highly volatile liquid: ir ($CHCl_3$) 1550, 1445, 1348, 1295, 1285, 1188, and 775 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.50 (m, 2, olefinic), 2.84 (m, 2, allyl), 1.03 (s, 9, methyls), and 0.93 (s, 3, methyl).

Anal. Calcd for $C_{11}H_{17}$: C, 89.12; H, 10.88. Found: C, 89.26; H, 10.92.

Pyrolysis of 26. A sealed tube containing 176 mg (1.0 mmol) of **26** was heated in a furnace at 200° for 4 hr. The resulting product mixture was separated into its components by preparative scale vpc (98°, 10% SE-30 on Chromosorb W). The first fraction (15 mg, 13.3%) was found to be 1,2,2,3-tetramethylbicyclo[3.2.0]-hepta-3,6-diene (**28**): ir (neat) 3021, 2941, 1451, 951, 894, 850, 824, 754, and 742 cm^{-1}; $\lambda_{\max}^{\mathrm{isooctane}}$ end absorption only; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.46 (d, $|J| = 3.0$ Hz, 1, H_7), 6.13 (dd, $|J| = 3.0$ and 1.2 Hz, 1, H_6), 5.45 (br m, $|J_{4,5}| = 2.3$ Hz, 1, H_4), 3.01 (br m, 1, H_5), 1.58 (m, $|J| =$ 1.5 Hz, 3, C_3-methyl), 1.29 (s, 3, methyl), and 0.97 (s, 6, methyls).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.15; H, 10.85.

The second fraction (78.1 mg, 69.4%) was 1,6,7,7-tetramethylcycloheptatriene (**29**): ir (neat) 2933, 1443, 1387, 1370, 1355, 829, and 736 cm^{-1}; $\lambda_{\max}^{\mathrm{isooctane}}$ end absorption (at 211 nm, ϵ 6900) and 277 nm (1900); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.38 (m, 2, H_3 and H_4), 6.13 (m, 2, H_2 and H_5), 1.95 (br s, 6, sp^2-bound methyls), and 1.03 (s, 6, C_7-methyls). Double irradiation of the δ 1.95 absorption resulted in collapse of the 6.13 multiplet to a pattern identical with that seen at 6.38.

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.87; H, 11.12.

The third fraction (19.4 mg, 17.2%) was unreacted starting material.

Thermal Rearrangement of 27. A solution of 15 mg of **27** in $CDCl_3$–TMS contained in an evacuated nmr tube was heated at 144° for varying periods of time. The appearance of **28** and **29** was assessed by integration of the nmr spectra: 2 hr, **28** (38%) and **29** (62%); 6 hr, **28** (42%) and **29** (58%); 12 hr, **28** (43%) and **29** (57%).

In order to assess the thermal stabilities of these two products, the following experiments were conducted. Heating of **28** at 150° for 8 hr (neat) led to no reaction; after 4 hr at 200° ($Cl_2C{=}CCl_2$ solution), however, 59% conversion to **29** was seen. In a separate study, a solution of **29** in $CDCl_3$ was found to be unchanged after 14 hr at 200°.

Photorearrangement of 29. A solution of 40 mg of **29** in $CDCl_3$-TMS contained in an nmr tube was irradiated at room temperature for various periods of time with a 200-W Hanovia lamp until the nmr revealed the absence of starting material (12 hr). At this point, the spectrum was identical with that of **28**.

Cycloaddition of 29 and *N*-Phenyltriazolinedione (22). A solution of 29.6 mg (0.02 mol) of **29** and 35.0 mg (0.02 mol) of **22** in 15 ml of acetone was stirred at room temperature until colorless (2 hr). Evaporation of the solvent and chromatography on silica gel (elution with chloroform) gave **30** in high yield (64 mg). As with **23**, this adduct was unstable to heat and upon standing in solution (development of pink color). The nmr spectrum showed no cyclopropyl hydrogens: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.46 (br s, 5, aryl), 6.32 (m, 2, olefinic), 4.90 (m, 2, bridgehead), 1.28 (s, 6, methyls), 1.20 and 1.05 (s, 3 each, methyls).