(35) E. J. Corey and W. R. Hertler, *J. Am. Chem. Soc.*, **82**, 1657 (1960).
(36) F. Kamper, H. J. Schafer, and H. Luftman, *Angew. Chem.*, **88**, 334 (1976).
(37) IR and NMR spectra were recorded on a JASCO IR-E spectrophotometer and JEOL JMN-PS-100 spectrometer, respectively. GLC analyses were performed on a Shimadzu gas chromatograph GC-3BF with a flame ionization detector. Preparative GLC was carried out using a Shimadzu gas chromatograph GC-3a with TCD.
(38) J. E. Malowan, *Inorg. Synth.*, **4**, 61 (1953).
(39) F. R. Atherton, H. T. Oppenshow, and A. R. Todd, *J. Chem. Soc.*, 660 (1945).
(40) W. R. Kerner and G. H. Richter, *J. Am. Chem. Soc.*, **51**, 2503 (1929).

Photochemical Rearrangements of an Unsaturated Nitro Compound. Mechanistic and Exploratory Organic Photochemistry[1,2]

Howard E. Zimmerman,* Luther C. Roberts, and Roberta Arnold

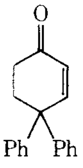
Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received July 13, 1976

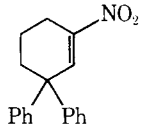
3,3-Diphenyl-1-nitrocyclohexene was synthesized for photochemical study in order to compare nitro n–π* photochemistry with carbonyl n–π* reactivity. Both direct and sensitized irradiations in benzene gave rise to *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane; the preference for formation of trans product was shown to be kinetic. Additionally, the photolysis afforded 3,3-diphenylcyclohexanone. Quantum efficiencies were determined, and these were found to be quite low compared with the corresponding enone analogue. Thus, for formation of bicyclic nitro compound the unsensitized and sensitized efficiencies were found to be $\phi = 3.05 \times 10^{-4}$ and 4.52×10^{-4} (acetophenone). Evidence favoring triplet multiplicity of the rearranging species is discussed as is the low reaction efficiency. It was observed that irradiation in isopropyl alcohol gave rise to 3,3-diphenylcyclohexanone oxime as the major product with the oxime to bicyclic product ratio increasing with increasing isopropyl alcohol concentration in isopropyl alcohol–benzene mixtures. Finally, *cis*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane was independently synthesized by reaction of 2-phenyl-1-nitrocyclopentene with diphenylsulfonium benzylide. This stereoisomer was converted, both in direct and sensitized irradiations, to the trans stereoisomer with a steady state favoring trans isomer over 1000:1.

Some of our previous studies[3–6] have involved the n–π* triplet photochemical rearrangement of 4,4-diphenylcyclohexenone (**1**) and substituted derivatives. The evidence favored promotion of a nonbonding (i.e., p_y or n) electron to the antibonding π system with rearrangement involving bonding of a γ aryl group to the β carbon.

Nitroalkenes also have an n–π* triplet as their lowest electronic excited state, although the literature on the subject is sparse.[7] Thus we were interested in seeing if the photochemistry of a nitro analogue of 4,4-diphenylcyclohexenone (**1**) would prove parallel to that of the ketone. For this study we selected 3,3-diphenyl-1-nitrocyclohexene (**2**).

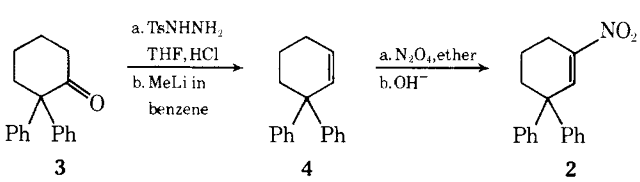


1



2

Synthesis of the Photochemical Reactant. The synthesis utilized 3,3-diphenyl-1-cyclohexene[8] (**4**) which was prepared from 2,2-diphenylcyclohexanone (**3**) using the method of Dauben.[9] Reaction of the diphenylcyclohexene **4** with nitrogen tetroxide in ether followed by hydroxide treatment gave a 19% yield of the desired 3,3-diphenyl-1-nitrocyclohexene (**2**), mp 106–107 °C. Note eq 1.



(1)

Exploratory Photochemistry. Exploratory irradiations were carried out using a 450-W medium-pressure immersion lamp along with either a Pyrex or a circulating sodium metavanadate filter, thus using light above 290 or 330 nm. A slow reaction was observed and could be monitored with analytical GC; two products were observed and these appeared linearly with time.

Preparative isolation employed column chromatography on Florisil. One product proved to be the known 3,3-diphenylcyclohexanone.[10] The major product, **5**, was a solid, mp 127.5–129 °C; at the end of 10 h a 9% yield of this photoproduct was formed. The minor diphenylcyclohexanone product was found in 0.5% yield. Thus, qualitatively, this contrasts with the very facile rearrangement of 4,4-diphenylcyclohexenone (**1**) where a similar conversion is complete in ca. 0.5 h.

Photoproduct Structure Elucidation. The first evidence regarding photoproduct **5** was the appearance of 6.59- and 7.37-μ bands in the infrared suggesting that this was a nitro compound. Substantial further evidence derived from the 270-MHz ^{1}H and 67.9-MHz ^{13}C NMR spectra (Tables I and II). The first point noted was the presence of two unsplit ^{13}C peaks at 79.8 and 53.3 ppm downfield from Me$_4$Si, indicating the presence of two quaternary carbons. The low field of the former suggested that it bore the nitro group (i.e., a C–NO$_2$ group present). Additionally, the doublet at 38.6 ppm proved suggestive of a benzylic cyclopropyl group (i.e., CHPh) bearing a hydrogen. Finally, the ^{1}H and ^{13}C NMR spectra both suggested the presence of three methylene groups (i.e., CH$_2$) and the former suggested that these formed a contiguous chain of three (–CH$_2$CH$_2$CH$_2$–); thus these are mutually coupled as indicated in Table II.

With evidence for these structural moieties in hand and with the course of the rearrangement of 4,4-diphenylcyclohexenone[3] in mind, a tentative assignment of **5** as *cis*- or *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane was made.

It seemed desirable to have the model compounds *cis*- and *trans*-1,6-diphenylbicyclo[3.1.0]hexane[8] (**8** and **7**, respectively), so these were prepared from the *cis*- and *trans*-5,6-

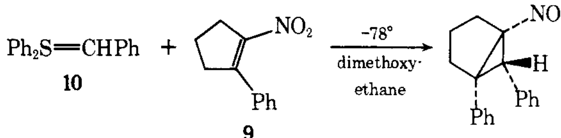
Table I. 67.9-MHz ^{13}C NMR Data

Compd	Carbon	Multiplicity	Chemical shift, ppm	$^1J_{^{13}CH}$, Hz
5	1	s	79.8	
	2	d of d	35.1	131
	3	d of d	21.1	132
	4	d of d	28.4	134
	5	s	53.3	
	6	d	38.6	155
6	1	s	79.7	
	2	d of d	40.8	132
	3	d of d	19.4	132
	4	d of d	33.3	134
	5	s	47.4	
	6	d	37.5	158
7	5	d	31.3	164
	2	d of d	26.4	130
	3	d of d	23.3	130
	4	d of d	31.8	129
	1	s	38.8	
	6	d	33.7	155
8	5	d	31.2	162
	2	d of d	28.5	128
	3	d of d	21.8	130
	4	d of d	36.8	130
	1	s	42.4	
	6	d	30.0	158

diphenylbicyclo[3.1.0]hexan-2-ones of known[3] structure. Synthetic details are given in the Experimental Section and the NMR spectra are detailed in Tables I and II. These spectra can be seen to show remarkable parallelism with that of photoproduct **5**.

With the preceding evidence in hand, we proceeded to obtain an unambiguous structure proof. This was obtained by synthesis of the stereoisomer of the photoproduct.

The reaction of 2-phenyl-1-nitrocyclopentene[11] (**9**) with diphenylsulfonium benzylide[12] (**10**) led to a product (**6**), mp 110–111.5 °C. The infrared spectrum again revealed the presence of a nitro group and was reminiscent of, but different from, that of the photoproduct (**5**). The ^{13}C NMR spectrum of this product was exceptionally similar to that of the photoproduct; note Table I. Literature analogy[13] had suggested that the nitrocyclopentene plus sulfonium benzylide reaction should lead to three-ring formation as shown in eq 2. Thus,



10 **9** **6** (2)

it was apparent that the synthesis had led to the stereoisomer (i.e., **6**) of the photoproduct (i.e., **5**).

Table II. 270-MHz ^1H NMR Data[b]

Compd	Proton	Multiplicity	Chemical shift, τ	Coupling constants, Hz[a]
5	a	16-line mult	9.61	$J_{ab} = -13.7, J_{ac} = 8.5, J_{ad} = 11.2, J_{ae} = 8.3, J_{af} = 11.2$
	b	d of t	8.39	$J_{bc} = 0.3, J_{bd} = 9.1, J_{be} = 0.1, J_{bf} = 9.4$
	c	d of d	7.75	$J_{cd} = -14.0, J_{ce} = 0.0, J_{cf} = 0.0,$
	d	mult	7.63	$J_{de} = 0.0, J_{df} = 0.5$
	e	d of d	7.58	$J_{ef} = -13.6$
	f	pseudo q	6.73	
	g	s	5.70	
	Arom	10 H mult	2.64	
6	a	16-line mult	8.35	$J_{ab} = -13.8, J_{ac} = 11.8, J_{ad} = 8.0, J_{ae} = 8.3, J_{af} = 11.3$
	b	mult	8.06	$J_{bc} = 8.5, J_{bd} = 0.7, J_{be} = 0.4, J_{bf} = 8.6$
	c	mult	7.75	$J_{cd} = -13.1, J_{ce} = 0.0, J_{cf} = 0.0$
	d	mult	7.72	$J_{de} = 0.0, J_{df} = 0.0$
	e	d of d	7.23	$J_{ef} = -12.9$
	f	d of d of d	7.08	
	g	s	6.91	
	Arom	2 H d of d	3.09	$J = 7.5, 1.0$
	Arom	5 H mult	2.80	
	Arom	3 H mult	2.72	
7	a	16-line mult	9.80	
	b	mult	8.64	
	c, d, e, f, h	1 H d of d 4 H mult	8.11 7.87	$J = 11.4, 8.5$
	g	d	7.65	$J = 8.46$
	Arom	10 H mult	2.93–2.91	
8	a	16-line mult	8.47	
	b	d of t	8.19	$J = 14.8, 8.1$
	c, d, e, f, h	mult d of d	7.87–8.07 7.69	 $J = 12.7, 8.1$
	g	d	7.77	$J = 3.7$
	Arom	2 H d of d	3.78	$J = 8.5, 1.0$
	Arom	8 H mult	3.55	

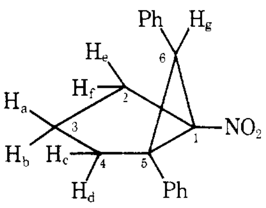
[a] The coupling constants listed for the methylene protons of compounds **5** and **6** are those obtained from a reiterative computer simulation of the observed spectrum. See the Experimental Section for details. [b] The observed and simulated methylene regions of the 270-MHz spectra of compounds **5** and **6**, along with a more complete discussion of their comparisons with the spectra of **7** and **8**, are given in the Ph.D. Thesis of L. C. Roberts, University of Wisconsin, 1976.

Table III. Summary of Quantum Yield Data

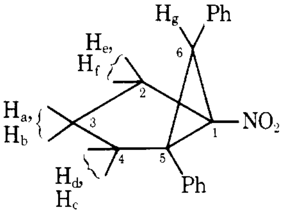
Concn of reactant, M	Added reagent (M)	λ_{irrad}, nm	Φ_r[a] bicyclic	Φ_r[b] ketone	Conversion, %
3.20×10^{-3}	None	317	3.06×10^{-4}	3.97×10^{-5}	3.240[c]
3.20×10^{-3}	None	317	3.03×10^{-4}	3.75×10^{-5}	1.630
3.20×10^{-3}	None	317	3.04×10^{-4}	2.63×10^{-5}	0.759
3.20×10^{-3}	None	317	3.05×10^{-4}	1.61×10^{-5}	0.361
1.00×10^{-3}	Acetophenone (5.25×10^{-1})	337	3.90×10^{-4}	4.22×10^{-4}	0.867
1.00×10^{-3}	Acetophenone (5.25×10^{-1})	337	4.37×10^{-4}	2.07×10^{-4}	0.343
1.00×10^{-3}	Acetophenone (5.25×10^{-1})	337	4.33×10^{-4}	1.65×10^{-4}	0.181

[a] Linear extrapolation to 0% conversion gave $\Phi_r = 3.05 \times 10^{-4}$ and $\Phi_r = 4.52 \times 10^{-4}$ for the formation of the bicyclic photoproduct in the direct and sensitized photolyses, respectively. [b] Linear extrapolation to 0% conversion gave $\Phi_r = 1.18 \times 10^{-5}$ and $\Phi_r = 8.70 \times 10^{-5}$ for the formation of the ketone in the direct and sensitized photolyses, respectively. [c] This run is less reliable than the others since at this extent of conversion the bicyclic photoproduct could have been absorbing up to 1% of the light.

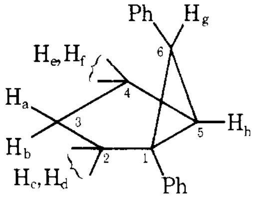
The assignment of stereochemistry to the two stereoisomers derives nicely from comparison of the ^{1}H NMR spectra of these compounds with those of the model compounds 7 and 8 of known stereochemistry. Primarily, the hydrogens labeled a in Table II, corresponding to the endo hydrogen at C-3, are shifted markedly upfield in photoproduct 5 and in model compound 7. Since the latter is known to have an endo C-6 phenyl configuration, we can conclude that the upfield shift is due to the high field hydrogen being in the shielding cone of the phenyl group. Also we can conclude that photoproduct 5 has the endo configuration. Stereochemical assignments are thus:



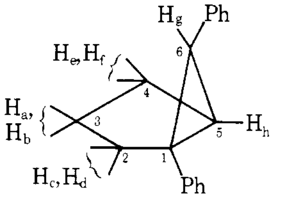
5



6



7



8

Final proof of the structure of photoproduct 5 derived from its formation in the acetophenone sensitized irradiation of the synthetically derived cis bicyclic isomer 6. Such stereoisomerization has literature precedent in the photochemical interconversion of cis and trans isomers of 5,6-diphenylbicyclo[3.1.0]hexan-2-one[14] and also of the cis and trans isomers of 2,3-diaryl-1-benzoylcyclopropanes.[15–17] Even in the absence of conjugating carbonyl or similar chromophores, diaryl cyclopropanes are known[18–20] to cis–trans isomerize photochemically.

Multiplicity and Quantum Efficiency Studies. One of the first questions of interest was whether the reaction would proceed via the triplet (i.e., under sensitized conditions). Accordingly, using the 450-W immersion apparatus and a combination Pyrex–copper–cobalt–nickel filter (290–390 nm bandwidth), an acetophenone-sensitized run was carried out. It was determined that minimally 99% of the light was captured by acetophenone sensitizer. From this run the same trans bicyclic photoproduct 5 was obtained (12% yield) along with 3,3-diphenylcyclohexanone (11) (14%) and recovered unphotolyzed reactant (23%).

For more quantitative studies the Black Box apparatus[21] was employed along with a narrower bandwidth solution filter of nickel–cobalt–copper (see Experimental Section for details). The conversions were monitored by GC. Under mild conditions (170 °C, SE-30, see Experimental Section) each of the compounds of interest—nitroalkene reactant 2, cis and trans bicyclic nitro compounds 5 and 6, 3,3-diphenylcyclohexanone, and tetraphenylethylene internal standard—gave nicely separable peaks. Ferrioxalate actinometry was used along with an integrating digital photometer.[22] The results are compiled in Table III. These runs were made from 3.2 to 0.4% completion in the direct irradiations and from 0.9 to 0.2% in the sensitized runs. Linear extrapolation to zero time gave nitrobicyclic quantum yields of $\phi = 3.05 \times 10^{-4}$ and 4.52×10^{-4} for the direct and sensitized runs, respectively. A major dependence of quantum yield on extent conversion was observed for 3,3-diphenylcyclohexanone product. Since this quantum yield increased with time, it seems unlikely that this ketone is a primary photoproduct.

An additional effort dealing with the nature of the excited state present was undertaken. This utilized the addition of isopropyl alcohol in order to determine if an efficient hydrogen abstracting excited state was present. With the addition of 10% isopropyl alcohol to the benzene solvent, a new product was obtained in addition to those ordinarily found. This proved to be 3,3-diphenylcyclohexanone oxime (12). Runs in pure isopropyl alcohol afforded oxime 12 as the major photoproduct (oxime 12:bicyclic 5:ketone 11, 5.7:1:0); note eq 3, Table IV, and the Experimental Section.

Interpretative Discussion. The first clear point deriving from the present study is the occurrence of a phenyl migration rearrangement parallel to that of enones [e.g., 4,4-diphenylcyclohexenone (1)]. In analogy to the ketone photochemistry,[3–6] it is the trans diphenyl product which is kinetically preferred. In the present instance this corresponds to inversion of configuration of C-3 during phenyl migration and bonding of C-3 to C-1.

The second point of interest is that the reaction appears to utilize an excited triplet, again in analogy to the ketone photochemistry.[3–6] Thus, successful rearrangement on sensitization means that, minimally, one knows that the triplet is capable of undergoing the rearrangement. The only uncertainty is whether the species involved in the direct irradiations is also the triplet. That the quantum yield in the direct runs is two-thirds of the sensitized runs is suggestive. Were these the same, one would tend to conclude that the same excited

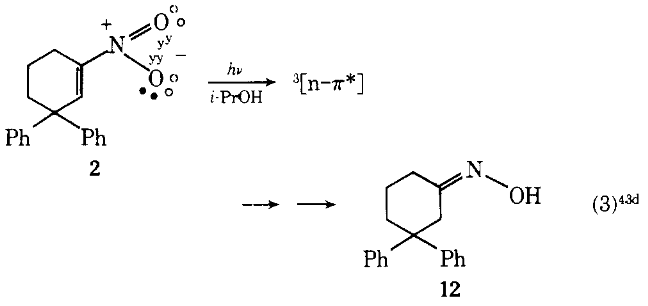
Table IV. Photolysis of 3,3-Diphenyl-1-nitrocyclohexene in Isopropyl Alcohol

Reactant (M)	Added reagent (M)	Solvent	λ_{irrad},[a] nm	Photolysis time, min	Conversion, %	Ratio of products[b]
Nitro olefin (3.58×10^{-3})	None	*i*-PrOH	>290	150	66.4	5.7:1.0:0
Nitro olefin (3.58×10^{-3})	None	10% *i*-PrOH in benzene	>290	150	19.5	0.9:1.0:-[c]
Nitro olefin (3.11×10^{-3})	None	10% *i*-PrOH in benzene	>330	150	15.5	1.3:1.0:0.2
Nitro olefin (3.11×10^{-3})	None	10% *i*-PrOH in benzene	>330	30	3.3	0.8:1.0:0.2
Nitro olefin (3.11×10^{-3})	Naphthalene (0.1)	10% *i*-PrOH in benzene	>330	150	13.0	1.0:1.0:0.2

[a] The filters used were Pyrex, for light of wavelength greater than 290 nm, and a combination of Pyrex and sodium metavanadate solution, for light of wavelength greater than 330 nm. [b] The ratio given is the mole ratio of 3,3-diphenylcyclohexanone oxime to *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane to 3,3-diphenylcyclohexanone, determined by NMR, using hand integrations of the expanded spectra. [c] Not detected by NMR at normal amplitude.

state species was rearranging in both direct and sensitized runs (i.e., the "fingerprint method" [6] type reasoning) and that intersystem crossing occurs with unit efficiency. With the two quantum yields being potentially orders of magnitude different but actually being not too different, the simplest conclusion is that the direct irradiations also involve the triplet but that the formation of triplet is only 67% efficient. Coincidentally, the intersystem crossing efficiency of nitrobenzene has been reported[23] to be 0.67.

The hydrogen abstraction reaction with isopropyl alcohol (note eq 3) seems ascribable to the n–π^* triplet. Thus, irradiation of nitro compounds in isopropyl alcohol has been reported[24] to give hydrogen abstraction via the n–π^* triplet. Hence, in the photochemistry under discussion evidence is available that the n–π^* triplet is present in solution.



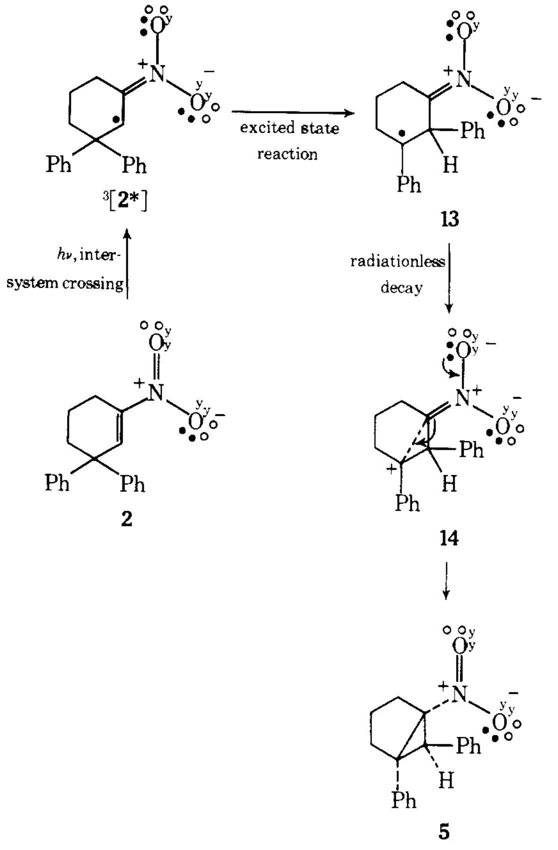
(3)[43d]

Still another point is the dramatically lowered quantum efficiencies of the nitroalkene rearrangement compared with the 0.043 efficiency[3b] observed for 4,4-diphenylcyclohexenone in a parallel process.

The last point before proceeding to consideration of an overall mechanism is that formation of 3,3-diphenylcyclohexanone (11) is unusual. The more common reaction of a nitroalkene is formation of the oximino ketone.[25]

A reasonable mechanism for formation of the rearranged, bicyclic photoproduct 5 is depicted in Chart I. The scheme in Chart I is quite analogous to that[3] given for the corresponding ketone rearrangement and conforms to the general scheme proposed by us 16 years ago.[26] The step we termed "rebonding" or "bond alteration" in the early days of our studies now corresponds to the triplet state reaction to give species 13. However, 13 is still a triplet and clearly a multiplicity change is needed to get to ground state product. This is written as a separate step giving zwitterion 14 in Chart I; 14 then bonds to afford photoproduct 5. However, it is conceivable that multiplicity change and radiationless conversion may lead 13 directly to photoproduct 5; thus the zwitterions in the enone photochemistry we reported[3] have never been intercepted by nucleophiles. This contrasts with the case of dienone photochemistry where numerous examples of intercepting[27] and generating[28,29] zwitterions have been reported. Thus, the stepwise nature of the reaction has not been defined with certainty.

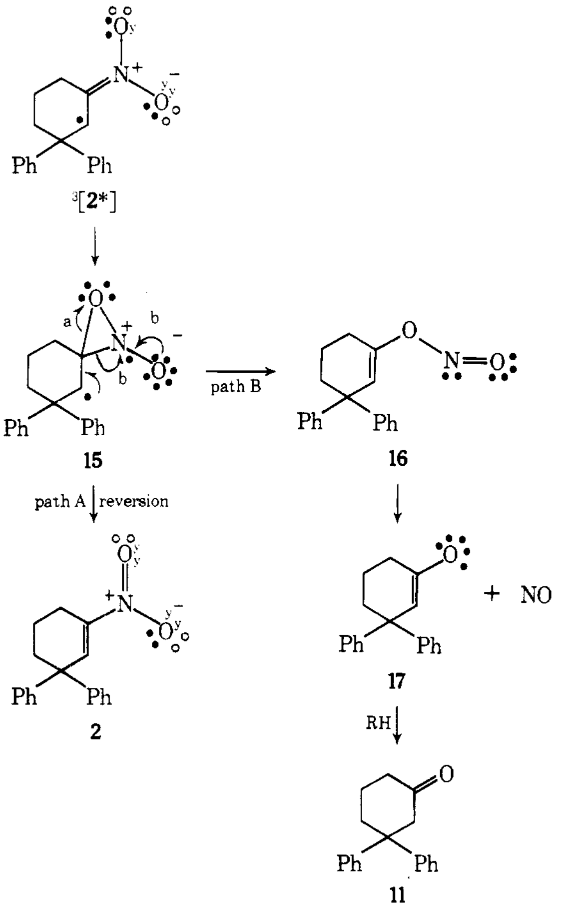
Chart I. Rearrangement Mechanism



The formation of ketone 11 seems most likely to involve the initial steps of the Chapman reaction[7e,25] except that with carbon 2 being quite hindered (adjacent to two phenyl groups), it seems more likely that the enoloxy radical 17 hydrogen abstracts to give enol which then affords the observed ketonic product. Note Chart II. This chart also includes a potential source of energy dissipation by reversion of the Chapman intermediate 15. This would then account for the low reaction efficiency.

We conclude by noting that nitroalkene photochemistry does parallel enone photochemistry in specialized, optimum cases such as that presently investigated. However, the availability of an efficient mode of energy dissipation derives from the capability of n–π^* nitro moieties to attack π systems.

Chart II. Mechanism of Formation of 3,3-Diphenylcyclohexanone



This leads to intrusion of an efficient competing reversion process and a lower efficiency.

Experimental Section[30]

2,2-Diphenylcyclohexanone. This compound was prepared by the method of Zaugg et al.[31] from cyclopentanone in an overall yield of 58%, after crystallization from hexane, mp 100.2–101.8 °C (lit.[3] 97–99 °C).

3,3-Diphenylcyclohexene. This compound has been previously reported by Dauben[8] and was prepared from 2,2-diphenylcyclohexanone by his general method.[9] A detailed procedure follows. A 50.1-g (0.20 mol) sample of 2,2-diphenylcyclohexanone was converted to its tosylhydrazone by refluxing for 26 h with 37.2 g (0.20 mol) of *p*-toluenesulfonylhydrazine in 400 ml of THF containing 0.6 ml of concentrated hydrochloric acid. Benzene (1.5 l.) was added, and the solvent distilled off at atmospheric pressure until the temperature of the distillate stabilized at 79 °C. The mixture was then cooled to 0 °C, mechanically stirred, and treated with 260 ml of a 1.7 M solution of methyllithium in ether over 40 min. The resulting solution was stirred at room temperature for 1.5 h, treated with 80 ml of water, poured into 400 ml of water, and extracted with pentane. The pentane was dried and concentrated in vacuo to give 51.0 g (0.20 mol) of 3,3-diphenylcyclohexene, pure by NMR, which was distilled to give 37.5 g (0.16 mol, 80%) of 3,3-diphenylcyclohexene, bp 115–145 °C (0.0025 mm). Recrystallization from pentane and then from methanol, at −78 °C, gave an analytical sample, mp 44–45 °C (lit.[8] 31–32 °C).

The spectral data follow: IR ($CHCl_3$) 3.27, 3.32, 3.40, 3.49, 3.51, 5.12, 5.31, 5.50, 6.27, 6.71, 6.92, 7.45, 8.46, 8.70, 9.01, 9.35, 9.71, 9.98, 10.88, 11.11, 11.68, 14.39 μ; 60-MHz ^{1}H NMR ($CDCl_3$) τ 2.80 (10 H, m, aromatic), 3.99 (2 H, m, vinyl), 7.40–8.81 (6 H, m, CH_2); UV (cyclohexane) 260 nm (ϵ 325); 254 (416), 250 (481), 269 (342).

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.30; H, 7.65.

3,3-Diphenyl-1-nitrocyclohexene.[32] A 25-ml (393 mmol) sample of dinitrogen tetroxide was vacuum distilled at 0.05 mm from a steel cylinder (Matheson Gas) into a trap cooled to −196 °C. The material was then allowed to thaw, and was passed, in a stream of dry air, into a stirred solution of 22.5 g (96.2 mmol) of 3,3-diphenylcyclohexene in 400 ml of dry ether at 0 °C. After all of the gas had been added (4 h), the reaction mixture was allowed to warm to room temperature and stir for 24 h. The resulting dark mixture was cooled to 0 °C and treated with 62 g (1.55 mol) of sodium hydroxide in 400 ml of water. The two-phase mixture was then magnetically stirred at room temperature for 24 h. The resulting mixture was ether extracted, and the ether solutions washed with water, dried, and concentrated in vacuo to give 17.8 g of a brown solid. Crystallization from hexane and then recrystallization from methanol gave 6.83 g (24.5 mmol, 25.4%) of 3,3-diphenyl-1-nitrocyclohexene, mp 104.0–106.5 °C, pure by NMR. Additional recrystallization from ether–hexane, treatment with Norit in refluxing methanol, crystallization from methanol, and recrystallization from ether–hexane gave 5.19 g (18.6 mmol, 19.3%) of pale yellow prisms of 3,3-diphenyl-1-nitrocyclohexene, mp 106.0–107.0 °C, >99.99% pure by GC (0.5% Carbowax 20M, 5% QF-1, and 5% SE-30).

The spectral data follow: IR (KBr) 3.26, 3.29, 3.38, 3.40, 3.48, 5.08, 5.26, 5.45, 5.63, 5.98, 6.25, 6.54, 6.67, 6.88, 6.94, 7.42, 8.26, 8.64, 9.26, 9.71, 10.70, 10.93, 11.63, 12.09, 12.99, 13.16, 13.51, 13.95, 14.22, 15.67, 16.39 μ; 100-MHz ^{1}H NMR ($CDCl_3$) τ 2.30 (1 H, br s, vinyl), 2.60–3.00 (10 H, m, aromatic), 7.40 (2 H, m, CH_2 adjacent to nitro substituted vinyl), 7.73 (2 H, m, CH_2CPh_2), 8.28 (2 H, m, CH_2); 15-MHz ^{13}C NMR ($CDCl_3$) 18.73 (br d of d, central CH_2), 24.20 (d of d, CH_2), 34.75 (d of d, CH_2 adjacent to nitro vinyl), 49.22 (s, Ph_2**C**), 126.73 (aromatic), 127.56 (aromatic), 128.55 (aromatic), 139.38 (d, vinyl β to nitro), 146.17 (s, tertiary aromatic), 149.60 ppm (s, nitro vinyl); UV (hexane) 244 nm (ϵ 8520), 325 sh (138); (95% ethanol) 253 nm (ϵ 7950); mass spectrum *m/e* (rel intensity) 279.12615 (0.5, calcd for $C_{18}H_{17}O$, 279.12593), 250 (0.2), 249.12840 (76.2, calcd for $C_{18}H_{17}O$, 249.12794), 234 (23.8), 233 (100.0), 205 (13.3), 204 (9.8), 203 (11.9), 202 (11.9), 193 (6.0), 192 (6.7), 191 (10.2), 190 (4.8), 189 (6.7), 180 (4.3), 179 (7.4), 178 (12.9), 177 (3.6), 165 (14.3), 156 (7.4), 155 (38.1), 154 (4.8), 153 (7.4), 152 (9.8), 130 (8.3), 129 (54.0), 128 (13.8), 127 (10.0), 117 (11.7), 116 (7.1), 115 (27.9), 105 (15.2), 91 (61.2), 77 (21.4).

Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.16; H, 6.30; N, 4.92.

Degradation of 3,3-Diphenyl-1-nitrocyclohexene. A 174-mg (0.623 mmol) sample of 3,3-diphenyl-1-nitrocyclohexene was reduced with zinc in acetic acid by the general method of Hassner.[34] The nitro olefin was dissolved in 15 ml of acetic acid containing 0.5 ml of water at 40 °C. Then 800 mg (12.2 g-atoms) of zinc dust was added portionwise over a period of 5 h. The mixture was heated to reflux, boiled for 4 h, stirred at room temperature for 10 h, reheated to 40 °C, and filtered hot. The zinc was washed with hot acetic acid, the acetic acid solutions diluted with 200 ml of water, ether extracted, and the extracts neutralized with saturated sodium bicarbonate solution, washed with saturated sodium chloride solution, dried, and concentrated in vacuo to give 116 mg (0.463 mmol, 74.4%) of 3,3-diphenylcyclohexanone, pure by NMR, whose spectral data were identical with those of a known sample of 3,3-diphenylcyclohexanone.[35] Recrystallization from ether gave 49 mg (0.175 mmol) of colorless crystals, mp 113–116 °C (lit.[10] 114–115 °C).

Previously unreported spectral data follow: 15-MHz ^{13}C NMR ($CDCl_3$) 210.0 (carbonyl), 147.3 (tertiary aromatic), 128.4 (aromatic), 126.9 (aromatic), 126.2 (aromatic), 53.7 (CH_2), 40.7 (CH_2), 35.8 (CH_2), 21.1 ppm (CH_2); UV (cyclohexane) 243 nm (ϵ 213), 250 (329), 255 (442), 259 (497), 263 (523), 270 (414), 283 (29), 291 (32), 298 (32), 308 (24), 320 (12); mass spectrum *m/e* (rel intensity) 251 (19.9), 250.13573 (100.0, calcd for $C_{18}H_{18}O$, 250.13576), 208 (12.2), 207 (40.4), 194 (17.4), 193 (98.8), 181 (5.3), 180 (31.2), 179 (22.0), 178 (26.6), 173 (10.1), 167 (9.3), 165 (21.5), 117 (6.5), 116 (5.5), 115 (34.3), 103 (12.9), 91 (25.0), 89 (8.6), 83 (8.4), 77 (14.0), 70 (22.6), 57 (9.9), 55 (25.2), 51 (6.9), 43 (15.0), 42 (53.2), 41 (11.0), 39 (5.9).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.55; H, 7.22.

Preparative Photolysis of 3,3-Diphenyl-1-nitrocyclohexene. A 435-mg (1.56 mmol) sample of 3,3-diphenyl-1-nitrocyclohexene in 500 ml of purified benzene was purged with vanadous-purified nitrogen[36] for 1 h prior to and during photolysis. The solution was irradiated through a 2-mm Pyrex filter with a 450-W Hanovia medium pressure mercury arc lamp, monitoring by GC (5% QF-1). After 9.75 h, the irradiation was discontinued, and concentration in vacuo gave 435 mg of dark orange oil. Chromatography on a 2.8 × 80 cm Florisil (Fisher, 60–100 mesh) column containing 2% of Sylvania no. 290 red phosphor, slurry packed with 1% ether in hexane, gave the following: fraction 1, 400 ml, 1% ether in hexane, 9.1 mg of unidentified oil; 2, 500 ml, 5% ether in hexane, 0.7 mg of unidentified oil; 3, 525 ml, 10% ether in hexane, 1.4 mg of unidentified oil; 4, 600 ml, 10% ether in hexane, 382 mg of 3,3-diphenyl-1-nitrocyclohexene and *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane, in a ratio of 9:1; 5, 600 ml, 15%

ether in hexane, 4.3 mg of unidentified oil; 6, 1000 ml, ether, 10.6 mg of 3,3-diphenylcyclohexanone; 7, 1000 ml, ether, 4.6 mg of an unidentifiable mixture. All fractions were analyzed by NMR and GC (5% QF-1).

Fraction 4 was rechromatographed on a 2.8 × 80 cm basic alumina (Fisher, 80–200 mesh, Brockman activity I) column containing 3% of Sylvania no. 290 red phosphor, packed in 1% ether in hexane, to give 40.7 mg of *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane (pure by NMR) upon elution with 50% ether in hexane. The 3,3-diphenyl-1-nitrocyclohexene could not be recovered, probably owing to decomposition or permanent adsorption on the alumina. Recrystallization from ether–hexane gave 18.6 mg of analytically pure colorless crystals of *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane, mp 127.5–129.0 °C.

The spectral data follow: IR (KBr) 3.26, 3.30, 3.36, 3.38, 3.40, 3.48, 5.10, 5.30, 5.51, 5.69, 6.24, 6.59, 6.91, 7.37, 7.54, 8.22, 9.28, 9.75, 9.92, 10.57, 10.86, 11.20, 11.74, 12.35, 12.87, 13.11, 13.64, 14.20, 14.77, 16.69 μ; 100-MHz ^{1}H NMR (CDCl$_3$) τ 2.64 (10 H, br s, aromatic), 5.72 (1 H, s, benzylic), 6.74 (1 H, m, CH$_2$), 7.65 (3 H, m, CH$_2$), 8.42 (1 H, m, CH$_2$), 9.64 (1 H, m, CH$_2$); UV (cyclohexane) 253 nm (ϵ 3936); (acetonitrile) 259 nm (ϵ 3240); mass spectrum *m/e* (rel intensity) 249 (6.5), 233.13322 (100.0, calcd for $C_{18}H_{17}$, 233.13302), 155 (29.4), 154 (2.2), 153 (5.0), 152 (6.1), 130 (5.0), 129 (38.1), 128 (13.1), 127 (8.0), 117 (10.9), 116 (6.1), 115)22.2), 105 (12.6), 91 (71.3), 77 (17.4).

Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.63; H, 6.25; N, 5.20.

Fraction 6 was rechromatographed on a 1.2 × 21 cm basic alumina (Fisher, 80–200 mesh) column deactivated with 10% water and containing 5% of Sylvania no. 290 red phosphor, packed in hexane to give 5.8 mg of 3,3-diphenylcyclohexanone upon elution with 85 ml of hexane and then 50 ml of ether. Trituration with chloroform gave 5.0 mg of colorless crystals, mp 110.5–113.5 °C, whose spectral data were identical with those of a known sample of 3,3-diphenylcyclohexanone.[35]

Preparative Photolysis of 3,3-Diphenyl-1-nitrocyclohexene for Quantitative Recovery. A 1.00-g (3.58 mmol) sample of 3,3-diphenyl-1-nitrocyclohexene in 1 l. of purified benzene was purged with vanadous-purified nitrogen[36] for 1 h prior to and during photolysis. The solution was irradiated through a 2-mm Pyrex filter and 4 mm of a 0.025 M solution of sodium vanadate in 0.05 M sodium hydroxide (circulated as lamp coolant) with a 450-W medium pressure mercury arc lamp, monitoring by GC (0.25% Carbowax). The Pyrex-vanadate filter transmitted light of wavelength above 330 nm. The irradiation was discontinued after 10 h 40 min, and the photolysate was concentrated and dried in vacuo to give 1.00 g of yellow oil. (The UV spectra of the photolysate and filter solution were not changed during photolysis.) Chromatography of the crude residue on a 3.4 × 28 cm Florisil (Fisher, 60–100 mesh) column, containing 2% of no. 2282 green Sylvania phosphor, slurry packed in hexane, collecting 1-l. fractions, gave the following: fraction 1, hexane, 1.4 mg of unidentifiable oil; 2, 2% ether in hexane, 0.8 mg of unidentifiable oil; 3–4, 2% ether in hexane, 732.4 mg of 3,3-diphenyl-1-nitrocyclohexene; 5, 2% ether in hexane, 19.2 mg of 3,3-diphenyl-1-nitrocyclohexene and 28.9 mg of *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane; 6–11, 2% ether in hexane, 60.7 mg of *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane; 12–15, 4–32% ether in hexane, 5.5 mg of overlap; 16, 64% ether in hexane, 4.8 mg of 3,3-diphenylcyclohexanone; 17–30, 33.3 mg of unidentified oil; 31–35, 3–40% methanol in ether, 106.7 mg of unidentified oil. Thus, the mass balance is 100%.[37]

2-Phenyl-1-nitrocyclopentene. The procedure of Bordwell[11] was followed to convert 15.1 g (105 mmol) of 1-phenylcyclopentene to 3.69 g (19.5 mmol, 18.6%) of 2-phenyl-1-nitrocyclopentene, mp 50.5–51.5 °C (lit.[11] 51.5–52.5 °C) after chromatography.

***cis*-5,6-Diphenyl-1-nitrobicyclo[3.1.0]hexane.** To a −77 °C slurry of 1.16 g (3.26 mmol) of benzyldiphenylsulfonium tetrafluoroborate[12] in 7.50 ml of dry DME was added, dropwise, 2.00 ml (2.94 mmol) of a 1.47 M solution of butyllithium in hexane. The resulting light orange suspension was treated dropwise with a solution of 309 mg (1.63 mmol) of 2-phenyl-1-nitrocyclopentene in 2.00 ml of dry DME. The dark orange mixture was then stirred under nitrogen at −77 to −78 °C for 102 h, monitoring by TLC. The reaction mixture was then diluted with 50 ml of water and ether extracted. The extracts were washed with water, dried, and concentrated in vacuo to give an orange oil. NMR analysis placed an upper limit of 1% on the possible yield of *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane, relative to the cis isomer. Chromatography on a 2.8 × 90 cm silica gel (Davison, 60–200 mesh) column containing 3% of Sylvania no. 290 red phosphor, slurry packed in hexane, gave the following: fraction 1, 2000 ml, hexane, 492 mg of diphenyl sulfide; 2, 1350 ml, 1% ether in hexane, nil; 3, 225 ml, 1% ether in hexane, 52.1 mg of 2-phenyl-1-nitrocyclopentene with several unidentified compounds; 4, 1875 ml, 1% ether in hexane, 265 mg of 2-phenyl-1-nitrocyclopentene and *cis*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane. All fractions were analyzed by GC (5% QF-1). The material from fraction 4 was recrystallized from ether–hexane to give 180 mg (0.645 mmol, 39.5%) of colorless prisms, mp 110.0–111.5 °C, identified as *cis*-5,6-diphenyl-1-nitrobicyclo-[3.1.0]hexane.

The spectral data follow: IR (KBr) 3.26, 3.30, 3.36, 3.37, 3.41, 3.48, 6.24, 6.61, 6.68, 6.91, 7.44, 8.31, 8.51, 9.64, 10.41, 12.02, 12.63, 13.14, 13.48, 14.10, 14.31, 15.22 μ; 100-MHz ^{1}H NMR (CDCl$_3$) τ 2.60–3.20 (10 H, m, aromatic), 6.95 (1 H, s, benzylic cyclopropyl), 7.20 (2 H, m, CH$_2$ adjacent to nitrosubstituted bridgehead), 7.74 (2 H, m, CH$_2$ adjacent to phenyl-substituted bridgehead), 8.26 (2 H, m, central CH$_2$ of three-bridge); UV (cyclohexane) 253 nm (ϵ 2668); mass spectrum *m/e* (rel intensity) 249 (23.7), 233.13256 (72.9, calcd for $C_{18}H_{17}$, 233.13302), 155 (28.8), 129 (67.8), 128 (16.9), 117 (13.6), 115 (30.5), 105 (28.8), 91 (100.0), 77 (23.7), 74 (28.8).

Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13, N, 5.01. Found: C, 77.59; H, 6.11; N, 5.03.

270-MHz ^{1}H NMR Spectra and Simulated Spectra of *cis*- and *trans*-5,6-Diphenyl-1-nitrobicyclo[3.1.0]hexane.[38] GC pure samples of both *cis*- and *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane were analyzed by 270-MHz NMR.

The spectral data are given in Table II.

The methylene regions of the 270-MHz NMR spectra of both *cis*- and *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane were simulated using the self-iterative computer program mentioned above.[30]

It should be noted that the <1.0 Hz coupling constants are necessary to make the simulated spectrum identical with the observed one, but the relative error is ca. 0.5 Hz.

Isomerization of *cis*-5,6-Diphenyl-1-nitrobicyclo[3.1.0]hexane to *trans*-5,6-Diphenyl-1-nitrobicyclo[3.1.0]hexane. A 100-mg (0.358 mmol) sample of *cis*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane and 11.7 ml(12.0 g, 100 mmol) of acetophenone in 100 ml of purified benzene was purged with vanadous-purified nitrogen[36] for 1 h prior to and during photolysis. The solution was irradiated through a 2-mm Pyrex filter with a 450-W Hanovia medium pressure mercury arc lamp, monitoring by GC (0.25% Carbowax). The concentration of acetophenone was such that it absorbed >99% of the ultraviolet light incident on the solution. After 25 min of irradiation, all of the starting cis isomer had been consumed. The solvent and sensitizer were removed to give 132 mg of dark orange oil, and NMR analysis of the crude photolysate showed *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane to be the only identifiable product. No 3,3-diphenyl-1-nitrocyclohexene was present either by NMR or GC. The crude product was dissolved in ether and filtered through a 1.2 × 5 cm silica gel column. Removal of the solvent gave 104 mg of an oil which was chromatographed on a 1.2 × 26 cm silica gel (Davison, 60–200 mesh) column containing 2% of no. 2282 green Sylvania phosphor, slurry packed in hexane. Elution, collecting 50-ml fractions, gave the following: fraction 1, hexane, nil; 2, 1% ether in hexane, nil; 3, 2% ether in hexane, 15.9 mg (0.0569 mmol, 15.9%) of *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane, mp 122–127 °C, after trituration with pentane. Recrystallization from hexane–ether gave 5.0 mg of colorless prisms, mp 127.0–129.0 °C. The IR, NMR, and mass spectrum were all identical with those of the major photoproduct of 3,3-diphenyl-1-nitrocyclohexene, previously identified as *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane (vide supra).

Photolysis of 3,3-Diphenyl-1-nitrocyclohexene to Extended Conversion. A 100-mg (0.358 mmol) sample of 3,3-diphenyl-1-nitrocyclohexene in 100 ml of purified benzene was purged with vanadous-purified nitrogen[36] for 1 h prior to and during the photolysis. The solution was irradiated through a 2-mm Pyrex filter with a 450-W Hanovia medium pressure mercury arc lamp, monitoring by GC (5% QF-1). The irradiation was discontinued after 19.0 h, when the ratio of major product to starting nitro olefin had reached 0.5:1. The only primary products seen were *trans*-5,6-diphenyl-1-nitrobicyclo-[3.1.0]hexane and 3,3-diphenylcyclohexanone. The solvent was then removed, and the residue was analyzed by GC (0.5% Carbowax). There was no *cis*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane, although as little as 0.1% (relative to the trans isomer) would have been detected by GC.

Photostationary State of *trans*- and *cis*-5,6-Diphenyl-1-nitrobicyclo[3.1.0]hexane. A mixture of 9.54 mg (0.0341 mmol) of *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane and 1.93 mg (0.00692 mmol) of *cis*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane in 50 ml of benzene was purged with vanadous purified nitrogen[36] for 1 h prior to and during photolysis. The solution was irradiated through a 2-mm Pyrex filter with a 450-W Hanovia medium pressure mercury arc lamp, monitoring by GC (0.25% Carbowax). The relative amount of the cis isomer rapidly decreased as the irradiation progressed, until, after 10 h, it was no longer present. (As little as 0.03% would have been detected.) Thus, the ratio of the cis isomer to the trans isomer is essentially zero at the potostationary state.

***cis-* and *trans*-5,6-Diphenylbicyclo[3.1.0]hex-2-ene.** These compounds were prepared by the general method of Dauben[9] from *cis*- and *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one using a procedure very similar to that of Zimmerman and Epling.[39]

***cis*-1,6-Diphenylbicyclo[3.1.0]hexane.**[40] A 88-mg (0.379 mmol) sample of *cis*-5,6-diphenylbicyclo[3.1.0]hex-2-ene and 1.75 g (9.01 mmol) of dipotassium azodicarboxylate in 20 ml of dry pyridine were treated at room temperature with 2.00 ml (32.5 mmol) of acetic acid in 10 ml of pyridine during 6 h. The resulting mixture was then stirred for 27 h, treated with 2.00 ml more of acetic acid over 1.25 h, stirred for 23 h, treated with a third 2.00-ml portion of acetic acid, and stirred for 4 h. The reaction mixture was then poured into 150 ml of water and pentane extracted. The extracts were washed with 10% hydrochloric acid, dried, and concentrated in vacuo to give 73.6 mg (0.314 mmol, 82.9%) of *cis*-1,6-diphenylbicyclo[3.1.0]hexane, pure by NMR. Chromatography on a 2.8 × 11 cm silica gel (Davison, 60–200 mesh) column, slurry packed in hexane, eluting with 750 ml of hexane, gave 69.7 mg (0.279 mmol, 78.3%) of colorless crystals, mp 74–77 °C (lit.[8] 66–68 °C), identified as *cis*-1,6-diphenylbicyclo[3.1.0]hexane. One crystallization from methanol sharpened the melting point to 73–75 °C and gave 56.1 mg.

The spectral data follow: IR (KBr) 3.27, 3.38, 3.46, 5.13, 5.32, 6.22, 6.63, 6.84, 6.86, 7.59, 7.81, 8.13, 8.25, 8.50, 9.03, 9.09, 9.18, 9.51, 9.55, 10.22, 10.55, 10.80, 11.31, 12.25, 12.84, 12.99, 13.87, 14.01, 16.47 μ; 100-MHz ^{1}H NMR ($CDCl_3$) τ 2.80–3.40 (10 H, m, aromatic), 7.60–8.80 (8 H, m, CH_2 and cyclopropyl); mass spectrum *m/e* (rel intensity) 235 (12.6), 234.14121 (58.9, calcd for $C_{18}H_{18}$, 234.14085), 207 (7.3), 206 (15.5), 193 (5.0), 192 (6.3), 191 (10.5), 179 (4.1), 178 (8.5), 177 (1.6), 165 (9.1), 157 (7.9), 156 (24.0), 155 (14.9), 152 (4.7), 144 (14.3), 143 (51.0), 131 (5.5), 130 (46.7), 128 (23.3), 119 (4.6), 117 (44.9), 116 (9.4), 115 (23.7), 105 (3.0), 104 (5.5), 103 (7.7), 102 (9.9), 101 (8.9), 92 (8.7), 91 (100.0), 89 (11.8), 79 (5.1), 78 (7.0), 77 (16.6), 65 (11.1), 63 (6.4), 51 (10.9).

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.20; H, 7.84.

***trans*-1,6-Diphenylbicyclo[3.1.0]hexane.**[40] A 272-mg (1.17 mmol) sample of *trans*-5,6-diphenylbicyclo[3.1.0]hex-2-ene and 1.49 g (7.67 mmol) of dipotassium azodicarboxylate in 37 ml of dry pyridine were treated at room temperature with 1.5 ml (26 mmol) of acetic acid in 7 ml of pyridine over 0.5 h and then stirred for 43 h. Another portion (3.76 g, 19.4 mmol) of dipotassium azodicarboxylate was added to the colorless slurry, followed by the addition of 1.5 ml (26 mmol) of acetic acid in 7 ml of pyridine over a period of 4 h. The resulting mixture was stirred for 7.5 h, treated with a final 1.60-ml (29 mmol) portion of acetic acid in 7 ml of pyridine, and stirred for 25 h. The colorless reaction mixture was then poured into 150 ml of water and pentane extracted. The extracts were washed with 10% hydrochloric acid, washed with saturated sodium bicarbonate solution, dried, and concentrated in vacuo to give 248 mg (1.06 mmol, 90.5%) of a colorless oil, pure by NMR and TLC. The oil was chromatographed on a 2.8 × 17 cm silica gel (Davison, 60–200 mesh) column, slurry packed in hexane, eluting with 700 ml of hexane, to give 228 mg (0.973 mmol, 83.2%) of analytically pure (GC on 5% QF-1 and 0.25% Carbowax 20M) *trans*-1,6-diphenylbicyclo[3.1.0]hexane.

The spectral data follow: IR (neat) 3.23, 3.27, 3.30, 3.37, 3.41, 3.49, 5.14, 5.32, 5.53, 5.69, 6.02, 6.24, 6.34, 6.67, 6.78, 6.89, 7.47, 7.61, 7.89, 8.01, 8.33, 8.47, 8.64, 9.12, 9.32, 9.73, 10.78, 11.01, 11.48, 11.89, 12.74, 13.23, 13.79, 13.97, 14.37, 14.97, 15.70 μ; 100-MHz ^{1}H NMR ($CDCl_3$) τ 2.60–3.10 (10 H, m, aromatic), 7.70 (1 H, d, benzylic cyclopropyl, J = 8 Hz), 7.80–8.40 (5 H, m, CH_2 and cyclopropyl methine), 8.70 (1 H, m, central CH_2 of three-bridge, exo proton), 9.73 (1 H, m, central CH_2 of three-bridge, endo proton); UV (cyclohexane) 253 nm (ϵ 789), 260 (743), 267 (614), 276 (281); mass spectrum *m/e* (rel intensity) 235 (20.9), 234.14099 (100.0, calcd for $C_{18}H_{18}$, 234.14085), 207 (11.8), 206 (25.4), 193 (8.5), 192 (11.0), 191 (33.7), 189 (11.6), 179 (6.3), 178 (14.8), 176 (2.7), 165 (14.6), 157 (12.8), 156 (38.2), 155 (26.3), 152 (8.7), 144 (22.3), 143 (85.6), 131 (8.7), 130 (79.9), 128 (28.1), 118 (7.4), 117 (76.1), 116 (16.7), 115 (43.4), 105 (6.4), 104 (8.7), 103 (13.9), 102 (15.7), 101 (13.9), 92 (16.0), 91 (90.5), 89 (21.6), 79 (8.8), 78 (13.3), 77 (30.9), 65 (21.5), 63 (11.2), 51 (21.0).

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.35; H, 7.70.

270-MHz ^{1}H NMR Spectra of *cis*- and *trans*-1,6-Diphenylbicyclo[3.1.0]hexane. Analytically pure samples of both *cis*- and *trans*-1,6-diphenylbicyclo[3.1.0]hexane (vide supra) were analyzed by 270-MHz NMR. The spectral data are given in Table II.

Preparative Sensitized Photolysis of 3,3-Diphenyl-1-nitrocyclohexene. A 212-mg (0.759 mmol) sample of 3,3-diphenyl-1-nitrocyclohexene in 650 ml of purified benzene containing 50 ml (0.428 mol) of acetophenone was purged with vanadous-purified nitrogen[36] for 1 h prior to and during photolysis. The solution was irradiated through a 2-mm Pyrex filter with a 450-W Hanovia medium pressure mercury arc lamp. Additional filtration of the light was accomplished by circulating the following filter solution[4] around the lamp as coolant: 20.0 g of cupric sulfate pentahydrate, 157 g of nickelous sulfate hexahydrate, 300 g of cobaltous sulfate heptahydrate, and 23.5 g of potassium nitrate in 1 l. of distilled water. The concentrations of nitro olefin and acetophenone were such that the acetophenone absorbed >99% of the light incident on the photolysis solution. After 8.5 h, secondary photolysis began to be apparent, monitoring by GC, 0.25% Carbowax, so the irradiation was discontinued and the solvent was removed in vacuo. The bulk of the acetophenone was removed by distillation at 40–50 °C (0.8–0.1 mm), and the residue was analyzed by GC (0.25% Carbowax) for the possible presence of *cis*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane. None of the cis bicyclic was detected although as little as 0.1%, relative to the trans isomer, would have been seen. Chromatography of the ether-soluble portion of the crude photolysate on a 2.8 × 86 cm Florisil (Fisher, 60–100 mesh) column containing 2% of Sylvania no. 2282 green phosphor, slurry packed in hexane, collecting 1-l. fractions, gave the following: fraction 1, hexane, nil; 2–4, 1% ether in hexane, nil; 5–8, 1% ether in hexane, 47.9 mg of 3,3-diphenyl-1-nitrocyclohexene; 9–10, 1% ether in hexane, 2.0 mg of overlap; 11–13, 2% ether in hexane, 25.7 mg of *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane; 14–20, 2% ether in hexane, 5.3 mg of an unidentified mixture; 21, 8% ether in hexane, 8.2 mg of an unidentified mixture; 22–23, 32% ether in hexane, 27.1 mg of 3,3-diphenylcyclohexanone; 24–26, 32% ether in hexane, 15.8 mg of an unidentified mixture. All fractions were identified by GC (0.25% Carbowax) and NMR.

Preparative Photolysis of 3,3-Diphenyl-1-nitrocyclohexene in Isopropyl Alcohol. A 75.6-mg (0.271 mmol) sample of 3,3-diphenyl-1-nitrocyclohexene in 115 ml of isopropyl alcohol (Mallinckrodt Reagent) was purged with vanadous-purified nitrogen[36] for 1 h prior to and during photolysis. The solution was irradiated with a 450-W Hanovia medium pressure mercury arc lamp, monitoring by GC (0.25% Carbowax). The irradiation was discontinued after 150 min, and the solvent was removed in vacuo to give 84.5 mg of an oil which was almost totally a single compound, by NMR. Trituration with ether and crystallization from ether gave 16.4 mg (0.062 mmol, 22.8%) of 3,3-diphenylcyclohexanone oxime, mp 181–191 °C, which had all spectral data identical with those of a known sample (vide infra). Chromatography on a 1.2 × 10 cm Florisil (Davison, 60–100 mesh) column, eluting with 10% ether in hexane, followed by recrystallization from methanol gave an analytical sample, mp 190–199 °C.

Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22. Found: C, 81.29; H, 7.17.

3,3-Diphenylcyclohexanone Oxime. A 100-mg (0.399 mmol) sample of 3,3-diphenylcyclohexanone was stirred for 12 h with 277 mg (3.99 mmol) of hydroxylamine hydrochloride and 41 mg (0.5 mmol) of sodium acetate in ethanol–water (5:1 v/v). The reaction mixture was then poured into water, ether extracted, dried, and concentrated in vacuo to give 64.0 mg of a colorless, crystalline solid. Recrystallization of 55 mg from methanol gave 46 mg (0.173 mmol, 51.8% based on total crude product) of colorless crystals, mp 191–199 °C.

The spectral data follow: IR (KBr) 3.08, 3.17, 3.26, 3.37, 6.17, 6.68, 6.90, 7.40, 7.51, 7.74, 7.92, 8.06, 9.17, 9.64, 10.08, 10.49, 10.72, 10.95, 11.98, 13.00, 13.18, 14.03, 14.27 μ; 60-MHz NMR ($CDCl_3$) τ 1.92 (1 H, br s, OH), 2.80 (10 H, m, aromatic), 6.84 (2 H, s, CH_2), 7.20–7.80 (4 H, m, CH_2), 8.00–8.60 (2 H, m, CH_2); UV (95% ethanol) 262 nm (ϵ 519), 268 (377); mass spectrum *m/e* (rel intensity) 266 (19.7), 265.14652 (100.0, calcd for $C_{18}N_{19}NO$, 265.14666), 249 (21.5), 248 (96.9), 193 (23.5), 191 (22.7), 179 (14.3), 178 (27.2), 170 (24.5), 167 (17.3), 165 (24.0), 130 (16.5), 129 (52.0), 128 (10.9), 115 (46.7), 105 (19.1), 103 (12.4), 98 (10.4), 91 (58.5), 77 (21.2).

Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22. Found: C, 81.32; H, 7.22.

Photolysis of 3,3-Diphenyl-1-nitrocyclohexene in Isopropyl Alcohol. A 200-mg (0.716 mmol) sample of 3,3-diphenyl-1-nitrocyclohexene in 200 ml of isopropyl alcohol was purged with vanadous-purified nitrogen[36] for 1 h prior to and during photolysis. The solution was irradiated with a 450-W Hanovia medium pressure mercury arc lamp, through a 2-mm Pyrex filter, monitoring by GC (0.25% Carbowax). After 150 min of irradiation, the solvent was removed in vacuo to give a yellow oil which was analyzed by NMR and found to contain

3,-diphenylcyclohexanone oxime, *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane, and 3,3-diphenyl-1-nitrocyclohexene in a ratio of 5.73:1.00:3.40. The product ratio was determined by hand integration of the expanded 100-MHz NMR spectrum. If any 3,3-diphenylcyclohexanone were present, it was not present in sufficient amount to be detected. Crystallization of the crude product from methanol, treatment with Norit, and a second crystallization from methanol gave 89.2 mg (0.336 mmol, 46.9%) of 3,3-diphenylcyclohexanone oxime, mp 184–195 °C.

Photolysis of 3,3-Diphenyl-1-nitrocyclohexene in 10% Isopropyl Alcohol. A solution of 3,3-diphenyl-1-nitrocyclohexene in 10% isopropyl alcohol in benzene (v/v) was purged with vanadous-purified nitrogen[36] for 1 h prior to and during the photolysis. In runs 1–3 the solution was irradiated with a 450-W Hanovia medium pressure mercury arc lamp through 2 mm of Pyrex and a 4-mm thickness of 0.025 M sodium vanadate in 0.05 M sodium hydroxide, circulated as lamp coolant. In run 4, only Pyrex was used as a filter. The filters were such that the light transmitted was of wavelength longer than 330 or 290 nm, respectively. The nitro olefin absorbed >99% of the incident UV light, relative to any other species in solution. After the irradiation, the photolysate was concentrated in vacuo and (in the quenched run) the naphthalene was removed by sublimation at 40 °C (0.05 mm). The ultraviolet spectrum of the photolysate and filter were the same before and after photolysis. By a combination of NMR and GC analysis (tetraphenylethylene internal standard) the quantities of *trans*-5,6-diphenyl-1-nitrobicyclo[3.1.0]hexane, 3,3-diphenylcyclohexanone, and 3,3-diphenylcyclohexanone oxime produced were determined. The details of each run are given below.

Run 1. Starting nitro olefin, 0.358 mmol in 115 ml of 10% isopropyl alcohol in benzene; 150 min photolysis time; bicyclohexane formed, 0.0225 mmol; cyclohexanone formed, 0.0045 mmol; oxime formed, 0.0284 mmol; 15.5% conversion.

Run 2. Starting nitro olefin, 0.358 mmol in 115 ml of 10% isopropyl alcohol in benzene containing 0.1 M naphthalene; 150 min photolysis time; bicyclohexane formed, 0.0207 mmol; cyclohexanone formed, 0.00456 mmol; oxime formed, 0.0213 mmol; 13.0% conversion.

Run 3. Starting nitro olefin, 0.358 mmol in 115 ml of 10% isopropyl alcohol in benzene; 30 min photolysis time; bicyclohexane formed, 0.00578 mmol; cyclohexanone formed, 0.00121 mmol; oxime formed, 0.00488 mmol; 3.3% conversion.

Run 4. Starting nitro olefin, 0.358 mmol in 100 ml of 10% isopropyl alcohol in benzene; 150 min photolysis time; ratio of oxime to bicyclohexane, 0.94:1.00; 19.5% conversion.

Apparatus for Quantum Yields. The quantum yield photolyses were run on the "Black Box" apparatus.[21] Light output was measured by ferrioxalate actinometry.[41] The light absorbed in the reaction cell was determined by the splitting ratio technique.[21] The light was filtered through a three-compartment cell containing one of the following solution filter combinations. Filter A, (a) 0.1 M cupric sulfate pentahydrate in 1% sulfuric acid, (b) 1.0 M cobaltous sulfate heptahydrate in 5% sulfuric acid, (c) 2.0 M nickelous sulfate hexahydrate in 5% sulfuric acid; this combination gave a maximum transmission (39%) at 317 nm and was opaque below 280 nm and above 360 nm. Filter B, (a) 1.0 M cupric sulfate pentahydrate in 5% sulfuric acid, (b) 2.0 M cobaltous sulfate heptahydrate in 5% sulfuric acid, (c) 0.5 M nickelous sulfate hexahydrate in 1.5% sulfuric acid; this combination gave a maximum transmission (24%) at 337 nm and was opaque below 310 nm and above 375 nm.

Direct Quantum Yields. The direct photolyses for quantum yield determinations were run in purified benzene. The photolysis solution was purged with vanadous-purified nitrogen[36] for 1 h prior to and during irradiation. The photolysates were analyzed by GC on a 4 ft × 0.25 in. column of 5% SE-30 on Varaport 30, 100/120 mesh, at 170 °C using tetraphenylethylene as internal standard. Data for the quantum yields are as follows.

Run 1. Filter A; starting nitro olefin, 2.40 mmol in 750 ml; 225.1 mEinsteins absorbed; bicyclohexane formed, 0.0688 mmol; Φ = 0.000306; ketone formed, 0.00895 mmol, Φ = 0.0000397; 3.24% conversion.

Run 2. Filter A; starting nitro olefin, 2.40 mmol in 750 ml; 110.4 mEinsteins absorbed; bicyclohexane formed, 0.0335 mmol, Φ = 0.000303; ketone formed, 0.00414 mmol, Φ = 0.0000375; 1.63% conversion.

Run 3. Filter A; starting nitro olefin, 2.40 mmol in 750 ml; 54.65 mEinsteins absorbed; bicyclohexane formed, 0.0166 mmol, Φ = 0.000304; ketone formed, 0.00162 mmol, Φ = 0.0000263; 0.759% conversion.

Run 4. Filter A; starting nitro olefin, 2.40 mmol in 750 ml; 26.96 mEinsteins absorbed; bicyclohexane formed, 0.00822 mmol, Φ = 0.000305; ketone formed, 0.000440 mmol, Φ = 0.0000161; 0.361% conversion.

Sensitized Quantum Yields. The sensitized photolyses for quantum yield determinations were run in purified benzene containing enough acetophenone to absorb >99% of the light incident on the solution. The photolysis solution was purged with vanadous-purified nitrogen[36] for 1 h prior to and during irradiation. The acetophenone was removed in vacuo (0.04 mm) at 40–50 °C before GC analysis, performed as in the direct quantum yields. Data for the quantum yields are as follows.

Run 1. Filter B; starting nitro olefin, 0.752 mmol in 750 ml; 8.03 mEinsteins absorbed; bicyclohexane formed, 0.00313 mmol, Φ = 0.000390; ketone formed, 0.00339 mmol, Φ = 0.000422; 0.867% conversion.

Run 2. Filter B; starting nitro olefin, 0.749 mmol in 750 ml; 3.99 mEinsteins absorbed; bicyclohexane formed, 0.00174 mmol, Φ = 0.000437; ketone formed, 0.000826 mmol, Φ = 0.000207; 0.343% conversion.

Run 3. Filter B; starting nitro olefin, 0.751 mmol in 750 ml; 2.27 mEinsteins absorbed; bicyclohexane formed, 0.000982 mmol, Φ = 0.000433; ketone formed, 0.000375 mmol, Φ = 0.000165; 0.181% conversion.

Acknowledgment. Support of this research by the National Science Foundation is gratefully acknowledged.

Registry No.—**2**, 60934-67-0; **4**, 31158-25-5; **5**, 60909-09-3; **6**, 60965-82-4; **7**, 31186-81-9; **8**, 31186-82-0; **11**, 17245-76-0; **11** oxime, 56740-40-0; dinitrogen tetroxide, 10544-72-6; benzyldiphenylsulfonium BF$_4^-$, 1763-99-1; 2-phenyl-1-nitrocyclopentene, 29787-31-3; *cis*-5,6-diphenylbicyclo[3.1.0]hex-2-ene, 27995-70-6; *trans*-5,6-diphenylbicyclo[3.1.0]hex-2-ene, 27995-69-3.

References and Notes

(1) This is part 103 of our photochemical series.
(2) For the previous paper on Mechanistic and Exploratory Organic Photochemistry, see H. E. Zimmerman, R. J. Boettcher, N. E. Buehler, G. E. Keck and M. G. Steinmetz, *J. Am. Chem. Soc.*, **98**, 7680 (1976).
(3) (a) H. E. Zimmerman and J. W. Wilson, *J. Am. Chem. Soc.*, **86**, 4036 (1964); (b) H. E. Zimmerman and K. G. Hancock, *J. Am. Chem. Soc.*, **90**, 3749 (1968).
(4) H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *J. Am. Chem. Soc.*, **89**, 2033 (1967).
(5) (a) H. E. Zimmerman and N. Lewin, *J. Am. Chem. Soc.*, **91**, 879 (1969); (b) H. E. Zimmerman and W. R. Elser, *ibid.*, **91**, 887 (1969).
(6) H. E. Zimmerman and R. L. Morse, *J. Am. Chem. Soc.*, **90**, 954 (1968).
(7) (a) C. Leibovici and J.-F. Labarre, *J. Chim. Phys. Phys.-Chim. Biol.*, **67**, 1664 (1970); (b) K. L. McEwen, *J. Chem. Phys.*, **32**, 1801 (1960); (c) G. Snatzke, *J. Chem. Soc.*, 5002 (1965); (d) E. A. Braude, E. R. H. Jones, and G. G. Rose, *ibid.*, 1104 (1947); (e) O. L. Chapman, D. C. Heckert, J. W. Reasoner, and S. P. Thackaberry, *J. Am. Chem. Soc.*, **88**, 5550 (1966); (f) K. R. Loos, U. P. Wild, and H. H. Günthard, *Spectrochim. Acta, Part A*, **25**, 275 (1969).
(8) W. G. Dauben and W. A. Spitzer, *J. Am. Chem. Soc.*, **92**, 5817 (1970).
(9) W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *J. Am. Chem. Soc.*, **90**, 4762 (1968).
(10) H. E. Zimmerman and G. A. Epling, *J. Am. Chem. Soc.*, **94**, 7806 (1972).
(11) F. G. Bordwell and E. W. Garbisch, Jr., *J. Org. Chem.*, **28**, 1765 (1963).
(12) A. W. Johnson, V. J. Hruby and J. L. Williams, *J. Am. Chem. Soc.*, **86**, 918 (1964).
(13) J. Asunskis and H. Shechter, *J. Org. Chem.*, **33**, 1164 (1968).
(14) H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *J. Am. Chem. Soc.*, **90**, 4892 (1968).
(15) H. E. Zimmerman and T. W. Flechtner, *J. Am. Chem. Soc.*, **92**, 6931 (1970).
(16) H. E. Zimmerman and C. M. Moore, *J. Am. Chem. Soc.*, **92**, 2023 (1970).
(17) H. E. Zimmerman, S. S. Hixson, and E. F. McBride, *J. Am. Chem. Soc.*, **92**, 2000 (1970).
(18) S. S. Hixson and J. Borovsky, *J. Am. Chem. Soc.*, **97**, 2930 (1975).
(19) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson and G. Klose, *J. Am. Chem. Soc.*, **87**, 1410 (1965).
(20) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *J. Am. Chem. Soc.*, **86**, 2532 (1964).
(21) H. E. Zimmerman, *Mol. Photochem.*, **3**, 281 (1971).
(22) H. E. Zimmerman and T. P. Cutler, to be published.
(23) R. Hurley and A. C. Testa, *J. Am. Chem. Soc.*, **90**, 1949 (1968).
(24) (a) R. Hurley and A. C. Testa, *J. Am. Chem. Soc.*, **88**, 4330 (1966); (b) J. K. Brown and W. G. Williams, *Chem. Commun.*, 495 (1966); (c) Y. Kitaura and T. Matsuura, *Tetrahedron*, **27**, 1583 (1971); (d) reasonable mechanisms require a two-photon process.
(25) (a) O. L. Chapman, P. G. Cleveland, and E. Hoganson, *Chem. Commun.*, 101 (1966); (b) G. B. Howarth, D. G. Lance, W. A. Szarek, and J. K. N. Jones, *Can. J. Chem.*, **47**, 81 (1969); (c) G. W. Shaffer, *ibid.*, **48**, 1948 (1970); (d) R. Hunt and S. T. Reid, *J. Chem. Soc., Perkin Trans. 1*, 2527 (1972); (e) J. T. Pinhey and E. Rizzardo, *Tetrahedron Lett.*, 4057 (1973).
(26) (a) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961); (b) *ibid.*, **84**, 4527 (1962); (c) H. E. Zimmerman, Abstracts of the

17th National Organic Chemistry Symposium of the American Chemical Society, p 31; (d) *Adv. Photochem.*, **1**, 183 (1963); (e) *Science*, **153**, 837 (1966); (f) *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969).

(27) (a) D. J. Patel and D. I. Schuster, *J. Am. Chem. Soc.*, **90**, 5137 (1968); (b) D. I. Schuster and D. J. Patel, *ibid.*, **90**, 5145 (1968); (c) D. I. Schuster and V. Y. Abraitjs, *Chem. Commun.*, 419 (1969); (d) D. I. Schuster and K. Liu, *J. Am. Chem. Soc.*, **93**, 6711 (1971); (e) P. J. Kropp and W. F. Erman, *ibid.*, **85**, 2456 (1963); (f) P. J. Kropp, *ibid.*, **86**, 4053 (1964); (g) C. Ganter, E. C. Utzinger, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 2403 (1962); (h) M. H. Fisch, *Chem. Commun.*, 1472 (1969); (i) L. L. Barber, O. L. Chapman, and J. D. Lassila, *J. Am. Chem. Soc.*, **91**, 3664 (1969); (j) R. E. Harmon and B. L. Jensen, *J. Heterocycl. Chem.*, **7**, 1077 (1970); (k) H. V. Secor, M. Bourlais, and J. F. DeBardeleben, *Experientia*, **27**, 18 (1971); (l) D. Caine, P. F. Brake, J. F. DeBardeleben, Jr., and J. B. Dawson, *J. Org. Chem.*, **38**, 967 (1973); (m) J. K. Crandall and R. P. Haseltine, *J. Am. Chem. Soc.*, **90**, 6251 (1968); (n) R. Noyori and M. Kato, *Tetrahedron Lett.*, 5075 (1968).

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

(29) T. M. Brennan and R. K. Hill, *J Am. Chem. Soc.*, **90**, 5614 (1968).

(30) All melting points were determined on a hot-stage apparatus calibrated with known compounds. Mass spectra were taken on an AEI MS-902 mass spectrometer at 70 eV. Proton nuclear magnetic resonance spectra were taken on a Varian T-60, JEOL-MH-100, or Bruker WH-270 spectrometer. Computer simulations of 270-MHz ^{1}H NMR spectra were done using the ITRCAL program (Nicolet N17-30712) on a Nicolet/Bruker B-NC computer with 36K core and a Diablo Model 31 moving head storage disk. Carbon nuclear magnetic resonance spectra were taken on a JEOL FX-60, a Bruker WH-270, or a Varian XL-100 pulsed Fourier transform spectrometer. Chemical shifts are given in parts per million from tetramethylsilane. Gas chromatographic analyses were carried out on a Varian Aerograph Series 2100 chromatograph with flame ionization detectors, using 4 ft × 0.25 in. glass columns of 0.25% Carbowax 20M, 0.5% Carbowax 20M, 5% QF-1, or 5% SE-30 on Varaport 30, 100/120 mesh. Column chromatography was done with Vycor columns and Sylvania phosphors mixed in the column packing to allow monitoring with a hand-held ultraviolet lamp. Benzene for photolysis was purified by repeated washing with acidic saturated potassium permanganate solution followed by repeated washing with concentrated sulfuric acid and then distilled through a 30-cm column of metal helics. Acetophenone for use as a sensitizer was purified by fractional distillation at reduced pressure followed by repeated crystallization under nitrogen.

(31) H. E. Zaugg, M. Freifelder, and B. W. Horrom, *J. Org. Chem.*, **15**, 1191 (1950).

(32) This compound was previously reported by Arnold.[33]

(33) R. Arnold, B.S.Thesis, University of Wisconsin, 1975.

(34) A. Hassner, J. E. Kropp, and G. L. Kent, *J. Org. Chem.*, **34**, 2628 (1969).

(35) The 3,3-diphenylcyclohexanone used for spectral comparisons was prepared by G. A. Epling; see ref 10.

(36) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

(37) In a control run in which 1.000 g of 3,3-diphenyl-1-nitrocyclohexene was chromatographed on Florisil under the same conditions as those used for the photolysate, a recovery of 98.1% of the material was realized. Thus, one can expect to lose 1.9% of the nitro olefin from a chromatographed photolysate.

(38) We are most grateful to Dr. D. F. Hillenbrand for running both the 270-MHz spectra and the computer simulations.

(39) H. E. Zimmerman and G. A. Epling, *J. Am. Chem. Soc.*, **94**, 8749 (1972).

(40) This compound was previously reported by Dauben et al.,[8] without spectral data or experimental details.

(41) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).

9-*tert*-Butyl-9-azabicyclo[3.3.1]nonan-3-one

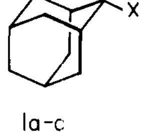
John R. Wiseman,* Herman O. Krabbenhoft, and Robert E. Lee

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

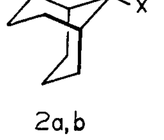
Received August 13, 1976

The title compound **7** has been synthesized by reaction of *tert*-butylamine with cycloocta-2,7-dienone. ^{13}C NMR and pK_a measurements of **7** show that the nitrogen atom of **7** is either a flattened pyramid or planar.

Six-membered cyclic compounds in chair conformations bearing axial *tert*-butyl groups are rare, as would be anticipated based upon the severe 1,3-diaxial steric interactions inherent in such conformations.[1] For instance, in order to avoid having an axial *tert*-butyl group, twist boat conformations are preferred for *trans*-1,3-di-*tert*-butylcyclohexane,[2a–c] *cis*-1,4-di-*tert*-butylcyclohexane,[2c,d] and *cis,trans*-1,3,5-tri-*tert*-butylcyclohexane;[2e] however, for both *cis*- and *trans*-1,2-di-*tert*-butylcyclohexane chair conformations with axial *tert*-butyl groups have been found to be important.[2f,g] Other carbocyclic examples are 2-*tert*-butyladamantane (**1c**),[3a] 2-*tert*-butyladamantan-2-ol (**1a**),[3b] and 9-*tert*-butylbicyclo[3.3.1]nonan-9-ol (**2a**).[3c] The corresponding *p*-nitrobenzoates **1b** and **2b** exhibit extraordinarily high solvolytic reactivities due to relief of strain during ionization.[3b–d]



1a-c

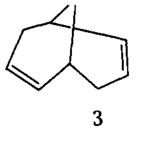


2a, b

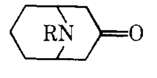
a, X = OH
b, X = p-NO$_2$C$_6$H$_4$CO$_2$
c, X = H

Heterocyclic compounds[4,5] such as *cis*-2-alkyl-5-*tert*-butyl-1,3-dioxanes[4a] and 5-*tert*-butyl-1,3,2-dioxaphosphorins[5e] with axially disposed *tert*-butyl groups have also been described. In these molecules the severe 1-*tert*-butyl-3-hydrogen diaxial interactions present in carbocyclic compounds are absent.[6]

Recently Cuthbertson and MacNicol have reported the preparation of 9-*tert*-butyl-9-azabicyclo[3.3.1]nona-2,6-diene (**3**),[7] a compound in which the 1,3-diaxial interactions are diminished by flattening of the carbon bridges. We now report the synthesis and interesting properties of 9-*tert*-butyl-9-azabicyclo[3.3.1]nonan-3-one (**7**). For comparison we have also prepared the *N*-methyl, *N*-ethyl, and *N*-isopropyl analogues **4–6**. We were intrigued with the possibility of detecting a flattening of the nitrogen pyramid to relieve some of the steric



3



4, R = Me
5, R = Et
6, R = i-Pr
7, R = t-Bu