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THE REACTION OF BENZOTROPENIUM ION, 1,2-BENZOCYCLOHEPTATRIENE-7-METHYL ETHER AND 3,4-BENZOCYCLOHEPTATRIENE-7-METHYL ETHER WITH METHYL AND 2-PROPYL GRIGNARD REAGENTS

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Abstract—Benzotropenium ion reacts with sodium methoxide to give only 1,2-benzocycloheptatriene-7-methyl ether. This sole product results from an equilibrium and not a kinetic controlled process. The reaction of benzotropenium ion with MeMgI leads to approximately an equal mixture of 7-methyl-1,2- and 7-methyl-3,4-benzocycloheptatriene. Essentially the same product ratio is derived from the reaction of 3,4-benzocycloheptatriene-7-methyl ether with MeMgI, while 1,2-benzocycloheptatriene-7-methyl ether gives predominantly 7-methyl-1,2-benzocycloheptatriene.

IN seeking a method of preparing 7-alkyl-1,2- and 3,4-benzocycloheptatrienes, it appeared feasible to extend the reaction of cycloheptatriene-7-methyl ether with alkyl magnesium halides[1] to the benzocycloheptatriene system. From the report that the neutralization of benzotropenium ion with sodium carbonate gave a product which was approximately a 50:50 mixture of 1,2-benzocycloheptatriene-7-ol and 3,4-benzocycloheptatriene-7-ol,[2] it was anticipated that a mixture of the corresponding 7-methyl ethers could be prepared by a similar neutralization reaction with sodium methoxide in methanol. However, the neutralization of benzotropenium ion with sodium methoxide does not follow this anticipated course. Furthermore, the reaction of benzocycloheptatriene-7-methyl ethers with alkyl magnesium halides leads to a mixture of products which would not be expected from a simple displacement mechanism.

Addition of crystalline benzotropenium fluoroborate to a solution of sodium methoxide in methanol resulted in the isolation of a major ether product accompanied by minor amounts of 1,2-benzocycloheptatriene and an approximately 2:1-mixture of 4,5-benzotropone and 1,2-benzotropone. These various components could be detected by and identified through VPC, IR, and NMR analysis. VPC analysis of the ether component of this mixture indicated that only a single compound was present in this fraction at column temperatures below 100°, and that two products were present at temperatures above 110°. Collection of the two ether samples which were produced at higher temperatures during VPC separation, and examination of their infrared and NMR spectra indicated that the second compound was a vinyl ether which was not present in the original ether component, and must have resulted from thermal isomerization.[3] Similar analysis of samples collected at column temperatures at or below 100° indicated no change had occurred in the ether upon vapor phase chromatography.

The NMR spectrum of this ether component (Table 1) could be interpreted to infer

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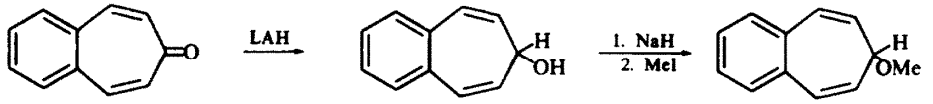
that it was 1,2-benzocycloheptatriene-7-methyl ether (**4**), but did not provide conclusive evidence that this was the only isomer present. In order to determine if 3,4-benzocycloheptatriene-7-methyl ether was also present, this compound was synthesized by an unambiguous route. Reduction of 4,5-benzotropone (**1**) with LAH



1 2 3

gave the corresponding alcohol 3,4-benzocycloheptatriene-7-ol (**2**) which was directly converted to the sodium salt with sodium hydride and alkylated with methyl iodide. The NMR spectrum (Table 1) of the ether product of this reaction sequence

TABLE 1. NMR CHEMICAL SHIFTS IN-τ-UNITS RELATIVE TO INTERNAL TMS

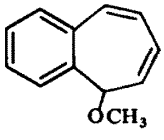
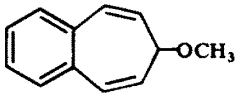
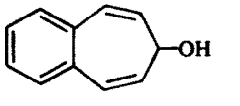
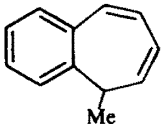
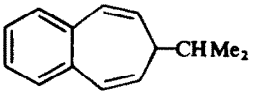
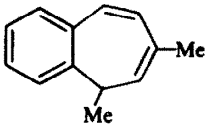
Compound	Benzene hydrogens	Vinyl hydrogens	Methylene hydrogen	Methyl hydrogen	Hydroxyl hydrogen
	2·48 (m)	3 – AB doublet J = 12 c/s overlaps with aromatic protons 4 – 3·33 $J_{3,4}$ = 12 c/s $J_{4,5}$ = 4 c/s (further split 1 c/s) 5 + 6 – 3·95 (m)	5·87 (d) $J_{6,7}$ = 3 c/s	6·53 (s)	
	2·72 (s)	2 + 5 – 3·46 $J_{1,2}$ = 11 c/s $J_{5,6}$ $J_{2,7}$ = 2 c/s $J_{5,7}$ 1 + 6 – 4·15 $J_{1,2}$ = 11 c/s $J_{5,6}$ $J_{1,7}$ = 4 c/s $J_{6,7}$	6·16 – 7 peaks $J_{1,7}$ = 4 c/s $J_{6,7}$ $J_{2,7}$ = 2 c/s $J_{5,7}$	6·68 (s)	
	2·81 (s)	2 + 5 – 3·59 $J_{1,2}$ = 11 c/s $J_{5,6}$ $J_{2,7}$ = 2 c/s $J_{5,7}$ 1 + 6 – 4·16 $J_{1,2}$ = 11 c/s $J_{5,6}$ $J_{1,7}$ = 4 c/s $J_{6,7}$	5·60 – overlaps the OH proton		5·60 (s)

TABLE 1—*continued*

Compound	Benzene hydrogens	Vinyl hydrogens	Methylene hydrogen	Methyl hydrogen	Hydroxyl hydrogen
	2·71 (m)	3 – overlaps aromatic multiplet	7.28 – five broad peaks $J_{Me\ 7} = 7$ c/s $J_{6,7} = 5$ c/s	8·52 (d) $J = 7$ c/s	
		4 – 3·51 $J_{3\ 4} = 12$ c/s $J_{4,5} = 5$ c/s			
		5 – 3·98 $J_{5,6} = 10$ c/s $J_{4,5} = 5$ c/s			
		6 – 4·50 $J_{5\ 6} = 10$ c/s $J_{6,7} = 5$ c/s			
	2·70 (d) $J = 2$ c/s	2 + 5 – 3·38 $J_{1,2}^{5,6} = 10$ c/s	no. 7 ring proton and secondary isopropyl hydrogen 7·98 (m)	9·00 (d)	
		$J_{2,7}^{5,7} = 1$ c/s			
		1 + 6 – 4·23 $J_{1,2}^{5,6} = 10$ c/s			
		$J_{1,7}^{6,7} = 5$ c/s			
	2·70 (m)	3 – overlaps aromatic multiplet 4, 5, 6 – 3.80 (m)	no. 7 ring proton and secondary hydrogen on isopropyl group 7·60 (m)	isopropyl methyls—two doublets of unequal intensity (A) 9·01 $J = 6$ c/s (B) 9·43 $J = 6$ c/s	
	2·93 (s)	3 – 3·14 (d) $J_{3,4} = 11$ c/s	7·32 (m)	vinyl Me 8·21 (d) $J = 1$ c/s	
		4 – 3·74 (d) $J_{3,4} = 11$ c/s		7-Me 8·57 (d) $J = 7$ c/s	
		6 – 4·89 (d) $J_{6,7} = 7$ c/s (doublet is broadened by second order splitting by vinyl Me group)			

[a] s, singlet; d, doublet; m, multiplet.

was completely consistent with an assigned structure of 3,4-benzocycloheptatriene-7-methyl ether (3). Comparison of the NMR spectrum of this 3,4-benzocycloheptatriene-7-methyl ether (3) with the NMR spectrum of the ether product from the neutralization of benzotropenium ion with sodium methoxide, demonstrated that the unique ether isolated from this neutralization reaction is 1,2-benzocycloheptatriene-7-methyl ether (4). This conclusion could be verified by the different chemical shifts of the hydrogens on the MeO groups in the two ethers,* as well as differences in the aromatic and vinyl region of the NMR spectra.

Since the results of neutralizing benzotropenium ion with sodium methoxide were contrary to what would have been expected in light of the reported data for the reaction of benzotropenium ion with sodium carbonate, these reactions were investigated more thoroughly. In order to determine if the neutralization of benzotropenium ion with sodium methoxide was giving an equilibrium or rate controlled product, the two ethers 3 and 4 were equilibrated with acid. Treatment of either ether 3 or 4 with a trace of hydrogen chloride in carbon tetrachloride and following the reactions by their NMR spectra demonstrated that 1,2-benzocycloheptatriene-7-methyl ether is the only product at equilibrium. Thus 3,4-benzocycloheptatriene-7-methyl ether (3) isomerizes completely to 1,2-benzocycloheptatriene-7-methyl ether (4) within a few minutes.† However, 1,2-benzocycloheptatriene-7-methyl ether shows no change in the presence of acid over a period of several hours in carbon tetrachloride. Therefore, the neutralization reaction of benzotropenium ion with sodium methoxide was forming an equilibrium product, but did not indicate if the equilibrium and kinetic controlled products are identical.

In order to ascertain what the rate controlled neutralization of benzotropenium ion might be, benzotropenium fluoroborate was reduced with both LAH and cycloheptatriene.‡ In each case approximately equal mixtures of 1,2-benzocycloheptatriene and 3,4-benzocycloheptatriene were formed (Table 2).§ This data indicated that a rate controlled neutralization would lead to an approximately equal mixture of 1,2- and 3,4-isomers, consistent with the product ratio reported for the neutralization of benzotropenium ion with sodium carbonate. Since it was still unclear how the neutralization of benzotropenium ion with sodium methoxide gave an equilibrium product, this point was further examined. It could be demonstrated that 3,4-benzocycloheptatriene-7-methyl ether is not isomerized to the 1,2-isomer by treatment with sodium methoxide in methanol. However, treatment of a solution containing two equivalents of sodium methoxide and one equivalent of 3,4-benzocycloheptatriene-

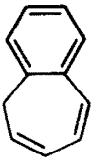
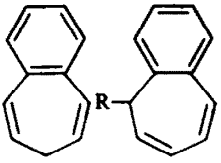
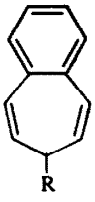
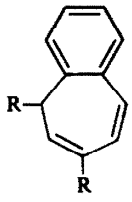
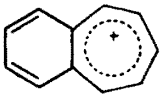
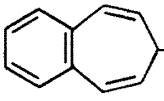
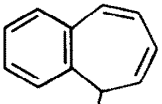
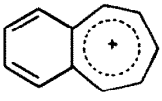
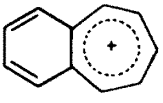
* The NMR spectrum of a mixture of the two ethers exhibited two clearly resolved MeO hydrogen peaks, eliminating any source of error due to concentration effects in determining the chemical shifts of the pure ethers.

† This equilibration of the 3,4-isomer was accompanied by a small amount of disproportionation to give minor amounts of 1,2-benzocycloheptatriene and, after hydrolysis, a mixture of the benzotropones. In all of the disproportionations observed in this work, the benzocycloheptatriene fractions always contained 90% or greater of the 1,2-benzo isomer indicating that equilibration to the more stable isomer can compete with the remaining reactions.

‡ Although neither of these reducing agents are ideal models for the bases used in the neutralization reactions under investigation, other more appropriate nucleophiles could also be subject to equilibration under the reaction conditions. In fact, tropenium ion will isomerize 3,4-benzocycloheptatriene to 1,2-benzocycloheptatriene, but at a rate which is too slow to be of significance under the conditions employed.

§ Equilibration of 1,2-benzocycloheptatriene or 3,4-benzocycloheptatriene with benzotropenium ion yields only 1,2-benzocycloheptatriene at equilibrium.

TABLE 2

Reactants	% Product				
					
 LAH	58	42			
„ Cycloheptatriene	40	60			
 —OMe , MeMgI			52(5)	48(6)	
„ $Me_2CHMgBr$			48(7)	52(8)	
 OMe , MeMgI			75(5)	25(6)	
„ $Me_2CHMgBr$			62(7)	38(8)	
 a , MeMgI	31		43	18	8
 b . MeMgI	5		52	41	2

[a] Salt not rapidly dispersed; [b] High-speed stirring.

7-methyl ether with one equivalent of benzotropenium fluoroborate resulted in the isolation of only 1,2-benzocycloheptatriene-7-methyl ether. Therefore, under the neutralization conditions it is possible for an equilibration reaction to compete with the reaction of benzotropenium ion with methoxide ion, and any 3,4-benzocycloheptatriene-7-methyl ether formed converted to the more stable 1,2-isomer. This equilibration reaction can be most readily envisioned through methoxide exchange between benzotropenium ion and already formed benzocycloheptatriene ethers.

Since it was apparent that the neutralization of benzotropenium ion with sodium methoxide followed a considerably different course than a similar neutralization with sodium carbonate, this latter reaction was reinvestigated. Repetition of the neutralization of benzotropenium ion by the method reported[2] leads to a complex mixture of products containing a benzocycloheptatriene-7-ol species* along with

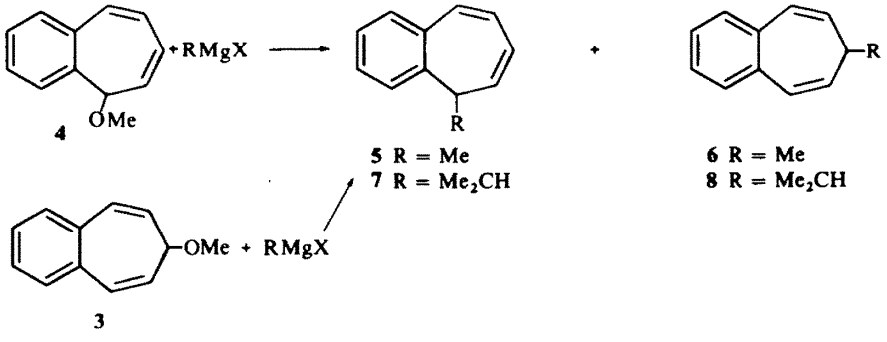
* Our analytical methods could not indicate if both possible isomers were present, because the alcohols were too unstable for purification.

2,3-benzotropone, 4,5-benzotropone, 1,2-benzocycloheptatriene and 3,4-benzocycloheptatriene.

The presence of these components could be established by IR, NMR, and vapor phase chromatographic analyses. Therefore, this latter neutralization reaction is accompanied by a disproportionation process from which the above products would be expected to originate.

At this point the data fits into a pattern in which hydride exchange occurs between benzotropenium ion and the benzocycloheptatrienols to give the benzotropones and benzocycloheptatrienes, and both hydride exchange and methoxide exchange occur between benzotropenium ion and the benzocycloheptatriene-7-methyl ethers to give the observed equilibrium ether product as well as disproportionation products. Although hydroxide exchange between benzotropenium ion and the benzocycloheptatrienols may occur, this process would remain undetected because of our inability to analyze the isomeric content of the benzocycloheptatrienols. Assuming the reduction of benzotropenium ion gives a realistic picture of the reaction with nucleophiles, it can be postulated that both neutralization reactions give approximately equal mixtures of ethers or alcohols which are converted to secondary products by rapid exchange reactions. The observation of 4,5-benzotropone as a major disproportionation product demonstrates that formation of 3,4-benzocycloheptatriene-7-methyl ether or alcohol competes favorably with the formation of the 1,2- isomers.

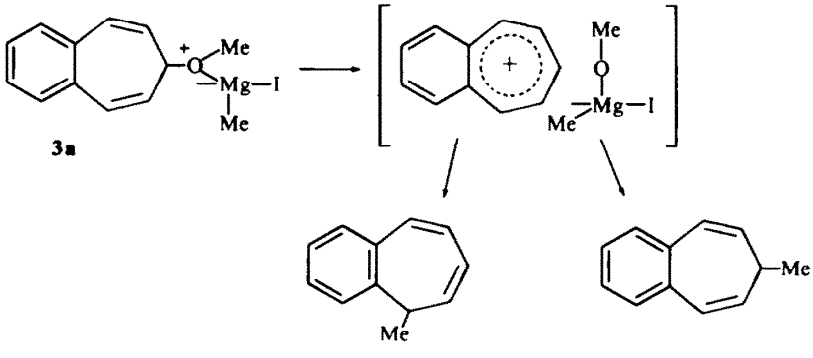
Having established synthetic routes to the desired benzocycloheptatriene-7-methyl ethers, their reactions with alkyl magnesium halides was then investigated. Addition of 1,2-benzocycloheptatriene-7-methyl ether to methyl magnesium iodide unexpectedly gave a 3:1 mixture of 7-methyl-3,4-benzocycloheptatriene (**6**) and 7-methyl-1,2-benzocycloheptatriene (**5**) (Table 2). Addition of 3,4-benzocycloheptatriene-7-methyl ether to MeMgI gave an approximately equal mixture of the same two methyl benzocycloheptatrienes (**5** and **6**). The reaction of isopropyl magnesium bromide with 1,2-benzocycloheptatriene-7-methyl ether gave a 2:1-mixture of 7-isopropyl 1,2- and 3,4-benzocycloheptatrienes (**7** and **8**), while reaction with 3,4-benzocycloheptatriene-7-methyl ether again gave an approximate equal mixture of isopropyl benzocycloheptatrienes (Table 2).



Since the hydrocarbons formed from the reaction of the benzocycloheptatriene-7-methyl ethers with alkyl magnesium halides apparently involves a pathway which leads to alkylation at a carbon not initially bonded to oxygen, carbon-oxygen bond

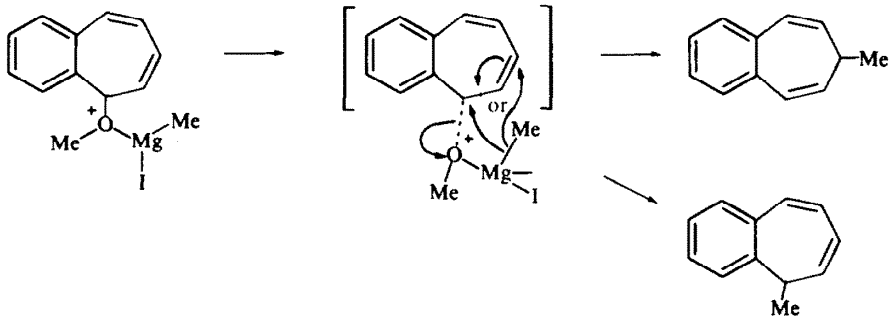
cleavage may occur before alkylation. To gain a better insight into this possibility the reaction of benzotropenium ion with MeMgI was also investigated. As can be seen from Table 2 the reaction of benzotropenium ion with MeMgI leads to more than simple alkylation, but under proper conditions the two methyl benzocycloheptatrienes are the major products. Because of the heterogeneous nature of the reaction, the product distribution is dependent on the particle size of the salt and the stirring speed. Thus, when the benzotropenium salt is not rapidly dispersed benzocycloheptatriene and 5,7-dimethyl-1,2-benzocycloheptatriene (**9**) are formed in appreciable amounts, while rapid dispersal of the salt significantly decreases the amount of disproportionation products. Additionally, it can be seen that 9 must arise from disproportionation of **6**, and not from **5**. Therefore, in terms of evaluating the yield of **6**, the yield of **9** should also be included. Also, it can be demonstrated that treatment of a 50:50 mixture of **5** and **6** with one half an equivalent of triphenylcarbonium hexachloroantimonate yields only 1-methyl-4,5-benzotropenium hexachloroantimonate. This data is consistent with the observation that during the reaction of benzotropenium ion with MeMgI only **6** disproportionates. Therefore, the yield of **6** from this latter reaction would probably better be approximated by the sum of the observed yields of **6** and benzocycloheptatriene.* This latter assumption leads to the conclusion that the reaction of benzotropenium ion with methyl iodide gives essentially an equal mixture of the two expected methyl benzocycloheptatrienes.

The data of Table 2 shows that the reaction of 3,4-benzocycloheptatriene-7-methyl ether with MeMgI gives, within experimental error, the same product ratio as benzotropenium ion. However, 1,2-benzocycloheptatriene-7-methyl ether gives a product ratio which favors alkylation α to the benzene ring. The product distribution from the two ethers indicates that the mechanistic pathway is not identical for the



two isomers. The data appears best fit into a scheme in which 3,4-benzocycloheptatriene-7-methyl ether is initially coordinated with a magnesium species which cleaves to an ion pair which collapses to the products expected for the reaction of benzotropenium ion. Conversely, 1,2-benzocycloheptatriene-7-methyl ether, after initial coordination with a magnesium species, must maintain some covalent character between the C—O bond of the ether which directs alkylation at the original ether carbon. In this case a benzotropenium ion never occurs on the reaction coordinate.

* The disparity in yields between benzocycloheptatriene and 9 can be explained by the fact that 1-methyl-4,5-benzotropenium ion is very unstable in ether. Apparently the ion will deprotonate to benzoheptafulvene which then polymerizes during the reaction or workup.



We have observed that **4** is more stable than **3** by at least 3 Kcal. Therefore, ionization of **3a** is favored by at least this amount. Additionally, the reaction of isopropyl magnesium bromide with 1,2-benzocycloheptatriene-7-methyl ether to give a ratio of products closer to that observed for the 3,4-isomer is consistent with the above hypotheses. The bulk of the isopropyl group could cause a steric acceleration for the carbon–ether oxygen bond cleavage leading to more ionic character in the transition state.

EXPERIMENTAL

All NMR spectra were obtained on a Varian A-60 spectrometer. All IR spectra were determined on a Perkin–Elmer 337 spectrophotometer. Analysis was carried out by Galbraith Laboratories Inc., Knoxville, Tenn.

7-Methoxy-1,2-benzocycloheptatriene (**4**)

To a soln of MeONa (1·0 g; 0·018 mole) in MeOH (25 ml) was added benzotropenium fluoroborate (3·2 g; 0·014 mole). The yellow salt turned red as it mixed with the soln but the red color disappeared as the salt reacted. The soln was allowed to stand 20 min at room temp. Then the MeOH soln was diluted with 75 ml water. The water soln was extracted 5 times with 25 ml portions pentane. The combined yellow pentane extracts were dried with K_2CO_3 and evaporated on a rotary evaporator yielding 2·1 g (88%) of a yellow oil. Evaporative distillation resulted in a colorless liquid.

IR spectrum (neat, cm^{-1}): CH stretching 3030 (m), 2940 (m), 2830 (m); C=C aromatic 1455 (m); C—O stretching 1125 (s); CH bending 800 (s), 775 (s), 695 (s).

This ether was too reactive to obtain a satisfactory carbon hydrogen analysis. The structure is verified by its facile reconversion to benzotropenium ion. 7-Methoxy-1,2-benzocycloheptatriene (0·11 g; 0·00064 mole) was dissolved in 2 ml anhydrous ether, and conc perchloric acid (0·10 g, 70%; 0·0007 mole) was added to the soln causing benzotropenium perchlorate, 0·14 g (91%) to precipitate. The decomposition point 160° and the UV spectrum were identical with those found in the literature[2] for benzotropenium perchlorate.

Compound **4** could also be prepared by the procedure used for preparing **3**. 2,3-Benzotropone (0·15 g; 0·001 mole) was added to a slurry of LAH (0·030 g; 0·0008 mole) in 5 ml ether. Upon workup, the reaction yielded 0·12 g (75%) of 7-hydroxy-1,2-benzocycloheptatriene.[2]

The crude 7-hydroxy-1,2-benzocycloheptatriene was treated with NaH (0·030 g; 0·0012 mole) in 5 ml dimethylformamide. After stirring for ½ hr, MeI (0·33 g; 0·0024 mole) was added to the reaction soln. The product 0·90 g (69%) displayed IR and NMR spectra of 7-methoxy-1,2-benzocycloheptatriene as prepared above.

7-Methoxy-3,4-benzocycloheptatriene (**3**)

4,5-Benzotropone (0·48 g; 0·0031 mole), dissolved in 10 ml ether, was added as rapidly as possible to a soln of LAH (0·05 g; 0·0014 mole) in ether (10 ml) cooled to −10°. The resulting soln was stirred for 2 min and immediately quenched by the careful addition of 10 ml sat aqueous sodium tartrate. The ether layer

was separated and the aqueous layer washed twice with 10 ml portions ether. The combined ether extracts were dried over K_2CO_3 and concentrated on a rotary evaporator to a pale yellow oil 0·38 g (78%). The NMR spectrum was consistent with the assigned structure of **2**.

IR spectrum (neat, cm^{-1}): O—H stretching 3350 (b) CH 3010 (w); C=C 1640 (m); C—O stretching 1065 (s); CH bending 800 (s), 750 (m).

The crude alcohol from above was added to a suspension of NaH (0·087 g; 0·0035 mole) in 10 ml dimethylformamide. The soln was stirred for ½ hr during which time it turned deep red. Then MeI (1·0 g; 0·0071 mole) was added to the alkoxide causing the red–brown soln to turn yellow. After ½ hr the soln was poured into 75 ml water and the water was extracted 5 times with 25 ml portions pentane. The combined pentane extracts were dried over K_2CO_3 and the solvent was removed on a rotary evaporator yielding a yellow liquid 0·33 g (79%), of **3**. Attempts to purify this compound by VPC only lead to decomposition. Proof of structure was demonstrated by the NMR spectrum which was consistent with the assigned structure, and by the fact that it readily isomerized to **4** by a trace amount of acid.

IR spectrum (neat, cm^{-1}): CH 3000 (w), 2900 (s), 2800 (w); C=C 1640 (w); C—O 1105 (s); CH 800 (s).

The NMR of 7-methoxy-3,4-benzocycloheptatriene shows that 5-methoxy-1,2-benzocycloheptadiene is formed as a by-product. This product arises by 1,2 addition of the LAH across the carbonyl double bond followed by 1,2-addition of LAH across the C=C double bond.[4] If 4,5-benzotropone was allowed to react with LAH at room temp for ½ hr and then the subsequent reaction completed as above, a single product was obtained that exhibited a NMR which was consistent with an assigned structure of 5-methoxy-1,2-benzocycloheptadiene.

Isomerization of 7-methoxy-3,4-benzocycloheptatriene to 7-methoxy-1,2-benzocycloheptatriene

7-Methoxy-3,4-benzocycloheptatriene (0·090 g; 0·0052 mole) was dissolved in 0·5 ml CCl_4 and the soln was placed in an NMR tube. To this soln was added 3 drops CCl_4 which had been saturated with HCl gas. Immediately after addition of the acid, a NMR spectrum of the sample was taken. The first spectrum showed two distinct MeO groups present while the remainder of the spectrum was complex. After 10 min the spectrum taken of the reaction mixture was identical to that of 7-methoxy-1,2-benzocycloheptatriene.

Attempted equilibration of 7-methoxy-3,4-benzocycloheptatriene by base

To a soln of MeONa (0·060 g; 0·011 mole) in MeOH (25 ml) was added 7-methoxy-3,4-benzocycloheptatriene (0·10 g; 0·0058 mole). After standing 20 min, the reaction was worked up by the general procedure for the preparation of 7-methoxy-1,2-benzocycloheptatriene. The only product was unchanged starting material.

Isomerization of 7-methoxy-3,4-benzocycloheptriene by benzotropenium ion

The above reaction was re-run with the same amounts of starting materials but after the 7-methoxy-3,4-benzocycloheptatriene was added to the MeONa–MeOH soln, benzotropenium fluoroborate (0·13 g; 0·0058 mole) was also added. This time, upon workup, the reaction afforded 7-methoxy-1,2-benzocycloheptatriene as the only product as identified by NMR and IR spectra.

7-Methyl-1,2-benzocycloheptatriene (**5**) *and 7-methyl-3,4-benzocycloheptatriene* (**6**)

Method one from 7-methoxy-1,2-benzocycloheptatriene (**4**). To a soln of MeMgI (1·0 g; 0·0063 mole) in ether (30 ml), 7-methoxy-1,2-benzocycloheptatriene (0·44 g; 0·0026 mole) was added dropwise and with mechanical stirring. After stirring for 2 hr sat NH_4Cl aq (20 ml) was added dropwise to the reaction soln. The ether layer was separated, washed with $NaHCO_3$ aq, dried over $MgSO_4$, and removed under vacuum. The yield of both methylbenzocycloheptatrienes was 0·30 g (75%). VPC of the mixture on a 12 ft diethylene glycol succinate (DEGS) column showed that it was 75% 7-methyl-1,2-benzocycloheptatriene and 25% 7-methyl-3,4-benzocycloheptatriene. After separation by VPC, conversion to the hexachloroantimonate salts of both pure isomers gave IR spectra (KBr) identical with the IR spectra of authentic 3-methylbenzotropenium hexachloroantimonate and 5-methylbenzotropenium hexachloroantimonate.[5]

Method two from 7-methoxy-3,4-benzocycloheptatriene (**3**). The procecure was identical with the one above. 7-Methoxy-3,4-benzocycloheptatriene (0·40 g; 0·0023 mole) was added to MeMgI (1·2 g; 0·0072 mole) yielding 0·28 g) (80%) of a yellow oil. By VPC it was determined that the mixture contained 52% 7-methyl-1,2-benzocycloheptatriene and 48% 7-methyl-3,4-benzocycloheptatriene.

7-Isopropyl-1,2-benzocycloheptatriene and 7-isopropyl-3,4-benzocycloheptatriene

The general procedure, as used previously, for the reaction of a Grignard reagent with an alkoxybenzocycloheptatriene was followed. Method one: from 7-methoxy-1,2-benzocycloheptatriene (**4**). 7-Methoxy-1,2-benzocycloheptatriene (1·0 g; 0·0058 mole) was added to iPrMgBr (1·6 g; 0·011 mole) affording 0·73 g (68%) of a yellow oil a mixture of **7** and **8**. VPC on a DEGS column showed that the mixture was 62% **7** and 38% 7-isopropyl-3,4-benzocycloheptatriene. The NMR spectrum of each pure isomer was consistent with the assigned structure.

IR spectrum of **7** (neat, cm^{-1}): CH stretching 3000 (s), 2945 (s); CH bending 755 (s), 700 (s).

IR spectrum of **8** (neat cm^{-1}): 3000 (s), 2950 (s), 2860 (m); CH bending 795 (s).

(Found: C, 91·37; H, 8·90. Calc. for $C_{14}H_{16}$: C, 91·25; H, 8·75%.)

Method two: from 7-methoxy-3,4-benzocycloheptatriene. 7-Methoxy-3,4-benzocycloheptatriene (0·073 g; 0·00042 mole) was added to iPrMgBr (0·14 g; 0·00095 mole) yielding 0·063 g (80%), of a mixture of **9** and **8**. The mixture was 48% 7-isopropyl-1,2-benzocycloheptatriene and 52% 7-isopropyl-3,4-benzocycloheptatriene, identified by VPC.

Reaction of benzotropenium fluoroborate with methyl magnesium iodide

(a) To a soln of MeMg I (4·0 g; 0·24 mole) in 250 ml ether, cooled to $-10°$, was added in small amounts solid benzotropenium fluoroborate (5·16 g; 0·023 mole). The addition was done under N_2 and with mechanical stirring. Stirring was continued until all the salt dissolved, then 60 ml sat NH_4Cl aq was added dropwise to the Grignard soln. The ether layer was separated and the aqueous layer was extracted once with 25 ml ether. The combined ether extracts were dried over $MgSO_4$ and the solvent was removed on a rotary evaporator. The product was a dark yellow oil 2·7 g (74%). VPC of the product on a DEGS column showed that it consisted of 4 main components: 12% 1,2-benzocycloheptatriene, 35% 7-methyl-3,4-benzocycloheptatriene, 48% 7-methyl-1,2-benzocycloheptatriene and 5% **9**. The components were separated by VPC and identified by their NMR spectra. The NMR spectrum of 5,7-dimethyl-1,2-benzocycloheptatriene was completely consistent with the assigned structure. IR spectrum of **9** (neat, cm^{-1}) CH stretching 3000 (m), 2950 (m), 2860 (w); C=C aromatic 1450 (m), CH bending 790 (s), 740 (s).

(b) By varying the particle size of the benzotropenium fluoroborate and by changing the stirring speed, it was possible to alter the product ratios. In one case by adding only one large particle of salt to the Grignard soln with slow speed stirring the product ratio was 31% 1,2-benzocycloheptatriene, 18% 7-methyl-3,4-benzocycloheptatriene, 43% 7-methyl-1,2-benzocycloheptatriene, and 8% 5,7-dimethyl-1,2-benzocycloheptatriene. In another case by adding only small amounts of the salt over a long period of time and with high speed stirring, the product ratios were 5% 1,2-benzocycloheptatriene, 41% 7-methyl-3,4-benzocycloheptatriene, 52% 7-methyl-1,2-benzocycloheptatriene, and 2% 5,7-dimethyl-1,2-benzocycloheptatriene. Products were identified by VPC retention times.

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