Tetrahedron Vol 25, pp. 2417 to 2425. Pergamon Press 1969. Printed in Great Britain

NEW SYNTHESES OF BENZOBICYCLO[2.2.2]OCTA-DIENE AND -TRIENE, AND THERMAL DECOMPOSITION OF THE HYDROCARBONS AND RELATED ONES[1]*

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(*Received in Japan* 29 *November* 1968; *Received in the UK for publication* 16 *January* 1969)

Abstract—A convenient synthesis of benzobicyclo[2.2.2]octadiene (I) from dicyclohexa-1,3-diene (III) by dehydrogenation with chloranil and a new route leading to benzobicyclo[2.2.2]octatriene (VI) from the unsaturated ketone VII are described. Thermal decomposition rates of these hydrocarbons, and bicyclo[2.2.2]octa-diene and -triene were compared. Naphthalene was the main product by LAH reduction of the oxime VIII.

SYNTHESIS OF BENZOBICYCLO[2.2.2]OCTADIENE

PARALLEL with the active researches on the chemistry of the benzonorbornene series,[2] syntheses and reactivities of the benzobicyclo[2.2.2]octene and benzobicyclo[3.2.1]octene compounds have recently been studied from a variety of interests.[3–7] Benzobicyclo[2.2.2]octadiene (I)[3,8] is one of the most important compounds for the syntheses of the benzobicyclo-octene derivatives. We have synthesized many sorts of the compounds[3,5,6] containing benzobicyclo-octene ring starting from I.

The hydrocarbon I was first synthesized by Simmons[8] through cycloaddition of benzyne to cyclohexa-1,3-diene (CHD). However, this method is not satisfactory, because the yield of I is low and its isolation from the raw product containing many other hydrocarbons[9] is tedious. In a previous paper,[3] we have reported the synthesis of the hydrocarbon I from 2,3-benzobicyclo[2.2.2]octene-5,6-*trans*-dicarboxylic acid (II)[10] by means of bis-decarboxylation with lead tetraacetate according to the method of Grob *et al.*[11] In this case, isolation of I from the products was easy, but its yield was not so high. This paper reports another convenient method for the synthesis of the hydrocarbon I.

We first tried to prepare I by converting the dicarboxylic acid II to a dibromide by the modified Hunsdiecker reaction using mercuric oxide and bromine,[12] followed by reduction with zinc. However, the expected dibromide was not obtained, and the acid was mostly recovered. Photo-iodination of II with lead tetraacetate and iodine[13] did not proceed.†

We have found a new synthetic pathway leading to I consisting of dehydrogenation of dicyclohexadiene (III), which is easily obtainable from CHD. There are many reports[14–17] on the dimerization of CHD. We have also carried out the dimerization of CHD in different conditions (see Experimental section). Heating CHD at 178–186°

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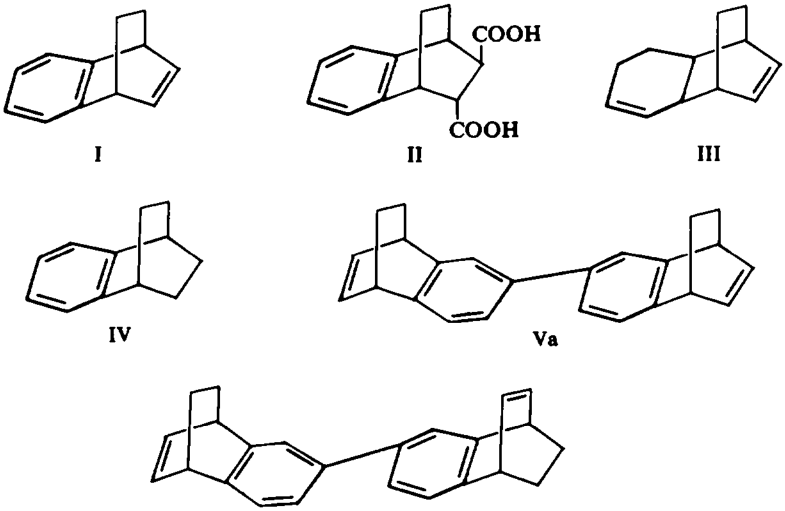
* Part of this paper has been presented in a preliminary communication.[1]

† The reaction of β-naphthol with *trans*-dichloroethylene at 200° did not form a Diels–Alder adduct and, instead, afforded a small amount of naphtho[2,1-b]furan.



I II III

IV Va

Vb

Fig. 1

in a stainless autoclave for 24 hr gave the most satisfactory yield of the dimer III (*endo* and *exo*).*

The dimer III was subjected to dehydrogenation without separation of the *endo*- and *exo*-isomer. Dehydrogenation of III with chloranil in xylene at 130–140° gave the expected benzobicyclo[2.2.2]octadiene (I) after easy purification by column-chromatography on alumina or by rectification. The hydrocarbon I was identified by comparison of IR and VPC with a standard sample[3] and by its hydrogenation to benzobicyclo[2.2.2]octene (IV).[3,15] When 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was used instead of chloranil, the yield of I was lower. Examples of the dehydrogenation experiments are shown in Table 1. Starting hydrocarbon was recovered in shorter reaction periods. As a by-product, biphenyl was obtained in small amounts.† In one experiment where the dehydrogenation mixture was subjected to chromatography on alumina without distillation, another by-product, m.p. 159–161° was obtained in a small amount. Structure Va or Vb was assigned by elemental analysis, molecular weight determination and spectral data (see experimental part). As expected, thermal decomposition of the hydrocarbon at 250° for

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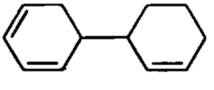
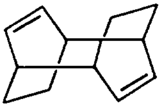
[*] Detailed mechanistic study on the dimerization and polymerization of CHD was carried out by Nakata and Choumei[17] of our Laboratory.

We had also realized that both the *endo*- and *exo*-dimer are produced by thermal dimerization of CHD, as reported by Valentine *et al.*[16]

[†] It is not yet clear whether biphenyl was formed from the dimer III or from some other hydrocarbons such as **a**[17] or **b**[16,17] involved slightly in the dimer III. The possibility of the formation of the by-product from I can not be excluded, but seems unlikely.



a



b

TABLE 1. DEHYDROGENATION OF DICYCLOHEXADIENE (III)

Exp. No.	Dicyclohexadiene (III) (g)	Chloranil* (g)	Xylene (ml)	Reaction temp (bath)	Reaction time (hr)	Yield of I g (%)	Recovered III g (%)
1	0·333	1·214	5	130 ~ 140	6·5	0·176 (54·3)	0·043 (12·8)
2	3·406	12·579	53	135 ± 2	10	2·281 (68·7)	0·272 (8·0)
3	11·98	46·0	170	136 ~ 141	22·5	8·316 (71·3)	0·140 (1·2)
4†	1·601	6·165	25	83 ~ 86	30	0·562 (36·0)	—

* Amounts of chloranil were about 1·2 equivalent of the theory.

† In this run, DDQ and benzene were used instead of chloranil and xylene, respectively.

4 hr in a sealed tube produced ethylene (identified by IR) and 2,2′-binaphthyl, m.p. 188–191° (Lit. m.p. 188°; characteristic UV[18] and IR spectrum). The product Va or Vb is thought to be formed through the dimerization of I or III, or a coupling of I with III, very likely *via* radical mechanisms.

As III is easily accessible and the yield of its dehydrogenation is fairly good, this route provides a convenient synthesis of the hydrocarbon I.

SYNTHESIS OF BENZOBICYCLO[2.2.2]OCTATRIENE (VI)

Benzobicyclo[2.2.2]octatriene (VI) is an interesting compound in view of the benzo-homolog of bicyclo[2.2.2]octatriene.[19] The hydrocarbon VI was found by Miller and Stiles[4] in the products of the reaction of benzyne with benzene. The procedure of its synthesis has been recently improved by Friedman *et al.*[20] Independently, we had also synthesized the hydrocarbon starting from 2,3-benzobicyclo-[2.2.2]octa-2,7-dien-5-one (VII) by the following route.

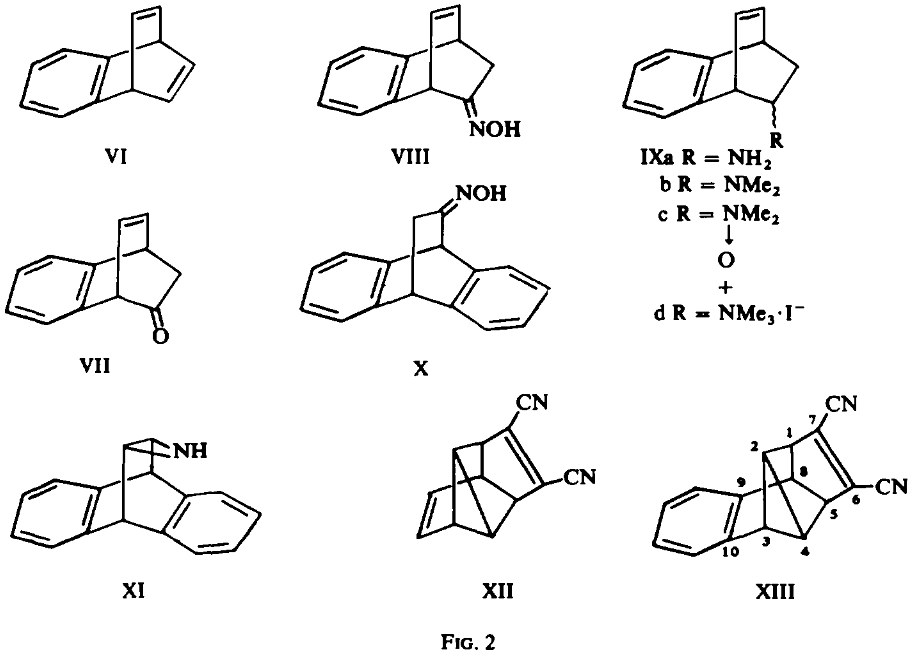


FIG. 2

The oxime VIII, m.p. 154–156°, of the ketone VII was reduced with sodium and ethanol to an oily amine IX*a*, which was assumed to be a mixture of the *endo*- and *exo*-isomers by paper chromatography. Because the separation of the isomers was not easy, the following reaction sequence leading to VI was carried out using mixtures of the isomers. The dimethylamino derivative IXb was obtained by methylation of IXa with formic acid and formaline. In this reaction, the ketone VII (18%) was produced as a by-product. Oxidation of IXb with hydrogen peroxide in methanol gave the N-oxide IXc, thermal decomposition of which at 120–150° *in vacuo* gave an almost colorless distillate, which soon solidified. Column chromatography of the distillate on alumina gave the desired benzobicyclo[2.2.2]octatriene (VI), m.p. 65·5–66·5° (Lit.[4] m.p. 65·0–65·5°), in 40–49% yields from VII, removing the first eluted naphthalene (ca. 10%). The structure of the obtained hydrocarbon VI was confirmed by the spectral data (IR, UV[3] and NMR), which agreed with those reported,[4] and its conversion to the saturated hydrocarbon IV.[3, 15] The Hofmann degradation of the ammonium hydroxide prepared from the methiodide IXd afforded also VI, but in lower yield, producing much naphthalene.*

When the oxime VIII was reduced with lithium aluminum hydride (LAH) in boiling tetrahydrofuran (THF), naphthalene was formed in about 60% yield, unexpectedly, and the yield of basic products (crude IXa) was only 30%. The unusual results prompted us to examine the reported reduction of dibenzobicyclo[2.2.2]-octadienone oxime X by LAH in THF.[5] Here again anthracene was formed in 50% yield besides the aziridine derivative XI (34%) and a small amount of the corresponding primary amine (3%). Aziridine formation was not observed on the reduction of VIII. Although we could not isolate the cleaved counter part in the formation of napththalene or anthracene and the mechanism of the reaction is not clear, it is noteworthy that the reductive cleavage of the bridge bearing an oximino function occurs under rather mild conditions to give rise a new aromatic ring from such bridged ring systems.

Incidentally, we have examined the reaction of VI with dicyanoacetylene, because bicyclo[2.2.2]octatriene has been reported[21] to react with the dienophilic reagent to give the adduct XII, which on heating undergoes interesting rearrangement leading to 1,2-dicyanonaphthalene. When VI was warmed with dicyanoacetylene at 52–56° in a sealed tube, an adduct, m.p. 188–188·4°, was obtained in 30% yield. The structure of the adduct was easily assigned based on the elemental analysis and spectral data (see experimental section) analogous to those of XII and the adduct[22] of norbornadiene and dicyanoacetylene. In contrast to XII, the adduct XIII is thermally more stable, since heating XIII at 200° caused no conversion into an anthracene derivative.

THERMAL DECOMPOSITION OF BENZOBICYCLO[2.2.2]OCTADIENE AND RELATED HYDROCARBONS

Thermal decomposition of bicyclo[2.2.2]octadiene and bicyclo[2.2.2]octatriene (barrelene) have been reported by Grob *et al.*[3] and Zimmerman *et al.*,[19] respectively. In this connection, we are interested in investigating the thermal stability or decomposition of the saturated and unsaturated hydrocarbons of the benzobicyclo-

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* We have also synthesized VI by decarboxylation of 2,3-benzobicyclo[2.2.2]octa-2,7-diene-5,6-*trans*-dicarboxylic acid with lead tetraacetate. Details will be reported elsewhere.

[2.2.2]octene series, which can be regarded as benzo-homologs of the above bridged compounds.

The hydrocarbons I, IV and benzobicyclo[2.2.2]octatriene (VI)[3,4] were heated in a sealed tube for appropriate periods, and the products were analysed by VPC. The results are summarized in Table 2 with the relevant data.[19,23] Thermal decomposition of the hydrocarbon I at 200° produced naphthalene and ethylene, which were identified by retention time analysis on VPC. The rate of thermal decomposition of the triene VI into naphthalene and acetylene is much smaller than that of I. The saturated hydrocarbon IV was not decomposed at all in the conditions cited.

TABLE 2.
RATES OF THERMAL DECOMPOSITION OF BENZOBICYCLO[2.2.2]OCTADIENE (I) AND THE RELATED HYDROCARBONS[*]

Hydrocarbon	Rate of decomposition (%) 200°		250°	
	1 hr	24 hr	1 hr	24 hr
I[†]	79	100	100	—
VI[‡]	0	5·7	3·9	31
IV	—	0	—	—
Bicyclo[2.2.2]octatriene[§]	—	29	—	100
Bicyclo[2.2.2]octadiene[‖]	—	93	—	—

[*] Small amounts of the hydrocarbons (6–20 mg) were heated in a sealed glass tube and the products were analyzed by VPC.

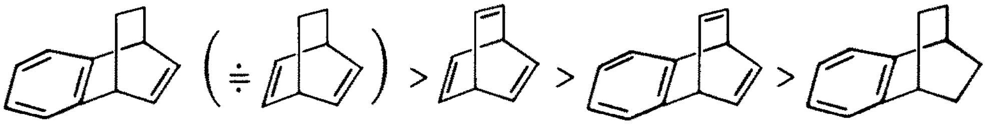
[†] Heating of I at 150° for 1 hr caused no decomposition.

[‡] Miller *et al.*[4] reported that VI was decomposed completely to naphthalene and acetylene by heating at 310° for 1·5 hr.

[§] Data reported by Zimmerman *et al.*[19]

[‖] Rate reported by Grob *et al.*[23]

Accordingly, the rates of thermal decomposition of these hydrocarbons and the related bicyclo[2.2.2]octanes at 200° decrease in the following order:



I VI IV

The results are understandable in view of that (i) decomposition proceeds smoothly if it leads to an aromatic system and (ii) an Sp^3–Sp^3 bond requires an activation energy for cleavage less than an Sp^2–Sp^3 bond.

EXPERIMENTAL

M.ps were taken by capillary, and are uncorrected. The NMR spectra were determined at 60 Mc with Varian A-60 spectrometer using TMS as internal standard in $CDCl_3$. The IR spectra were measured using a Koken Model D.S. 301 double-monochromatic spectrophotometer and the UV spectra were measured using a Hitachi Model E.P.S.-2 UV spectrometer. Solutions were dried over anhyd Na_2SO_4 unless otherwise stated.

Attempted decarboxylation of 2,3-*benzobicyclo*[2.2.2]*octene*-5,6-*trans-dicarboxylic acid* (II) *according to the method of Cristol*[12]

The acid II (3·109 g) was mostly dissolved in $CHCl_3$ (700 ml) by refluxing, and HgO (5·746 g) was added. After refluxing for 2·5 hr Br_2 (4·2 g) in $CHCl_3$ (30 ml) was added dropwise for 45 min, and the mixture was refluxed for another 3·5 hr. After work up, crude acid II (ca. 2·3 g, 74%) was recovered and the expected dibromide was not obtained.

By a similar procedure stearic acid was decarboxylated to give heptadecyl bromide in good yield (90·2%) as reported[12] using CCl_4 as a solvent.

Attempted decarboxylation of II *according to the method of Barton*[13]

A hot soln of II (0·860 g) in $CHCl_3$ (200 ml) was added to a suspension of $Pb(OAc)_4$ (2·62 g) in $CHCl_3$ (40 ml). To the stirred mixture refluxed by irradiation with a 500 W tungsten lamp, I_2 (0·763 g) in $CHCl_3$ (60 ml) was added gradually, and refluxing was continued for 17 hr (CO_2 gas produced was 27% of the theory). After filtration of the reaction mixture the $CHCl_3$ solution was washed with 5% $NaHCO_3$aq and H_2O, dried, and evaporated to give residue (700 mg), which was extracted with petroleum ether (572 mg) and recrystallized from the same solvent affording plates, m.p. 71·5–73° (m.p. 178–180°, in a sealed tube). This was identified with hexachloroethane[24] by elemental analyses, mixed m.p. and comparison of IR with a standard sample. Decarboxylated compound could not be isolated. From the $CHCl_3$-insoluble substance, the acid II (669 mg, 75·3%) was recovered after acid and alkali treatment.

Thermal dimerization of cyclohexa-1,3-*diene* (CHD)

CHD was prepared from *trans*-1,2-dibromocyclohexane by dehydrobromination with NaOH in ethylene glycol.[25]

Thermal dimerization of CHD was carried out in a stainless autoclave by heating at different ranges between 178–210° in an atmosphere of hydrogen or nitrogen. In some runs, a small amount of 2,5-di-*tert*.-butylhydroquinone (Di-*t*-BuHQ) or 1,1-diphenyl-2-picrylhydrazyl (DPPH) was added, but the yield of the dimer was not improved. Examples of the dimerization are shown in Table 3.

Dehydrogenation of the dimer III *leading to* I (*see Table* 1)

Dimer III (11·98 g) and chloranil (46·0 g) in dry xylene (commercial grade, mixture of isomers; 170 ml) were heated at 136–141° (bath temp.) for 20 hr. The brown soln was cooled and diluted with petroleum

TABLE 3. THERMAL DIMERIZATION OF CYCLOHEXA-1,3-DIENE (CHD)

CHD	Yield[*]			Reaction conditions		
(g)	Monomer† (%)	Dimer (III)‡ (%)	Polymer§ (%)	Temp	Time (hr)	Atmosphere third additive (mg)
37·0	14·4	52·8	27·9	178–186	24	Hydrogen
276·9	25·4	42·8	29·1	184–187·5	24	Hydrogen
41·7	20·2	39·9	24·2	180–185	24	Hydrogen Di-*t*-BuHQ (200)
45·3	22·7	43·8	24·1	180–185	24	Nitrogen DPPH (22)
40·3	30·1	36·9	24·1	182–186	12	Nitrogen DPPH (20)
43·3	20·2	32·7	34·9	200–210	12	Nitrogen DPPH (22)
40·6	24·3	39·1	27·1	181–185	24	Nitrogen

[*] Calculated from the weight of the product obtained by fractional distillation.

† Fraction boiling below 83°, mainly 80–83°. This fraction is probably a mixture of cyclohexene, CHD, cyclohexa-1,4-diene and benzene as reported by Nakata *et al.*[17]

‡ Fraction with b.p. 83–87° (6·5 mm) (mixture of *endo*- and *exo*-isomer); a small amount of the initial fraction and end fraction was discarded.

§ Residue on the distillation.

ether (b.p. 33–38°, 130 ml), and the precipitates (mainly tetrachlorohydroquinone) was filtered and washed with petroleum ether. The filtrate was washed several times with 5% KOHaq (total, 200 ml) and water, dried over K_2CO_3 and evaporated carefully to give a brown residue (15·85 g), which was chromatographed on Al_2O_3 (Woelm, neutral, grade I; 1000 g). First fraction eluted with petroleum ether (b.p. 33–38°) gave the recovered III (ca. 140 mg). The subsequent fractions eluted with the same solvent, and then petroleum ether–benzene (9:1–1:1) gave a colorless oil (8·32 g, 71·3%) of I (A distilled pure sample showed N_D^{20} 1·5711, N_D^{25} 1·5685). The products were identified by IR spectra and VPC retention time analyses with standard samples.[3] The obtained hydrocarbon gave on hydrogenation over Pd–C in EtOH gave the crystalline IV.[3,15]

When the dehydrogenation was carried out on a larger scale (dimer, 76·7 g) and the crude product was fractionated twice by distillation, almost pure I was obtained. On chromatography on alumina of the end fractions (6·34 g) on its distillation, a small amount of biphenyl (ca. 130 mg) was obtained by elution with petroleum ether containing 5% benzene after the main fractions of I.

In another experiment where III (12·85 g) was dehydrogenated similarly for 11 hr and the raw product was subjected to chromatography on alumina, a crystalline product (69 mg, m.p. 155–158°) was eluted with petroleum ether–benzene (1:1) after the fraction of I. A pure sample Va or Vb was obtained on recrystallization from petroleum ether as needles, m.p. 159–161°. (Found: MW (vapour pressure osmometry), 294; C, 93·00; H, 7·12. $C_{24}H_{22}$ requires: MW, 310·42; C, 92·86; H, 7·14%). IR ν_{max}^{Nujol} (cm^{-1}) 705 (—HC═CH—, *cis*); $\nu_{max}^{CHCl_3}$ (cm^{-1}) 813, 825, 1609, 2999, 3044; UV $\lambda_{max}^{n\text{-heptane}}$ 212·7 mμ (ε = 47,500), 266 mμ (ε = 17,650), substituted biphenyl type absorption without substituent on 2,2'- position *ortho* to the bond linking the benzene rings; NMR τ: about 2·7–2·8 (6H, aromatic, a complex signal pattern of an ABC spin system having one strong coupling (J_{ortho})), ~3·53 (4H, olefinic, 4 peaks as X_2 part of an A_2X_2 system), ~6·07 (4H, bridge-head, multiplet), ~8·50 (8H, bridge-methylene, multiplet).

A sample of this hydrocarbon was decomposed by heating at 250° for 4 hr in a sealed glass tube in N_2 atmosphere. The IR spectrum of the resulted gas *in vacuo* was identical with that of pure ethylene, and sublimation of the crystalline product gave plates, whose m.p. (188–191°) and the UV spectrum[18] in 95% EtOH was in good agreement with the reported of 2,2'-binaphthyl; its IR spectrum in KBr was also identical with that of authentic 2,2'-binaphthyl.

Thermal decomposition of the hydrocarbon I, IV *and* VI

A pure sample (6 ~ 22 mg) of each hydrocarbon (single peak on VPC analysis) was put into a sealed glass tube (dia., 5 mm; length, 120 mm) and heated at constant temp. for appropriate periods. The content was subjected to VPC analysis using a Shimazu IB apparatus with TCD. Column: Thermol-2; dia., 6 mm; length, 3 m; temp., 151°. Carrier gas: H_2, 200 ml/min. The percentage of the decomposition of the hydrocarbon was obtained by comparison of the peak areas of the formed naphthalene and recovered hydrocarbon. The calculation was justified by the similar VPC analysis of the mixture of naphthalene and the hydrocarbon prepared in known ratios. The retention times of naphthalene and the hydrocarbons are as follows: naphthalene, 12 min; I, 19 min; IV, 20 min; VI, 21 min. The results obtained are listed in Table 2. No other products except ethylene and acetylene gas were detected, even when some decomposition products showed light brown colour.

In an experiment of the decomposition of I, ethylene gas which began to evolve on heating at about 180°, was captured and identified with a standard sample by VPC analyses; from the leaving residue almost quantitative amount of naphthalene was obtained.

Benzobicyclo[2.2.2]*octadienone oxime* (VIII)

A mixture of the ketone VII (1·073 g), abs EtOH (6 ml), NH_2OH–HCl (0·684 g) and pyridine (10·5 ml) was refluxed in an oil bath (160°) for 4 hr and evaporated to dryness under reduced press. After the addition of 5% HCl (6 ml), the oily substance was extracted with CH_2Cl_2, washed with water and evaporated to give a crystalline residue (1·152 g), which on recrystallization from EtOH–H_2O afforded the oxime VIII (0·952 g, 81·7%) as rods, m.p. 154–156°. (Found: C, 77·98; H, 6·22; N, 7·43. $C_{12}H_{11}ON$ requires: C, 77·81; H, 5·99; N, 7·56%). IR ν_{max}^{Nujol} 3223 cm^{-1}.

2,3-*Benzobicyclo*[2.2.2]*octa*-2,7-*dienylamine* (IXa)

To a stirred soln of the oxime VIII (2·328 g) in absolute EtOH (125 ml), Na (12 g) was added in small portions at 75–95° for 80 min in an N_2 atmosphere, and heating at 95° was continued for 20 min. After dilution with water (100 ml) under cooling and extraction with ether, the organic layer was shaken with 5% HClaq (150 ml). The aqueous soln was basified with 10% NaOHaq, extracted with ether, and washed with water. Evaporation of the solvent gave the crude amine IXa as an oil (1·87 g, 86·9%), which showed two spots (*endo*- and *exo*-amine) on PPC. Oxalate: colorless prisms, m.p. 231–233°, recrystallized twice from MeOH. (Found: C, 71·81; H, 6·60. $(C_{12}H_{13}N)_2 \cdot C_2H_2O_4$ requires: C, 72·20; H, 6·53%). Benzoate: cubic crystals, m.p. 134·5–136°, recrystallized thrice from ether. (Found: C, 82·73; H, 6·32; N, 5·14. $C_{19}H_{17}ON$ requires: C, 82·88; H, 6·22; N, 5·09%). IR ν_{max}^{Nujol} 3385, 1634 cm^{-1} (—$NHCOC_6H_5$).

Dimenthylamino derivative IXb, *N-oxide* IXc *and methiodide* IXd

A mixture of the amine IXa (1·412 g), formic acid (6 ml) and 37% formalin (4 ml) was refluxed in a bath (140°) for 12·5 hr. After evaporation of the mixture, addition of 5% HClaq (15 ml) to the residue and washing with ether, the aqueous layer was basified with 20% NaOHaq, extracted with ether and dried over anhyd K_2CO_3. Evaporation of the solvent gave 1·332 g (81·0%) of crude IXb as an oil, which showed two spots on PPC. As a neutral by-product, ketone VII (ca. 18%) was obtained from the foregoing ether-washings.

To a cold soln of IXb (1·80 g) in MeOH (3·5 ml), 30% H_2O_2 (3·3 ml) was added with stirring, and the soln was kept at room temp (23°) for 24 hr. After destroying the excess H_2O_2 with Pt-black, the filtrate was evaporated *in vacuo* under 40° to give a viscous oil (2·12 g) of the crude IXc.

A soln of IXb (228 mg) and MeI (822 mg) in MeOH (1 ml) was refluxed for 2 hr. After evaporation, the residue was recrystallized four times from EtOH to give needles, m.p. 222·5–223° (dec), of IXd. (Found: C, 52·53; H, 5·89; N, 4·00. $C_{15}H_{20}IN$ requires: C, 52·80; H, 5·91; N, 4·11).

Benzobicyclo[2.2.2]*octatriene* (VI)

(a) *From the* N-*oxide* IXc. The crude *N*-oxide IXc (2·12 g) described above was gradually heated in a distillation flask under a vacuum (2 mm Hg). The distillate was produced by elevating the temp from 120 to 140° (bath) during 10 min and maintaining at 140° for 20 min. The distilled solid (987 mg) was dissolved in petroleum ether, washed with 4% HClaq and H_2O and dried. Evaporation gave crystals, m.p. 44–57°, which was chromatographed on 1% H_2O-containing Al_2O_3 (Woelm, neutal, 260 g) using petroleum ether. The early eluted fractions gave crystals of naphthalene (116 mg, 10% from IXb), which was identified by mixed melting point determination and IR spectra. The later eluted fractions gave 685 mg (49·1% from IXb) of crystals, m.p. 56–60°, which was recrystallized twice from petroleum ether to afford a pure sample of the triene VI as needles, m.p. 65·5–66·5° (Lit.[4] m.p. 65·0–65·5°). (Found: C, 93·57; H, 6·64. $C_{12}H_{10}$ requires: C, 93·46; H, 6·54). UV $\lambda_{max}^{n\text{-heptane}}$ 174·9 mμ (ε = 33,100), 187·7 mμ (ε = 19,700), 190·8 mμ (ε = 19,900), 205·7 mμ (ε = 28,100), 230·8 mμ (shoulder) (ε = 1200), 262·7 mμ (ε = 498), 269·7 mμ (ε = 688), 276·6 mμ (ε = 768). NMR τ: ~5·11 (2H, bridgehead, multiplet), ~3·16 (4H, olefinic, multiplet).

(b) *From methiodide* IXd. Ammonium hydroxide prepared from crude IXd (585 mg) by treatment with AgO in the usual manner was decomposed in a distillation flask. The distillate obtained by heating gradually up to 150° *in vacuo* (150 → 50 mm) and at 160° (12 mm) for 1 hr was worked up as the above, giving a mixture (71 mg) of naphthalene and VI (ca. 1 : 1, as analysed by VPC and UV).

Benzobicyclo[2.2.2]*octatriene-dicyanoacetylene adduct* XIII

A mixture of triene VI (186 mg) and dicyanoacetylene (133 mg) was heated in a sealed tube at 52–56° for 46 hr. The brown mass was chromatographed on silica gel (Woelm, grade II, 4 g). From the fractions eluted with petroleum ether and with petroleum ether–benzene 124 mg (66·5%) of the triene VI was recovered and further elution with benzene gave the crude adduct XIII (85 mg, 30·5%), which on recrystallization from CH_2Cl_2–EtOH gave a pure sample (53·4 mg) as needles, m.p. 188–188·5°. (Found: C, 83·23; H, 4·59; N, 11·92. $C_{16}H_{10}N_2$ requires: C, 83·46; H, 4·38; N, 12·17). IR ν_{max}^{Nujol} 2225 cm^{-1} (CN). NMR τ: 6·78 (C_3-H, triplet, *J* = 6·4 c/s), 7·93 (C_2, C_4-H, doublet-multiplet, *J* = 6·4 c/s), ~7·32 (C_1, C_5-H, multiplet), ~6·85 (C_8—H, multiplet). UV $\lambda_{max}^{95\%}$ EtOH 254 mμ (ε = 9710), 295 mμ (ε = 4510). Heating of this adduct at 200° in a glass tube caused no change.

Reduction of the oxime VIII *with LAH*

The oxime VIII (609 mg) in THF (10 ml) was added to a slurry of LAH (538 mg) in THF (6 ml), and refluxed for 6 hr. After usual work up, basic fraction gave crude oily amine IXa (183 mg, 33%), which showed to be a mixture on PPC. From the neutral fraction, 251 mg (60%) of crystals (m.p. 77°) was obtained, and identified with naphthalene by mixed melting point and comparison of the IR spectra.

When the reduction was carried out in boiling ether, the yield of amine was higher and naphthalene formation was decreased.

Acknowledgements—We wish to thank Mr. Fumihiko Matsubara for his skillful technical assistance and Dr. Tadashi Nakata for helpful discussions.

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