Tetrahedron. Vol 30, pp. 2353 to 2356. Pergamon Press 1974. Printed in Great Britain

SOME CHEMISTRY OF 6,7-BENZOTRICYCLO[3.3.1.$0^{2,8}$]-NONA-3,6-DIEN-9-ONE (BENZOBARBARALONE)

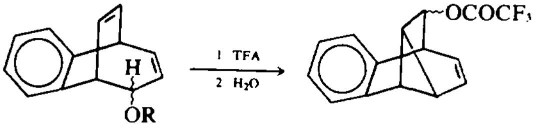
A. EISENSTADT*
Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel

(*Received in the UK* 10 *August* 1973; *Accepted for publication* 25 *February* 1974)

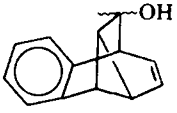
Abstract—Some reactions of benzobarbaralone **3** have been studied. Ring expansion occurs in reaction of **3** with diazomethane–lithium chloride to yield benzobullvalone **5** and the spirooxirane **6**. The tosylhydrazone of **5** was converted to the fluxional benzobullvalene **9**. Decarbonylation of **3** to benzocyclooactatetraene occurs upon irradiation. On reaction with $Fe_2(CO)_9$, **3** gives a σ-π allyl tricarbonyliron complex, **11**, with rearranged skeleton.

INTRODUCTION

We have recently reported the isolation of epimeric benzobarbaralols **2**[1] by quenching the trifluoroacetic acid solution of the two isomeric benzobicyclo[3.2.2]nonatrienols **1a** in ice-water followed by hydrolysis of the resulting trifluoro esters on basic alumina column. (The rearrangement process probably occurs via 1,2 shift path in benzobicyclo[3.2.2]nonatrienyl cation).



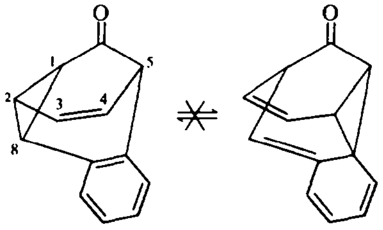
1a: R = H
1b: R = PNB



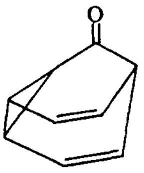
2

Preparative solvolyses of the epimeric 3,5-dinitrobenzoates **1b** in 80% aqueous acetone have been reported to give mainly the epimeric benzobarbaralols.[2]

Oxidation of the **2a** with CrO_3-pyridine in dry methylene–chloride alcohol-free has recently been reported to give the benzobarbaralone **3**.[3] Benzobarbaralone is a white crystalline compound, m.p. 82–83°. We had independently obtained **3** in 90% yields by oxidation of the mixture of epimeric benzobarbaralols **2**. The NMR spectrum of **3** (Fig 1) at room temperature reveals a frozen structure of divinyl–cyclopropane system where one of the double bonds is a part of a fused benzene ring. This is in contrast to the parent compound, barbaralone **4**, the NMR spectrum of which represents a fluxional character at room temperature or above, by the averaging of the two rapidly equilibrating valence tautomers.[4] Obviously, the aromatization energy precludes double bond shifting in this system:



3 **3′**



4

RESULTS AND DISCUSSION

Reaction of **3** with excess diazomethane at 3° in methanol–chloroform–ether, using lithium chloride as catalyst followed by chromatography on neutral alumina, yielded benzobullvalone **5**, (22%) and the epoxide **6**, (31%), both as oily products. In the absence of lithium chloride, the hemiacetal **7** was isolated as a mixture of stereoisomers.* Again, the

---

*The material left was insufficient for analysis, but the mass spectrum provided convincing evidence.

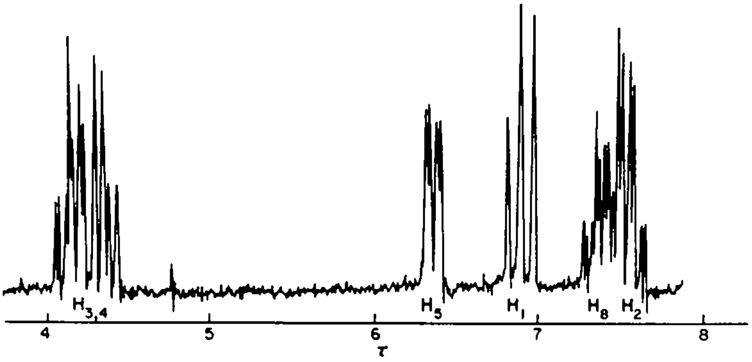
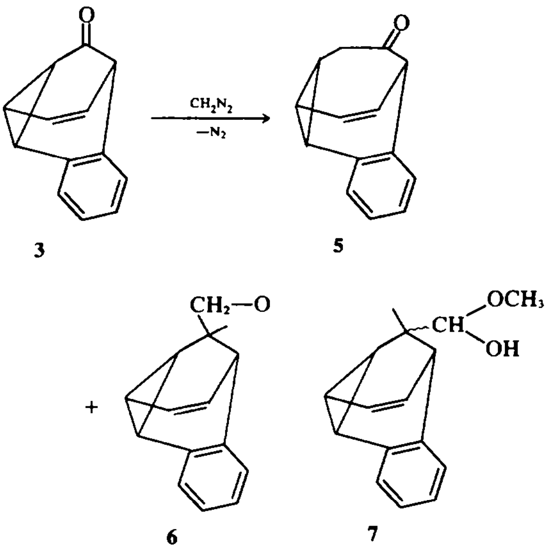


Fig 1. NMR spectrum, 100 MHz, of Benzobarbaralone 3, in CDCl$_3$.

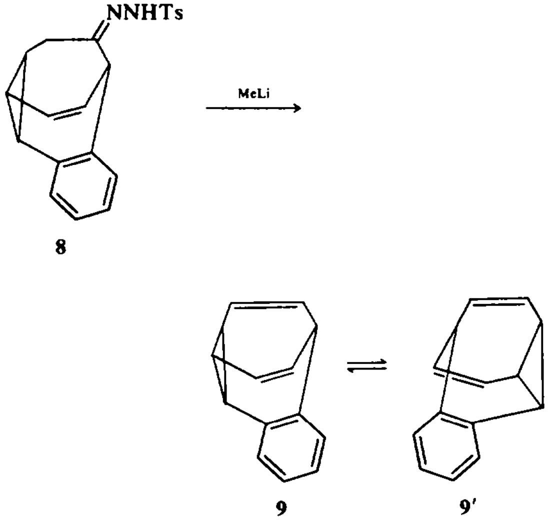
NMR spectrum of **5** reveals *no* tautomeric equilibrium of the type exhibited by bullvalone (at room temp).



3 **5** **6** **7**

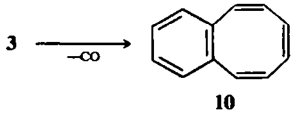
The tosylhydrazone of benzobullvalone **8**, was converted by methyl–lithium (excess)[5] in hexane–ether mixture at room temperature to the unknown benzobullvalene **9**, (30%).

The fast and reversible valence isomerization of $9 \rightleftharpoons 9'$ (which involve only *two* isomers) is easily recognized from the temperature-dependence of the NMR spectra (in CD$_2$Cl$_2$). $\Delta G^{\ddagger}_{258}$ for isomerization as calculated from the temperature of coalescence (at − 15°) is 11·5 kcal/mol. This value is similar to that which has been found for the parent bullvalene.[6],* The NMR spectrum of **9** in CCl$_4$ at room temperature shows a very broad signal centered at τ 6·08 (about 24 Hz width of half-height of the peak) which results from the averaging of the chemical shift of two cyclopropyl and two olefinic protons, triplet of relative area 2 centered at τ 7·22 (J = 9 Hz) and a triplet of relative area 2 centered at τ 4·32 (J = 8·5 Hz) with each wing being further split into a triplet (J = 1·5 Hz).



8 **9** **9′**

Direct irradiation of **3** in acetonitrile at 254 nm afforded benzocyclooctatetraene **10**[7] (20%) accompanied by polymeric material. This is in accord with the facile decarbonylation of , β, γ unsaturated ketones[8a,9] as well as their rearrangement involving allylic bonds.[8b] Mukai *et al.*[9a] have reported the photodecarbonylation of barbaralone **4**, using a high pressure Hg-lamp to give a single product identified as cyclooctatetraene. Our result repres-



10

---

*Only substituted derivatives of **9** so far have been described.

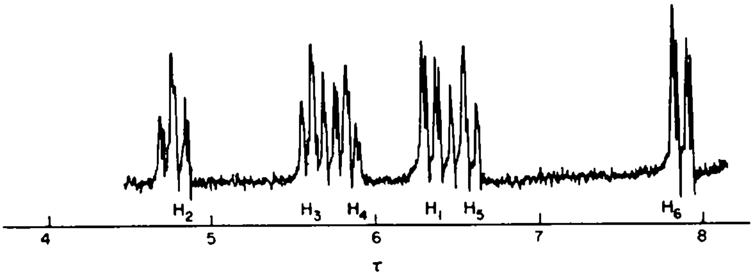
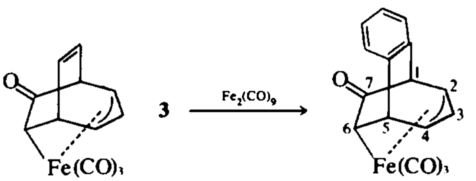


Fig 2. NMR spectrum, 100 MHz, of irontricarbonyl complex **12**, in $CDCl_3$.

ents another new example of decarbonylation of cyclic unsaturated ketone in the condensed phase.

It has recently been shown that barbaralone **4**[10a,b] and also some other bridged polycyclics[11] containing the divinylcyclopropyl group react with diiron nonacarbonyl to give irontricarbonyl complexes in which the iron is involved in a σ-bond and π-allyl complex. These results directed our attention towards benzobarbaralone **3** since it consists of a vinylcyclopropyl system within a rigid tricyclic ring system, but lacks the additional double bond present in barbaralone **4**. Complex **11*** was indeed obtained in 40% yield by reaction of **3** with $Fe_2(CO)_9$ in benzene. The CH skeleton of **11** was determined by H^1 NMR analysis in $CDCl_3$, 100 MHz (Fig 2), including double resonance irradiation experiments. As in the Fe complex, **12**, obtained from **4**,[10a,b] the NMR spectrum of **11** shows no symmetry and each of the six non-benzenoid protons exhibits separate and well-resolved absorption.



12 **11**

The highest field proton (relative to TMS) at τ 7·88 is due to H_6 on the carbon atom σ-bonded to the Fe atom (dd, $J_{6,5}$ = 8·5 Hz). The bridgehead protons: H_5 appears at τ 6·55 (dt, $J_{5,4}$ = 7·0 Hz) and H_1 at τ 6·33 (dd, $J_{1,2}$ = 8·0 Hz). The multiplicity of the three allylic protons is very similar to that observed for **12**, where the chemical shifts are: H_2 at τ 4·77 ($J_{4,2}$ = 2·0; $J_{4,3}$ = 6·0), H_3 at τ 5·62 and H_4 at τ 5·83.

EXPERIMENTAL

M.ps were taken on Unimelt-Thomas and Hoover's capillary m.p. apparatus and are uncorrected. IR spectra were recorded on Perkin-Elmer Infracord models 337 and 257 spectrophotometers. NMR spectra were measured with Varian HA-100 and Jeol CH-60 spectrophotometers. Mass spectra were determined with an Atlas CH4 mass spectrometer fitted with TO-4 ion source with direct inlet system.

Reaction of 3 with diazomethane

I. Etheral diazomethane (100 ml) (prepared from 4 g Nitrosomethylurea) at 0° was added all at once to a soln of **3** (800 mg) in MeOH (8 ml)—$CHCl_3$ (16 ml) containing LiCl (70 mg) at 0°. The mixture was stored at 3° over-night. AcOH (3 ml) was used to destroy excess of diazomethane and the mixture was extracted with water, 5% $NaHCO_3$ aq and sat NaCl aq and dried over $MgSO_4$. Removal of the solvent gave oily residue which was chromatographed on neutral alumina. Using hexane -CH_2Cl_2 (20%) as eluent, the first compound to be removed was **6** (252 mg, 31%) followed by benzobullvalone **5** (171 mg, 22%). Elution with CH_2Cl_2 removed unreacted starting benzobarbaralone (75 mg).

Compound **5**, oil, mass spectrum *m/e* 196; IR absorption: $\gamma_{max}^{CHCl_3}$ 1695 cm^{-1} (C=O); NMR ($CDCl_3$): τ 2·6–3·0 (m, 4H), 7·72–6·45 (m, vinyl protons, 2H), 6·31 (dd, J = 9 and 1·5 Hz, 1H), 6·75 (m, 2H), 7·53 (dd, J = 10 and 7·5 Hz), 8·05 (m, 2H); **6**, is an oil, mass spectrum *m/e* 196; NMR ($CDCl_3$): τ 2·8–3·1 (m, 4H), 3·85–4·5 (m, 2H), 6·25 (dd, 1H), 6·9 (m, 1H), 7·4 (m, 2H) and 7·92 (m, 2H). Compound **5** and **6**: (Found: C, 85·45; H, 6·13%, $C_{14}H_{12}O$ requires: C, 85·7; H, 6·12%).

II. *Reaction in the absence of lithium chloride.* Diazomethane in ether (prepared from 6 g N-nitrosomethylurea) was treated with **3** (1·33 g) dissolved in 50 ml MeOH, at 0°. After the work up as above, the residue was chromatographed on basic alumina to give **5** (366 mg, 24%) followed by the mixture of hemiacetals **7** (877 mg, 48%) eluted with $CHCl_3$ as an oily product. Mass spectrum *m/e* 228 (M^+), 197 (M^+-OCH_3) and 165. $\gamma_{max}^{CHCl_3}$: 3650, 3450 and 1720 cm^{-1}.

Conversion of 5 into benzobullvalene 9

To suspension of tosyhydrazone **8** prepared from **5** (350 mg) (according to the procedure in Ref 9*b*) m.p. 172–176°, in dry ether were added 4 equiv of MeLi (2M soln in ether) at room temp. After stirring the mixture for 1 h, water was added, and the layers were separated, the aqueous soln was extracted with 2 × 25 ml ether. The combined extracts washed with dil HCl acid, 5% $NaHCO_3$ aq, satd NaCl, dried ($MgSO_4$) and evaporated at reduced pressure. The oily residue was chromatographed on basic alumina to give the only isolable product **9** (90 mg, 30%) as eluted with hexane. Recrystallization from pentane gave

---

*Compound **11**: (Found: C, 59·49; H, 3·28; $C_{16}H_{10}FeO_4$ requires: C, 59·4; H, 3·11%).

m.p. 89°. Mass spectrum *m/e* 180 (M^+). Compound **9**: (Found C, 93·0; H, 7·02, $C_{14}H_{12}$ requires: C, 93·4; H, 6·6). m.p. is given in the text.

Photolysis of 3 *in acetonitrile*

An acetronirile soln (40 ml) of **3** (130 mg) was purged with N_2 for 5 h and then irradiated directly at room temp for 2 h at 2537 Å in quartz vessel. A positive N_2 pressure was maintained over the photolysis soln during the entire experiment. The soln was concentrated and the residue then chromatographed on basic alumina. Using hexane as eluent, the first compound to be removed was identified as **9** (20 mg) by its unique NMR spectrum.[7]

Reaction of 3 *with* $Fe_2(CO)_9$

To a soln of **3** (450 mg, 2·5 mmoles) in dry benzene (30 ml), was added $Fe_2(CO)_9$ (1·2 g, 3·3 mmoles) and the mixture was stirred for 1·5 h at 55°. The dark soln was filtered, and evaporated at room temp under reduced pressure and the residue was chromatographed on basic alumina. Starting material was eluted with CH_2Cl–hexane (1 : 1), 218 mg, followed by the σ-h^3 complex, eluted with CH_2Cl_2, 156 mg, crystallized from hexane, m.p. 125–127°. ν_{max}^{hexane}; 1695 cm^{-1} (carbonyl C=O); 2060, 2065 and 1985 cm^{-1} (C≡O); $(_{max}^{CHCl_3}$ for the keto carbonyl 1665 cm^{-1}). Mass spectrum *m/e* 322 (M^+), 294 (M^+–CO), 266 (M^+–2CO), 238 (M^+–3CO) and 210 (M^+–4CO).

Acknowledgements—The author wishes to thank Mrs. S. Weinman (synthesis) and Mrs. R. Weininger (NMR determinations) for technical assistance and Professor A. Mandelbaum for the mass spectra.

REFERENCES

[1] A. Eisenstadt, *J. Organometal. Chem.* **38**, C32 (1972)
[2] J. S. Blair, J. Clark and G. V. Meehan, *Tetrahedron Letters* 3097 (1972)
[3] The ketone first prepared by Dr. P. T. Izzo: see Z. Goldschmidt and A. S. Kende, *Ibid.* **48**, 4625 (1971); Ref 13
[4] Von. E. Doering *et al.*, *Tetrahedron* **23**, 3943 (1967)
[5] R. Shapiro and M. Heath, *J. Am. Chem. Soc.* **89**, 5734 (1967)
[6] G. Schroder and J. F. M. Oth, *Angew. Chem.* Inter. Ed. **6**, 414 (1966)
[7] H. E. Zimmerman, R. S. Givens and R. M. Pagni, *J. Am. Chem. Soc.* **90**, 6096 (1968)
[8a] B. Fuchs, *J. Chem. Soc.* (C), 68 (1968) and refs cited; [b] U. Klinsman, J. Gauthier, K. Schaffner, M. Pasternak and B. Fuchs, *Helv. Chim. Acta* **55**, 2643 (1972)
[9a] T. Makai and K. Kurabayaski, *J. Am. Chem. Soc.* **94**, 4493 (1970); [b] H. Shechter *et al.*, *Ibid.* **94**, 5366 (1972)
[10a] A. Eisenstadt, *Tetrahedron Letters* 2005 (1972); [b] R. Aumann, *Angew. Chem.* **84**, 583 (1972)
[11] R. H. Moriarty, C. L. Yeh, K. N. Chein and R. Srinivasan, *Tetrahedron Letters* 5325 (1972) and refs therein