

LIGHT-INDUCED TRANSFORMATIONS OF A SPIRONORCARADIENE^{1, 2}

R. H. LEVIN³ and M. JONES, JR.⁴

Department of Chemistry, Princeton University, Princeton, New Jersey 08540

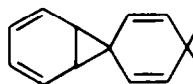
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Abstract—Norcaradiene **2** undergoes two kinds of photochemical reaction. 4,4-Dimethylcyclohexadienylidene is extruded on irradiation through quartz, but not when **2** is shielded by Pyrex. The carbene can be trapped with various olefins and a comparison of the properties of the carbene formed from **2** and on photolysis of 4,4-dimethyldiazocyclohexadiene reveals them to be identical. In either quartz or Pyrex an isomer of **2** is formed which is thought to possess structure **3d**. Heating of **3d** at 100° produces still another isomer, **4a**, which can be reconverted to **3d** on irradiation. Structures for **3d** and **4a** are proposed and mechanisms for their formation suggested.

EMANATING from recent investigations of the addition reactions of cyclopentadienylidene⁵ and 4,4-dimethylcyclohexadienylidene^{6, 7} was the astounding discovery that these carbenes formed norcaradienes **1** and **2** on reaction with benzene. The reasons for the preference of **1** and **2** for the norcaradiene form remain at least partially



1



2

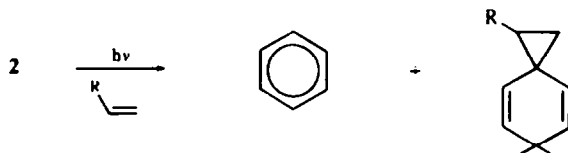
obscure at this time, but probably derive mainly from the ideal geometry for interaction between the 7-substituents and the 3-membered ring made obligatory by the rigid structure.⁸

The thermal chemistry of **2** has been briefly described⁷ and consists of an aromatization reaction occurring as low as 70° unenlivened by detectable Berson-Willcott rearrangements.^{9, 10.} * The photochemical reactions of **2** are varied and interesting, though, and it is these we wish to describe.

It was anticipated that if enough energy could be conveyed to **2**, the reversal of the initial cycloaddition might be effected. Such an event is not unprecedented in simple norcaradienes¹¹ and has even been observed in less propitious systems.¹²⁻¹⁷ Should the extrusion occur, it would become possible to compare the carbene generated by conventional decomposition of the diazo compound⁷ with that from **2**. In turn, this would allow an assessment of the importance of reactions of excited diazo compounds in supposed carbene reactions.

* This does not mean such processes are not occurring at a rate which makes detection by NMR spectroscopy impossible.

Irradiation of olefinic solutions of **2** with an unfiltered, medium pressure mercury arc led to the decomposition of **2** and the formation of two products. One of these proved to be the product of the addition of 4,4-dimethylcyclohexadienylidene to the host olefin and the other was isomeric with **2**. We shall return to this isomer and its further reactions later. Identification of the carbene adducts was by comparison of properties with those of the compounds previously identified.⁷ A sensitive test of



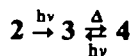
the identity of the species produced from **2** and the diazo compound seemed to us to be the relative rates of addition of the two (or one) species to olefins. Host olefins were chosen so as to span the entire range of rates previously found on photolysis of the diazo compound. In no case is there a significant difference in rate (Table 1).

TABLE I. RELATIVE RATES OF OLEFIN ADDITION

Olefin	Diazo ⁷	K_{rel}	2
3,3-Dimethylbutene-1	0.21		0.23
2-Methylbutene-2	1.00		1.00
2,3-Dimethylbutene-2	1.23		1.07
2,3-Dimethylbutadiene-1,3	3.00		3.07

The adducts themselves are not stable to the photolysis conditions, but relatively little decomposition occurs during the photolysis times employed (*ca* 15 min). We conclude that excited diazo compounds are not likely to contribute significantly as sources of the products formed on photolysis of the diazo compound in olefins.*

The second product (**3**) found in the irradiations through quartz is independent of the host olefin and isomeric with **2**. This compound is also formed on irradiation of **2** in non-olefinic solvents and the yield appears to be maximized by irradiation through Pyrex under which conditions the retro-cycloaddition does not take place. Compound **3** is converted nearly quantitatively to **4** on refluxing for 10–12 hr in



carbon tetrachloride or acetonitrile. Compound **4** is reconverted to **3** in *ca* 50% yield on irradiation through Pyrex.

Let us first look at compound **4**, as it is the simpler of the two unknowns. The similarity of the spectra of **4** to those of 1-vinylcycloheptatriene (**5**)¹⁸ and the mixture

* Of course we lie exposed to whim of nature, and an unlikely accidental equivalence in properties of the two species would render this experiment irrelevant.

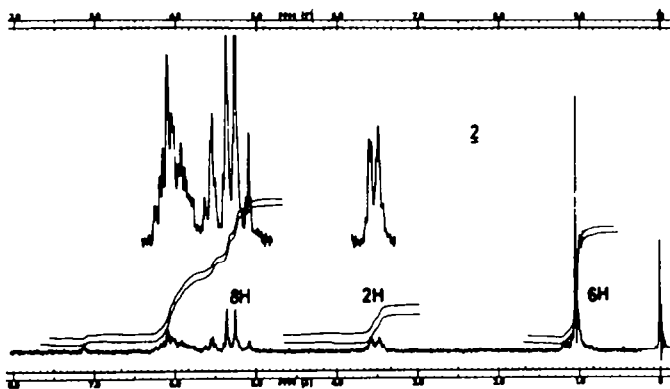


FIG 1. NMR spectrum of 2

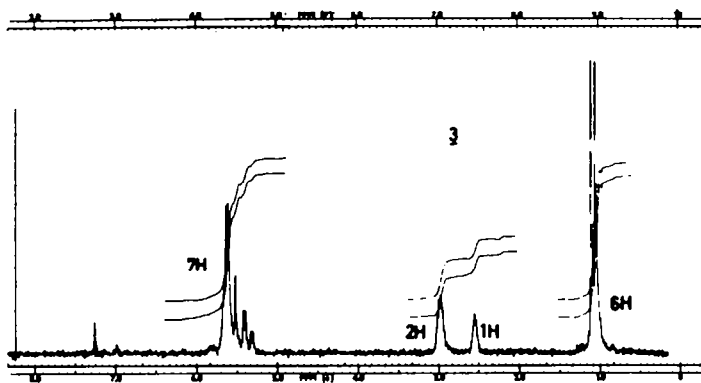


FIG 2. NMR spectrum of 3

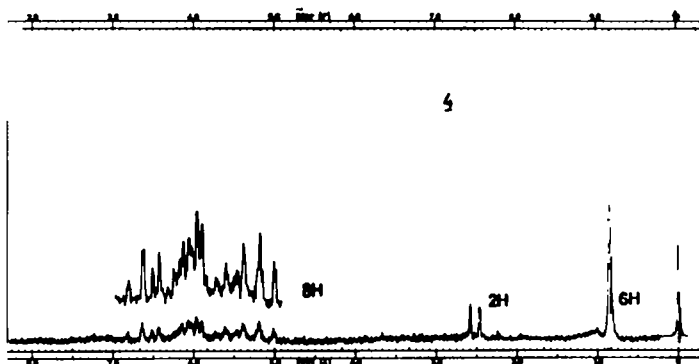


FIG 3. NMR spectrum of 4

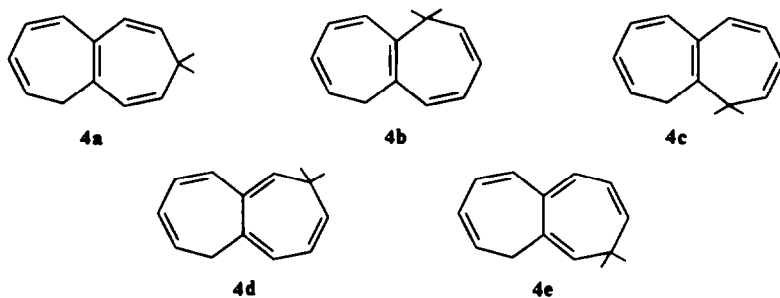
TABLE 2. UV SPECTRA OF 3, 4 AND MODEL COMPOUNDS

Compound	UV		Reference
	λ	ϵ	
3 ^a	300	160	this work
	268	6640	
	259	8700	
	249	8260	
	240	6530	
4 ^a	309	6900	this work
	250	11,400	
	213	~22,500	
	1-Vinylcycloheptatriene ^b (5)	298	
2-Vinylcycloheptatriene ^b (6)	264	3020	20
3-Vinylcycloheptatriene ^b (7)	280	10,720	20
(8) ^a	252	7860	21
	308	3680	21

^a In hexane ^b In cyclohexane

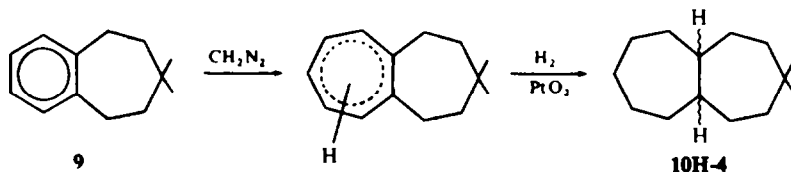
of Dauben and Bertelli (8)¹⁹ led us to concentrate on compounds containing fused cycloheptatriene rings. Heptafulvenes were eliminated from consideration because of the lack of color in 4,²⁰⁻²² and perhaps surprisingly, structures composed of fused 6 + 8, 5 + 9, 4 + 10 or 3 + 11 membered rings are all lacking in one or more of their expected spectral properties. Further, they often lack an appropriate photoisomer and demand extreme mechanistic contortions for their presence. The methylene position of one ring must be adjacent to the ring fusion as these protons appear as a doublet at τ 7.44, $J = 6.9$ Hz (compare to 5: doublet, $\tau = 7.38$, $J = 7$ Hz²⁰). The other methylene position must bear the nondiastereotopic methyl groups.

From these constraints only five structures (4a-4e) emerge as possibilities. Of these, 4c and 4d are 2-vinylcycloheptatrienes, and 4e is a 3-vinylcycloheptatriene. These compounds would be expected to mimic the UV spectra of their parents (Table



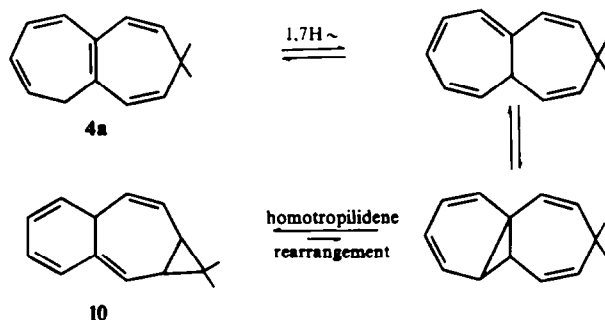
2), which 4 does not. That the additional double bond does not importantly change the system can be seen from the mixture 8 which has an UV maximum quite close (10 nm) to the parent 1-vinylcycloheptatriene. This leaves 4a and 4b as possibilities.

In an attempt to synthesize perhydro 4a, the known^{23, 24} compound 9 was treated

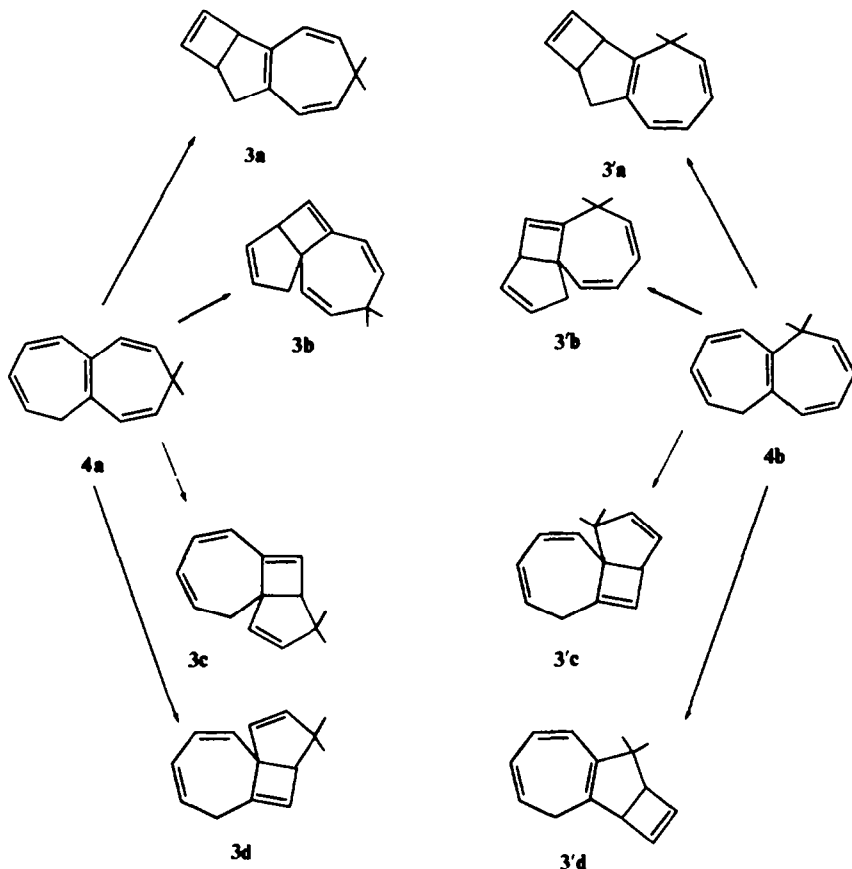


with diazomethane according to the Gaspar-Roth recipe²⁵ to give a mixture of cycloheptatrienes which was then hydrogenated to give decahydro-4 (10H-4) of unproven stereochemistry. Compound 4 was then hydrogenated to give a mixture of partially hydrogenated compounds from which only the octahydro isomer could be cleanly separated. The mass spectrum of the remaining mixture contained all the peaks of the decahydro-4 made previously, and in the correct ratio, except for a tiny peak at $m/e = 152$, which may be due to the *trans*-isomer. This evidence, while of a permissive nature rather than compelling, is complimented by mechanistic considerations.

Let us for now carry both 4a and 4b as possibilities and consider unknown 3. The general mechanistic paths available to 4 include three common in cycloheptatriene chemistry, 1,7-hydrogen shift,^{26, 27} formation of a norcaradiene, and photochemical closure to a bicyclo[3.2.0] system.²⁸ Of course the latter two processes could occur from any cycloheptatriene formed by a series of hydrogen shifts. There seems no reason to suppose that any of the possible norcaradienes would be stable relative to the related cycloheptatrienes and we reject this path. Hydrogen shifts also do not directly yield appropriate structures, but further transformations of compounds produced by hydrogen-shift must be examined carefully. We can find no suitable candidate for 3 this way but our closest approach is shown below (10).

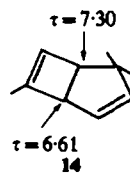
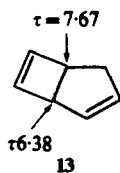
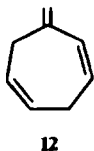
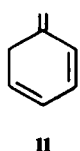


While 10 might fit the NMR, the ultraviolet spectrum of 3 is not appropriate for compound 10. Application of Woodward's rules²⁹ to 10 yields a calculated λ_{\max} of 303 nm. In fact methylenecyclohexadiene-1,3 (11) has $\lambda_{\max}^{\text{isooctane}} = 303$. ($\epsilon = 4400$).³⁰ In addition one would expect 10 to aromatize on standing.³⁰ Formation of a bicyclo[3.2.0] system does yield an acceptable structure, however. The eight possibilities from 4a and 4b are shown below. Three of these (3a, 3'a, 3'd) can be eliminated immediately because they possess one fewer than the required 7 vinyl hydrogens. Another (3b) should have no UV maximum at wavelength as long as 268 nm. Thus 12 has



$\lambda_{\text{max}}^{\text{EtOH}}$ 235 nm ($\epsilon = 13,900$).³¹ Of the remaining four, **3d** is to be preferred to either **3c**, **3c'** or **3b'** because it possesses a doubly allylic pair of methylene hydrogens and a singly allylic methine hydrogen. In the nmr spectrum of **3**, it is the two-proton multiplet which appears downfield of the one-proton multiplet. Good models are **13** and **14** which both show the doubly-allylic protons 0.7–1.3 ppm downfield of the singly allylic ones. We find a two-proton signal at $\tau = 7.00$ and a one-proton signal at $\tau = 7.48$.

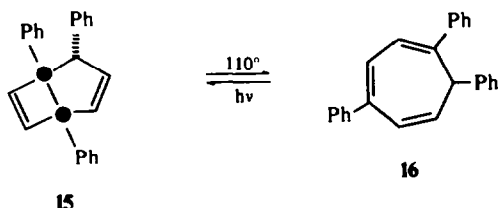
We feel **3d** fits the spectral data better than the other possibilities. Additionally, precedent exists which shows that **4a** should close on photolysis to **3d** while **4b** should give **3d'**, a molecule definitely out of consideration. Brember *et al.*³² have developed semi-empirical predictions which are claimed to predict correctly the



direction of every known cycloheptatriene ring closure. Their predictions agree with our independent formulation of **3d** as the structure of **3** and give weight to our rejection of **3c**, and any structure in the **3'** series (and hence **4b** as well).

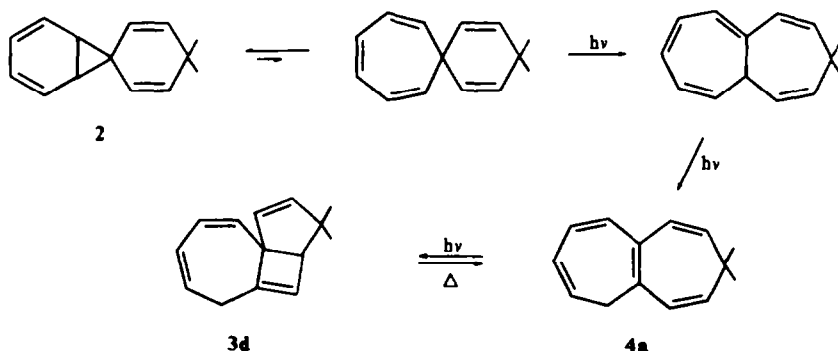
One may legitimately ask two questions: (1) why does **3** open to **4** at such a low temperature, and (2) how is **3** formed from **2**?

The thermal opening of **3** very probably is not concerted, as the formulations of Woodward and Hoffmann³³ allow the sure prediction that the thermal opening of **3** should be conrotatory. This would oblige one double bond in **4** to be *trans*, an unhappy situation indeed. Could a non-concerted ring opening occur at these temperatures? As precedent one may mention the complete conversion of **15** to **16** on heating at 110° for 10 min.³⁴



The formation of **3** from **2** probably goes through **4**. A mechanism is suggested below which requires a photochemical 1,7 alkyl shift^{35, 36} in the cycloheptatriene related to **2**, followed by a 1,7 hydrogen shift.^{26, 27} Compound **4**, which in Pyrex is absorbing light more strongly than **2**, then cyclizes to **3**.

We stress that **3** and **4** cannot be considered to possess *rigorously* proven structures, but we feel the evidence strongly favors the structures proposed.



EXPERIMENTAL

General. All m.ps and b.ps are uncorrected. NMR spectra were obtained on a Varian Associates A-60A instrument using CCl_4 as solvent and TMS as internal standard. Mass spectra were recorded on an AEI MS-9 mass spectrometer.³⁷ Gas-chromatographic analyses and collections were performed with a Varian Aerograph A-90P instrument.

Condition A. 0.3 m, 10% FFAP on 60/80 mesh Chromosorb P column operated at 60° with a detector of 100°, injector temp of 95° and a He flow of 150 ml/min.

Condition B. 0.5 m, 20% Carbowax 20M on 60/80 mesh Chromosorb P column operated at 132° with a detector temp of 190°, injector temp of 160° and a He flow of 100 ml/min.

Preparation of diazo-4,4-dimethylcyclohexadiene. This preparation was modelled after Method B in ref. 7. To a homogeneous soln of 4,4-dimethylcyclohexadienone tosylhydrazone (5.0 g, 0.017 mole) in ca 70 ml dry THF, NaOMe (0.92 g, 0.017 mole) was added. The soln was stirred and within minutes, a viscous white slurry formed. The slurry was stirred for ca 12 hr after which time the THF was removed at the water-pump and the resultant tan solid evacuated to 0.05 mm in a flask attached to a cold trap at -78°. The flask was gradually heated in an oil bath and ca 300-400 mg purple diazo compound distilled over between 90-105° (0.05 mm). Care had to be exercised at the higher temp limit in order to prevent the azine from flashing over. A soln of the diazo compound in the olefin in which it was to be irradiated was washed with two portions cold water (25 ml) to remove traces of THF which inevitably co-distilled with the diazo compound. The aqueous washings were separated and discarded and the purple organic soln was rapidly dried over Na₂SO₄. This soln was then used to generate the carbene as described below.

Photolysis of diazo-4,4-dimethylcyclohexadiene in benzene. Preparation of spiro[bicyclo(4.1.0)hepta-3,5-diene-1,1'-4,4'-dimethylcyclohexa-2,5'-diene] (**2**), and its photoisomer, **3**. A purple soln of ca 300 mg diazo compound in 1 l. degassed benzene was irradiated with a G.E. sunlamp through Pyrex while N₂ was continually bubbled through the system. External cooling was effected by running cold tap water over the face of the flask. Within 15 min the purple color had been completely dissipated and the soln was yellow. When the photolysis was stopped the benzene was removed by rotary evaporation (care being exercised to keep the product soln below 40°) leaving a few ml of a clear yellow liquid. This liquid was analyzed under Condition A. other gas-chromatographic conditions causing **2** to aromatize. If the photolysis was stopped after 1 hr, then **2** could be isolated as the major product in ca 10% yield as a white solid, m.p. 42-45° (lit.⁶ 40-43°). If the photolysis was allowed to proceed for ca 7 hr, then a white solid melting just below room temp to a clear liquid, **3**, was the major product (ca 5% yield) with only a trace of norcaradiene **2** remaining. In all cases varying but usually small, amounts of the liquid ketone 4,4-dimethylcyclohexadienone and the related alcohol were formed.

Precise mass measurement (3). Found: 184.125175. Calcd. for C₁₄H₁₆: 184.125194.

Photolysis of norcaradiene 2 through quartz. A few mg of **2** was dissolved in 100 ml tetramethylethylene. The colorless soln was placed in a quartz tube and irradiated with a Hanovia type L 450-w medium pressure mercury arc. The reaction was followed by gas-chromatography under Condition A. After 15 min irradiation two new peaks were present, each in ca 25% yield, while only a trace of **2** remained. One peak was identified as **3** by comparison of retention time data. The other peak was identified as the cycloadduct of 4,4-dimethylcyclohexadienylidene and tetramethylethylene by comparison of retention time and mass spectrum to an authentic sample.⁷ Further irradiation caused a gradual disappearance of the carbene-olefin adduct. Similar irradiations were carried out in the presence of 2,3-dimethyl-1,3-butadiene, trimethylethylene and t-butylethylene. Competition experiments were run in measured mixtures of olefins.

Photolysis of 3 through quartz. This photolysis was performed as delineated above, but with the substitution of **3** for **2**. The irradiation in tetramethylethylene resulted in the gradual disappearance of **3** without the formation of any new products.

Pyrolysis of 3. A sample of **3** was heated in refluxing CCl₄ or MeCN for 10-12 hr. Collection of the major product under Condition A yielded the rearranged compound **4** as a clear pale yellow liquid. Only a trace of **3** could be detected.

Precise mass measurement (4). Found: 184.125824. Calcd. for C₁₄H₁₆: 184.125194.

Photolysis of 4. Irradiation of a CCl₄ soln of **4** in Pyrex with a G.E. sunlamp for 3.5 hr resulted in its reversion to **3** in ca 50% yield. The reaction was monitored by NMR spectroscopy.

Reaction of 3,3-dimethylbenzocycloheptane with diazomethane. Hydrogenation of the adduct. Diazomethane, generated by the Gaspar-Roth technique,²⁵ was bubbled into a magnetically stirred soln of 3,3-dimethylbenzocycloheptane and ca 100 mg cuprous chloride. The catalyst soon became black and the reaction was followed by gas-chromatography under Condition B. After 8 hr the reaction was stopped and filtered to yield a clear yellow liquid. Collection of the major new product which was formed in ca 17% yield, provided a clear colorless liquid. Mass spectral analysis of this material revealed a compound with *m/e* = 188, contaminated with a compound with *m/e* = 206. The collected material was then hydrogenated over PtO₂ in hexane. 93% of the theoretical (assuming the material to be 100% *m/e* = 188) amount of H₂ was absorbed after 2 hr. Gas-chromatographic analysis under Condition B produced two peaks which were collected as clear colorless liquids and further analyzed by mass spectroscopy. The minor peak had *m/e* = 206 while the major peak gave *m/e* = 194, as expected for *cis* and/or *trans*-10H-4.

Hydrogenation of 4. A sample of **4** was hydrogenated over PtO₂ in hexane. 90% of the theoretical amount of H₂ was absorbed after 1 hr, no further uptake occurring. The reaction was filtered and analyzed under Condition B. Two peaks were detected and collected. Mass spectroscopic analysis indicated one peak to have *m/e* = 192, corresponding to octahydro-**4** while the other peak, a much broader one, contained molecular ions at *m/e* = 194, 192, 190, 188 and 186, corresponding to dihydro to decahydro-**4**.

REFERENCES

- ¹ This work was generously supported by the National Science Foundation through Grants GP-7819 and GP-12759. This work is taken in part from the Ph.D. thesis of R.H.L. submitted to Princeton University
- ² The reader will perhaps excuse the uninformative title. The proper name, Spirobicyclo[4.1.0]hepta-3,5-diene-1,1'-4',4'-dimethylcyclohexa-2',5'-diene is unwieldy
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