

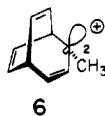
Table I. ¹H NMR Spectrum Data of the 9-Methyl-9-barbaralyl Cation^a

δ , prepared from alcohol 3 ^b	δ , from tetraene 1
6.18	6.18
5.93	5.95
5.80	5.80
5.21	5.20
4.77	4.75
2.94	2.92

^a Reference: internal CHDCl₂ at δ 5.30. ^b Reference 2.

retical models. The stability of the bicyclo[4.3.0]nonatrienyl cation was attributed to its bishomoaromaticity.^{2,3,6} The instability of the 2-bicyclo[3.2.2]nonatrienyl cation was attributed to its antibicycloaromaticity.⁴ If, instead, the 2-methylbicyclo[3.2.2]nonatrienyl cation (2) were as stable as had originally been reported,¹ the power of the bicycloaromatic model would seriously have been compromised.

3. The apparent conflict, between prediction and reality, might yet be resolved by the ¹³C NMR spectrum that was reported for this cation. The observation of *ten* distinct signals would exclude any element of symmetry. Structure 6 accommodates this constraint by representing a 2-methylbicyclo[3.2.2]nonatrienyl cation that is pyramidal rather than trigonal at C2. However unprecedented, this



structural possibility might yet allow adjacent allylic stabilization, while also inhibiting antibicycloaromatic interaction with the other two bridges.

For all these reasons, it seemed important to repeat the preparation of the cation, to obtain a more thorough NMR analysis, and to confirm the original structural assignment by nucleophilic quenching experiments.

Results

The tetraene 1 was prepared at Cornell University according to procedures that had earlier been developed at The Ohio State University.⁷ Samples were then sent to the investigators at Uppsala (92 mg) and at the University of Southern California (217 mg). In none of the three laboratories, however, could the originally reported ¹H NMR spectrum of the purported 2-methylbicyclo[3.2.2]nonatrienyl cation (2) be duplicated.

The best resolved ¹H NMR spectrum was obtained at the University of Uppsala (Table I). It leaves no doubt but that the only cation which the tetraene 1 provides is the 9-methyl-9-barbaralyl cation (4). (The spectrum obtained at Cornell University differs only marginally; it fails to resolve the broadened singlets at δ 5.80 and 5.95.) In none of the three laboratories could a second characteristically sharp methyl signal (reported¹ at δ \approx 3.8) be detected above the base-line noise.

Conclusions

The 2-methylbicyclo[3.2.2]nonatrienyl cation (2) can not be prepared from the tetraene 1. The instability of that

hydrocarbon was not fully appreciated when the original spectra were taken. As a result, it might well have been transformed into the precursor of an apparent allylic cation, either during transit or storage. Tertiary methyl carbinols clearly do produce the same cations as do the corresponding exo methylene derivatives.

Whatever other limitations the bicycloaromatic model might possess,⁸ there is now no reason to doubt but that it correctly anticipated the instability of the bicyclo[3.2.2]nonatrienyl cation.

Experimental Section

¹H NMR spectra at the University of Uppsala were obtained with a JEOL-FX 100 spectrometer, at Cornell University with a Varian Associates CFT-20 spectrometer operating at 79.56 MHz, and at the University of Southern California with a Varian Associates HA-100 spectrometer.

2-Methylenebicyclo[3.2.2]nona-3,6,8-triene (1) was obtained as described:⁷ NMR (CDCl₃) δ 6.59 (t), 6.27 (t), 6.02 (d, 5.09 H), 5.49 (d, *J* = 10 Hz, 1.08 H), 5.06 (s, 0.96 H), 4.70 (s, 1.03 H), 3.71 (t), and 3.43 (q, 1.85 H). Reported:⁷ NMR (CDCl₃) δ 6.75-5.90 (m, 5 H), 5.48 (d, *J* = 10 Hz, 1 H), 5.05 (s, 1 H), 4.7 (s, 1 H), and 3.87-3.20 (m, 2 H).

Sample Preparation. At the University of Uppsala, 3 μ L of 1 in 60 μ L of CD₂Cl₂ was mixed into ca. 0.4 mL of FSO₃H-SO₂ClF-SO₂F₂ (1:14:5, by volume) at ca. -136 °C, using the apparatus described elsewhere.⁹ At Cornell University, 14 mg of 1 and 205 mg of FSO₃H were concurrently condensed from the vapor phase at -198 °C onto a surface of 2.4 mL of SO₂ClF and 1.0 mL of SO₂F₂. The apparatus was a modified version of that described by Saunders.¹⁰ The condensed material was thawed at -136 °C and poured into an attached NMR tube, which was then sealed.

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Registry No. 1, 38898-40-7; 2, 78217-65-9; 3, 38694-37-0; 4, 28830-19-5; 5, 78217-66-0.

(8) (a) Goldstein, M. J.; Nomura, Y.; Takeuchi, Y.; Tomoda, S. *J. Am. Chem. Soc.* 1978, 100, 4899-4900. (b) Grutzner, J. B.; Jorgensen, W. L. *J. Am. Chem. Soc.* 1981, 103, 1372-1375. (c) Kaufmann, E.; Mayr, H.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1981, 103, 1375-1380.

(9) (a) Ahlberg, P.; Engdahl C. *Chemica Scripta* 1977, 11, 95-96. (b) Ahlberg, P.; Engdahl C. *J. Am. Chem. Soc.* 1979, 101, 3940-3946.

(10) (a) Saunders, M.; Cox, D.; Ohlmstead, W. *J. Am. Chem. Soc.* 1973, 95, 3018-3019. (b) Saunders, M.; Cox, D.; Lloyd, J. R. *J. Am. Chem. Soc.* 1979, 101, 6656-6658.

Air Oxidation of an Isoindene: Formation of Isobenzofuran and Acetone

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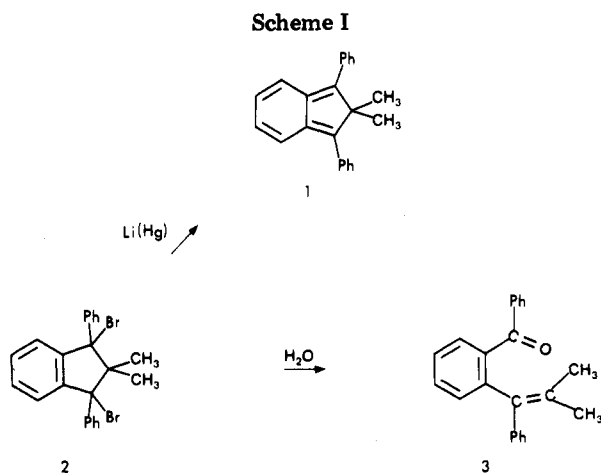
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In connection with work on addition reactions of selected dienes, we required an isoindene (2*H*-indene). The only isoindene which is claimed to be stable enough for isolation is the 2,2-dimethyl-1,3-diphenyl derivative (1).¹ Even

(1) K. Alder and M. Fremery, *Tetrahedron*, 14, 190 (1961).

(6) Warner, P. M. In "Topics in Nonbenzenoid Aromatic Chemistry"; Nozoe, T.; Breslow, R. Itô, S.; Hafner, K.; Murata, I., Eds.; Hirokawa Publishing Co., Inc.: Tokyo, 1977; Vol. 2, pp 283-352.

(7) Paquette, L. A.; Broadhurst, M. J. *J. Org. Chem.* 1973, 38, 1893-1902.



2,2-dimethylisobenzofuran has been reported to possess considerable stability, albeit only in oxygen-free solutions.² An account of isobenzofuran as reaction intermediates has recently appeared.³ The present note deals with a modified synthesis of 1, its pertinent NMR data, and its oxidation by air.

Results and Discussion

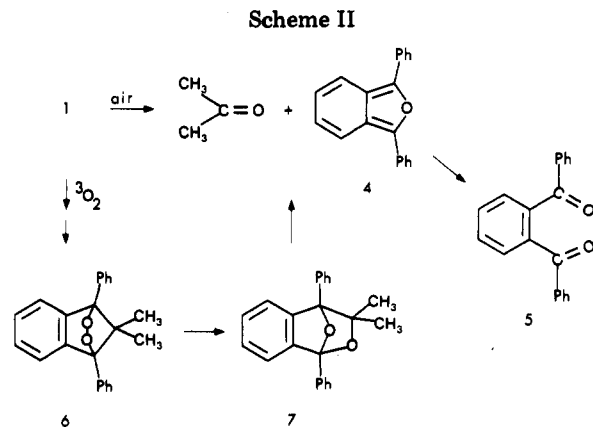
Three different procedures have been applied to the synthesis of 1, all involving reduction of the dibromide (Scheme I) as the final step. Two groups used zinc amalgam in toluene at 100 °C or zinc dust in dimethylformamide at 40 °C,^{1,4} and one group used copper refluxing benzene as the reducing method.⁵ It is interesting to note that only one group actually claims to have isolated 1.¹

We used lithium amalgam in benzene solution at room temperature for the conversion of 2 to 1 in a modified version of the method which has been published for the synthesis of 2,2-dimethylisobenzofuran.²

However, 2 proved very labile to hydrolytic ring opening, both in solution and especially on TLC plates. Accordingly the reduction had to be carried out with the careful exclusion of water and oxygen (vide infra). The hydrolysis product was identified (NMR, IR, mass spectra) as 2-(2-methyl-1-phenylpropenyl)benzophenone (3), which also was formed when the corresponding diol was treated with acid.⁶

We found that 1, generated in a dry oxygen-free atmosphere, has an orange color which in benzene or chloroform solutions appears bright orange-red. Solutions of 1 reacted quantitatively with maleic anhydride and *N*-phenylmaleimide to give the known^{1,5} Diels-Alder adducts.

To our knowledge only one report has been published containing NMR data of 1. McCullough and Yarwood et al.⁴ reported that the methyl protons of 1 absorb at δ 1.70 (CDCl₃). Our results are different. We found that the methyl protons produce a sharp 6 H singlet at δ 1.25 in CDCl₃ and at δ 1.14 in C₆D₆. This agrees with the reported² value for the methyl protons of 2,2-dimethylisobenzofuran (δ 1.16). We suggest that the NMR spectrum reported⁴ for 1 may actually have been due to the ring-opened ketone 3 which gives an NMR singlet for the



methyl protons at δ 1.70 (CDCl₃)⁶ and may be produced from 2 as demonstrated above.

When solutions of 1 were exposed to air at ambient temperature, the color changed from orange to colorless and finally to yellow with a bright green-blue fluorescence. When this process was followed by ¹H NMR in CDCl₃ solution, the change in the signals from the methyl protons was especially rewarding. After air had been admitted to the NMR tube, the signal at δ 1.25 decreased fairly rapidly whereas a new, slightly broadened singlet at δ 1.20 appeared. In a period of a few hours the latter signal was replaced by a sharp singlet at δ 2.15 and the solution attained the yellow color with the green-blue fluorescence. We assign this last signal to the methyl protons of acetone. The presence of acetone was confirmed by GC/MS on the reaction mixture as well as by comparison (NMR, IR, mass spectra) with an authentic sample.

TLC revealed the presence of two further products in the reaction mixture. These were isolated by preparative TLC and identified as 1,3-diphenylisobenzofuran (4) and 1,2-dibenzoylbenzene (5) (Scheme II) by comparison (NMR and mass spectra, TLC, melting point) with authentic samples. When the reaction mixture was allowed to be in contact with air for more than 24 h, most of 4 was converted to 5. Obviously it is the isobenzofuran 4 which is responsible for the green-blue fluorescence. This compound has λ_{max} for emission at 458 nm.⁷ It is further known that 4 is oxidized by oxygen to 5.⁸

The question of the structure of the colorless primary product has not been completely settled, but we have reason to believe it is the endoperoxide 6. It gives a positive iodide test for peroxides, but attempted isolation by TLC resulted only in the formation of 4 and 5. Although the NMR signal from the methyl protons appears as a broad singlet (vide supra) rather than the expected doublet, the ¹³C NMR spectrum revealed two signals (δ 21.2 and 22.3), demonstrating the nonequivalence of the methyl groups of 6.

It is important to point out that this oxidation also takes place in the dark, indicating the involvement of triplet oxygen.

The formation of 4 and acetone from the endoperoxide 6 may occur via the diether 7. Analogues of 7 have been reported as products of the thermal decomposition of cyclic peroxides.⁹ The driving force for the elimination of acetone is apparently the formation of the carbonyl bond in acetone and the extended conjugated π -electron system in 4 (at the expense of some aromatic stabilization).

(2) W. R. Dolbier, Jr., K. Matsui, H. J. Dewey, D. V. Horák, and J. Michl, *J. Am. Chem. Soc.*, **101**, 2136 (1979).

(3) J. J. McCullough, *Acc. Chem. Res.*, **13**, 270 (1980).

(4) K. Kamal de Fonseka, C. Manning, J. J. McCullough, and A. J. Yarwood, *J. Am. Chem. Soc.*, **99**, 8257 (1977).

(5) J. M. Holland and D. W. Jones, *J. Chem. Soc., Perkin Trans. 1*, 927 (1973).

(6) K. R. Huffman and E. F. Ullman, *J. Am. Chem. Soc.*, **89**, 5629 (1967).

(7) W. Friedrichsen, *Adv. Heterocycl. Chem.*, **26**, 200 (1980).

(8) W. Friedrichsen, *Adv. Heterocycl. Chem.*, **26**, 203 (1980).

(9) R. G. Salomon, M. F. Salomon, and D. J. Coughlin, *J. Am. Chem. Soc.*, **100**, 660 (1978).

The thermal formation of cyclic peroxides from cis,cis dienes and triplet oxygen has precedence in the literature. Barton et al.¹⁰ have suggested that the spin barrier is overcome by reversible formation of a tetroxide from the primarily produced triplet diradical and decomposition of the tetroxide to two molecules of singlet diradical which cyclize to the endoperoxide.

Experimental Section

General Methods. ¹H and ¹³C NMR spectra were obtained on Varian HA-100 and JEOL FX 60 spectrometers, respectively, using CDCl₃ or C₆D₆ as solvents and Me₄Si as an internal standard. Mass spectral measurements were recorded on an AEI MS 902 spectrometer and the GC/MS results were obtained with a Carlo Erba gas chromatograph combined with a Micromass 7070 F mass spectrometer.

Melting points are uncorrected. TLC analyses were carried out on silica gel plates, mostly with petroleum ether/ethyl acetate as eluent. Authentic samples of 4 and 5 were purchased from Ventron and Aldrich, respectively.

2,2-Dimethyl-1,3-diphenylisoindene (1). The reaction vessel consisted of a two-necked 25-mL reaction flask fitted with two rotatable side arms, one connected to a two-necked 10-mL addition flask (from which solid 2 could be added to the reaction flask) and the other connected to a two-necked 10-mL conical receiver flask via a glass filter. An N₂ inlet and an outlet to a vacuum pump completed the reaction vessel.

The reaction flask was loaded under N₂ with Hg (19 g), a piece of Li (0.5–1 g) and a Teflon-coated stirring bar. After 50 min of stirring, the excess Li was removed with a pair of tweezers and 2.5 mL of solvent (C₆H₆ or C₆D₆) was added to the lithium amalgam. The system was degassed four times and crystalline 2¹ (400 mg) was transferred from the addition flask to the reaction flask by rotation of the side arm. After a few minutes the solution turned orange-red. The suspension was stirred for 5 h and then filtered through the glass filter into the receiving flask. For the NMR measurements the solution was filtered directly into the NMR tube (which was connected to the side arm) and then sealed off with a gas burner. When CDCl₃ was used as NMR solvent, this solvent was added under N₂ after evaporation of the benzene: ¹H NMR (C₆D₆) δ 1.14 (s, 6 H), 5.97–6.15 (q, 2 H), 6.65–6.82 (q, 2 H), 7.0–7.3 (m, 10 H); ¹H NMR (CDCl₃) δ 1.25 (s, 6 H), 6.28–6.39 (q, 2 H), 6.74–6.85 (q, 2 H), 7.0–7.3 (m, 10 H); ¹³C NMR (C₆D₆) δ 20.5 (CH₃, J_{CH} = 129 Hz), 56.5 (C₂), 124.2–128.6 (C₄, C₅, C₆, C₇, *o*-, *m*-, and *p*-phenyl), 137.0 and 137.5 (C₈, C₉, and ipso-phenyl), 149.7 (C₁, C₃).

When solutions of 1 were treated with *N*-phenylmaleimide, the orange-red color instantly disappeared and a white solid precipitated. After crystallization from ethanol the Diels–Alder adduct with mp 276–279 °C (lit.⁵ mp 265–266 °C) was obtained; mass spectrum, *m/e* 469.2047 (30%) calcd. for C₃₃H₂₇NO₂ 469.2042), 296.1563 (100%, calcd for C₂₃H₂₀ 296.1565). The base peak is obviously due to a retro-Diels–Alder reaction. A similar treatment with maleic anhydride resulted in the corresponding adduct, mp ca. 350 °C dec (lit.¹ mp 344 °C).

Treatment of the dibromide 2 as described above, but without rigorous drying of the solvent and glass apparatus, resulted in appreciable amounts of the ring-opened ketone 3, identified by NMR, IR and mass spectra. This ketone was isolated by column chromatography (silica gel and petroleum ether/ethyl acetate). The ¹H NMR values were found to be in complete agreement with published values⁶ (both in CDCl₃ and C₆D₆ solutions). The ¹³C NMR (CDCl₃) gave signals for the methyl carbons at δ 21.96 and 23.07; mass spectrum, *m/e* 312 (33%), 297 (100%).

An especially fast conversion of 2 to 3 was found to take place on TLC plates with silica gel.

Treatment of 1 with Air. When air was bubbled through a solution of 1 in C₆D₆ as prepared above, the orange-red solution first turned colorless and then after a few hours yellow with a green-blue fluorescence. The colorless solution gave the following: ¹H NMR (CDCl₃) δ 1.20 (br s, 6 H), 7–8 (m, 14 H); ¹³C NMR

(CDCl₃) δ 21.2 (CH₃), 22.3 (CH₃). The other ¹³C signals were less well resolved but not incompatible with the peroxide structure 6. A peroxide test with the iodide/starch reagent was positive. The TLC analysis of this compound is reported below.

The yellow, fluorescent solution was first analyzed by combined gas chromatography and mass spectrometry which showed the presence of acetone. TLC revealed two further components, identified as 1,3-diphenylisobenzofuran (4) and 1,2-dibenzoylbenzene (5) by comparison with authentic samples. NMR analysis of the crude reaction mixture confirmed the presence of these three products. After more than 24 h of contact with air, ost of 4 had been oxidized to 5.

When solutions containing the colorless compound believed to be the peroxide 6 were analyzed by TLC a band with an *R_f* value between the *R_f* values for 4 and 5 was found. When this band on the TLC plate was exposed to air after evaporation of the solvent, an interesting rapid change of color took place: colorless → bright yellow → colorless. Isolation of the band revealed an almost quantitative conversion to 5. Obviously the same reaction takes place on the TLC plates as in solution.

Registry No. 1, 64836-60-8; 2, 42003-48-5; 3, 18949-20-7; 4, 5471-63-6; 5, 1159-86-0; 6, 78020-04-9; 3a,4,9,9a-tetrahydro-10,10-dimethyl-2,4,9-triphenyl-4,9-methano-1*H*-benz[*f*]isoindole-1,3(2*H*)-dione, 78087-14-6; 3a,4,9,9a-tetrahydro-10,10-dimethyl-4,9-diphenyl-4,9-methanonaphtho[2,3-*c*]furan-1,3-dione, 78020-05-0; *N*-phenyl maleimide, 941-69-5; maleic anhydride, 108-31-6.

Strained Benzene Rings: Preparation and Crystal Structure of a Dithiahexahydro[3.3]paracyclophane, S₂C₁₆H₂₂

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Introduction

The most stable conformations of strained molecules such as paracyclophanes may be computed, in principle, by quantum mechanical procedures, but semiempirical molecular mechanics calculations generally are used for such molecules of interest to organic chemists.^{1,2} The required force field parameters are often obtained by reference to observed structures. Accordingly, the structure of 2,11-dithia-4,5,6,7,8,9-hexahydro[3.3]paracyclophane (3), which is clearly strained because it includes a bent benzene ring,³ is of interest because of the variety of chemical linkages it presents. It is the first structurally characterized molecule of the paracyclophane class in which one unit is a cyclohexane ring. One might have supposed that the intramolecular strain would have been relieved through distortions of the saturated cycle; however, only part of the strain is relieved in this way; the cyclohexane moiety has bond distances and angles close to those expected for a typical *cis*-1,4-dialkylcyclohexane.

Compound 3 was prepared in 31% yield from the reaction of α,α' -dichloro-*p*-xylene (1) and *cis*-1,4-bis(mercaptomethyl)cyclohexane (2) in an alcoholic NaOH solution, using the high dilution technique described by Davis.⁴ The *cis*-1,4-bis(mercaptomethyl)cyclohexane was prepared either by hydrolysis of the diisothiuronium salt which was

(1) Allinger, N. L.; Tribble, M. T.; Miller, M. A.; Wertz, D. H. *J. Am. Chem. Soc.* 1971, 93, 1637–1648.

(2) Engler, E. M.; Andose, J. D.; von R. Schleyer, P. *J. Am. Chem. Soc.* 1973, 95, 8005–8025.

(3) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* 1971, 4, 204–213.

(4) Davis, A. C. *Chem. Ind.* 1977, 203–204.

(10) D. H. R. Barton, R. K. Haynes, G. Leclerc, P. D. Magnus, and I. D. Menzies, *J. Chem. Soc., Perkin Trans. 1*, 2055 (1975).