Tetrahedron. Vol. 28, pp. 4285 to 4297. Pergamon Press 1972. Printed in Great Britain

$C_{11}H_{12}$ HYDROCARBONS—II

PREPARATION OF TRICYCLO[5.4.0.$0^{2,5}$]UNDECA-3,8,10-TRIENE A NORBORNENONE ROUTE FROM CYCLOHEPTATRIENE*

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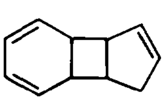
(*Received in USA* 3 *March* 1972; *Received in UK for publication* 4 *May* 1972)

Abstract—A stereoselective 6-step synthesis of the $C_{11}H_{12}$ hydrocarbon *cis,anti,cis*-tricyclo[5.4.0.$0^{2,5}$]-undeca-3,8,10-triene (**2a**) is described. The dichloro compound **3c** was prepared by the selective reduction of **3a** with chromous perchlorate-ethylenediamine complex, a general reagent for this type of transformation. Irradiation of **3c** produced **6a** and **7a** in a ~7:1 ratio. Reduction of the mixture with sodium produced ketal mixture **6b** and **7b**. The ketals were hydrolyzed to ketones **6c** and **7c** and the ketones decarbonylated to **2a** and an isomeric hydrocarbon tentatively assigned as homobasketene **2b'**. Hydrocarbon **2a** was readily obtained pure by a silver nitrate extraction procedure and **2b'** by preparative VPC. It was shown that pure **6c** gives only **2a** and therefore, **7c** is the source of **2b'**. The stereochemical assignments, based on both spectral and chemical evidence, are discussed.

INTRODUCTION

IN THE preceding paper,[1] we noted the ease with which the tricyclic $C_{11}H_{12}$ hydrocarbon **1**, prepared in several steps from cyclooctatetraene, fragments both thermally and photochemically to benzene and cyclopentadiene. Our interest in examining the energy surface on which $(CH)_nCH_2$ hydrocarbons traverse has prompted efforts directed towards synthesizing several other isomeric $C_{11}H_{12}$ hydrocarbons. In this report, we wish to describe a 6-step synthesis of tricyclo[5.4.0.$0^{2,5}$]undeca-3,8,10-triene (**2**) from 1,3,5-cycloheptatriene (CHT) using a norbornenone decarbonylation step to generate the cyclohexadiene ring.[2] A useful step in the synthetic sequence resulted from our observation that Kochi's reagent (chromous perchlorate-ethylenediamine, $Cr^{II}(en)_x$ complex in aqueous N,N-dimethylformamide)[3] selectively reduces bridgehead chlorine atoms of 1,2,3,4-tetrachloronorbornene derivatives in good yield.[4]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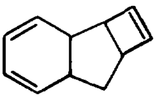
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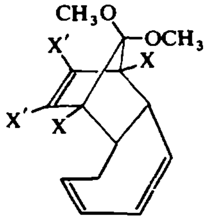
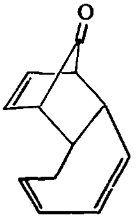
* A preliminary account of this study was presented at the 160th National Meeting of the ACS (Chicago, Illinois, 1970) and at the Sixth Western ACS Regional Meeting (San Francisco, California, 1970). This study was generously supported by grants from the Petroleum Research Fund (3369-A1) administered by the American Chemical Society and the Intramural Fund of the University of California at Riverside. Address correspondence to W. H. O. This work was taken in part from the doctoral thesis of J.F.M.

RESULTS AND DISCUSSION

General scheme. The appropriate annelation of a four carbon fragment to CHT can be envisioned as leading to the necessary C_{11} skeleton. After several trials,[†,5] we chose the known substance **3a**[6] as a starting point. We considered that **3a** might be dechlorinated to **3b**, which upon acid hydrolysis should lead to ketone **4**. The latter was expected to undergo ready cheleotropic elimination[7] of carbon monoxide to afford **5**.[2] This route was thwarted at the outset by our observation that **3a** could not be dechlorinated to **3b** by a standard method[8] or by variations of this method. The reduction of **3a** appeared to be complicated by concomitant reduction of the 1,3-diene function in the molecule. The partial dehalogenation of **3a** to **3c** was readily achieved, however (*vide infra*).



3a: X = X' = Cl
b: X = X' = H
c: X = H, X' = Cl



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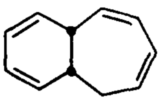

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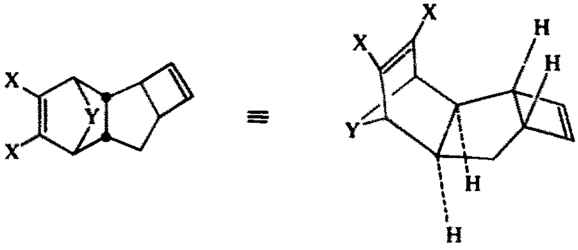
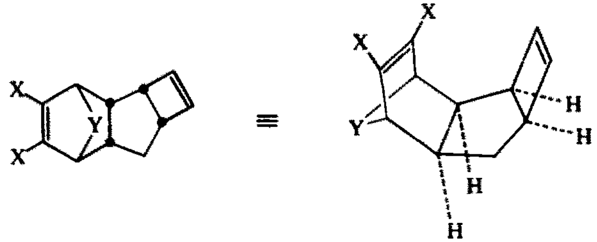
Concurrent with the study directed towards synthesizing $C_{11}H_{12}$ substances was a study of the photochemistry of **3a**. The irradiation of **3a** was examined in order to induce skeletal rearrangement through a [3.5]sigmatropic shift.[7] This shift was expected to be photochemically allowed[7b] in the same sense that the Woodward–Katz Rearrangement[9] (a [3.3]sigmatropic shift) is thermally allowed.[7b] The irradiation of **3a** appeared to be complicated by photodechlorination[10] as evidenced by the evolution of acidic vapours (hydrogen chloride). The photolysis of **3c** did not result in a [3.5] shift, but led instead to the cyclobutene derivatives **6a** (major) and **7a** (minor). While **3c**, like **3a**, could not be further dechlorinated,[8] the derivatives **6a** and **7a** could. Thus, the resulting ketals **6b** and **7b** represented the logical sources of the $C_{11}H_{12}$ hydrocarbon **2** in the manner we had envisioned originally for the synthesis of **5**.

[†] Routes initiated by combining or attempting to combine CHT or tropone[5a] with cyclobutadiene,[5b] benzocyclobutadiene,[5c] thiophene-1,1-dioxide,[5d] 5,5-dimethoxycyclopentadiene,[5e] cyclopentadiene,[5f] α-pyrone,[5g] or 1,4-diacetoxy-1,3-butadiene[5h] have thus far proved unsuccessful in this laboratory as a useful approach to $C_{11}H_{12}$ hydrocarbons.

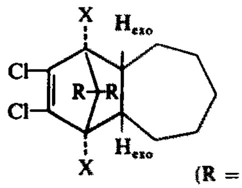


6a: X = Cl, Y = $C(OCH_3)_2$
b: X = H, Y = $C(OCH_3)_2$
c: X = H, Y = C=O



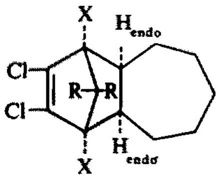
7a: X = Cl, Y = $COCH_3)_2$
b. X = H, Y = $C(OCH_3)_2$
c: X = H, Y = C=O

The synthesis. The adduct **3a**,[6] prepared by reacting CHT with 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (**8**), was obtained as an air-sensitive, viscous oil. Some of the spectral properties of the **3a** obtained in this manner were not in full accord with the previously described data.[6] It was not unreasonable that **3a** could actually have been a mixture of isomers, for CHT and **8** can in theory add regiochemically[11] and stereochemically in a number of ways.[12] However, it was observed that **3a** absorbed 2.1 molar-equivalents of hydrogen to afford solely the crystalline



(R = OCH_3)

9a: X = Cl
b: X = H



9'

substance **9a** (64%), which was also formed as the only isolable product in the Diels-Alder reaction between **8** and *cis*-cycloheptene (68%). That **3a** possesses the 1,3-cycloheptadiene chromophore is evidenced by its UV spectrum (λ_{sh} 240(ε 3750)),[13] by previously reported degradation studies,[6] and by the observation that it undergoes an intramolecular Diels-Alder reaction to form a cage.[14] The latter intramolecular reaction would also tend to support the *endo* stereochemistry assigned to **3a** and therefore **9a**. The assigned stereochemistry is further supported by the fact that the NMR spectrum of **9b**, prepared by reducing **9a** (*vide infra*), reveals that the molecule possesses a plane of symmetry and that its bridgehead protons X (τ 7·25) appear significantly coupled (triplet, $J \sim 2{\cdot}2$ Hz; see the discussion of **3c** below) to the adjacent protons (H_{exo}). Had **9b** actually been **9'b**, the resonance due to the protons

X should have appeared as a much narrower adsorption.[15] Several other dienophiles are known to react with **8**[16] and related derivatives[17] in the analogous *endo* fashion.

Our failure to reduce **3a** to **3b** with the usual reagents[8] led us to consider the several transition metal reducing agents uncovered by Kochi[3] and by others.[18] In our hands, Kochi's Cr^{II} (en) complex proved particularly useful for reducing one or both bridgehead chlorine atoms of 1,2,3,4-tetrachloronorbornene derivatives.[4] The derivatives **3a** and **9a** were reduced to **3c** (68%) and **9b** (66%) respectively. Two preparatively useful procedures are described in the experimental.

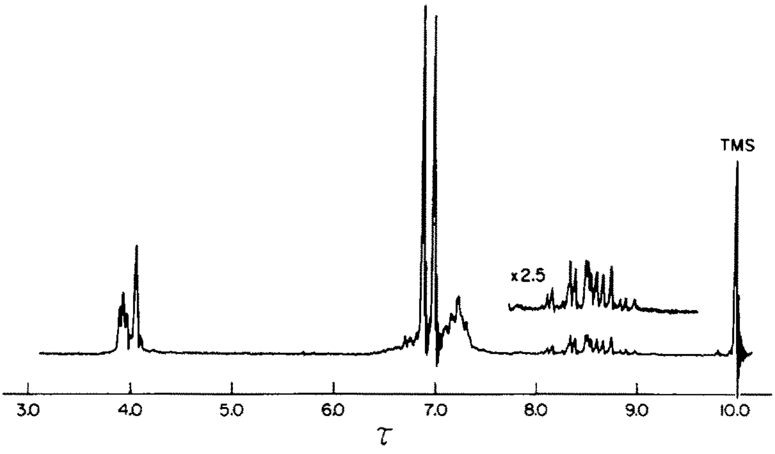


FIG 1. NMR spectrum of major ketal **6b** (60 MHz, CCl_4)

The air-sensitive solid **3c**, like **3a** described above, revealed a shoulder at 245 nm (ε 2960) in its UV spectrum.[13] Its 60 MHz NMR spectrum was similar to that of **3a**, while its IR spectrum was not inconsistent with the assignment. The 220 MHz NMR spectrum‡ was particularly revealing in that besides the other resonances, the spectrum revealed two one-proton triplets centered at τ 7·02 ($J \sim 2·5$ Hz) and 7·27 ($J \sim 2·5$ Hz) presumably attributable to the non-equivalent norbornyl bridgehead H atoms (X in structure **3c**). The magnitude of the coupling constant further supports the *endo* stereochemical assignment discussed above[15] although the magnitude of the observed coupling constant is slightly smaller than those reported for unchlorinated norbornene derivatives (~3–5 Hz).[15] The smaller observed coupling appears characteristic of 2,3-dichloronorbornenes.[4]

The photolysis of **3c** (pentane, quartz vessel, Rayonet Photoreacter, 2537 Å light source) afforded a 42% yield of a mixture of **6a** and **7a** in a ~7:1 ratio (by VPC). Dechlorination of the mixture (**6a** and **7a**) with t-BuOH—Na—THF[8] afforded at 71% yield of **6b** (~80%) and **7b** (~20%). The structures assigned to **6b** and **7b** were deduced from spectral and chemical evidence obtained for the samples separated and purified by preparative VPC.

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‡ Recorded with the instrument at the California Institute of Technology, Pasadena, California.

The NMR spectrum of the major isomer, **6b**, (Fig. 1) revealed, besides other approproate resonances, a two proton triplet ($J \sim 2·0$ Hz) at τ 3·95 assigned to and characteristic[15,§] of the norbornene olefinic protons and a two proton (broad) singlet at τ 4·05 assigned to the cyclobutene vinyl protons.[19] That the major ketal is **6b** and the minor ketal **7b** rests importantly on the fact that the minor ketal was in fact also isolated and found to possess key spectral characteristics which served tentatively to distinguish it as **7b**.

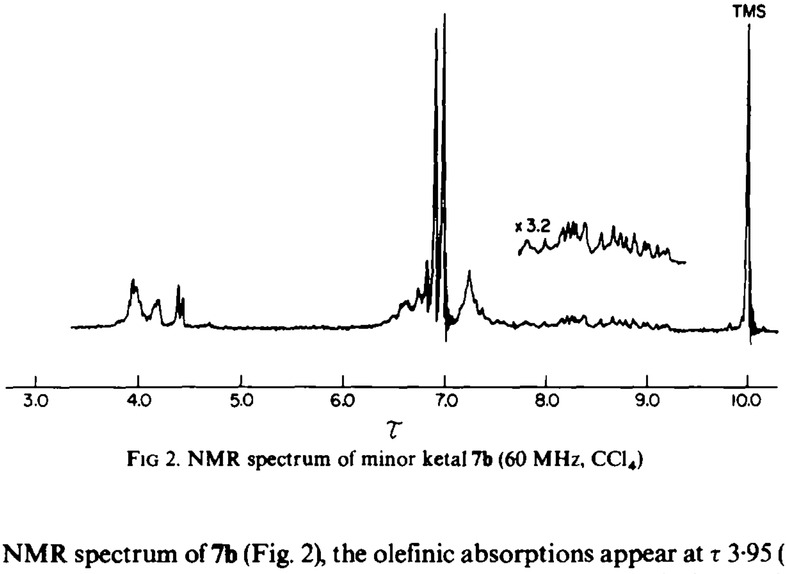

FIG 2. NMR spectrum of minor ketal **7b** (60 MHz, CCl_4)

In the NMR spectrum of **7b** (Fig. 2), the olefinic absorptions appear at τ 3·95 (2H, m) 4·18 (1H, m), and 4·42 (1H, d, $J \sim 2·5$ Hz). In a double resonance study, it was observed that irradiation of the broad resonance near τ 7·2 (where the allylic protons of the norbornene ring should appear (see above) results in the collapse of the low field resonance to an AB quartet ($J_{AB} \sim 6$ Hz, $\Delta\nu_{AB} \sim 5$ Hz).[20,†] Irradiation near τ 6·6 (where the allylic cyclobutene protons might be expected to appear)[19] causes the remaining olefinic resonances to collapse to another AB quartet (the τ_A 4·18 peak becomes a doublet and the τ_B 4·42 peak sharpens, $J_{AB} \sim 2·5$ Hz, $\Delta\nu_{AB} \sim 14$ Hz).[20] These data emphatically suggest that the τ 3·95 resonance, which normally appears as a triplet,[15] be assigned to the norbornene olefinic protons and the two remaining resonances to the cyclobutene olefinic protons. Molecular models suggest that the

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§ For 7,-dimethoxynorbornene, the olefinic protons appear at τ 4·03 (t, $J \sim 2·0$ Hz) and allylic protons at τ 7·32 (m); for norbornenone, the corresponding protons appear at τ 3·52 (t, $J \sim 2·5$ Hz) and 7·23 (m) respectively. We are grateful to Professor M. F. Rettig and Mr. G. Albelo of this Department for this information. The allylic protons of 8,8-dimethoxytricyclo[3.2.1.0^{2,4}]oct-6-ene, a cyclopropane fused compound, appear at τ 7.25 [S. C. Clarke and B. L. Johnson, *Tetrahedron Letters* 617 (1967)].

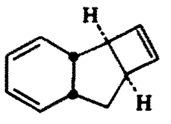
† *cis*-Vicinal olefinic coupling constants for norbornenes fall characteristically in the 5·0–6·0 Hz range[15b] while that for cyclobutenes in the 2·5–3·7 Hz range.[19a]

close proximity of the two double bonds in structure **7b** is such that shielding due to the diamagnetic anisotropy of the C=C double bonds[21] could influence the chemical shifts of the olefinic protons. This influence would appear negligible for structure **6b**. The more distorted appearance of the olefinic resonances of the minor ketal relative to that of the major ketal and the observation that the cyclobutene vinyl protons of the former appear at higher fields are the most important reasons for suggesting that the former is **7b** and the latter **6b**.

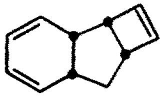
Chemical evidence for these structures was provided by hydrolysis experiments. The acid hydrolysis[22] of pure **6b** afforded a single ketone **6c**. The NMR spectrum of **6c** is, with not unexpected differences, very similar to that of **6b** and the IR spectrum shows the CO absorption at 1780 cm^{-1} characteristic of norbornenones.[4,8] Similar hydrolysis of **7b** produced low yields (< 10%) of the impure ketone **7c**. The NMR of this crude material indicated that it consisted mainly of **7c** and that **7b** was absent. The amount of material available from this experiment precluded isolation of pure **7c**. However, when a mixture of **6b** and **7b** was hydrolyzed[22] on a relatively large scale (9·9 g), careful chromatography of the ensuing product afforded fractions containing ketones **6c** and **7c**, but enriched (>50% **7c**, ~450 mg) in the latter. Rechromatography afforded a 85/15 mixture of **7c**/**6c**. The ketone **7c** showed an NMR spectrum which was quite similar to that of **7b**, and again, with not unexpected differences. Its IR revealed the characteristic[4,8] norbornenone carbonyl stretch at 1789 cm^{-1}.

Finally, it should be noted that other IR spectral data also provides important structural information. The spectra of the ketals **6b** and **7b** are quite remarkably similar, while those of the ketones **6c** and **7c** show moderate similarities. All of the compounds, **6bc** and **7bc**, reveal the weak band at around 3120 cm^{-1}, characteristic of the cyclobutene C—H stretch,[19b,23] while **6bc** and **7b** also show the weak 1560 cm^{-1} band characteristic of the cyclobutene C=C stretch.[19b,23] The characteristic norbornene C=C stretch[15j,24] was observed only for **6b**, but all of the compounds (**6bc**, **7bc**) revealed bands characteristic of *cis*-disubstituted olefins in the 650–800 cm^{-1} region.[25]

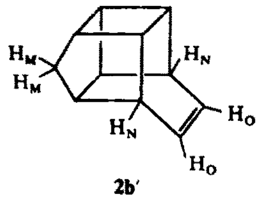
When pure **6c** was heated (140°, 3 h) in a sealed tube, decarbonylation occurred with production of a single hydrocarbon identified as **2a**. Its NMR spectrum (Fig. 3) revealed the presence of an equal number of aliphatic and olefinic protons; its IR spectrum showed bands at 3115 and 1563 cm^{-1} characteristic of cyclobutenes;[19b,23] and its UV spectrum revealed two maxima at 262 (ε 3090) and 270 (ε 2820) nm characteristic of related *cis*-bicyclo[4.3.0]nona-2,4-dienes.[26] Storage of **2a** without rigorous exclusion of air for prolonged periods caused decomposition and oxidation to **10**,



2a



2b



2b′

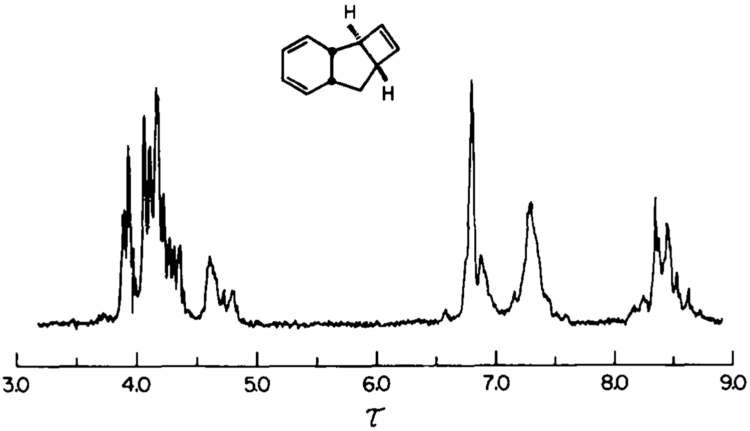
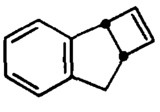


FIG. 3. NMR spectrum of major $C_{11}H_{12}$ hydrocarbon **2a** (60 MHz, CCl_4, TMS as internal standard).

a known substance.‡ This observation proves that the stereochemistry between the 5 and 4-membered ring is *cis* for **2a** (and therefore for its precursors), which was tacitly assumed for the photochemical formation **3c** → **6a** + **7a**.

When a mixture of **6c** (80%) and **7c** (20%) was heated for 3 h at 140°, a mixture of **2a** (80%) and an isomeric hydrocarbon (20%) was produced. The major isomer **2a** was obtained pure by extraction into aqueous silver nitrate from a pentane solution of the mixture. The remaining pentane solution is left with a ~ 6/1 mixture (isomer/**2a**), from which the new isomer was obtained pure by preparative VPC. The isomer was not the expected triene **2b**, however, but it is tentatively assigned as the homobasketene[27] **2b**′. Besides other resonances, the NMR spectrum of **2b**′ revealed key absorptions of equal intensity at τ 3·5–4·2, 6·6–7·1, and 8·3–8·9 assigned to H_O, H_N, and H_M respectively. The olefinic region (H_O) consists of an AB quartet (J_{AB} ~ 8·3 Hz, $\Delta\nu_{AB}$ ~ 16·0 Hz centered at τ_A 3·68 and τ_B 3·98) further split into double-doublets (A part, J ~ 1·7, 6·6 Hz; B part, J ~ 1·4, 6·6 Hz). These coupling constants are similar to those reported for basketene itself (J_{AB} ~ 8·5 Hz with further splittings of 1·0 and 6·8 Hz).[27] The τ 6·9 signal is assigned to the allylic protons (H_N) because its irradiation simplifies the olefinic signal. The highest field signal is assigned to the methylene group (H_M) and consists of an AB quartet (J_{AB} ~ 10·6 Hz, $\Delta\nu_{AB}$ ~ 10·0 Hz centered at τ_A 8·54 and τ_B 8·71) with fine splittings. The fine splittings disappear when the region near τ 7·3 is irradiated. The magnitude of the geminal coupling constant (~10·6 Hz) is appropriate for the assigned structure.[28] The formation of **2b**′ by pyrolysis of **7c** should not be wholly unexpected, for its formation can readily



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‡ We are grateful to Professor Martin Pomerantz (Yeshiva University) for providing us with comparison spectra and a sample of **10**.

be rationalized on the basis that **2b** is the intermediate which undergoes an intramolecular Diels–Alder reaction to give the observed cage **2b'**.

We have observed an intermediate by VPC examination of a mixture of hydrocarbons produced by pyrolyzing a **6c/7c** mixture in a different manner. The ketones were decarbonylated by distillation at ~45 mm. The hydrocarbons distilled over rapidly as decarbonylation occurred. The intermediate is observed as a shoulder on the **2a** peak (VPC) and the NMR spectrum of this mixture integrates appropriately for a mixture of **2a** and **2b**. The **2b'** peak (negligible at first) in the VPC trace appears to increase at the expense of the shoulder if the initially produced distillate is allowed to stand. The NMR spectrum of the latter mixture shows the presence of **2b'**. The formation of cage further attests to the stereochemical assignments described above.

The availability of these $C_{11}H_{12}$ hydrocarbons now makes possible a study of their chemistry. The photochemistry of *cis*-8,9-dihydroindanes has stimulated much interest recently as a route to medium rings.[26b,d] We have initiated a study of the photochemistry of **2a** in order to explore the possibility of synthesizing cycloundecapentaene. The subject of a future report will concern the photochemical and thermal behavior of these interesting hydrocarbons.

EXPERIMENTAL

General. IR spectra were determined with a Perkin-Elmer 621 Grating Spectrophotometer and UV spectra with a Cary Model 14 Spectrophotometer. NMR spectra were recorded with a Varian 60 MHz spectrometer (A60, A60-D, or T-60) and unless otherwise indicated, the spectra produced integrals appropriate for the structural assignments. Mass Spectra were taken on a Hitachi–Perkin Elmer Model RMU-6D spectrometer: for Cl- containing compounds, *m/e* values are based on ^{35}Cl. VPC was carried out on a Varian-Aerograph A90-P apparatus. Mp and bp are uncorrected. Microanalysis were carried out by C. F. Geiger, Ontario, California.*

Preparation of **3a**. Reaction of cycloheptatriene with **8** according to the described procedure afforded **3a** as a viscous, air-sensitive yellow oil: bp 119–121°/0·09 mm (lit.,[6] bp 121–2°/0·05 mm): NMR (CCl_4) τ 3·9–4·5 (m with broad singlet centered at τ 4·14, 4H, olefinic) 6·4–7·1 (m with sharp singlets due to non-equivalent methoxyls centered at τ 6·48 and 6·53, 8H), and 7·3–8·5 (m, 2H): IR (film) ν_{max} 1604 cm^{-1} (lit.,[6] 1592 cm^{-1}): mass spectrum (80 eV) *m/e* 354 (parent ion); UV (n-hexane) λ_{max} 212 nm (ε 10,300) and 240 sh nm (ε 3750).

The adduct **3a** becomes dark on prolonged standing and trituration of aged material with pentane causes the deposition of a non-crystalline substance. Pentane solutions of **3a** were filtered, delocalized with charcoal, then rapidly chromatographed on neutral alumina (weight alumina to weight **3a** ~2:1) with hydrocarbon solvents. The colorless oil resulting from this purification procedure possessed spectral properties identical with freshly distilled material and was found sufficiently pure for use in subsequent steps.

Preparation of **9a** *by catalytic hydrogenation of* **3a**. The ketal **3a** (1·0272 g, 2·89 mmoles) in MeOH (25 ml) containing 5% Pt-C (47·4 mg) readily absorbed 2·1 molar equiv of H_2 (25°, one atm). The mixture, after filtration and concentration, produced a residual solid containing small amounts of a yellow oil. Recrystallization of the residue from MeOH (13 ml) afforded 655 mg (64%) of **9a** as a colorless, crystalline solid: mp 98·5–100·0°: NMR (CCl_4) τ 6·43 and 6·49 (s, 6H, non-equivt methyls), 7·1–7·7, 7·8–8·4, and 8·6–9·2 (series of broad m, 12H); IR (CCl_4) ν_{max} 1605 cm^{-1} (C=C); UV (hexane) λ_{max} 210 nm with no shoulder at higher wavelengths. The sample submitted for microanalysis was purified by sublimation. (Found: C, 46·66: H, 5·02: Cl, 39·46. Calcd. for $C_{14}H_{18}O_2Cl_4$: C, 46·69: H, 5·04: Cl, 39·38).

Preparation of **9a** *from cycloheptene.* A mixture of cycloheptene (9·62 g, 0·1 mole) and **8** (26·8 g, 0·1 mole) was heated at reflux for 4·5 hr. Recrystallization of the residue from MeOH afforded 24·4 g (68%) of cry-

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* The small amounts and air-sensitivity of some of the substances reported in this work precluded obtaining better microanalytical data. Mass spectral data was obtained for those clearly unacceptable cases. Purification by distillation was insufficient and preparative VPC proved superior.

stalline material identified as **9a** by comparison of the spectral properties of this material with that obtained in the preceding experiment. A second recrystallization afforded 18 g (50%) of **9a**, which upon sublimation afforded material with mp 95–99°.

Reduction of **3a** *with chromous perchlorate-ethylenediamine in aqueous N,N-dimethylformamide. Preparation of* **3c**. Cr metal was obtained from Alfa Inorganics (flakes, m4N5-t3N3 grade), perchloric acid (70·0–72·2% assay reagent) from Baker and Adamson, ethylenediamine (98% grade, redistilled before use) from Mallinckrodt, and N,N-dimethylformamide (DMF, reagent grade) from Matheson, Coleman, and Bell. All operations with chromous ion soln were conducted under N_2 and solvents were thoroughly purged with N_2 before use.

Cr (66·43 g, 0·128 g-atoms) was added to a soln of perchloric acid (362 g, 2·55 moles) and water (494 ml). The mixture was stirred magnetically for ~24 hr, at which point most of the Cr had usually dissolved and the soln was deep blue in color. The deep blue soln was added to the ice cooled soln of **3a** (37·9 g, 0·106 mole) in DMF (1800 ml) at such a rate that the mixture stayed below room temp. Ethylenediamine (191·4 g, 3·19 mole) was added to the ice-cooled mixture which was stirred at ambient temp for 48–72 hr. The determination of an adequate reaction time was obtained in preliminary experiments which were monitored by VPC (5′ × $\frac{1}{8}$″ 10% SE-30 on 60/80 chromosorb W, 180°, 30 ml/minute helium). As noted above, all operations up to this point were carried out with exclusion of air.

The mixture was doubled in volume with water, saturated with ether, then extracted with ether (6 × 200 ml). The combined ether extracts were washed with water (3 × 200 ml) and saturated brine (1 × 200 ml), then dried ($MgSO_4$). After filtration the soln was concentrated under vacuum to afford 31·6 g crude material. NMR and VPC examination of the crude material confirmed the absence of **3a** and the presence of only one major product **3c**. The crude material was sufficiently pure for use in subsequent steps.

Distillation afforded 20·4 g (67·5%) of **3c** (air-sensitive) as an oil which solidified on standing: bp 99–101° (0·11 mm): NMR (CCl_4) τ 4·14 (broad s, 4H, olefinic), 6·6–7·1–7·3, and 7·8–8·1 (series of m with singlets at τ 6·85 and 6·87 due to methyls, 12H): IR (CCl_4) ν_{max} 1613 cm^{-1} (C=C): UV (n-hexane) λ_{max} 208 nm (ε 9345) and 245sh nm (ε 2960); partial mass spectrum (80 eV) *m/e* (rel intensity) 290 (1·8), 288 (8·4), 286 (11·8), and 91 (100). The solid was recrystallized (MeOH) then sublimed (35°/0·5 mm) to afford the sample submitted for analysis, mp 42·0–43·3°. (Found: C, 58·41: H, 5·66. Calcd. for $C_{14}H_{16}O_2Cl_2$: C, 58·55: H, 5·62).

Preparation of **9b**. The cycloheptene adduct **9a** was reduced in a manner differing somewhat from the procedure described for the reduction of **3a**. The two procedures gave comparable results. The chromous perchlorate soln was prepared as described above from Cr metal (20·45 g, 0·395 g-atoms), perchloric acid (111·4 g, 0·78–0·80 mole) and water (170 ml). Ethylenediamine (59 g, 0·99 mole) in DMF (1200 ml) was added to the ice cold chromous ion soln. The ketal **9a** (9·1 g, 0·025 mole) in a small volume of DMF was added to the reducing soln, then the mixture was stirred for one day. VPC (1′ × $\frac{1}{4}$″ 20% SE-30 on 60/80 firebrick, 190°, 200 ml/minute helium) of a small aliquot after quenching showed the absence of **9a**, traces of an unknown substance (presumably the trichloro compound), and **9b**.

The mixture was doubled in volume with water, saturated with ether, then extracted with ether (4 × 300 ml). The combined ether extracts were washed with water (3 × 200 ml) and saturated brine (1 × 200 ml), then dried over $MgSO_4$. After filtration, the soln was concentrated under vacuum to afford a syrupy residue (7·3 g) which crystallized on trituration with MeOH. Recrystallization afforded **9b** in 66% yield (4·8 g): mp 64·0–65·0°; NMR (CCl_4) τ 6·87 (two closely spaced singlets, 6H, methoxyls), 7·25 (broad t, *J* ~ 2·2 Hz, 2H, norbornyl bridgehead), 7·3–7·8, 7·9–8·5, and 8·6–9·1 (broad m, 12H); IR (CCl_4) ν_{max} 1615 cm^{-1} (C=C). Sublimation preceded by preparative VPC purification of the recrystallized substance afforded the sample submitted for analysis mp 65·0–65·5°. (Found: C, 57·83, H, 6·83. Calcd. for $C_{14}H_{20}O_2Cl_2$: C, 57·74; H, 6·92).

Preparation of **6a–7a**. The Srinivasan–Rayonet–Griffin Photochemical Reactor (Southern New England Ultraviolet Company, Middetown, Connecticut) equipped with a 2537 Å light source was used for the photolysis. The fan-cooled quartz reaction vessel equipped with a water cooled condenser was purged continuously with N_2 to remove O_2 and to effect mixing during the course of the reaction. The photoisomerization was monitored by VPC (10% LAC on 60/80 chromosorb W, 6′ × $\frac{1}{8}$″, 175°, 30 ml/minute helium flowrate).

The dichloroketal **3c** (3·63 g) in 175 ml of spectrograde hexane (0·09 molar) was irradiated to >90% disappearance of starting material (~7 hr). The product mixture consisted of two components present in a ratio of ~7:1. The solvent was removed at reduced pressure. The residue from two such photolyses (total weight **3c** 6·69 g, 0·0233 mole) afforded a total of 2·95 g (42%) of colorless oil upon fractional distillation (bp 92–95°/0·08 mm). The distillate was shown by VPC to consist of the same two components observed in the crude photolysate. The minor component (**7a**) was eluted at longer retention times on several VPC columns and was found enriched in the later fractions resulting from the distillation. A sample containing >90% of the major component (**6a**), obtained by preparative VPC, was submitted for analysis. (Found: C, 58·18; H, 5·73. Calcd. for $C_{14}H_{16}O_2Cl_2$: C, 58·55; H, 5·61).

The purified photoisomer, containing mainly the major isomer **6a**, revealed the following properties: NMR (CCl_4) τ 3·94 (broad s, 2H, olefinic), 6·5–7·3 and 8·2–8·6 (broad multiplets with methoxyl singlets centered at τ 6·86 and 6·88, 14H); IR (film) ν_{max} 1614 cm^{-1} (s, ClC=CCl) and 1568 cm^{-1} (w. cyclobutene C=C); partial mass spectrum (80 eV) *m/e* (rel intensity) 290 (8·2), 288 (45·6), 286 (72·3), 219 (100), and 91 (40·5).

Preparation of **6b–7b**. Finely chopped Na (7·5 g, 0·33 g-atoms) was added to a soln under N_2 of **6a–7a** (9·2 g, 0·032 mole) and t-butyl alcohol (26·2 g, dried over K) in THF (450 ml, freshly distilled from LAH) contained in a one liter round bottom flask equipped with a water cooled condenser and N_2 inlet. The magnetically stirred mixture was heated at ~60° for 8 hr, then maintained at room temp for 7 hr. A small aliquot, upon examination by VPC (see below), indicate the presence of some starting material. An additional amount of Na (1·5 g, 0·065 g-atoms) was added to the mixture and the mixture was refluxed for 5 additional hr. MeOH (75 ml) was added slowly to the cooled mixture to remove unreacted N_2 then the mixture was poured onto 500 ml of a crushed ice-water mixture. The aqueous mixture was extracted with low boiling light petroleum (4 × 125 ml), then the combined organic extracts were washed successively with water (3 × 40 ml) and saturated brine (1 × 40 ml). The organic phase was dried ($MgSO_4$) and filtered. The solvent was removed at reduced pressure to give 8 g of crude **6b–7b**. Distillation afforded 5·28 g (75%) of material, bp 58–62° (0·09 mm), which was found by VPC to consist of a 80:20 mixture of two components. Both preparative and analytical VPC were carried out with a SE-30 column (8% on 60/80 chromosorb W, 10′ × ¼″, 150°, 120 ml/minute helium flow). A sample (220 mg), upon subjection to preparative VPC, afforded a *major component* (165 mg, eluted first) of greater than 95% purity (by NMR and VPC) and a *minor component* (43 mg).

The *major component* was further purified by resubjection to preparative VPC and the resulting material was found to contain >98% (analytical VPC) **6b**: NMR (CCl_4, see figure 1) τ 3·95 (t, 2H, J ~ 2·0 Hz, norbornene olefinic), 4·05 (broad s, 2H, cyclobutene olefinic), 6·5–7·4 (m with two singlets centered at τ 6·89 and 7·01, 12H, methine and Me protons), and 8·0–9·0 (complex m, 2H, methylene); IR (film) ν_{max} 3150 (vw), 3124(w) (cyclobutene C—H), 3·6· (mw), 3030 (m), 1577 (vw) (norborene C=C), 1563 (w) (cyclobutene C=C), 1452 (m) (CH_2), 790 (m), 752 (s), 736 (m), and 701 (w) cm^{-1}. (Found: C, 76·76; H, 8·66. Calcd. for $C_{14}H_{18}O_2$: C, 77·03; H, 8·31).

The *minor component* described above was found by analytical VPC to contain ~85% of isomer **7b** and ~15% of isomer **6b**. The following properties were observed for **7b** in this mixture: NMR (CCl_4, see Fig 2) τ 3·95 (m, 2H, norbornene olefinic; collapses to AB quartet, J_{AB} ~ 6 Hz and $\Delta\nu_{AB}$ ~ 5 Hz, on irradiating at ~τ 7·2), 4·18 (m, 1H, cyclobutene olefinic; collapses to d, J ~ 2·5 Hz, on irradiating at ~τ 6·6), 4·42 (broad d, 1H, J ~ 2·5 Hz, remaining cyclobutene olefinic; sharpens on irradiating near ~τ 6·6), 6·3–8·0 (m with sharp singlets at τ 6·92 and 7·01 and broad peak at 7·21, 12H, methine and Me protons), and 8·0–9·2 (complex m, 2H, methylene); IR (film ν_{max} 3147 (vw), 3120 (w) (cyclobutene C—H), 3064 (mw), 3027 (m), 1561 (vw, obscure) (cyclobutene C=C), 1447 (m) (CH_2), 801 (m), 776 (m), 748 (m) and 728 (s) cm^{-1}. (Found: C, 76·60; H, 8·43. Calcd. for $C_{14}H_{18}O_2$: C, 77·03; H, 8·31).

Preparation of ketone **6c–7c**. The ketals **6b–7b** (2·9 g, 0·0135 mole) in glacial AcOH (20 ml) containing Ac_2O (5 drops) was heated under anhyd conditions for 72 hrs at 65°. After this period, hexane (50 ml) was added, then the mixture was ice cooled. NaOH aq (13·5 g in 45 ml water) was slowly added to the cold mixture, and then the organic phase was separated. The aqueous portion was extracted with hexane (3 × 20 ml) and the combined organic extracts were washed successively with water (3 × 15 ml) and saturated brine (1 × 20 ml). Drying ($MgSO_4$) then concentrating under vacuum afforded 2·6 g of crude ketones. A portion (1·35 g) of this material was vacuum distilled to afford 1·10 g (92%) of **6c–7c** consisting mainly of **6c** (bp 50–54°/0·05 mm). Spectral properties are described in the following section.

Preparation of pure major ketone **6c** *from* **6b**. The ketal **6b** (49·4 mg, 0·226 mmole, >98% pure) in glacial AcOH (1·5 ml) containing Ac_2O (0·3 ml) was heated under anhyd conditions for 72 hr at 65°. NaOHab (1·4 g in 4·5 ml water) was added to the ice cooled mixture, then the mixture was extracted with pentane. Upon drying ($MgSO_4$) and concentrating, the pentane soln afforded 30·6 mg (79%) of a single ketone **6c** with spectral properties identical to that of a material purified by preparative VPC (2·5′ × ¼″, Ucon 50 HB2000, 12·5% on 60/80 Chromosorb W, 118°, 300 ml/min helium flowrate). The purified sample (containing >98% by VPC) of **6c** exhibited the following properties: NMR (CCl_4) τ 3·55 (t, 1·9H, $J \sim$ 2·5 Hz, norbornene olefinic), 4·03 (broad s, 2·0H, cyclobutene olefinic), 6·3–7·6 (complex m, 5·9H, aliphatic methine), and 7·9–9·0 (complex m, 2·1H, methylene); IR (film) ν_{max} 3119 (w) (cyclobutene C—H), 3036 (m), 3000 (m), 1791sh (s) and 1775 (s) (C=O), 1450 (m) (CH_2), 771 (ms), 741(ms), and 729 (m) cm^{-1}; IR (CCl_4 solution) ν_{max} 3125 (w), 3040 (m), 3005 (m), 1780 (s), 1560 (vw) (cyclobutene C=C), 1448 (m), 734sh (m), and 726 (s) cm^{-1}; mass spectrum (80 eV, ~100°) *m/e* (rel intensity) 172 (~0·2), 171 (~0·2), 170 (~0·2), 144 (16), 129 (100), 128 (40), 91 (48), and 66 (61). (Found: C, 83·27; H, 7·01. Calcd. for $C_{12}H_{12}O$: C, 83·69; H, 7·02).

A second sample was resubjected to preparative VPC, then submitted for re-analysis. (Found: C, 84·25: H, 7·26).

Preparation of pure minor ketone **7c**. *A. From large scale hydrolysis of* **6b–7b**. A sample of **6b–7b** (9·9 g, ~87% **6b**, ~13% **7b**) was hydrolyzed in essentially the same manner as described above. The crude residue (~7·5 g) from this reaction was chromatographed on a silica gel (175 g, J. T. Baker) column prepared with low boiling light petroleum (P.E.). The elution was carried out successively with the following solvents: P.E. (900 ml), 5% benzene-P.E. (250 ml), 10% (500 ml), 15% (750 ml), 20% (750 ml), then 25%. Relatively pure major ketone was eluted with 15–20% benzene–P.E. while a ~1:1 mixture (by vpc and nmr) of major and minor ketone (~450 mg) was eluted with 25% benzene-P.E. The latter mixture was rechromatographed in a similar way on 15 g of silica gel. The elution was carried out successively with 7·5% (100 ml) and 15% (400 ml) benzene-P.E. The last 100 ml of eluate afforded the purest sample of **7c** (45 mg, 82% **7c** to 18% **6c**); NMR (CCl_4)§ τ 3·57 (m, ~2H, norbornene olefinic), 4·10 (m, ~1H, cyclobutene olefinic; irradiation at ~τ 6·5 collapses this signal to a doublet, $J \sim$ 2·7 Hz), 4·42 (d, $J \sim$ 2·7 Hz, ~1H, cyclobutene olefinic; this signal sharpens on irradiating near ~τ 6·5), 6·3–9·1 (complex m, ~8H); IR (CCl_4 soln) ν_{max} 3122 (w) (cyclobutene C—H), 3040 (mw) 300 (mw), 1789 (s) (C=O), 1449 (mw) (CH_2), and 719 (m) cm^{-1}. No further studies were carried out with this sample as it deposited an ether insoluble material on standing overnight in the cold under N_2.

B. From pure **7b**. The ketal **7b** (70·0 mg, 0·32 mmole, ~90% **7b** and ~10% **6b**) in glacial AcOH (1·5 ml) and Ac_2O (5 drops) was heated under anhyd conditions for 72 hr at 65°. After quenching and working up the mixture as above, only small amounts of crude residue (10·4 mg) remained. The NMR spectrum (CCl_4) of this material showed that it contained mainly **7c** (**7b** was absent), but was contaminated by material with aliphatic high field protons (the olefinic region was relatively clean with resonances at τ 3·63 (m, ~2H), 4·16 (m, ~1H), and 4·50 (d, $J \sim$ 3 Hz)). At shorter reaction times (24 hr, 55°), the ketal **7b** only partly hydrolyzed.

Preparation of **2a** *and* **2b′**. A mixture of ketones (1·4 g, 0·0081 mole, 22% **7c** and 78% **6c** by NMR) was heated (140°) under N_2 for 2·8 hr. CO evolved rather rapidly during the first 1·3 hr, then quite slowly thereafter. The cooled, crude residue was eluted rapidly on silica gel (13 g) with low boiling light petroleum to remove small amounts of unreacted ketone and a solvent insoluble material. The first 175 ml of eluate was combined and concentrated under vacuum to afford a mixture of $C_{11}H_{12}$ hydrocarbons (1·05 g, ~90%; 78% **2a** and 22% **2b′** by VPC, 10′ × $\frac{1}{4}$″ column, 8% SE–30 on 60/80 chromosorb W, 90°, ~200 ml helium/minute, **2a** elutes first). The mixture was dissolved in pentane (6 ml), then the pentane soln extracted with 50% (w/w) $AgNO_3$ aq (8 × 1 ml). At this stage, the organic phase contained a ~2/3 mixture (by VPC) of **2b/2a**. Further extraction of the organic phase with sat $AgNO_3$ aq (3 × 1·5 ml) afforded an organic phase containing a ~6/1 mixture of **2b′/2a**.

The aqueous Ag ion soln (separatory funnel) was quenched with ice cold 65% aqueous ammonia (40 g concentrated ammonium hydroxide and 20 g of ice) and the mixture extracted with pentane (5 × 5 ml). The combined pentane extracts were washed with 65% aqueous ammonia (1 × 3 ml), water (2 × 3 ml), and saturated brine (1 × 3 ml). After drying ($MgSO_4$) and filtering, the solvent was removed under vacuum to afford 0·55 g of oil consisting of pure **2a** (<1% **2b′**). This material or material purified by VPC or distillation is sufficiently pure for further studies (see spectral data below).

The organic phase enriched in **2b′** was washed with 65% aqueous ammonia (1 × 1 ml), water (2 × 1 ml), and saturated brine (1 × 1 ml) and then dried ($MgSO_4$). Filtration then concentration afforded 0·38 g of a ~6/1 mixture of **2b′/2a**. Preparative VPC of the mixture on a $AgNO_3$-glycerine† column (2′ × $\frac{1}{4}$″, 30°,

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§ The resonances due to **6c** were substracted from the spectrum. The olefinic to aliphatic integration ratio was 4·0 to 8·8 (calculated, 4·0 to 8·0).

† Packing prepared from 3 g $AgNO_3$, 10 g glycerine, and 39 g 60/80 firebrick. See J. Herling, J. Shabtai, E. Gil-AV, *J. Chrom.* **8**, 349 (1962).

240 ml helium/minute; **2b**′ elutes first) afforded pure **2b**′ ($<1\%$ **2a**) as a waxy solid: NMR (CCl_4) τ 3·5–4·2 (m, 2·04H, olefinic), 6·6–7·1 (m, 2·07H, allylic), 7·1–8·3 (m, 5·68H nonallylic methine), and 8·3–8·9 (m, 2·15H, methylene) (a more detailed discussion is given in the main text): IR (film) ν_{max} 3044 (mw), 2966 (s), 2863 (mw), 1610 (w), 1451 (w), 1378 (w), 1310 (w), 1294 (mw), 1285 (w), 1280–800 (many w to vw bands), 792 (w), 780 (m), 749 (m), 689 (ms), and 671 (m) cm^{-1}: mass spectrum (80 eV) *m/e* (rel intensity, $>1\%$) 144 (2·4), 143 (6·3), 141 (2·5), 130 (2·8), 129 (28), 128 (13), 127 (3·2), 117 (2·2), 116 (3·1), 115 (7·7), 91 (6·0), 79 (4·9), 78 (7·3), 77 (6·0), 67 (7·5), 66 (100), and 65 (6·0).

Preparation of **2a** *from* **6c**. The major ketone **6c** (55 mg, 0·32 mole, $>98\%$ pure by VPC) contained in a sealed glass ampoule (~one atm) was heated at 142–144° for 3 h. The residue was chromatographed on 9 g of Flurosil (eluted with low boiling light petroleum). After discarding a small forerun, a 20 ml fraction was collected, which afforded 33·6 mg (72%) of quite pure **2a** (**2b**′ was absent). A subsequent fraction contained $<0·2$ mg of residue. Further purification of the **2a** obtained in this experiment by preparative VPC (10′ × ¼″, 15% LAC on 60/80 chromosorb W, 98°, 300 ml helium/minute) afforded 17·5 mg (38%) of pure **2a**. The $AgNO_3$ extraction procedure described above afforded the largest quantities of pure **2a**: bp 100° (25 mm); NMR (CCl_4) τ 3·65–4·48 (m, 5·00H, olefinic), 4·48–4·90 (m, 0·91H, olefinic), 6·50–7·05 (m, 2·12H), 7·05–7·55 (m, 1·92H), and 8·05–8·90 (m, 2·04H, methylene) (Fig. 3); IR (film) ν_{max} 3115 (w) (cyclobutene C—H), 3030 (s), 2920 (s), 2840 (m), 1580 (vw), 1563 (vw) (cyclobutene C═C), 1440 (w) (methylene), 1400–800 (series of w to vw bands), 770 (w), 750 (s), 720 (m), and 685 (s) cm^{-1}; UV (hexane) λ_{max} 262 (ε 3090) and 270 (ε2820) nm; mass spectrum (80 eV) *m/e* (rel intensity, $>10\%$) 144 (24), 143 (17), 129 (75), 128 (34), 116 (12), 115 (24), 91 (39), 78 (16), 77 (16), 66 (100), 65 (30), 63 (15), 53 (33), 52 (11), 51 (25), 50 (11), 40 (22), and 39 (53).

Preparative VPC on the LAC column described above afforded a sample submitted for microanalysis. (Found: C, 90·18; H, 8·25. Calcd. for $C_{11}H_{12}$: C, 91·61; H, 8·39%).

A second sample, purified by distillation, also gave a poor analysis (Found: C, 90·18; H, 8·51%) and this may be due to the fact that **2a** is quite air-sensitive. A sample, on brief exposure to air, deposits an insoluble material upon addition of pentane. When a sample was stored without rigorous purging with N_2 at 0° (in a glass stoppered vessel) for 4 months, a total of ~35% of hydrocarbons was recovered consisting of 55% **2a** and 45% **10** (by NMR or VPC). The oxidation product **10** was identified by isolation and then by comparison of its IR, NMR, and VPC behavior with those of an authentic sample. Samples of **2a** appear stable when stored under N_2 at −50°.

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