8.52, 9.25, 9.80, 10.00, 10.90, and 12.75 μ; $\lambda_{max}^{CH_3CN}$ 300 mμ (ϵ 13,730), 290 (13,250), 247 (51,300), and 238 (43,480).

Anal. Calcd for $C_{19}H_{25}N_5O$: C, 67.2; H, 7.42; N, 20.6. Found: C, 67.0; H, 7.32; N, 20.5.

1,1'-Bis(tetracyanocyclopentadienido)ethyl Ether (16).—A mixture of tetraethylammonium acetyltetracyanocyclopentadienide (16.5 g, 55.9 mmoles), sodium borohydride (1.65 g, 43.5 mmoles), and ethanol (500 ml) was heated to reflux, allowed to cool (0.5 hr), and then reheated to reflux and allowed to cool (0.5 hr). The solution was concentrated to dryness, and the residue was treated with cold 1 *N* sulfuric acid (200 ml). Bis(tetraethylammonium) 1,1'-bis(tetracyanocyclopentadienido)methyl ether (13.0 g, 78% yield) was collected and recrystallized from water–CH_3CN three times and ethylene chloride once: mp 211–213°; λ_{max}^{KBr} 3.35, 4.54, 6.82, 7.15, 7.27, 7.55, 7.65, 8.45, 9.32, 9.70, 9.96, 10.45, and 12.60 μ; $\lambda_{max}^{CH_3CN}$ 303 mμ (ϵ 29,300), 292 (27,300), 248 (96,000), and 239 (84,100); nmr (CD_3CN·), in addition to the tetraethylammonium peaks, a quartet at τ = 5.67 ppm (2 H) and a doublet at τ = 8.54 ppm (6 H, J = 7.0 cps).

Anal. Calcd for $C_{38}H_{48}N_{10}O$: C, 68.9; H, 7.30; N, 21.2. Found: C, 68.8; H, 7.29; N, 21.3.

(1-Pyridiniumethyl)tetracyanocyclopentadienide (17).—Tetraethylammonium (1-hydroxyethyl)tetracyanocyclopentadienide (12.7 g, 37.4 mmoles) was dissolved in pyridine (300 ml), thionyl chloride (3.0 ml, 41.7 mmoles) was added, and the solution was allowed to stand at room temperature (2.5 hr). The solution was concentrated to dryness, and the residue was washed with water. (1-Pyridiniumethyl)tetracyanocyclopentadiene (7.5 g, 75% yield) remained. An analytical sample (decomposition point 170°) was recrystallized from acetonitrile four times: λ_{max}^{KBr} 3.17, 3.24, 4.52, 6.18, 6.65, 6.72, 6.85, 7.15, 7.90, 8.45, 8.62, 9.45, 10.64, 12.96, and 14.88 μ; $\lambda_{max}^{CH_3CN}$ 297 mμ (ϵ 10,160), 283 (13,300), 266 (10,380), 247 (58,940), and 240 (46,700); nmr (CD_3COCD_3), complex multiplet centered at τ = 1.34 ppm (5 H), quartet at τ = 3.57 ppm (1 H), and doublet at τ = 7.79 ppm (3 H), J = 7.0 cps).

Anal. Calcd for $C_{16}H_9N_5$: C, 70.8; H, 3.34; N, 25.8. Found: C, 70.8; H, 3.30; N, 24.9.

Vinyltetracyanocyclopentadienide (18).—A solution of (1-pyridiniumethyl)tetracyanocyclopentadienide (9.40 g, 34.8 mmoles) in pyridine (200 ml) was heated under reflux (15 hr). The solution was concentrated to dryness and the residue was stirred with water (300 ml) containing tetraethylammonium chloride (10 g). Tetraethylammonium vinyltetracyanocyclopentadienide (11.5 g, quantitative yield) was collected. An analytical sample was recrystallized from ethylene chloride (three times): it melted and polymerized at 136°; λ_{max}^{KBr} 3.30, 3.35, 4.51, 6.12, 6.72, 6.86, 7.09, 7.16, 7.31, 8.52, 9.50, 10.00, 10.16, 11.29, 12.70, and 13.45 μ; $\lambda_{max}^{CH_3CN}$ sh 330 mμ (ϵ 3060), sh 315 (6620), 298 (9900), 271 (52,100), and 262 (45,600); nmr (CD_3CN), vinyl multiplet centered at τ = 3.9 ppm (J_{trans} = 17 cps, J_{cis} = 11 cps, and J_{gem} = 2 cps).

Anal. Calcd for $C_{19}H_{23}N_5$: C, 71.0; H, 7.21; N, 21.8; mol wt, 162. Found: C, 70.7; H, 7.16; N, 22.5; mol wt (freezing point of dimethyl sulfoxide), 173.

An acetonitrile-soluble polymer was obtained by heating the vinyl compound at 135–140° for 15 min under nitrogen. The nmr of the polymer showed no vinyl absorption.

Synthetic Approaches to Cyclohept[*f*]indenes[1a]

F. G. BORDWELL AND MARTIN WINN[1b]

The Chemistry Department, Northwestern University, Evanston, Illinois

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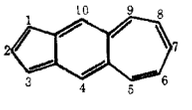
In the process of developing a method of synthesis of the cyclohept[*f*]indene derivatives **2b** and **3b**, a method of preparing benzo[*d*]tropones from *o*-bisbromomethylarenes and ketone enamines has been devised. Nitration and bromination of benzo[*d*]tropones in sulfuric acid solution have been observed to occur excusively in the α positions of the benzene ring. On quenching the carbanion of **2b** (formed in dimethyl sulfoxide) with deuterium oxide all three hydrogen atoms of the indene ring were exchanged, but the cyclohept[*f*]indenol was not produced. Attempts to obtain the cyclohept[*f*]indene system by removal of a proton from the tropylium ion **3b** were unsuccessful.

Some time ago we initiated a synthetic program designed to prepare derivatives of cyclohept[*f*]indene (**1**), a 14 π-electron system. In the meantime Bertelli[2] published the synthesis of the cyclohep[*f*]indene derivatives **2a** and **3a**. Since our synthetic approach and the derivatives prepared (**2b** and **3b**) differed somewhat from those described by Bertelli, we are hereby presenting a summary of our results.



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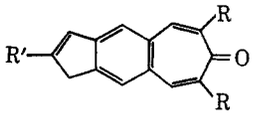
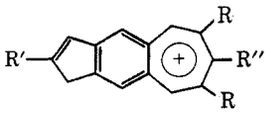
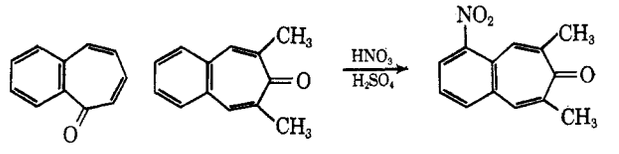


2a, R = C_6H_5; R' = H
b, R = CH_3; R' = C_6H_5



3a, R = C_6H_5; R' = R'' = H
b, R = CH_3; R' = R'' = C_6H_5

Reactions of Benzotropones with Electrophilic Reagents.—Our first approach to the cyclohept[*f*]-indene system was to fuse a five-membered carbocyclic ring onto the benzene ring of a benzotropone system using a Friedel–Crafts or Meerwein reaction.[3] Although neither of these reactions succeeded, some useful information concerning electrophilic substitution of benzotropones was obtained. Tropone **4**, when treated with nitric acid, dinitrated in the seven-membered ring.[4] Under comparable conditions the



4 **5** **6**

dimethylbenzo[*d*]tropone **5** (readily obtained from phthalaldehyde and ethyl ketone[5]) failed to react; yet with nitric acid in sulfuric acid, **5** gave an almost quan-

(1) (a) Abstracted in part from the Ph.D. dissertation of M. Winn, Northwestern University, Aug 1965. (b) National Science Foundation Predoctoral Fellow 1962–1963; Texaco Fellow, 1963–1964; Ethyl Corp. Fellow, 1964–1965.

(2) D. Bertelli, *J. Org. Chem.*, **29**, 3032 (1964); **30**, 891 (1965).

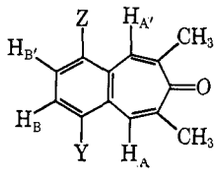
(3) H. Meerwein, E. Büchner, and K. van Emster, *J. Prakt. Chem.*, [2] **152**, 237 (1939); C. F. Koelsch and V. Boekelheide, *J. Am. Chem. Soc.*, **66**, 412 (1944).

(4) G. L. Buchanan and D. R. Lockhart, *J. Chem. Soc.*, 3586 (1959).

(5) J. Thiele and E. Weitz, *Ann.*, **377**, 1 (1911); see also D. Meuche, H. Strauss, and E. Heilbronner, *Helv. Chim. Acta*, **41**, 2220 (1958)

TABLE I

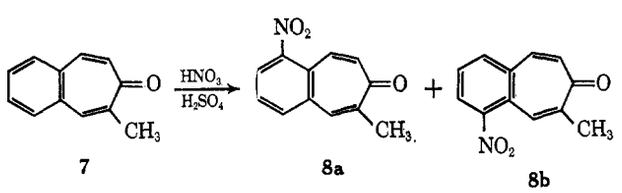
NMR AND ULTRAVIOLET PEAKS[a,b]



Compd	Y[c]	Z	$H_{B'}$ and H_B[c] ($CDCl_3$)	H_A and $H_{A'}$ ($CDCl_3$)	H_A and $H_{A'}$ (F_3CCO_2H)	$H_{B'}$ and H_B[c] F_3CCO_2H	λ_{max}, mμ	ϵ_{max}
5	H	H	7.20	7.20	9.35	8.30–8.80	271	43,500
2	H	NH_2	6.85–7.50	7.67, 7.83	...	...	300	31,200
14	H	NHAc	...	...	8.98, 9.11	8.05–8.45	280	36,600
15	H	OCH_3	6.60–7.15	7.22, 7.95	...	...	286	33,100
16	H	Br	7.00–7.65	7.15, 7.86	9.00, 9.57	7.80–8.55	277	33,900
17	H	OH	...	...	9.22, 10.10	7.75–8.50	287	44,200
18	NO_2	NHAc	...	...	7.80–8.30	7.80–8.30	280	36,600
19	NO_2	NH_2	...	...	8.00–8.30	8.00–8.30	299	29,000
20	Br	Br	...	...	8.62	7.71	281	25,000
21	H	NAc_2	7.30–7.80	7.30–7.80	8.35, 8.52	7.85–8.35	271	42,400
6	H	NO_2	...	...	7.80–8.40	7.80–8.40	265	34,100
22a	H	NH_3^+	...	...	7.80–8.40	7.80–8.40	...	...

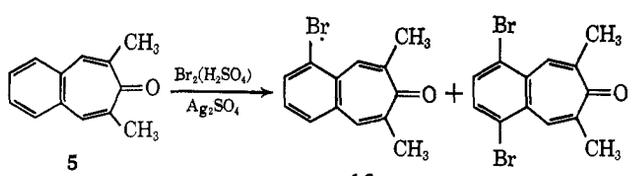
[a] The nmr peaks are δ values relative to TMS. [b] Only the strongest ultraviolet peak is recorded. [c] When Y = H, the signal appears with that of H_B and $H_{B'}$.

titative yield of **6**. The exclusive formation of **6** can be rationalized by assuming that it is the hydroxy tropylium ion that is undergoing nitration, and that attack of the nitronium ion will occur so as to form that intermediate which will allow a maximum separation and delocalization of the two positive charges. This will dictate substitution in the benzene ring, rather than the tropone ring, and at an α rather than a β position. The markedly different behavior of **4** suggests that it is highly susceptible to electrophilic attack at positions α and γ to the carbonyl group. In order to rule out the possibility that failure of attack in the tropone ring of **5** is caused by blocking of attack at the α positions by the two α-methyl groups, the behavior of the monomethyl derivative **7** was investigated. Once again nitration with concentrated nitric acid failed and nitration in sulfuric acid resulted in exclusive substitution in the benzene ring rather than the tropone ring (as shown by nmr).



7 **8a** **8b**

It would appear from the above that benzo[*b*]tropones are much more susceptible to electrophilic attack (of nitronium ion) than are benzo[*d*]tropones. However, their behavior toward bromine seems to be similar. Bromine is reported to add to **4**;[4] an addition product is also formed from **5**. In the dark **5**, like **4**,[4] reacts with bromine in carbon tetrachloride to form an insoluble, unstable complex. On standing, the complex forms the dibromide **9**. No further reaction occurs in the dark, which is not surprising in view of the hindered nature of the potential tetrabromide (**4** does give a tetrabromide[4]). In the light, additional bromine reacts with **9** to give methyl substitution products. Methyl substitution, rather than addition, occurs with **5** and N-bromosuccinimide. The results are summarized as shown in Scheme I. If one converts **5** into the tropylium ion by dissolving it in sulfuric acid, bromination (catalyzed by Ag^+) occurs on the benzene ring.



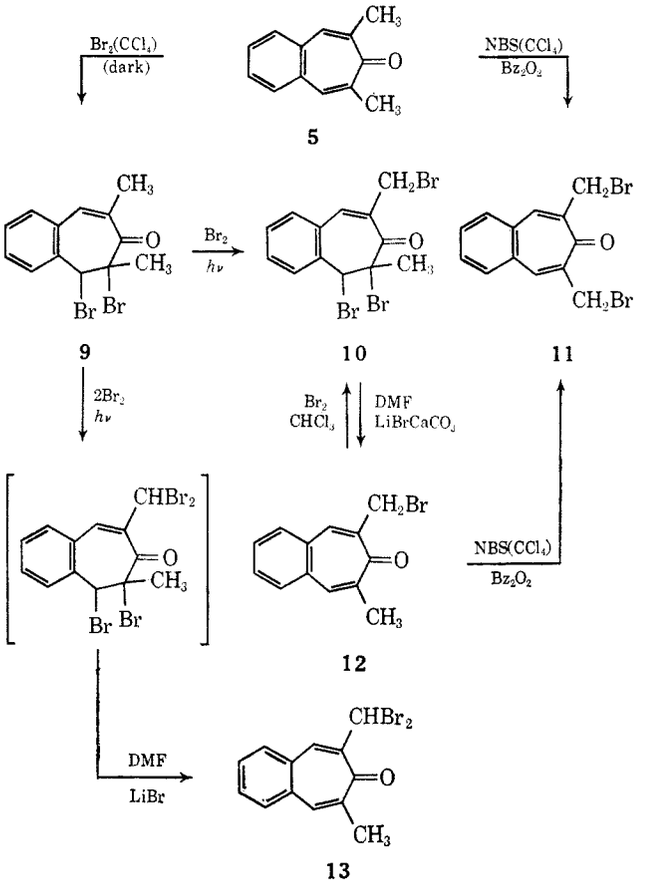
5 **16** **20**

Structure assignments for the nitration and bromination products of **5** were made by degradation and interrelation experiments, coupled with nmr spectroscopy. The details are given in the Experimental Section. In the course of this work the nmr and ultraviolet spectra of a variety of derivatives of **5** having substituents in the benzene ring were recorded. Part of these data are summarized in Table I.

Comparison of the spectrum of **5** in deuterated chloroform with that in trifluoroacetic acid (Table I) shows that in the latter solvent the tropone is converted almost completely into the tropylium ion. Note that the signal for the H_A and $H_{A'}$ protons of the tropone ring shifts to a much greater extent when the change is made from deuteriochloroform to trifluoroacetic acid (δ 7.20 to 9.35) than do the H_B and $H_{B'}$ protons (δ 7.20 to 8.30–8.80). A comparable shift for H_A and $H_{A'}$ protons is noted in the tropylium salt **36**.

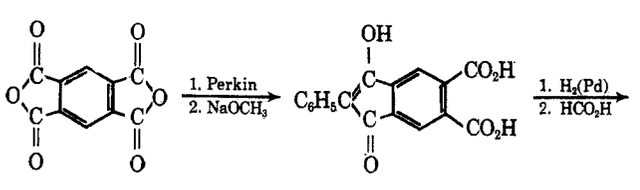
The five compounds listed directly below **5** in Table I also exist largely as the tropylium salts in trifluoroacetic acid solution, but the last six, each of which contains one or more electron-withdrawing groups, are not converted into tropylium salts. One bromine atom fails to prevent tropylium ion formation (**16**), but two bromine atoms do inhibit tropylium ion formation (**20**).

SCHEME I

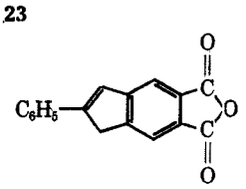


Substitution of a group into the benzene ring of **5** that can enter into electron-pair-donor resonance with the carbonyl function (NH_2, NHAc, OCH_3, Br, OH) results in a shift of the principal absorption maximum to longer wavelengths. On the other hand, the nitro group, which causes a large red shift in benzene, has relatively little effect in **5**. This is understandable since the electron-pair-acceptor properties of the nitro group are in competition with those of the carbonyl group.

Synthesis of Benzotropones from Enamines.—A different approach to cyclohept[*f*]indene is to fuse a seven-membered ring to an indene system. The ready availability of 2-phenyl-1,3-indanedione-5,6-dicarboxylic acid (**23**) (from pyromellitic dianhydride by a Perkin condensation with phenylacetic acid and subsequent rearrangement[6]) made this an attractive

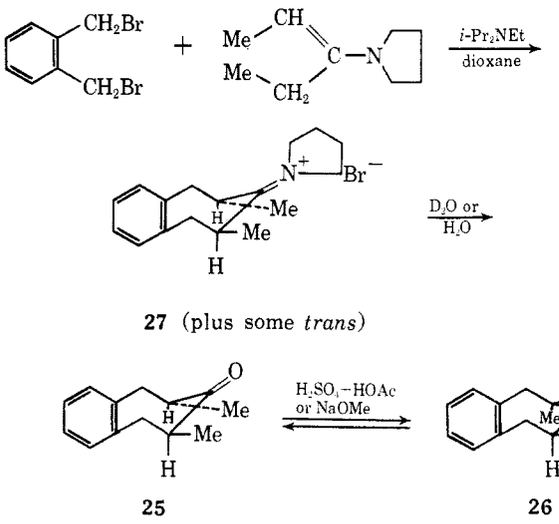


23



24

SCHEME II



27 (plus some *trans*)

starting material. Hydrogenation of **23** over palladium gave a complex mixture of products which, nevertheless, gave a 40% yield of 2-phenylindene-5,6-dicarboxylic anhydride (**24**) on heating with formic acid.

Preparation of a dialdehyde corresponding to **24** would allow easy access to an indenotropone, but efforts to prepare the dialdehyde in satisfactory yields from **24** by a variety of approaches failed.[7] It seemed advisable, therefore, to seek an alternative route for the construction of the tropone ring. The observation of Opitz and Mildenberg[8] that a tricyclic system can be generated by the action of α,α'-dibromo-*o*-xylene with the enamine of cyclohexanone suggested that this approach could be used to prepare tetrahydrobenzotropones and thence benzotropones. This approach was indeed successful.

Before attempting the synthesis of an indenotropone it was decided to work out the conditions by synthesizing the benzotropone **5**. Under conditions similar to those described,[8] except that diisopropylethylamine was used in place of dicyclohexylethylamine, α,α'-dibromo-*o*-xylene and the pyrrolidine enamine of ethyl ketone condensed in acetonitrile solution to give a 65% yield of a mixture of the *cis*- and *trans*-tetrahydro derivatives of **5** [*cis*- and *trans*-6,8-dimethyl-6,7,8,9-tetrahydro-5H-benzocycloheptene-7-ones (**25** and **26**, respectively)]. A comparable yield of product was obtained in dioxane solution, using either collidine or diisopropylethylamine as the base, but the *cis*/*trans* ratio in dioxane was about 20:1, whereas in acetonitrile it was about 3:1. When dioxane was the solvent the product separated as a solid during the reaction. This product was shown to be a quaternary immonium salt (**27**), rather than the tautomeric protonated enamine, both by the absence of an unsplit methyl in its nmr spectrum and by its failure to incorporate deuterium on deuterolysis. (See Scheme II.)

Equilibration of ketones **25** and **26** in acetic acid–sulfuric acid solution gave about a 1:4 ratio of **25** and **26**. Treatment of **25** with sodium methoxide in methanol gave a mixture of about equal amounts of **25** and **26**. (The apparent difference in the equi-

(6) A. Schönberg and G. Schutz, *Chem. Ber.*, **94**, 667 (1961).

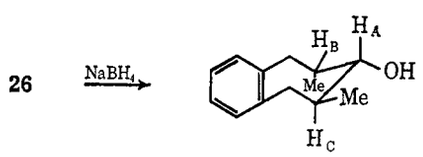
(7) Bertelli[2] obtained a 20% yield of the dialdehyde used in his synthesis of **2a** starting from 5,6-(dibromomethyl)indane.

(8) G. Opitz and H. Mildenberg, *Ann.*, **650**, 115 (1961).

librium position is probably due to the existence of the ketone in the protonated form under acid conditions.) The *cis* quarternary salt (**27**) was not converted into its *trans* isomer by heating with diisopropylethylamine in acetonitrile solution. These experiments show that the formation of **27** as the predominate product is the result of kinetic control in both acetonitrile and dioxane solutions.

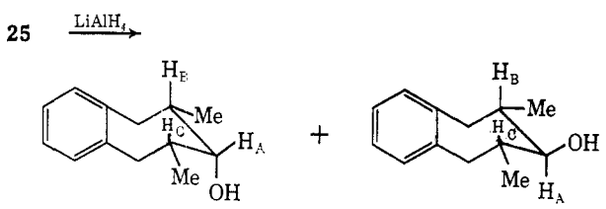
The structures of **25** and **26** were established by reduction to the corresponding alcohols with sodium borohydride or lithium aluminum hydride. The *cis* structure **25** was assigned to the ketone which gave two alcohols on reduction. The *trans* structure **26** was assigned to the ketone which gave a single (and different) alcohol on reduction.

Reduction of the *trans* ketone **26** can give only one alcohol, the *cis,trans* alcohol (**28**; the OH is taken as the reference point). Assuming a chair conformation for **28**,[9] the dihedral angles between the proton (H_A) attached to the carbon atom holding the hydroxyl group and the protons (H_B and H_C) on the adjacent carbon atoms will be 60 and 180°, respectively. The appearance of a double doublet pattern ($J_{AB} \cong 3$ cps; $J_{AC} \cong 7$ cps) at 3.58 ppm for the proton α to the hydroxyl group fits this geometry.[10]



cis,trans-**28**

Reduction of the benzocycloheptanone **25** with lithium aluminum hydride gave about a 9:1 ratio of two alcohols. The major product appears, on the basis of its nmr spectrum, to be the *cis,cis* alcohol **29**. Assuming the chair conformation shown for **29**, H_B and H_C will each be in essentially axial positions and H_A will be essentially equatorial. The dihedral angles will each be about 60°. The broad signal at 3.65 ppm for H_A is consistent with this (triplet with $J_{AB} \cong J_{AC} \cong$ 2 cps expected).[10] In **30**, H_A, H_B, and H_C are all axial.



cis,cis-**29**, 80% *trans,trans*-**30**, 11%

The observed triplet ($J_{AB} \cong J_{AC} \cong 8$ cps) agrees with the structure shown in which the dihedral angles are 180°

Since **29** is probably the less stable of the two products the course of the reduction is controlled by "steric approach" rather than by "product development,"[11] which is contrary to the result that might have been expected by analogy with the cyclohexanone series.[11]

(9) H. Hart and J. L. Corbin, *J. Am. Chem. Soc.*, **87**, 3135 (1965).

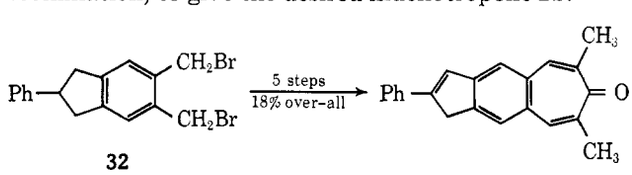
(10) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p 87.

(11) W. G. Dauben, G. J. Fonken, and D. S. Noyce, *J. Am. Chem. Soc.*, **78**, 2579 (1956).

It seemed desirable to compare these products with those obtained by hydrogenation of **5**. When **5** was hydrogenated over palladium, hydrogen was absorbed slowly until about 1 mole had reacted. The rate of hydrogen uptake then increased markedly (about 10-fold), and the reaction proceeded rapidly until about 2.5 moles of hydrogen had been absorbed at which point it stopped abruptly.[12a] The products from the reduction were the *cis* ketone **25** (43%), the *trans* ketone **26** (24%), the *cis,cis* alcohol **29** (18%), and the *trans,trans* alcohol **30** (2%). It would appear that the benzotropone is hydrogenated at a relatively slow rate, as is consistent with its inherent aromatic character, and that it also adheres strongly to the catalyst surface. Since the saturated ketones themselves do not react with hydrogen, the alcohols must come from the tropone or the dihydro intermediate.

Bromination of **25** gave a mixture of *cis*- and *trans*-bromo ketones. Dehydrobromination of this mixture with dimethylformamide–calcium carbonate–lithium chloride gave **5** in an over-all yield of 85% from **25**.

Application of the enamine synthesis to 2-phenyl-5,6-bis(bromomethyl)indene (**31**) gave polymeric material (presumably polymerization is initiated by a base-catalyzed dehydrobromination involving the hydrogen atom at C-3). The enamine reaction worked smoothly, however, on the dihydro derivative, 2-phenyl-5,6-bis(bromomethyl)indan (**32**). Bromination followed by dehydrobromination gave the indanotropone **33**. The C=C bond was reintroduced into the five-membered ring by an additional bromination–dehydrobromination, to give the desired indenotropone **2b**.



32 **2b**

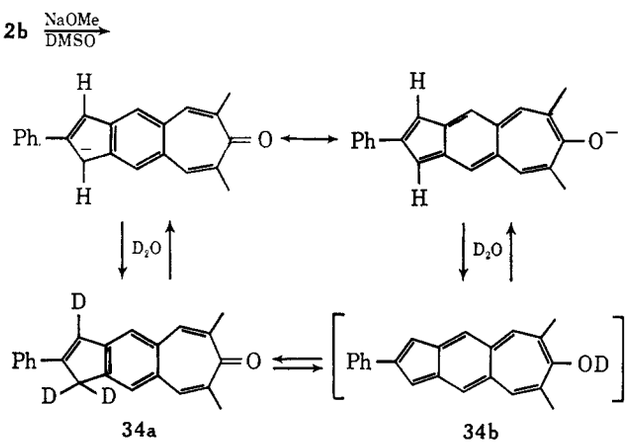
Attempts to Generate a Cyclohept[*f*]indene System.—The infrared and nmr spectra of **2b** show that it exists as a tropone and not as the tautomeric enol. There are two strong bands in the infrared at 6.19 and 6.28 μ, which are characteristic of the tropone grouping; no OH band was evident. In the nmr spectrum the ten protons in the aromatic–vinylic envelope (δ 7.19–7.80) must include five on the phenyl group, two on the benzene ring, two on the tropone ring, and one on the indene ring. In trifluoroacetic acid, the signal for six of these protons remains in the same region (7.26–7.50 ppm). These must be the five protons on the phenyl group and the one on the indene ring, since the others shift in a manner comparable with that described previously for **5** (Table I). The signal for the two protons which constitute the methylene group of the indene ring remains in essentially the same position in trifluoroacetic acid (δ 3.75) as in deuteriochloroform (δ 3.80). Apparently the positive charge on the tropylium ion is delocalized to the ben-

(12) (a) M. E. Volpin and A. F. Plate [*Dokl. Akad. Nauk, SSSR*, **70**, 843 (1950); *Chem. Abstr.*, **44**, 6846 (1950)] have observed this phenomenon in the reduction of **5** but isolated no products. (b) However, Hückel molecular orbital calculations by R. Zahradnik, J. Michl, and J. Kopecky [*Collection Czech. Chem. Commun.*, **31**, 640 (1966)] suggest that cyclohept[*f*]indene should exhibit some aromatic character, although not so much as the angular isomer, cyclohept[*e*]indene.

zene ring to some extent, but there is no evidence to indicate that the indene ring is included in delocalization.

The indenotropone **2b** is insoluble in dimethyl sulfoxide, but dissolves in the presence of excess sodium methoxide to give a green-black solution. When deuterium oxide was added to this solution, the recovered indenotropone was found to have all three hydrogen atoms of the indene replaced by deuterium (see Scheme III).

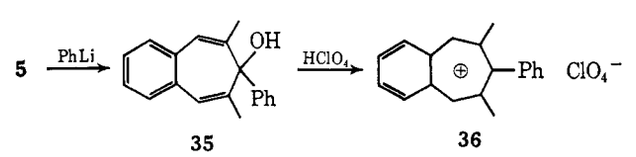
SCHEME III



It is clear from these results that the carbanion is formed rapidly and reversibly from **2b** under these conditions. Since protonation at oxygen is usually much more rapid than at carbon, it seems likely that the enol form **34b** would be produced if the cyclohept[*f*]indene system has inherent stability. Apparently it has little or none and the enol form is either not formed or is much less stable than the keto form **34a**. None of the other hydrogen atoms in the molecule was exchanged under these conditions, even after extended reaction times. Since dimethyl 2-phenylindene-5,6-dicarboxylate also exchanges three hydrogen atoms under these conditions, this is a property of the indene group irrespective of the presence of the tropone grouping.

The deuterium atoms in **34a** were not exchanged by hydrogen in trifluoroacetic acid solution even after standing for 2 weeks in an nmr tube. Evidently the trifluoroacetate ion is not sufficiently basic to remove a deuterium atom from protonated **34a** to form the enol **34b**.

Another approach to the cyclohept[*f*]indene hydrocarbon system would be to remove a proton from an indenotropylium salt. In a preliminary experiment, it was found that phenyllithium could be added to **5** to form the tertiary alcohol **35**. Treatment of **35** with perchloric acid gave a crystalline benzotropylium per-



chlorate **36**. Its nmr spectrum in nitromethane was comparable with that of **35** in trifluoroacetic acid.

Extension of this reaction to the indenotropone **2b** gave the corresponding alcohol (**3**) and a corresponding perchlorate (**3b**). Attempts to convert either of these into the desired hydrocarbon were unsuccessful.

In the light of these results and the work of Bertelli[2] it must be concluded that cyclohept[*f*]indene has little, if any, inherent aromatic character.[12b]

Experimental Section[13]

6,8-Dimethyl-7H-benzocyclohepten-7-one (5).—The method of Theile[5] with double the theoretical amount of 3-pentanone gave 85% of colorless crystals, mp 84–85° (benzene–hexane) (lit.[5] mp 85–86°).

6,8-Dimethyl-1-nitro-7H-benzocyclohepten-7-one (6).—Tropone **5** (6 g, 32.5 mmoles) was dissolved in 18 ml of concentrated sulfuric acid, and concentrated nitric acid (7.00 ml, 112.0 mmoles) was added slowly with stirring and cooling. The dark solution was stirred for 20 min at 25° and poured into 100 ml of ice–water. The resulting solid was recrystallized from chloroform–ethanol to give 7.15 g (31.2 mmoles, 96.0%) of pale yellow needles, mp 206–207°.[14]

Anal. Calcd for $C_{13}H_{11}NO_3$: N, 6.11. Found: N, 6.16.

Oxidation of 6,8-Dimethyl-1-nitro-7H-benzocyclohepten-7-one to 3-Nitrophthalic Acid.—Tropone **6** (500 mg, 2.29 mmoles) in 30 ml of hot acetone was treated with potassium permanganate until the purple color persisted. After standing overnight at 25° the manganese dioxide was dissolved in hydrochloric acid, and the reaction mixture was extracted with ether giving 100 mg (0.47 mmole, 20.5%) of 3-nitrophthalic acid, mp 217–218° (benzene–ether), identified by infrared.

6-Methyl-7H-benzocyclohepten-7-one (7).—The method of Theile[5] gave 59% of white crystals, mp 61–64° (ether–hexane).

1-and 4-Nitro-6-methyl-7H-benzocyclohepten-7-one (8a and b).—Tropone **7** (1.20 g, 7.05 mmoles) in 6.0 ml of concentrated sulfuric acid at 0° was treated with 2.0 ml (32.0 mmoles) of concentrated nitric acid and kept at 0° for 30 min. Treatment with ice–water and chloroform gave 0.732 g (3.40 mmoles, 48%) of white crystals, mp 105–120° (ether–chloroform). The isomers were never separated but an nmr spectrum of the mixture showed that the proton α to the carbonyl was present in both isomers.

Anal. Calcd for $C_{12}H_9NO_3$: C, 66.96; H, 4.22. Found: C, 66.69; H, 4.20.

5,6-Dibromo-6,8-dimethyl-6,7-dihydro-5H-benzocyclohepten-7-one (9).—To 4.00 g (21.7 mmoles) of **5** in 20 ml of chloroform in the dark, was added 6.00 g (37.5 mmoles) of bromine. After 2 min, a solid separated; the mixture was stirred 2 hr at 25° and then treated with sodium bisulfite, water, and chloroform to give 4.17 g of product (crystallized from heptane). The mother liquors were retreated with 3.00 g of bromine in the dark to give 1.52 g of additional product. A total of 5.64 g (15.8 mmoles, 75.1%) was obtained as white crystals from heptane, mp 98–99°.

Anal. Calcd for $C_{13}H_{12}Br_2O$: C, 45.39; H, 3.52. Found: C, 45.51; H, 3.55.

8-Bromomethyl-5,6-dibromo-6-methyl-6,7-dihydro-5H-benzocyclohepten-7-one (10) from 9.—To the above dibromide (**9**) (1.15 g, 3.34 mmoles) in 20 ml of carbon tetrachloride in sunlight, was added dropwise 0.535 g (3.34 mmoles) of bromine. After 30 min the reaction was treated withso dium bisulfite solution and chloroform, giving 1.03 g (2.45 mmoles, 72.5%) of white crystals, mp 114–116° (benzene–ether).

Anal. Calcd for $C_{13}H_{11}Br_3O$: C, 36.92; H, 2.62. Found: C, 37.20; H, 2.77.

6-Bromomethyl-8-methyl-7H-benzocyclohepten-7-one (12).—The tribromide **10** (500 mg, 1.19 mmoles) in 20 ml of dimethylformamide, containing 2.0 g of dry lithium bromide and 1.0 g of calcium carbonate, was heated on a steam bath for 25 min in a nitrogen atmosphere. The reaction mixture was extracted with ether and dilute hydrobromic acid giving 247 mg (0.94 mmole, 79.5%) of white crystals, mp 130–132° (ether–chloroform).

Anal. Calcd for $C_{13}H_{11}BrO$: C, 59.33; H, 4.21. Found: C, 59.57; H, 4.12.

8-Bromomethyl-5,6-dibromo-6-methyl-6,7-dihydro-5H-benzocyclohepten-7-one (10) from 12.—To bromotropone **8c** (350 mg,

(13) Melting points are uncorrected. Microanalyses were by Micro-Tech Laboratories, Skokie, Ill., and by Miss Hilda Beck, Northwestern University. Additional experimental details, including the positions of infrared and ultraviolet maxima and of nmr peaks may be found in the Ph.D. dissertation of M. Winn.[1a]

(14) A. V. El'tsov [*Zh. Organ. Khim.*, **1** (10), 1815 (1965); *Chem. Abstr.*, **64**, 3439*d* (1966)] reports mp 200–201° and gives 137–138° for the corresponding amine.

1.32 mmoles) in 5.0 ml of chloroform was added, in the dark, 320 mg (2.00 mmoles) of bromine. After 1 hr at 20°, the reaction was treated with sodium bisulfite solution to give 490 mg (1.16 mmoles) of the tribromide **8a**, mp 114–115°.

6-(Dibromomethyl)-8-methyl-7H-benzocyclohepten-7-one (13).—The tribromide **10** (500 mg, 1.19 mmoles) in 15 ml of carbon tetrachloride was treated with 250 mg (1.56 mmoles) of bromine in the sunlight. After 10 min the reaction was treated with sodium bisulfite. The residue was debrominated with dimethylformamide–calcium carbonate–lithium bromide, as with **8c**, to give 285 mg (0.83 mmole, 70.3%) of white crystals, mp 162–163° (chloroform–ether).

Anal. Calcd for $C_{13}H_{10}Br_2O$: C, 45.63; H, 2.95. Found: C, 45.77; H, 2.97.

6,8-Bis(bromomethyl)-7H-benzocyclohepten-7-one (11) from 12.—N-Bromosuccinimide (200 mg, 1.12 mmoles) and dibenzoyl peroxide (5 mg) were added to a boiling solution of **12** in 13 ml of carbon tetrachloride. After refluxing for 20 min, the mixture was cooled to 0° and filtered. The solid was washed with water to dissolve the succinimide, and the remaining solid was recrystallized from chloroform to give 1.95 mg (0.58 mmole, 61%) of white crystals, mp 211–212°.

Anal. Calcd for $C_{13}H_{10}Br_2O$: C, 45.63; H, 2.95. Found: C, 45.91; H, 2.99.

6,8-Bis(bromomethyl)-7H-benzocyclohepten-7-one (11) from 5.—Tropone **5** (500 mg, 2.71 mmoles) was brominated with 988 mg of N-bromosuccinimide (5.25 mmoles) as described above to give 680 mg (1.99 mmoles, 73.4%) of dibromide **8b**, mp 211–212°.

1-Bromo-6,8-dimethyl-7H-benzocyclohepten-7-one (16) and 1,4-Dibromo-6,8-dimethyl-7H-benzocyclohepten-7-one (20).—To a solution of 1.72 g (5.54 mmoles) of silver sulfate and 1.00 g (5.44 mmole) of **5** in 25 ml of concentrated sulfuric acid, was added 0.89 g (5.54 mmoles) of bromine in portions, while stirring. After 4 hr the mixture was treated with water and benzene. The crude product was chromatographed on silica gel eluting with 5–10% ether in hexane to give first 300 mg of the dibromide (0.88 mmole, 16.0%), mp 197–198°, next 920 mg (3.49 mmoles, 64.2%) of the monobromide, mp 114–115°, and finally 140 mg of starting material.

Anal. Calcd for $C_{13}H_{11}BrO$: C, 59.35; H, 4.21. Found: C, 59.52; H, 4.23.

Anal. Calcd for $C_{13}H_{10}Br_2O$: C, 45.63; H, 2.95. Found: C, 45.59; H, 2.86.

1-Amino-6,8-dimethyl-7H-benzocycloheptene-7-one (22).—Concentrated hydrochloric acid (12 ml) was added slowly to a stirred suspension of 4.00 g (17.5 mmoles) of **6**, 16 ml of ethanol, and 8.00 g (143 g-atoms) of iron powder. After the mixture was warmed on a steam bath for 15 min, 10 g of sodium hydroxide in 80 ml of water was added, and the resultant slurry was extracted four times with hot benzene to give 3.05 g (15.31 mmoles, 87.8%) of yellow crystals, mp 139–140° (benzene).[14]

Anal. Calcd for $C_{13}H_{13}NO$: C, 78.38; H, 6.59; N, 7.03. Found: C, 78.48; H, 6.58; N, 7.64.

Refluxing 1 g in 4.5 ml of acetic acid containing 0.8 g of acetic anhydride and 1 drop of sulfuric acid gave the acetyl derivative (**14**), mp 235–236° (ethanol).

Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.66; H, 6.27; N, 5.81. Found: C, 74.52; H, 6.28; N, 6.23.

1-Bromo-6,8-dimethyl-7H-benzocyclohepten-7-one (16) from 22.—One gram (5.0 mmoles) of **22** was diazotized by dissolving it in 5.0 ml of acetic acid, treating with 400 mg of sodium nitrite in 2.0 ml of concentrated sulfuric acid at 0°, and stirring for 1 hr. This solution was added to a cold, saturated solution of sodium bromide containing 1.50 g of cuprous bromide. The dark purple solution was heated on a steam bath for 45 min and extracted with ether giving 793 mg (3.01 mmoles 60%) of the bromide, mp 112–115°.

1-Methoxy-6,8-dimethyl-7H-benzocyclohepten-7-one (15).—Diazotization of **22** (2.3 g), as described above, and dilution with 30 ml of cold water and then with 60 ml of acetone gave, on cooling, 2.20 g of yellow crystals, mp 120–122° dec. This was heated with 25 ml of methanol, the solution was concentrated, and the solid was chromatographed on silica gel to give 200 mg (13.2%) of colorless crystals, mp 141–142°.

Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 77.90; H, 6.61.

1-Hydroxy-6,8-dimethyl-7H-benzocyclohepten-7-one (17).—Diazotized **22** (550 mg) was added dropwise to 65 ml of water heated to 90°. The solid formed was sublimed at 190° (0.3 mm) to give 220 mg of yellow crystals (40%), mp 274–275° dec.

Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.31; H, 5.86.

1-Acetylamino-4-nitro-6,8-dimethyl-7H-benzocyclohepten-7-one (18).—Compound **14** (910 mg, 3.78 mmoles) in 4.0 ml of concentrated sulfuric acid at 0° was treated dropwise with 1.00 ml of concentrated nitric acid. The solution was stirred for 7 min and poured into ice–water to give 500 mg (1.75 mmoles, 46.4%) of orange crystals, mp 232–233° (ethanol).

Anal. Calcd for $C_{15}H_{14}N_2O_4$: C, 62.93; H, 4.93; N, 9.79. Found: C, 62.83; H, 4.96; N, 9.48.

1-Amino-4-nitro-6,8-dimethyl-7H-benzocyclohepten-7-one (19).—Nitroamide **18** (3.40 g, 11.9 mmoles) was heated on a steam bath with 50 ml of concentrated hydrochloric acid for 2 hr. Diluting, cooling, and filtering gave 2.10 g (8.63 mmoles, 72.5%) of orange crystals melting above 300° (tetrachloroethane).

Anal. Calcd for $C_{13}H_{12}N_2O_3$: C, 63.92; H, 4.95; N, 11.47. Found: C, 64.16; H, 5.08; N, 11.44.

1-Diacetylamino-6,8-dimethyl-7H-benzocyclohepten-7-one (21).—Amine **22** (6.00 g, 30.1 mmoles) was refluxed for 2 hr in 25 ml of acetic anhydride and then poured into water to give 6.12 g (21.7 mmoles, 72.2%) of colorless crystals, mp 159–160° (ethanol).

Anal. Calcd for $C_{17}H_{17}NO_3$: N, 4.95. Found: N, 4.87.

Benzalphthalide-5,6-dicarboxylic Anhydride.—In a modification of the procedure of Schönberg and Schutz,[6] phenylacetic acid (16.0 g, 117.5 mmoles), pyromellitic dianhydride (34.0 g, 156.0 mmoles), and sodium acetate (3.20 g, 39.0 mmoles) were stirred at 240° (Wood's metal bath) for 3 hr. The resulting solid was pulverized and washed with methanol, sodium bicarbonate, and ether giving 19.0 g (65.2 mmoles, 56%).

2-Phenylindene-5,6-dicarboxylic Anhydride (24).—A crude sample of 10 g of 3-hydroxy-2-phenylinden-1-one-5,6-dicarboxylic acid (**23**)[6] in 175 ml of methanol was hydrogenated at 60 psi using 2.00 g of 10% palladium on charcoal. After 2.5 hr, 2.8 equiv of hydrogen was absorbed. The resultant, oily solid was refluxed in 75 ml 98% formic acid for 8 hr and the mixture was cooled and filtered. The solid was refluxed in fresh formic acid for 5 hr more giving 4.06 g (15.5 mmoles, 48%) of yellow crystals, mp 289–293° dec (tetrachloroethane).

Anal. Calcd for $C_{17}H_{10}O_3$: C, 77.85; H, 3.84. Found: C, 77.74; H, 4.01.

***cis*-6,8-Dimethyl-6,7,8,9-tetrahydro-5H-benzocyclohepten-7-one (25).**—A solution of 45.0 g (0.323 mole) of 3-(N-pyrrolidine)-2-pentene[15] in 200 ml of dioxane was added over a period of 1.5 hr to a solution of 84.0 g (0.318 mole) of α,α'-dibromo-*o*-xylene and 125 g (0.967 mole) of diisopropylethylamine in 300 ml of dioxane under nitrogen. A white solid appeared. The mixture was stirred at 25° for 1 hr and at 85° for 2 hr. Then 200 ml of water was added and the solution was kept at 90° for 45 min. The solution was concentrated and treated with dilute hydrochloric acid and ether to give 39.9 g (0.213 mole 67%) of colorless crystals, mp 52–53° (hexane). Chromatography on silica gel (5% ether in hexane) gave 3.4% of the *trans* isomer (see below).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.17; H, 8.58.

***cis*- and *trans*-6,8-Dimethyl-6,7,8,9-tetrahydro-5H-benzocyclohepten-7-one (25 and 26).**—The above procedure was repeated with 10.0 g (37.9 mmoles) of α,α'-dibromo-*o*-xylene, except that acetonitrile was used in place of dioxane, and the reaction was refluxed for 8 hr after addition. No solid appeared in the reaction. The crude product was chromatographed on silica gel (5% ether in hexane) giving 2.75 g (14.6 mmoles, 38.5%) of the *cis* ketone **25** and 1.53 g (8.15 mmoles, 21.5%) of the *trans* ketone **26**, mp 31–32°.

Anal. Calcd for $C_{13}H_{16}O$ (*trans* ketone): C, 82.93; H, 8.57. Found: C, 82.85; H, 8.88.

***cis*-6,8-Dimethyl-6,7,8,9-tetrahydro-5H-benzocyclohepten-7-(N-pyrrolidino)immonium Bromide (27).**—The above reaction in dioxane was repeated, to the point of hydrolysis. The colorless solid was collected on a filter, washed with dry ether, and dried under vacuum. From 5.00 g of α,α'-dibromo-*o*-xylene, there was obtained 7.21 g of dried solid. The nmr spectrum showed it be an equimolar mixture of **27** and diisopropylethylammonium bromide [an authentic sample had peaks at δ 1.45 (d, J = 7 cps, 12), 1.52 (t, J = 7 cps, 3), 3.18 (q, J = 7 cps, 2), and 3.71 (quintet J = 7 cps, 2)]. Subtracting the area of this from the

(15) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

spectrum for **27** gave δ 1.10 (d, J = 7 cps, 6), 2.10–4.50 (m, 18), 7.15–7.50 (m, 4). The δ 2.10–4.50 region should be m, 14 but the agreement is good, considering the crudity of the sample.

Reaction of 27 with Deuterium Oxide.—Three grams of the above product (representing about 5.64 mmoles of **27**) was heated to 90° with 1.80 g of diisopropylethylamine and 20 ml of dioxane, treated with 3.0 ml of deuterium oxide, and kept at 90° for 30 min. The reaction was processed as before to give 0.88 g (4.58 mmoles) of the *cis* ketone **25**. Nmr analysis showed that no deuterium was incorporated.

Reaction of 27 with Diisopropylethylamine in Acetonitrile.—A solution of 2.00 g of diisopropylethylamine, 25 ml of acetonitrile, and 4.21 g of **27** (containing about 7.92 mmoles) was refluxed under nitrogen for 30 min. Processing as before, but using deuterium oxide, gave only the undeuterated *cis* ketone **25** as shown by thin layer chromatography and nmr and infrared spectra.

Equilibration of *cis*- and *trans*-Dimethyl-6,7,8,9-tetrahydro-5H-benzocyclohepten-7-one (25). A. In Sulfuric Acid.—Purified **25** (7.50 g) was kept for 20 hr at 10° in 45 ml of concentration sulfuric acid and 15 ml of acetic acid, and then treated with ice and ether giving an oil which, when chromatographed as before, gave 1.73 g of *cis* ketone **25** and 5.41 g of *trans* ketone **26**. Pure *trans* ketone (1.21 g) was subjected to the same treatment, and gave 0.43 g of *cis* and 1.64 g *trans*.

B. In Sodium Methoxide Solution.—Pure **25** (450 mg) was kept for 2.5 days at 25° in 20 ml of methanol and 350 mg of sodium methoxide. After treating with ether and water, the resulting oil was found to contain 41% *cis* and 59% *trans* as shown by nmr (the methyl doublet for the *cis* isomer is at 1.10 ppm; for *trans* it is at 0.93 ppm). Treatment with sodium methoxide solution for an additional 3 days gave 46% *cis* and 54% *trans* ketones.

7-Hydroxy-*cis*,*trans*-6,8-dimethyl-6,7,8,9-tetrahydro-5H-benzocycloheptene (28).—Three grams (15.9 mmoles) of **26** in 25 ml of ethanol was treated with 500 mg (13.5 mmoles) of sodium borohydride at 25° for 1 hr. Treatment with dilute hydrochloric acid and ether and chromatography on silica gel (18% ether in hexane) gave 2.51 g (13.2 mmoles, 83.2%) of colorless crystals, mp 63–64°.

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.11; H, 9.47.

7-Hydroxy-*cis*,*cis*-6,8-dimethyl-6,7,8,9-tetrahydro-5H-benzocycloheptene (29) and 7-Hydroxy-*trans*,*trans*-6,8-dimethyl-6,7,-8,9-tetrahydro-5H-benzocycloheptene (30).—Lithium aluminum hydride (1.00 g, 30.0 mmoles), **25** (6.00 g, 31.9 mmoles), and 100 ml of ether were refluxed for 1 hr. Processing with ether and dilute hydrochloric acid and chromatography on silica gel (30% ether in hexane) gave 4.81 g (25.3 mmoles, 79.2%) of the *cis*,*cis* alcohol, mp 132–133°, and then 0.652 g (3.42 mmoles, 10.8%) of the *trans*,*trans* alcohol, mp 139–140°.

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found (for the *cis*,*cis* alcohol): C, 82.09; H, 9.58. Found (for the *trans*,-*trans* alcohol): C, 82.26; H, 9.44.

Hydrogenation of 5.—A solution of **5** (5.00 g, 21.7 mmoles) in 100 ml of ethanol was hydrogenated at 60 psi over 500 mg of 10% palladium on charcoal. (It took 1 hr to absorb 1 equiv of hydrogen, but in the next 10 min another 1.5 equiv was absorbed.) The product was chromatographed on silica gel. Elution with 5% ether in hexane gave ketone **25** (1.71 g, 41.4%) followed by ketone **26** (0.947 g, 23.1%); subsequent elution with 15% ether in hexane gave the *cis*,*cis* alcohol **29** (0.719 g, 17.3%) and 25% ether in hexane gave the *trans*,*trans* alcohol **30** (0.061 g, 1.5%). No trace of the *cis*,*trans* alcohol **28** was detected.

***cis*- and *trans*-6,8-Dibromo-6,8-dimethyl-6,7,8,9-tetrahydro-5H-benzocyclohepten-7-one.**—A solution of **25** in 30 ml of chloroform was saturated with hydrogen bromide, and (in the dark) a solution of 6.40 g (40.0 mmoles) of bromine in 10 ml of chloroform was added dropwise. After 3 hr the reaction was treated with dilute sodium bisulfite solution to obtain 6.32 g (18.3 mmoles, 91.5%) of a colorless oil. Nmr showed it to consist solely of *cis* and *trans* bromo ketones. Chromatography failed to separate the isomers.

A solution of dibromides (6.32 g, 18.3 mmoles) in 70 ml of dimethylformamide containing 8.6 g of calcium carbonate and 2.0 g of lithium chloride was heated on a steam bath for 20 min under a nitrogen atmosphere. Treatment with dilute hydrochloric acid and ether gave 3.09 g (16.8 mmoles, 92.0%) of colorless **5**, mp 84–85° (benzene–hexane).

Dimethyl 2-Phenylindene-5,6-dicarboxylate.—Anhydride **24** (23.40 g, 89.4 mmoles) was refluxed for 8 hr in 500 ml of methanol saturated with hydrogen chloride. Concentrating and cooling gave 26.01 g (84.5 mmoles, 94.5%) of colorless crystals, mp 153–154° (methanol).

Anal. Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 73.80; H, 5.35.

5,6-Bis(bromomethyl)-2-phenylindene (31).—Ten grams (32.5 mmoles) of the above indene diester was refluxed for 12 hr with 3.40 g (89.5 mmoles) of lithium aluminum hydride in 400 ml of ether. Treatment with dilute hydrochloric acid gave 4.48 g (17.8 mmoles, 55%) of 5,6-bis(hydroxymethyl-2-phenylindene, mp 216–217° (after crystallization from dioxane). This diol (3.00 g, 11.9 mmoles) was brominated by refluxing for 2 hr in 80 ml of chloroform containing 2 drops of pyridine and 16.5 g (61.0 mmoles) of phosphorus tribromide. Treatment with water and sodium bicarbonate gave 4.05 g (10.7 mmoles, 90.1%) of colorless crystals, mp 205–206° (chloroform–ether). (The action of an enamine or amine on this dibromide gave polymeric material.)

Anal. Calcd for $C_{17}H_{14}Br_2$: C, 54.10; H, 3.74. Found: C, 54.10; H, 3.78.

5,6-Bis(hydroxymethyl)-2-phenylindan.—2-Phenylindene-5,6-dicarboxylic acid dimethyl ester (24.16 g, 78.5 mmoles) was hydrogenated in 175 ml of dioxane over 2.0 g of 10% palladium on charcoal at 60 psi giving 22.86 g (74.2 mmoles, 94.5%) of colorless crystals, mp 73–74° (ether–hexane). This ester (21.62 g, 70.0 mmoles) was reduced by refluxing for 5 hr with 6.00 g (157.0 mmoles) of lithium aluminum hydride in 500 ml of ether to give 16.93 g (66.6 mmoles, 95.3%) of colorless crystals, mp 121–122° (chloroform–ether).

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 79.99; H, 7.08.

5,6-Bis(bromomethyl)-2-phenylindan (32).—The above diol (18.74 g, 73.9 mmoles) was refluxed for 2 hr with 40.0 g (147.5 mmoles) of phosphorus tribromide, 2 drops of pyridine, and 500 ml of chloroform to give 26.40 g (69.5 mmoles) of colorless crystals, mp 132–133° (chloroform–ether).

Anal. Calcd for $C_{17}H_{16}Br_2$: C, 53.71; H, 4.24. Found: C, 53.46; H, 4.23.

6,8-Dimethyl-2-phenyl-1,2,3,5,6,7,8-octahydrocyclohept[*f*]inden-7-one.—Dibromide **32** (18.5 g, 48.6 mmoles) was treated with 3-(N-pyrrolidine)-2-pentene by the same procedure described for **25** to give 9.79 g (32.1 mmoles, 66.0%) of colorless crystals, mp 124–126° (chloroform–ether). Despite the sharp melting point, changes in the infrared spectra on successive crystallizations indicated the presence of isomers.

Anal. Calcd for $C_{22}H_{24}O$: C, 86.80; H, 7.95. Found: C, 86.79; H, 8.07.

6,8-Dimethyl-2-phenyl-1,2,3,7-tetrahydrocyclohept[*f*]inden-7-one (33).—The above tricyclic ketone (1.52 g, 5.00 mmoles) was brominated by the procedure used for the bicyclic ketone **25** to give 2.23 g (4.82 mmoles, 96.4%) of a mixture of isomeric dibromo ketones, mp 132–135° (chloroform–ether). The mixture of dibromo ketones (14.35 g, 31.0 mmoles) was dehydrobrominated by the procedure used for the bicyclic dibromo ketone derived from **25** to give 8.14 g (27.2 mmoles, 87.8%) of pale yellow crystals, mp 138–138.5° (chloroform–ether).

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 88.08; H, 6.72.

6,8-Dimethyl-2-phenyl-1,7-dihydrocyclohept[*f*]inden-7-one (26).—Tricyclic tropone **33** (6.00 g, 20.1 mmoles) was refluxed for 30 min with 3.67 (21.1 mmoles) of N-bromosuccinimide and 25 mg of benzoyl peroxide. After cooling, the succinimide was removed, the solution was concentrated under vacuum, and a mixture of 100 ml of dimethylformamide, 3.0 g of lithium chloride, and 4.0 g of calcium carbonate was added immediately. After stirring under nitrogen for 2 hr at 30°, the reaction was treated with chloroform and dilute hydrochloric acid to give 2.01 g (6.75 mmoles, 33.6%) of light tan plates, mp 209–210°.

Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.29; H, 5.95.

6,8-Dimethyl-2-phenyl-1,1,3-trideuterio-1,7-dihydrocyclohept-[*f*]inden-7-one (34a).—Indenotropone **2b** (100 mg) was dissolved in 2.0 ml of dimethyl sulfoxide and 50 mg of sodium methoxide (giving a black solution). Deuterium oxide (2 ml) was added slowly. Concentrated hydrochloric acid (2 drops) was added to discharge the color, and the solid was collected on a filter. Recrystallization from chloroform gave 58 mg of tan crystals, mp 211–212°. Repetition of the procedure with dimethyl 2-

phenylindene-5,6-dicarboxylate gave the 1,1,3-trideuterio derivative.

6,8-Dimethyl-7-phenyl-7H-benzocyclohepten-7-ol (35).—Phenyllithium (4.0 ml of a solution in benzene–ether, 8.57 mmoles) was added slowly under nitrogen to a solution of 1.32 g (7.17 mmoles) of **5** in 15 ml of benzene at 10°. After 20 min at 25°, the reaction was treated with water and ether giving 1.75 g (6.67 mmoles, 93%) of colorless crystals, mp 109.5–110.5° (hexane).

Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 87.12; H, 7.19.

6,8-Dimethyl-7-phenylbenzotropylium Perchlorate (36).—Alcohol **35** (759 mg, 2.90 mmoles) in 6.0 ml of ether was treated with 1.0 ml of concentrated perchloric acid giving a yellow solid. Recrystallization from methylene chloride gave 942 mg (2.66 mmoles, 81.7%) of yellow, fluorescent crystals, mp 163–165°.

Anal. Calcd for $C_{19}H_{17}ClO_4$: C, 66.19; H, 4.97. Found: C, 66.38; H, 5.02.

6,8-Dimethyl-2,7-diphenyl-1,7-dihydrocyclohept[*f*]inden-7-ol (37).—A solution of **26** (605 mg, 2.03 mmoles) in 10 ml of benzene was treated with 2.10 ml (4.50 mmoles) of a phenyllithium solution in benzene–ether. After 45 min under nitrogen the reaction was treated with water and chloroform to give 577 mg (154 mmoles, 76%) of colorless crystals, mp 184–185° (chloroform).

Anal. Calcd for $C_{28}H_{24}O$: C, 89.32; H, 6.43. Found: C, 89.13; H, 6.42.

Attempts to dehydrate this alcohol with sodium methoxide in dimethyl sulfoxide or with alumina in benzene were unsuccessful.

6,8-Dimethyl-2,7-diphenyl-1H-cyclohept[*f*]indenium Perchlorate (36).—Concentrated perchloric acid (5.0 ml) was added to a solution of **37** (868 mg, 2.30 mmoles) in 40 ml of methylene chloride. Addition of 25 ml ether and cooling gave 959 mg (2.09 mmoles, 90.5%) of maroon crystals which did not melt at 300°.

Anal. Calcd for $C_{28}H_{23}ClO_4$: C, 73.29; H, 5.05. Found: C, 73.25; H, 5.29.

Attempted Synthesis of 6,8-Dimethyl-2,7-diphenylcyclohept[*f*]-indene.—Perchlorate **36** (166 mg) was suspended in 2.0 ml of dry methylene chloride and treated with 0.2 ml of dry triethylamine. After 1 min, the solution turned from dark red to yellow and the maroon crystals dissolved. Removal of solvents under vacuum gave 200 mg of a tan solid, whose infrared spectrum showed protonated amine and whose nmr spectrum showed aromatic, olefinic, and ethyl peaks with a reduced indene methylene peak.

Syntheses of Indolizino- and Dihydroindolizinoquinoxalines

ERNEST F. PRATT AND JOHN C. KERESZTESY, JR.[1,2]

The Department of Chemistry, University of Maryland, College Park, Maryland

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A 47% yield of the benzoindolizinoquinoxaline (**8**, Scheme I) was obtained in one step upon reaction of 2,3-dichloroquinoxaline (**1**) with ethyl cyanoacetate and isoquinoline. The assigned structure is based on the results of determinations of the molecular weight and infrared absorption spectrum as well as on analogies with related reactions carried out in these laboratories. An 80% yield of cyano ester **3** was obtained from ethyl cyanoacetate and 2,3-dichloroquinoxaline and a 74% yield of related dicyano compound **6** was obtained from malononitrile and 2,3-dichloroquinoxaline. Reaction of either **3** or **6** with isoquinoline gave **8**. Reaction of **3** with pyridine gave **23** (Scheme II), the expected analog of **8**, but reaction of **6** with pyridine gave dihydrodicyanoindolizinoquinoxaline **26** in 84% yield. Upon treating 2,3-dichloroquinoxaline with the sodium salt of 2-phenacylquinoline, a 24% yield of the benzoindolizinoquinoxaline (**2**, Scheme I) containing a ring system not available by the other methods was obtained. A number of analogs of the foregoing products were prepared and routes of reaction are proposed.

It has been found that 2,3-dichloroquinoxaline (**1**) reacts with isoquinoline and ethyl cyanoacetate to give a 47% yield of 14-cyanobenz[*a*]indolizino[2,3-*b*]-quinoxaline (**8**, Scheme I). Low yields of **8** and **9** were obtained when benzoylacetonitrile and ethyl acetoacetate were employed in place of the ethyl cyanoacetate. Here three bonds of the central pyrrole ring are established in one step. The molecular weight of **8** was found[3] to be close to the calculated value and bands ascribed to the cyano and carbonyl groups appeared at 2200 and 1675 cm^{-1} in the infrared absorption spectra of **8** and **9**. The close analogy of these reactions with the previously reported[4] reaction of 2,3-dichloro-1,4-naphthoquinone, isoquinoline, and ethyl cyanoacetate to give **12** supports the assigned structures. Other syntheses reported herein for **8**, and its analogs obtained with pyridines (**23**, **24**, and **25**; Scheme II), supply additional confirmation.

The one-step synthesis of **8** is most simply envisaged as proceeding *via* **1** → **3** → **10** → **11** → **8** (Scheme I). It was previously proposed[5] that the quinone analogs of **10** underwent solvolytic cleavage (*e.g.*, of the carbethoxyl group) before the cyclization (**10** → **11**), but such a cleavage or cleavage by loss of alkyl carbonate[6] appears improbable in the one-step synthesis of **8** since water, alcohols, and strong bases are absent. The isolation of compounds analogous to **11** (*cf.* **26** through **29**, Scheme II) further supports the proposal that the carbethoxyl group is eliminated (**11** → **8**) as ethyl formate.[7] This elimination is doubtlessly facilitated by the resonance stabilization of **8** involving contributing structures **13** and **14**. All seven of the indolizinoquinoxalines obtained are deeply colored, varying from orange to red, and hence may be of potential interest as dyes. No synthesis for these indolizinoquinoxaline ring systems was found in the literature.

The first reaction intermediate suggested above, compound **3**, and several of its analogs were readily obtained by interaction of 2,3-dichloroquinoxaline, an active methylene compound and potassium *t*-butoxide in *t*-butyl alcohol. The active methylene compounds used, the products, and the yields obtained under identical conditions were as follows: ethyl cyanoacetate, **3**, 80%; methyl cyanoacetate, **4**, 84%; *t*-butyl cyanoacetate, **5**, 59%; and malononitrile, **6**, 74%. Since the bands for the nitrile and carbonyl groups appeared in the infrared absorption spectra at

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(3) We wish to thank Mr. Donald Glover of the Naval Ordnance Laboratory for these determinations.

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(7) A related elimination for certain quinone analogs was first suggested by J. A. VanAllan, G. A. Reynolds, and R. E. Adel, *J. Org. Chem.*, **28**, 3520 (1963).