THE SYNTHESIS AND STUDY OF PSEUDO-AROMATIC COMPOUNDS—VIII

THE SYNTHESIS OF 2-CYCLOHEPTATRIENYLIDENEINDANONE

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Abstract—Indanone and 3-substituted indanones react with tropenium fluoroborate to give the corresponding 2-cycloheptatrienylideneindanones. Analysis of the NMR, UV and IR spectra of these systems indicates that they deviate from typical olefinic ketones.

THERE have been several examples of heptafulvenes and pentatriafulvalenes which are reported to possess significant π-electron delocalization due to important dipolar resonance contributors in the ground state.[1] 8,8-Dicyanoheptafulvene is considerably more stable than the parent hydrocarbon heptafulvene, and recent crystallographic studies have proven that 8,8-dicyanoheptafulvene is planar.[2] Since the source of this stabilization may be considered to arise by virtue of a substantial lowering of the ground state by dipolar resonance contributors (**1**) it should be possible to synthesize a series of heptafulvene derivatives (**2**) in which variation of A over a range of $-$ R
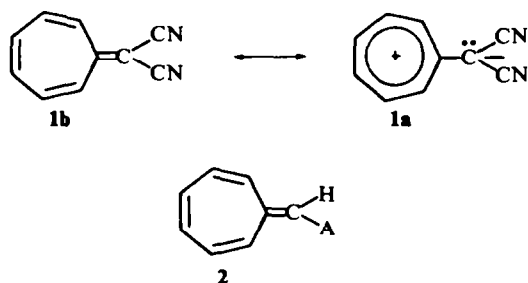

capability produces a recognizable trend in the physical and chemical properties with increasing dipolar resonance contributions. Also, it should be possible by such a study to determine the point where the 7-membered ring deviates from planarity, or to establish if the 7-membered ring in simple heptafulvene derivatives is planar.

We have initiated a study towards the elucidation of this point and herein report initial results produced by varying A through the sequence $-C\!\!=\!\!O$, $C\!\!=\!\!\overset{+}{O}H$ and

$-\overset{|}{C}+$. The changes brought about by this sequence would be expected to be reflected to a large extent in the UV and NMR spectra of these compounds which should be sensitive indicators of enhanced π-electron delocalization and development of charge separation.

Addition of two moles of tropenium fluoroborate to one mole of indanone pro-
duces two products, 2-(7-cycloheptatrienyl)indanone (3) and 2-cycloheptatrienyl-
indeneindanone (4) in a ratio of 1:4. The structures of these products were confirmed
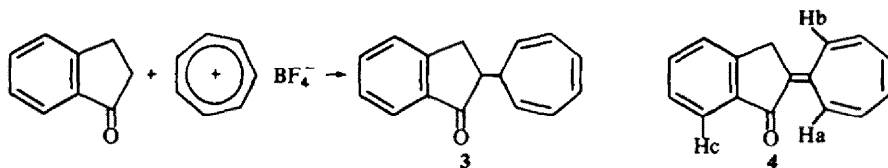
by their NMR spectra (Fig. 1) and conversion of 3 to 4 by hydride exchange with
benzotropenium ion and deprotonation. Contrary to the reaction reported for
cycloheptatrienyl acetone,[3] 3 reacted with triphenylcarbonium ion to give only
fragmentation.[4] However, benzotropenium ion or tropenium ion gave satisfactory
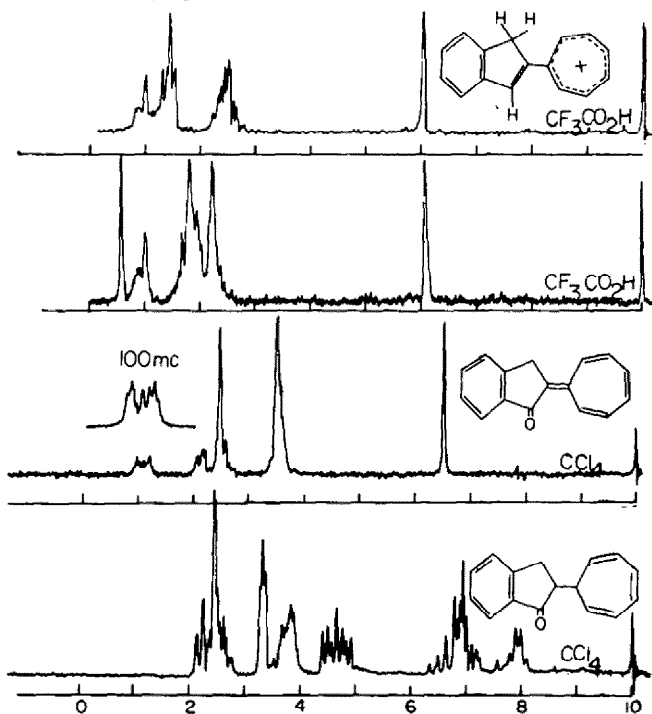yields of hydride exchange products.

FIG. 1. NMR spectra referenced to internal TMS. The inset in the NMR spectrum of
2-cycloheptatrienylideneindanone (4) shows the 1'-hydrogen at high resolution.

The 60 mcs NMR spectrum of 2-(7-cycloheptatrienyl)indanone (3) is essentially
that expected for a 7-substituted cycloheptatriene[5] except for a greater complexity
of the 1,6-hydrogens of the 7-membered ring. The pattern in Fig. 1 exhibiting seven
lines for these two hydrogens further separates into eight lines at 100 mcs, indicating
that the complexity is partially due to different chemical shifts. This difference of
magnetic environment can readily be attributed to the asymmetric center at carbon
two of the indanone system.

The multiplet at 1·10 τ in **4** corresponds to one hydrogen and by integration and decoupling can be shown to be on the 7-membered ring. This hydrogen is assigned to the one labeled Ha and is shifted downfield by the anisotropy of the CO group. The magnitude of this downfield shift (ca. 145 c/s at 60 mc) indicates that the average oxygen-Ha distance must be less than the oxygen-Hc distance. Molecular models of **4** indicate that for a nonplanar molecule Hc is ca. 20% closer to the oxygen than Ha. However, forcing the 7-membered ring into coplanarity with the remaining skeleton causes the oxygen-Ha distance to become ca. 20% shorter than the oxygen-Hc distance. Thus, this data indicates that the 7-membered ring is planar in this molecule.

Similar reactions of tropenium fluoroborate with 3-methylindanone and 3,3-dimethylindanone gave the corresponding **5** and **6**. These compounds gave similar NMR spectra to that of **4**, (Table 1) consistent with the assigned structures.
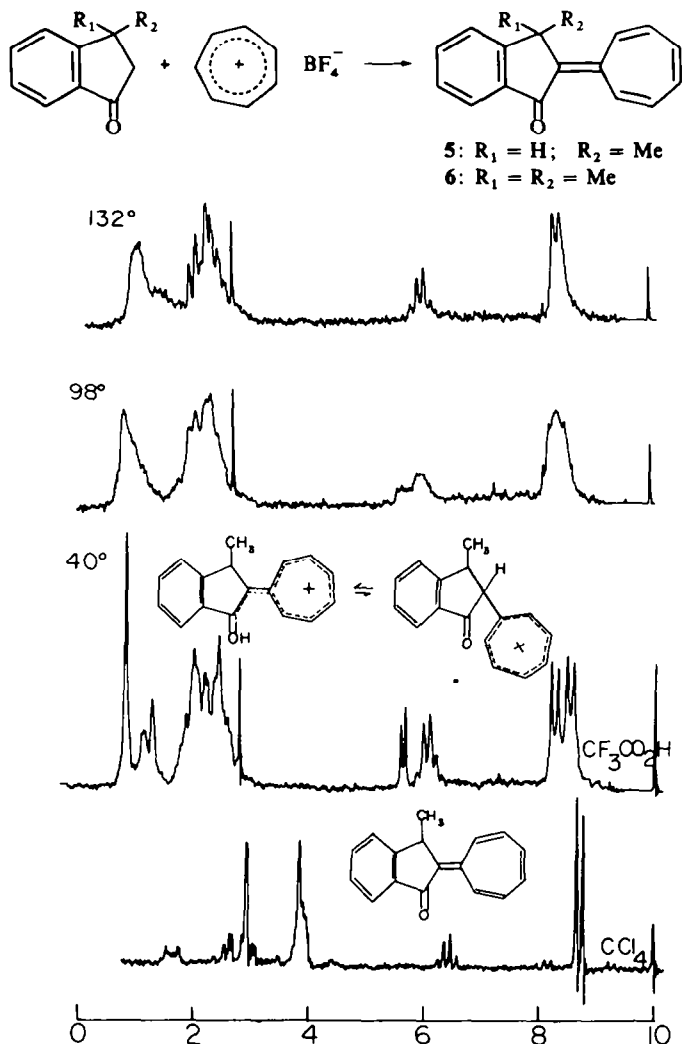

5: R$_1$ = H; R$_2$ = Me
6: R$_1$ = R$_2$ = Me

FIG. 2. NMR spectra reference to internal TMS. The sharp peak occurring at 2·8 τ in the variable temperature spectra is due to chloroform.

These compounds (4–6) were unusually basic for ketones, readily forming salts with fluoroboric acid. This property would be predicted on the basis of the important resonance contributors containing the tropenium moiety. The same ions could also be observed by dissolving the corresponding ketone in trifluoroacetic acid. The NMR spectra of these ions were complicated by equilibria between two possible structures for each protonated form, the oxygen protonated conjugate acids (7, 8 and 9) and the carbon protonated conjugate acids (10, 11, 12). The unexpected complexity

7: $R_1 = R_2 = H$ 10: $R_1 = R_2 = H$
8: $R_1 = H, R_2 = Me$ 11: $R_1 = H$ $R_2 = Me$
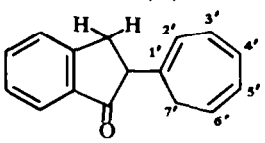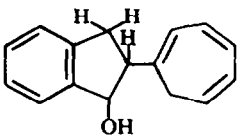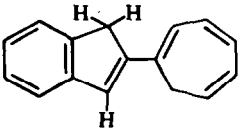9: $R_1 = R_2 = Me$ 12: $R_1 = R_2 = Me$
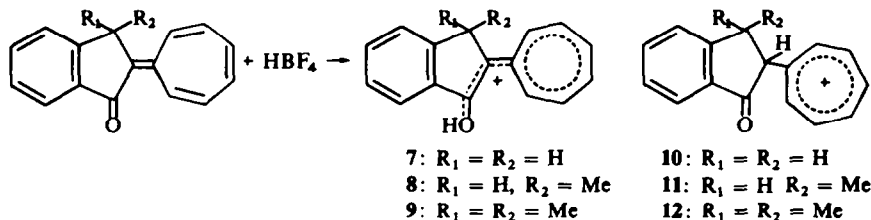
involving species 7, 8 and 9 in equilibrium with 10, 11 and 12 respectively can best be demonstrated by the NMR spectrum of 5 in trifluoroacetic acid (Fig. 2). The lowest field singlet is attributed to the 7-membered ring of 11, since in this form the positive charge is localized entirely in this ring. Consistent with this assignment, integration of this singlet at 0·80 τ, the doublet at 5·16 τ (the 2 indanone hydrogen) and the Me doublet at 8·23 τ give the correct ratios for structure 11. The multiplets at 1·20 τ and 1·97 τ and the Me doublet at 8·52 τ are in the correct ratio for structure 8. The remaining absorptions in this spectrum correspond to the hydrogens for the benzene ring and the 3-hydrogen on the indanone system which overlap for both compounds. Also consistent with the assignment of an equilibrium mixture giving the observed spectrum, the relative proportions of the various species were solvent dependent. This would be expected since solvents of lower dielectric constant would favor protonation on oxygen giving an ion in which the charge is more diffuse. Also, heating solutions of compound 8 and 11 in trifluoroacetic acid increases the rate of inter-conversion between the two conjugate acids to the point that the rate becomes fast

TABLE 1. 60 MC NMR CHEMICAL SHIFTS IN τ UNITS RELATIVE TO INTERNAL TMS[a]

Compounds	7-membered ring hydrogens	6-membered ring hydrogens	5-membered ring hydrogens	Me hydrogens
	H'_1, H'_6; 4·65 H'_2, H'_5; 3·76 (m) H'_3, H'_4; 3·30 (t) H'_7; 7·92 (m)	H_{4-6}; 2·41 (m) H_7; 2·10 (m)	H_2, H_3; 6·86 (m)	
	H'_1; 1·10 (m) H'_{2-6}; 3·51 (m)	H_{4-6}; 2·46 (s) H_7; 2·10 (m)	H_3; 6·50	

TABLE 1—*continued*

Compounds	7-membered ring hydrogens	6-membered ring hydrogens	5-membered ring hydrogens	Me hydrogens
5	H'_1; 1·65 (m), H'_{2-6}; 3·91 (m)	H_{4-6}; 2·91 (s) H_7; 2·56 (m)	H_3; 6·42 (q), $J = 6·0$ c/s	8·7 (d) $J = 6·0$ c/s
6	H'_1; 1·30 (m) H'_{2-6}; 3·66 (m)	H_{4-6}; 2·65 (s) H_7; 2·40 (m)	—	8·50 (s)
7 ⇌ 10	oxygen protonated conjugate acid H'_1, H'_6; 1·55 (m) H_{4-7}; ?·81 (s), H'_{2-5}; 2·30 (m) carbon protonated conjugate acid $H'_1–H'_6$; 1·21 (s) H_{4-7}; 2·81 (s)		H_3; 6·44 (s)	—
8 ⇌ 11	Oxygen protonated conjugate acid H'_1, H'_6; 1·54 (m) H_{4-7}; 2·73 (s) H'_{2-5}; 2·33 (m) Carbon protonated conjugate acid H'_{1-6}; 1·20 (s) H_{4-7}; 2·73 (s)		H_3; 6·18 (q) H_2; 5·80 (d) $J = 5$ H_3; 6·18 (q)	8·42 (d) $J = 7$ 8·32 (d) $J = 7$
9 ⇌ 12	Carbon protonated conjugate acid H'_{1-6}; 1·14 (s) H_{4-7}; 2·54 (m)		H_2; 5·41 (s)	6·55 (s) cis 8·97 (s), trans
Indenyltropenium ion (13)	H'_1, H'_6; 0·90 (m) H'_{2-5}; 1·43 (m) H'_2, H'_5; 4·00 (m) H'_3, H'_4; 3·60 (t), H'_6; 4·80 (q) $J = 6·5$ H'_7; 7·84 (d) $J = 6·5$	H_{4-7}; 2·46 (m) H_{4-6}; 2·63 (m) H_7; 2·56 (m)	H_1; 1·54 (s) H_3; 6·00 (s) H_{2-3}; 6·80 (m)	
	H'_2, H'_5; 3·99 (m) H'_3, H'_4; 3·58 (m) H'_6; 4·84 (q) $J = 7·0$ H'_7; 6·13 (d) $J = 7·0$	H_{4-7}; 2·87 (m)	H_{2-3}; 7·15 (m) —O—H; 4·94 (s)	
	H'_2, H'_5; 3·75 (m) H'_3, H'_4; 3·48 (t) H'_6; 4·60 (q) $J = 7·0$ H'_7; 5·62 (d) $J = 7·0$	H_{4-7}; 2·87 (m)	H_1; 3·05 (s) H_3; 6·50 (s)	

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* s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

on the NMR time scale and the two species exhibit a time averaged spectrum. This process can best be demonstrated by consideration of the change in the NMR spectrum of 8 and 11 in trifluoroacetic acid with temperature (Fig. 2). As the temperature increases the doublet for the 2-hydrogen of 11 is broadened by rapid exchange to the point that it is no longer observable, and is also decoupled from the 3-hydrogen causing this latter hydrogen to become a defined quartet. Concurrent with these changes, the two doublets for the Me groups coalesce into a broad partially resolved doublet and the hydrogens for the 7-membered ring coalesce into a broad unresolved multiplet while the benzene hydrogens become more defined. From the coalescence temperature, employing the usual assumptions,[6] the activation energy for the conversion 8 to 11 could be estimated (19·9 Kcal at 60 Mc, 20·9 Kcal at 100 Mc).

The relative populations of the conjugate acids of these ketones (5, 6 or 7) are listed in Table 2 for a specific concentration of ketone in trifluoroacetic acid. The conjugate acid salts could readily be prepared by adding perchloric or fluoroboric acid to ether solutions of the ketones. However, the composition varied and although the salts were well formed crystalline solids, C and H analyses were not reproducible due to formation of hydrates.

The NMR spectra of the crystalline fluoroborate or perchlorate conjugate acids of these ketones in trifuloroacetic acid were primarily the carbon protonated species (10, 11 or 12). However, solutions in this solvent do not equilibrate, indicating that perchlorate ion, fluoroborate ion or trifluoroacetic acid are not sufficiently strong bases to transfer a proton between the isomeric conjugate acids at a measurable rate. The conjugate acid perchlorates or fluoroborates of 4 or 5 will equilibrate entirely to the O-protonated form in a mixture of 30% trifluouroacetic acid-acetonitrile.

The relative ratios of C-protonated to O-protonated conjugate acids are also a function of the substituent at the 3-position on the indanone ring. Thus, the Me groups apparently create a steric interaction with the coplanar 7-membered ring in the ion 11 with respect to 10 increasing the relative population of 11. The second Me group increases this interaction to the point that ion 12 is the predominant species at equilibrium (Table 2). Using the equilibrium data of Table 2, the energy of this methyl-7-membered ring interaction can be calculated and is ca. 1·2 Kcal per Me group.

An additional fact to be gained from the NMR spectrum of 4 in trifluoroacetic acid is that the doublet at 1·0 τ integrates for two hydrogens indicating that the 7-membered ring is rapidly rotating on the NMR time scale so that the Ha and Hb signals have coalesced. From low temperature NMR experiments in trifluoroacetic


acid-acetonitrile it was possible to estimate the activation energy for this process for ion 7 as 10·9 Kcal. This low energy barrier would be expected since the transition state for rotation would be a tropenium ion. However, it is interesting that this barrier to rotation is observable, verifying that structure 7a is relatively important to the resonance hybrid indicating a significant amount of positive charge resides on the

oxygen atom in this ion. Similar low temperature NMR studies on the oxygen protonated conjugate acid (8) indicated that the energy barrier was too low to be accessible in suitable solvents. This is probably again a result of the steric interaction between the 3-Me group of the indanone ring and the 7-membered ring when the system is planar.

Variable temperature NMR experiments on the ketones (4, 5 or 6) indicated that coalescence of the Ha–Hb hydrogens of 6 could be observed at high temperatures. The activation energy for this process in this compound was 19·3 Kcal (60 Mc).

TABLE 2. EQUILIBRIUM RATIOS FOR 20% SOLUTIONS (w/v) IN TRIFLUOROACETIC ACID
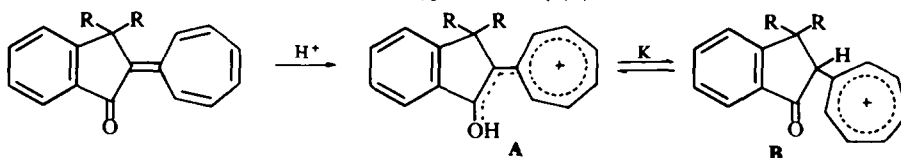
| Compound	%A	%B	K^a	ΔF (Kcal)	$\Delta\Delta F$
4	83·7	16·3	0 0·195	0·97	
5	34	66	1·94	−0·39	1·36
6	8	92	11·5	−1·44	1·05

a 25°.

The energy barrier was too high to be accessible in suitable solvents for 4 or 5 indicating that the steric interaction of the two Me groups is necessary to lower the energy barrier sufficiently to be observed. Using the previously determined methyl-7-membered ring interaction energy for these systems allows an estimation of the rotational energy for 2-cycloheptatrienylideneindanone (4) of 21·9 Kcal[*,7] The transition state for this process would be expected to be the dipolar structure which should possess a substantial resonance stabilization.

The synthesis of 2-indenyltropenium ion (13) could be readily accomplished starting with 2-cycloheptatrienylideneindanone (4). Reduction of this ketone with LAH gave the conjugate addition product 2(1-cycloheptatrienyl)indanone (14) rather than the alcohol. Reduction of 2(1-cycloheptatrienyl)indanone in a second step yielded 2(1-cycloheptatrienyl)indanol which was then directly dehydrated to 2(1-cyclo-

* This value for the ethylenic double bond in stilbene is 42·8 Kcal, and for p,p'-N,N-dimethylamino-nitrostilbene is 17·1 Kcal.

heptatrienyl)indene. This hydrocarbon readily reacted with triphenylcarbonium fluoroborate to give 2-indenyltropenium ion (13).

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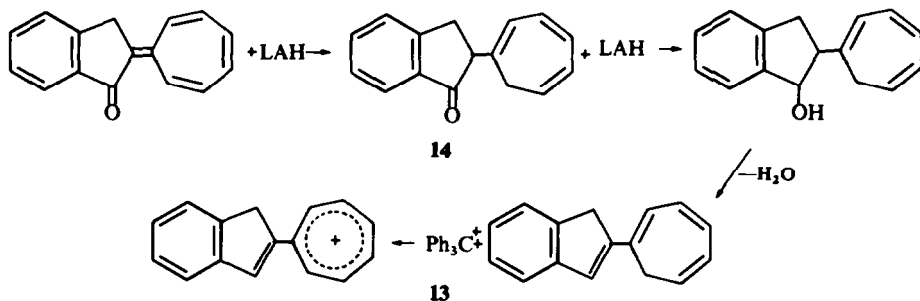
As would be anticipated, the resonance hybrid has as the major contributing structure (13a); and thus, there is no detectable barrier to rotation of the 7-membered ring.

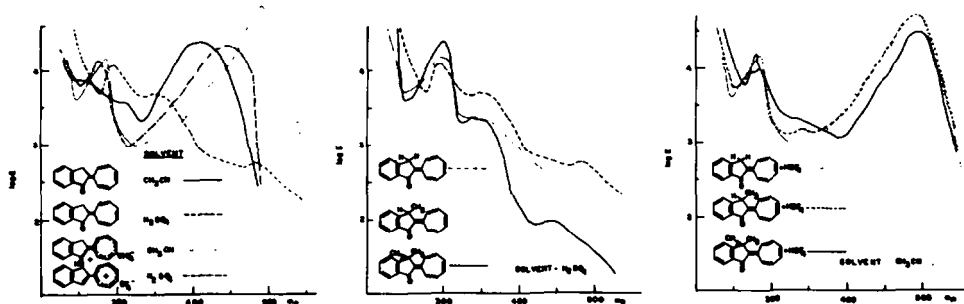**13a**   **13b**

FIG. 3. UV spectra.

The UV spectra of these compounds (Fig. 3) reaffirms the conclusions concerning the various equilibria established upon protonation of 4, 5, or 6. Thus, 2-indenyltropenium ion and the oxygen protonated conjugate acids of (4, 5 and 6) exhibit similar UV spectra. The C-protonated conjugate acids exhibit significantly different UV spectra consistent with the interrupted π-system in these latter ions. Also the UV spectra point out the solvent effects on the stability of the various conjugate acids. Thus, in sulfuric acid C-protonation is favored, but in acetonitrile the equilibrium populations are shifted towards protonation on oxygen.

It should be noted that the long wavelength band for the O-protonated conjugate acid of 2-cycloheptatrienylideneindanone (7) occurs at longer wavelength than the long wavelength band of indenyltropenium ion 13. This data is again consistent with the interpretation, that the oxygen atom is still significantly involved in the π-system and that the ion is not a 2(1-hydroxyindenyl)tropenium ion and that resonance structure 7a is important to the resonance hybrid.

Consideration of the chemical shifts of the 7-membered ring hydrogens in the NMR spectra of the series 2(7-cycloheptatrienyl)indanone (**3**), 2-cycloheptatrienylidene-indanone (**4**), the O-protonated conjugate acid of **4** and 2-indenyltropenium ion **13** (Table 1) should give some indication of charge distribution where applicable. The chemical shifts of the 7-membered ring hydrogens of 2(7-cycloheptatrienyl)-indanone (**3**) and 2-cycloheptatrienylideneindanone (**4**) are essentially identical. The downfield shift of the 1,6 hydrogens in going from **3** to **4** is consistent with conversion of the hybridization of C'_7 from sp^3 to sp^2. Therefore, to a first approximation, the introduction of the *heptafulvene* double bond in going from **3** to **4** apparently does not result in a significant build up of positive charge in the 7-membered ring, to the extent that chemical shifts measure this effect. This analysis would predict that dipolar resonance structures do not contribute significantly to the ground state of the molecule.

The chemical shifts of the 7-membered ring hydrogens in the series, 2-cyclohepta-trienylideneindanone (**4**), the O-protonated form of 2-cycloheptatrienylideneindanone (**7**) and 2-indenyltropenium ion **13** show an increasing downfield shift in the order of increasing positive charge in the 7-membered ring. This sequence defines the trend that would be expected in the NMR spectrum of these compounds with increasing charge and ring current due to aromatic character.

The IR spectra of these compounds are also of interest. Since 2-cycloheptatrienyl-ideneindanone is a vinylogous tropone, these two compounds should show some similarities. There is some controversy as to the actual assignment of the CO band in tropone.[8] Tropone exhibits two intense bands in the IR, one at 1645 cm^{-1}, and the other at 1595 cm^{-1}.[9] Originally the band at 1645 cm^{-1} was assigned to the CO stretching frequency,[10] but more recently the 1595 cm^{-1} band has been assigned to this vibration on the basis of solvent effects.[11] Considering 2-cycloheptatrienyl-ideneindanone (**4**), this compound exhibits a moderately strong band at 1665 cm^{-1} (Fig. 4) and an intense band at 1538 cm^{-1} (Table 3). Indenyltropenium ion (**13**)
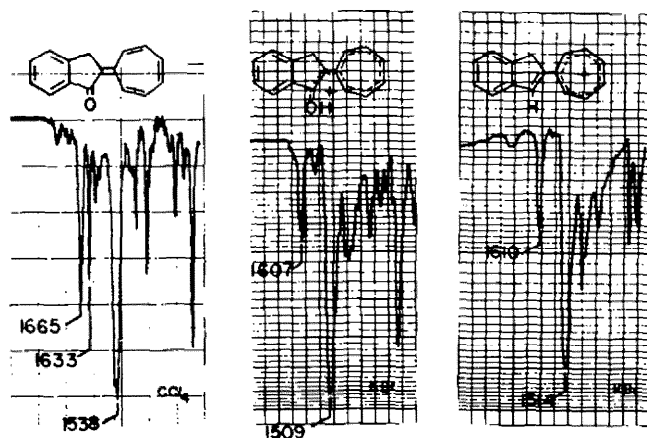

FIG. 4. IR spectra with units in cm^{-1}.

and the O-protonated conjugate acid of 2-cycloheptatrienylideneindanone (**7**) exhibit strong bands at 1514 cm^{-1} and 1509 cm^{-1} respectively. For this reason the 1538 cm^{-1} band in 2-cycloheptatrienylidene-1-indanone (**4**) is assigned to the heptafulvene

Solvent	Band I cm^{-1}	Band II cm^{-1}
Heptane	1671	1549
		(1538)[b]
Carbon tetrachloride	1665	1538
		(1545)[b]
Acetonitrile	1655	1532
Chloroform	1655	1531

[a] Measured with Perkin–Elmer 21 spectrophotometer
[b] Shoulder

bond or a molecular vibration coupled with it. The band at 1665 cm^{-1} in the IR spectrum of this compound is then assigned to the CO. Determination of the solvent effect on the IR spectrum of 2-cycloheptatrienylideneindanone (4) yields the data of Table 3. This data shows similar trends to the behavior of the IR spectrum of tropone[10] with varying solvents and based on a similar treatment as was applied to tropone could lead to the erroneous assignment of the 1538 cm^{-1} band of 2-cyclo-heptatrienylideneindanone to the CO. For this reason it appears highly unlikely that the solvent effect on the IR spectrum of highly polorizable molecules such as those studied in this work, or tropone has any validity as a criteria of assigning IR bands. We have recently suggested that the extent and importance of dipolar resonance in tropone has been over emphasized.[12] These data indicate that the more recent assignment of the IR spectrum of tropone requires additional verification before being accepted.

The CO stretching frequencies for 3,3-dimethyl-2-benzalindanone (15) and the enamine 16 occur at 1706 cm^{-1} and 1640 cm^{-1} respectively.[13] Comparison of the CO stretching frequencies in the series 2-cycloheptatrienylideneindanone,3,3-dimethyl-2-benzalindanone and the enamine 16 indicates that the cycloheptatrienyl-
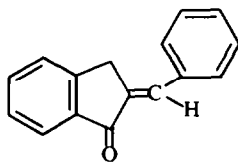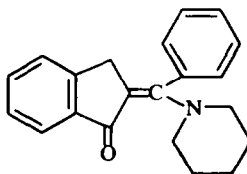

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idene ring and an enamine have approximately the same effect in lowering the energy of this mode.

The data provided in this work do not allow a clear assessment of the amount of *aromatic* character present in the compounds studied. The problem arises because of the difficulty choosing among different criteria of aromaticity. Thus, the keto heptafulvenes (4, 5 and 6) are stable solids. However, the NMR chemical shift data indicates little or no dipolar resonance in the ground state, but is apparently contradicted to some extent by the rotational barrier data. The IR data is also consistent with appreciable dipolar resonance contributors, but it is not clear what this data actually means on a quantitative basis.

The rotational barrier data is difficult to interpret because of insufficient available information. In order to fully evaluate resonance interactions from data of this type it is necessary to have the energy barrier to rotation about the 7, 8 C=C formal double bond and the same barrier about the C_8-C_9 formal single bond arising from dipolar resonance. The value for the C=C double bond is available from this work, but gives only half the picture. An excellent model compound for evaluating the rotational barrier about the C_8-C_9 formal single bond would be 8-acetylheptafulvene (17).
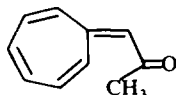

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The detection of a measurable barrier to rotation about the C_8-CO carbon bond would establish the importance of dipolar resonance contributors. Although a synthesis of 8-acetylheptafulvene has been reported,[3] in our hands repetition of this synthetic route on both the tropenylacetone cation 18 or the tropenylproprio-phenone cation 19 led only to rearrangement or cyclization, but yielded no acyl
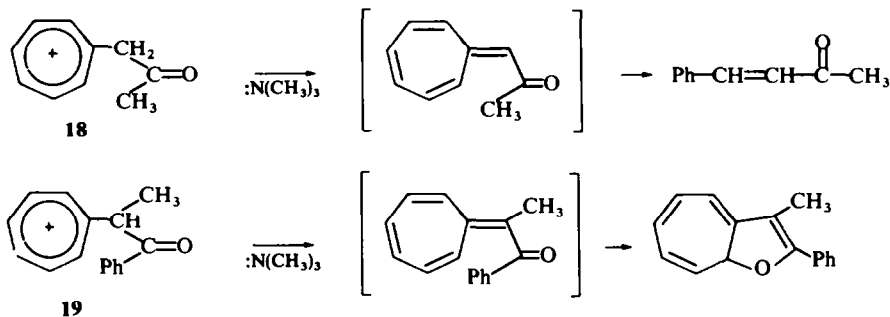
heptafulvene derivatives.* The fact that this cyclization step does not readily occur in the case of 2-cycloheptatrienylideneindanones may be a consequence of the slightly greater strain energy which would be involved in forming a compound such as 20. For these reasons the chemical reactivity and bond energy data cannot be adequately interpreted until more model compounds are available for study.
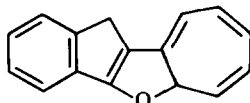
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It is clear that these compounds deviate from simple polyenones, however, the assessment of the amount of aromatic character which they might possess is still not possible. Additional study of these and related systems are in progress.

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* Work is presently in progress to verify the products of these reactions. However, the NMR spectra of the products resulting from deprotonation of either ion clearly demonstrates that they are not the corresponding ketoheptafulvene.

EXPERIMENTAL

NMR spectra were taken on Varian A-60 and Varian Ha-100 instruments. Temps were maintained with the Varian V-6040 controller and were calibrated with the standard samples of MeOH and ethylene glycol supplied by Varian. UV spectra were obtained from a Cary 14 recording spectrophotometer. All IR measurements were taken on a Perkin–Elmer 337 grating IR spectrophotometer or a Perkin–Elmer Model 21 double beam IR spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

2-(7-Cycloheptatrienyl)indanone (13) *and 2-cycloheptatrienylideneindanone* (4). Indanone (5·0 g, 0·038 Moles) dissolved in a minimal amount of acetonitrile was added to tropenium fluoroborate (16·2 g, 0·090 moles) dissolved in a soln made up of 50 ml acetonitrile, 25 ml water and 7 ml fluoroboric acid (50%). Within a few hr the soln turned deep red and became opaque. After standing for ca. 24 hr deep red crystals had formed along with a dark, almost black, oil. This mixture was poured into 300 ml water and extracted with ether (3 × 100 ml). The ether extracts were combined, dried over $MgSO_4$, and concentrated to give a dark red semisolid. Purification by column chromatography over alumina gave two bands. A yellow band was eluted with hexane. A second red band was stripped from the column with $CHCl_3$. Evaporation of the solvents gave crystalline materials in both cases.

Recrystallization of the yellow solid (1·43, 17%) gave pale yellow needles. Repeated recrystallization gave white needles, m.p. 75–76°. The NMR spectrum in CCl_4 (Fig. 1) and the IR spectrum, CO at 1707 cm^{-1}, were consistent with the assigned structure as 2-(7-cycloheptatrienyl)indanone (3). (Found: C, 86·33; H, 6·39. $C_{16}H_{14}O$ requires: C, 86·45; H, 6·35%.)

The dark red solid obtained from the $CHCl_3$ fraction (4·66 g, 56%) was recrystallized from heptane to give dark red needles, m.p. 157–158°. The NMR spectrum in CCl_4 (Fig. 1) was consistent with the structure as 2-cycloheptatrienylideneindanone. UV spectrum (acetonitrile, mμ) 410 (4·36). IR spectrum (CCl_4, cm^{-1}) 1665 (m); 1663 (w); 1538 (s). (Found: C, 87·07; H, 5·62. $C_{16}H_{12}O$ requires: C, 87·25; H, 5·25%.)

3-Methyl-2-cycloheptatrienylideneindanone (5). 3 Methyl-indanone (2·92 g, 0·020 moles) was dissolved in a minimal amount of acetonitrile and added to tropenium fluoroborate (8·0 g, 0·045 moles) dissolved in a mixture of 40 ml acetonitrile, 20 ml H_2O, and 5 ml fluoroboric acid (50%). The reaction conditions and work-up were exactly the same as above. Column chromatography over alumina gave a red fraction with $CHCl_3$ as the eluant. Evaporation of the $CHCl_3$ yielded a deep red oil, which was recrystallized from benzene–hexane (2·08 g, 44%). Recrystallization from heptane gave black red prisms, m.p. 114·5–115·5°. The NMR spectrum in CCl_4 (Fig. 2) was consistent with the proposed structure as 3-methyl-2-cycloheptatrienyl-ideneindanone. UV spectrum (dichloromethane, mμ) 412 (4·37). IR spectrum (KBr, cm^{-1}) 1650 (s); 1631 (s); 1600 (m); 1531 (s). (Found: C, 87·14; H, 6·02. $C_{17}H_{14}O$ requires: C, 87·08; H, 5·99%.)

3,3-Dimethyl-2-cycloheptatrienylideneindanone (6). 3,3-Dimethylindanone (10·0 g, 0·0625 moles) was dissolved in a minimal amount of acetonitrile and added to tropenium fluoroborate (22·3 g, 0·125 moles) dissolved in a mixture of 160 ml acetonitrile, 80 ml water, and 20 ml fluoroborate acid (50%). The reaction conditions and workup were the same as above. Column chromatography over alumina with hexane as eluent gave recovered 3,3-dimethylindanone (5·44 g, 54%), and a dark red oil was obtained from the $CHCl_3$ fractions. Repeated attempts to induce crystallization of this oil failed. This oil was dissolved in ether and addition of an excess of perchloric acid (70%) afforded a mahogany brown crystalline perchlorate adduct (3·25 g, 15%). Treatment of this salt with excess Et_3N in 10 ml of ether gave a quantitative yield (from the salt) of free ketone as a deep red oil. This oil again failed to crystallize after repeated efforts. The NMR spectrum (Table 1) was completely consistent and establishes the structure as assigned UV spectrum (CH_2Cl_2, mμ) 410 (4·24).

Conjugate acids of 2-cycloheptatrienylideneindanone. Addition of an excess of perchloric acid (70%) or fluoroboric acid (50%) to 2-cycloheptatrienylideneindanone (1·0 g, 4·76 mmoles) dissolved in 20 ml ether gave a quantitative yield of the perchlorate or fluoroborate conjugate acid salt. These adducts could be recrystallized from AcOH to give red needles which decomposed above 120°.

The NMR spectrum in trifluoroacetic acid was completely consistent with the assigned structures (Table 1). The UV spectrum (Fig. 5) showed the presence of two distinct conjugate acid forms, 7 and 10. Species 7 was observable in acetonitrile (containing 1% $HClO_4$) 490 mμ (4·85), and 10 was present in conc H_2SO_4, 295 mμ (4·08) and 350 mμ (3·70). IR (KBr, cm^{-1}) 1607 (m), and 1509 (s). Due to the hygroscopic nature of these salts correct analysis was unobtainable; however, the spectral data substantiate the proposed structure as the conjugate acid of 2-cycloheptatrienylideneindanone.

Conjugate acids of 3-methyl-2-cycloheptatrienylideneindanone. Adopting identical reaction conditions as above it was possible to obtain a quantitative yield of crystalline perchlorate and fluoroborate conjugate

acid salts from 3-methyl-2-cycloheptatrienylideneindanone. Either adduct could be recrystallized from AcOH to give bright red needles which decomposed above 120°. The UV spectrum was similar to that of the conjugate acid of 2-cycloheptatrienylideneindanone in acetonitrile and in conc H_2SO_4 showing the presence of **8** and **11**. The NMR spectrum of either conjugate acid adduct in trifluoroacetic acid was consistent with the assigned structures (Table 1). Due to the hygroscopic nature of these salts correct analysis was unobtainable; however, the spectral data substantiates the proposed structure as the conjugate acid of 3-methyl-2-cycloheptatrienylideneindanone.

Conjugate acids of 3,3-dimethyl-2-cycloheptatrienylideneindanone. Adopting the same reaction conditions as above, it was possible to obtain a quantitative yield of crystalline perchlorate or fluoroborate conjugate acid salts from 3,3-dimethyl-2-cycloheptatrienylideneindanone. Either adduct could be recrystallized from AcOH to yield mahogany brown needles, decomposing above 120°. The UV spectrum was similar to that of the conjugate acid of 2-cycloheptatrienylideneindanone in conc H_2SO_4 showing the presence of **9** and **12**. The NMR spectrum of either conjugate acid adduct in trifluoroacetic acid was consistent with the assigned structures (Table 1). Due to the hygroscopic nature of these salts correct analysis was unobtainable; however, the spectral data substantiates the proposed structure as the conjugate acid of 3-methyl-2-cycloheptatrienylideneindanone.

2-(1-Cycloheptatrienyl)indanone (**14**). 2-Cycloheptatrienylideneindanone (4·5 g, 0·0202 moles) as a fine powder was added to a suspension of LAH 10·5 g, in 200 ml anhyd ethyl ether. The mixture was stirred until all of the ketone had dissolved (ca. 40 min), and 14 ml EtOAc was added to the yellow mixture. Finally, 1N HCl was added dropwise until gas evolution ceased and an excess was then rapidly added (100 ml). The etherial layer was separated and the aqueous layer was extracted with 50 ml ether. The ether extracts were combined, dried over $MgSO_4$, and evaporated to give a red-orange oil. Crystallization occurred by addition of pentane (2·93 g, 65%). Recrystallization from hexane afforded pale yellow flakes, m.p. 84–85°. The NMR spectrum, Table 1 and the IR spectrum (KBr, cm⁻¹) 1700 (s), 1600 (m) were both consistent with the structure as 2-(1-cycloheptatrienyl)indanone. (Found: C, 86·24; H, 6·44. $C_{16}H_{14}O$ requires: C, 86·45; H, 6·35%.)

2-(1-Cycloheptatrienyl)indanol and 2-(1-cycloheptatrienyl)indene. 2-(1-Cycloheptatrienyl)-indanone (2·5 g, 0·0113 moles) dissolved in 60 ml of anhyd ether was added to a suspension of LAH (0·5 g) in 100 ml of anhyd ether. The yellow mixture was stirred for 20 min whereupon 1N HCl was added dropwise until gas evolution ceased; an excess was then added (100 ml). The ether layer was separated and the aqueous layer was extracted with 50 ml ether. The ether extracts were combined, dried over $MgSO_4$, and evaporated to give a viscous yellow oil which resisted crystallization attempts (2·31 g, 93%). The NMR spectrum (Table 1) and the IR spectrum (neat, cm⁻¹) 3200–3600 (w), 1601 (w) were both consistent with the structure as 2-(1-cycloheptatrienyl)indanol.

To the viscous oil, (2·31 g, 0·0113 moles) dissolved in 20 ml anhyd EtOH was added 10 ml EtOH saturated with HCl gas. The reaction mixture turned dark red. The soln was then warmed for 15 min. Finally it was poured into 100 ml water and extracted with hexane (3 × 25 ml). The organic extracts were combined, dried with $MgSO_4$ and evaporated to give a yellow-orange powder (1·56 g, 73%). Chromatography over alumina with hexane as the eluent afforded yellow flakes. Recrystallization from EtOH (95%) gave pale yellow needles, m.p. 80·5–82°. The NMR spectrum (Table 1) and the IR spectrum (KBr, cm⁻¹) 1450 (w), 1431 (w), 1381 (w) were consistent with structural assignment as 2-(1-cycloheptatrienyl)indene. (Found: C, 93·29; H, 6·76. $C_{16}H_{14}$ requires: C, 93·16; H, 6·84%.)

(2-Indenyl)tropenium fluoroborate (**13**). 2-(1-cycloheptatrienyl)indene (226 mg, 1·04 mmoles) was added to trityl fluorborate (400 mg, 1·21 mmoles) dissolved in 8 ml CH_2Cl_2 causing a very rapid precipitation of deep brown needles. Filtration gave **13** (295 mg, 96%). Recrystallization from AcOH afforded deep red needles which decomposed above 190°. The NMR spectrum (trifluoroacetic acid, Table 1), the UV spectrum (acetonitrile, Fig. 3), and the IR spectrum (KBr, Fig. 4) were all consistent with the proposed structure. (Found: C, 65·57; H, 4·36. $C_{16}H_{13}BF_4$ requires: C, 65·80; H, 4·49%.)

Activation energy parameters. Compound **6**: 60 Mc, T_c 137°, $\Delta\nu$ 122 c/s, Ea 19·3 Kcal/mole. Conjugate acid of 3-methyl-2-cycloheptatrienylideneindanone (**8** ⇌ **11**): 60 Mc, T_c 114°, $\Delta\nu$ 13 c/s, Ea 19·9 Kcal/mole; 100 Mc, T_c 142°, $\Delta\nu$ 22 c/s, Ea 20·9 Kcal/mole. Conjugate acid of 2-cycloheptatrienylideneindanone (**7**): 100 Mc, T_c −62°, $\Delta\nu$ 60 c/s, Ea 10·9 Kcal/mole.

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