Although soluble in organic solvents, it remains at the origin on TLC plates and is therefore easily separated from the desired products. The yellow color also remains in solution if the products are purified by crystallization instead of chromatography.

(28) The product derived from cyclohexene is especially crystalline and begins to crystallize if the chloroform phase is allowed to cool (this problem does not arise in the more dilute general procedure described above). A detailed procedure for oxyamination of cyclohexene on large scales is being readied for submission to "Organic Syntheses".

(29) As in procedure A (see ref 24), olefin may remain even after all of the Chloramine-T has been consumed (i.e., negative starch-iodide test). This is the case in example 8 of Table I. We suspect that part of the Chloramine-T is spent in side reactions with the ketone function. This hypothesis is supported by the observation that the olefin is completely consumed when the ketone is protected as the ethylene ketal (example 9, Table I).

(30) This replaces the aqueous bisulfite reduction procedure used earlier. We found that although the bisulfite method would slowly reduce osmate esters from unsym-disubstituted olefins, the osmate esters derived from trisubstituted olefins were inert to this treatment. As mentioned earlier (ref 25), the reddish-yellow osmate esters can be detected by TLC. Treatment with $NaBH_4$ reduces even these more hindered osmate esters rapidly at room temperature. As with the bisulfite reduction used in procedure A (ref 26), the nature of the reduced osmium species is unknown. The last of the black, osmium-containing particles is removed when the $MgSO_4$ is separated from the organic phase by filtration.

(31) The procedure for oxyamination of α-methylstyrene on large scales is being readied for submission to "Organic Syntheses".

(32) Chlorox brand commercial household bleach was employed. The bottle states that it contains 5.25% of sodium hypochlorite. The approximate density of the solution is 1.076; thus, 1 mL contains ca. 0.759 mmol of NaOCl. Slight variations in the strength of these bleach solutions have been observed: M. J. Mintz and C. Walling, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 184.

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(34) Since an explosion has recently been reported [*Chem. Eng. News*, **55** (49), 56 (1977)] while handling anhydrous Chloramine-T, it is important to emphasize the difference in stability between anhydrous Chloramine-T and the corresponding trihydrate, which is required in the present work. Commercially available Chloramine-T trihydrate is a very stable substance, and no special precautions are necessary in handling it.

Attempted Synthesis of 2,4,8,10-Tricyclo[5.4.0.0^{1,6}]undecatetraene: Bisnorcaradiene

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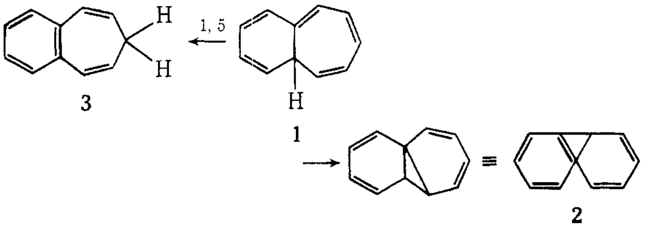
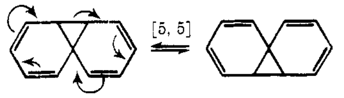
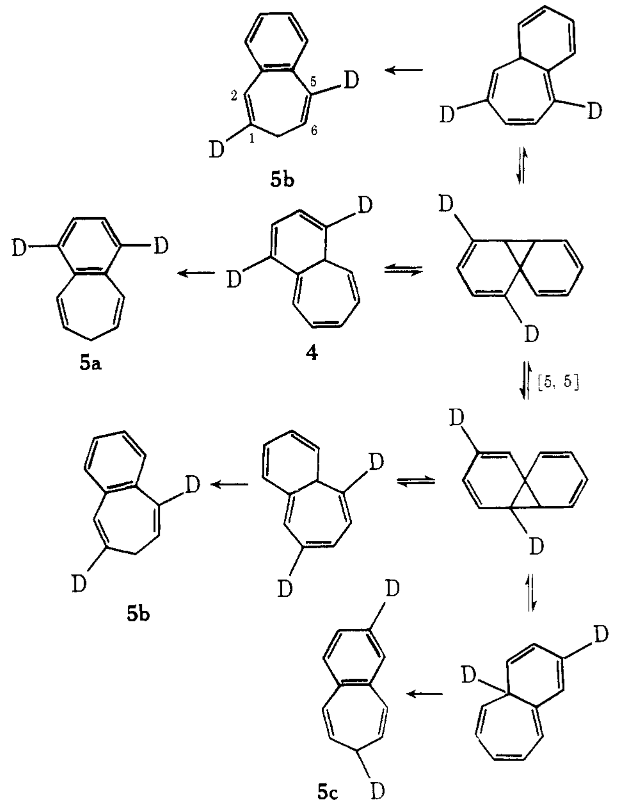
In addition to 1,5-sigmatropic rearrangement of hydrogen, 1,3,5,8,10-bicyclo[5.4.0]undecapentaenes are believed to undergo electrocyclic ring closure to 2,4,8,10-tricyclo[5.4.0.0^{1,6}]undecatetraenes 2 which have been euphemistically named "bisnorcaradienes." The latter have been suggested to explain substituent scrambling in a number of thermal and photochemical reactions[1] and have aroused further interest because they have the potential to undergo symmetry allowed, degenerate, concerted antara,antara[5,5]-sigmatropic rearrangements,[1b] reactions that are intriguingly reminiscent of semibullvalene rearrangements.[2]



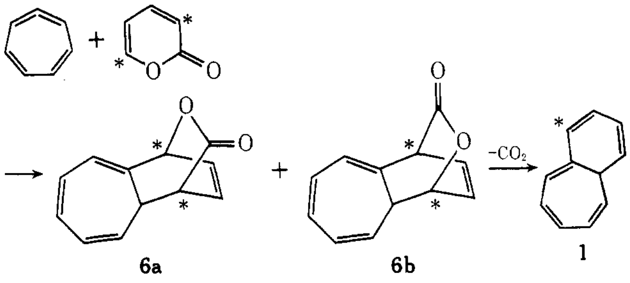


With an eye to exploring this interesting latter possibility, we undertook to generate a deuterium labeled 1,3,5,8,10-bicyclo[5.4.0]undecapentaene 4 which could reveal this degenerate rearrangement. Our plan of attack is outlined in Scheme I where it can be seen that a semibullvalene type of rearrangement would lead to a unique scrambling (**5c**) in the final product.

Scheme I



Scheme II



Our synthetic approach to the labeled bicyclopentaenes is outlined in Scheme II. The essence of the synthesis is a Diels–Alder addition of cycloheptatetraene to 2-pyrone (or, indistinguishably, addition of cycloheptatrienylidene followed by rearrangement) to give one or both of the polycyclic lactones **6a** and/or **6b** which could decarboxylate to the desired polyene.

Cycloheptatrienylidene–cycloheptatetraene has been generated by both base induced dehydrochlorination of a mixture of chlorocycloheptatrienes[3] and photolysis or pyrolysis of the sodium salt of tropone tosylhydrazone.[4] The sensitivity of 2-pyrone to strong base excluded the dehydrochlorination reaction as a viable alternative. The salt of tropone tosylhydrazone was therefore pyrolyzed (110 °C) and photolyzed (to −78 °C) in the presence of 2-pyrone. In no case was there any evidence of the bicyclopentaene **1** but in the pyrolysis reaction there was cleanly (NMR) obtained (30%) isolated 3,4-benzocycloheptatriene. The photolysis was not as clean (in some cases showing the isomeric 1,2-benzocycloheptatriene) but again, even at temperatures as low as −78 °C, there was no evidence for **1**. Again, the predominant product was the benzocycloheptatriene **3**.

Taking formation of **3** as presumptive evidence for **1**, we then undertook to explore the various degenerate rearrange-

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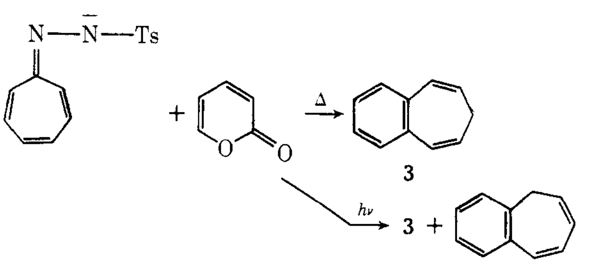
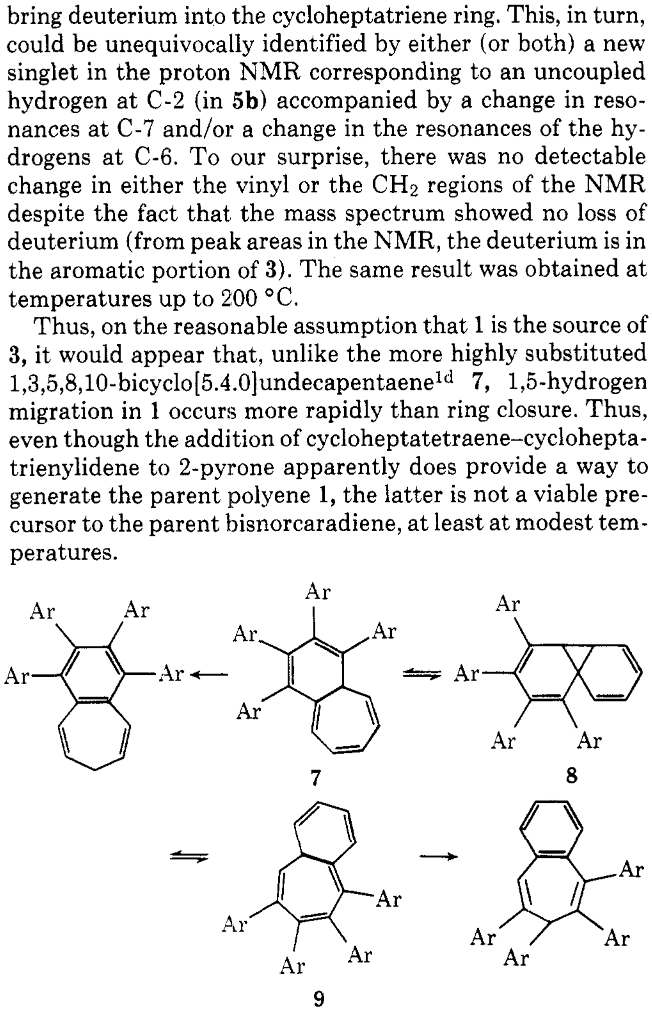


ments. Before attacking the more difficult synthesis of specifically labeled dideuterio-2-pyrone that could identify the semibullvalene rearrangement, we considered it judicious to first assure that the expected bisnorcaradiene rearrangement was faster than aromatization. To test this, 2-pyrone-*6-d* was synthesized by the method of Pirkle[5] and allowed to react at 110 °C with cycloheptatrienylidene–cycloheptatetraene. From Scheme I it can be seen regardless of the regiochemistry of the initial cycloaddition, bisnorcaradiene automerization would bring deuterium into the cycloheptatriene ring. This, in turn, could be unequivocally identified by either (or both) a new singlet in the proton NMR corresponding to an uncoupled hydrogen at C-2 (in **5b**) accompanied by a change in resonances at C-7 and/or a change in the resonances of the hydrogens at C-6. To our surprise, there was no detectable change in either the vinyl or the CH_2 regions of the NMR despite the fact that the mass spectrum showed no loss of deuterium (from peak areas in the NMR, the deuterium is in the aromatic portion of **3**). The same result was obtained at temperatures up to 200 °C.

Thus, on the reasonable assumption that **1** is the source of **3**, it would appear that, unlike the more highly substituted 1,3,5,8,10-bicyclo[5.4.0]undecapentaene[1d] **7**, 1,5-hydrogen migration in **1** occurs more rapidly than ring closure. Thus, even though the addition of cycloheptatetraene–cycloheptatrienylidene to 2-pyrone apparently does provide a way to generate the parent polyene **1**, the latter is not a viable precursor to the parent bisnorcaradiene, at least at modest temperatures.



It might be added in conclusion that from the different behavior of **1** and **7** it would appear that the relative rates of norcaradiene formation and aromatization from 1,5-hydrogen migration in systems of this type must be governed by a rather delicate balance of factors. In principle, these could be either acceleration of norcaradiene formation or retardation of aromatization by the aryl groups in **7**.

Experimental Section

^1H-NMR spectra were recorded on a Varian A-60 NMR spectrometer in $CDCl_3$ or CCl_4 relative to internal Me_4Si. Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer as a film between NaCl plates. Mass spectra were recorded on an AEI MS 30 double beam mass spectrometer. Reagents were not purified except as noted. Solvents were dried by stirring overnight with CaH_2 and filtered through basic alumina, activity grade I (Fisher Scientific Co), into dry septum bottles. The progress of column chromatography was followed by addition of 1% type 609 phosphor (DuPont Photoproducts Dept.) to the absorbent, employing a quartz column, and observing with a hand-held UV unit (Fisher Scientific). Sodium iodine and zinc were dried overnight in a vacuum oven at 130 °C.

2-Pyrone. Coumalic acid (30 g, 0.214 mol), prepared from malic acid by the method of Wiley and Smith,[6] was decarboxylated at 650 °C through copper turnings[7] to yield 12.3 g (0.128 mol, 60%) of 2-pyrone, bp 106–9 °C (26 mm) [lit.[7] bp 110 °C (26 mm)]. This was stored under nitrogen below 0 °C until used.

Sodium Salt of Tropone Tosylhydrazone. The sodium salt of tropone tosylhydrazone was prepared by the method of Jones and Ennis[4] by the reaction of tropone tosylhydrazone with sodium hydride in tetrahydrofuran. The resulting precipitate was recrystallized from 1% Me_2SO in THF to yield purple needles.

2-Pyrone-*6-d*. Glutaconic acid (10 g, 0.077 mol) (Aldrich Chemicals) was allowed to react with phosphorus pentachloride (30 g, 0.144 mol) by the method of Pirkle and Dines[5] to yield 7.1 g (0.054 mol, 71%) of 6-chloro-2-pyrone, bp 64–5 °C (0.5 mm) [lit.[5] 67 °C (9 mm)]. In 30 mL of dry THF 5.8 g of this material was stirred with 11.6 g of sodium iodide for 4 h. The resulting suspension was added[5] to a mixture of 30 g of zinc dust in 20 mL of deuterioacetic acid (Aldrich Chemicals 98 atom %) and allowed to stand overnight. Work-up with CH_2Cl_2, followed by distillation from a 115 °C bath at 25 mm, yielded 607 mg of 2-pyrone-*6-d*. The NMR and mass spectrum of this material were identical to the published spectra.[5,8] ^1H NMR ($CDCl_3$) δ 6.28 (s, H_3), 6.38 (s, H_5), 7.42 (m, H_4); mass spectrum *m/e* (rel intensity) 97 (99.9), 69 (100).

Pyrolysis of the Sodium Salt of Tropone Tosylhydrazone in the Presence of 2-Pyrone-*6-d*. In a typical run, 100 mg (1.04 mmol) of 2-pyrone-*6-d* was dissolved in 15 mL of dry diglyme and heated under nitrogen to the appropriate temperature. To this was added, in small portions through an addition tube, 500 mg (1.41 mmol) of the sodium salt over 30 min. The reaction was allowed to continue for another 30 min, then the reaction mixture was poured into 150 mL of water. This was extracted four times with 50 mL of pentane. The combined pentane extracts were washed six times with 50 mL of water and dried over magnesium sulfate. After removal of the pentane via rotary evaporation, the residue was chromatographed on alumina (Fisher basic, activity grade III) with pentane. Typical 3,4-benzocycloheptatriene yields were about 25%. This was identified by comparing its NMR and mass spectra with the same material synthesized from undeuterated α-pyrone (which, in turn, was identified by comparison of its properties with those reported for the known[9] compound). The mass spectrum of the product from monodeuterated 2-pyrone clearly indicated retention of the deuterium. The NMR spectra from monodeuterated and nondeuterated 2-pyrone were identical except for the relative areas of the resonance at δ 7.25 (3.3:4.0, phenyl). The only other product noted was heptafulvalene which was identified by comparison with a known sample:[4] ^1H NMR (CCl_4) 2.50 (t, 1.8 H, $J = 6$ Hz), 5.82 (d of t, 2.1 H, $J = 6, 10$ Hz), 6.59 (d, 2.0 H, $J = 10$ Hz), 7.25 (s, 3.3 H); mass spectrum *m/e* (rel intensity) 144 (9.6), 143 (90.0), 142 (100), 116 (26.9); for **3** 143 (8.6), 142 (79.4), 141 (100), 115 (29.8); IR (major peaks) 3010, 2950, 2820, 2220, 1480, 1450, 1430, 895, 820, 800.

Photolysis of the Sodium Salt of Tropone Tosylhydrazone in the Presence of 2-Pyrone. In a Pyrex photochemical immersion apparatus was stirred under nitrogen 1.4 g (0.014 mol) 2-pyrone in 100 mL of dry THF. While irradiating with a 550 W Hanovia medium pressure lamp, 0.5 g (1.4 mmol) of sodium salt was added in portions over 30 min. The mixture was irradiated for 3 h and then poured into 300 mL of water. This mixture was worked up in the same manner as the above reaction. The average yield of benzocycloheptatrienes was 25 mg. The ratio of **3** to 1,2-benzocycloheptatriene is 2:1. In an attempt to study this reaction at low temperature equivalent amounts of the tosylhydrazone salt and 2-pyrone-*6-d* were photolyzed at −78 °C. Unfortunately, the yield of benzocycloheptatriene was too low to be detected in the NMR. No pyrone was recovered suggesting that the cause of the low yield may be its known[10] photolability.

Acknowledgment. The authors gratefully acknowledge support of this work received from the National Science Foundation.

Registry No.—2, 65701-68-0; **3,** 264-09-5; 2-pyrone, 504-31-4; 2-pyrone-*6-d*, 20357-66-8; troponetosylhydrazone sodium salt, 18870-24-1; 6-chloro-2-pyrone, 20357-65-7; heptafulvalene, 531-45-3; 1,2-benzocycloheptatriene, 264-08-4.

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One-Step Dialkylation of Phenylacetonitrile in the Presence of Tertiary Amines

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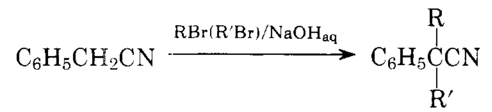
The alkylation of the activated methyne carbon atom is known to occur in aqueous organic medium under standard "phase-transfer" conditions, catalyzed by quaternary ammonium salts.[1-3]

In the course of our studies dealing with the use of macromolecular amines and derived ammonium salts as phase transfer catalysts[4] we have pointed out the activity of tertiary heteroaromatic bases in the monoalkylation of phenylacetonitrile (PAN).[5]

In the previously reported conditions[5] (molar ratio: alkylating agent/PAN = 1.2), the formation of a small amount (<15%) of dialkylated product became appreciable only at PAN conversions larger than 60%.

When an excess of alkylating agent with respect to the starting PAN [5/1 (mol/mol)] was used, conversions to dialkylation product of preparative value were obtained in the same time scale as for standard monoalkylation in the presence of both aliphatic and heteroaromatic amines (Table I).



$$C_6H_5CH_2CN \xrightarrow{RBr(R'Br)/NaOH_{aq}} C_6H_5\overset{R}{\underset{R'}{C}}CN$$

(R = or ≠ R′)

In the case of asymmetric dialkylation of PAN (R ≠ R′) an excess of the less reactive alkyl bromide (n-C_4H_9Br) was used and the reaction was temporarely stopped at PAN conversion >98% (monoalkylation 90–95% and dialkylation 5–10%). After the removal of the unreacted alkyl bromide under vacuum (no further workup of the reaction mixture) an excess of the more reactive alkyl bromide was added and the reaction was carried on until completion.

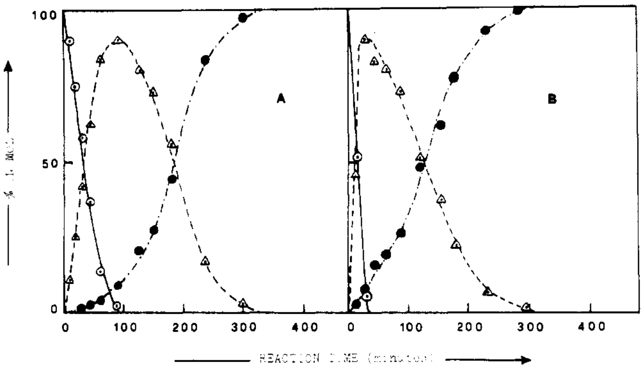


Figure 1. Mono- and dialkylation of phenylacetonitrile (PAN) in the presence of tri-n-butylamine (A) and tetra-n-butylammonium bromide (B): (– ⊙ –) PAN disappearance curve; (- ▲ -) 2-phenylbutanonitrile formation and disappearance curve; (- • ● - •) 2-ethyl-2-phenylbutanonitrile formation curve.

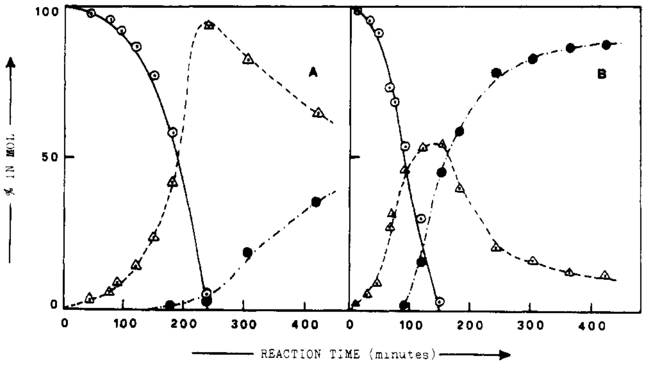


Figure 2. Mono- and dialkylation of phenylacetonitrile (PAN) in the presence of poly(4-vinylpyridine) (A) and 4-methylpyridine (B): (– ⊙ –) PAN disappearance curve; (- ▲ -) 2-phenylbutanonitrile formation and disappearance curve; (- • ● - •) 2-ethyl-2-phenylbutanonitrile formation curve.

The activity of amines, in the examined cases, appears to be comparable to that of the corresponding ammonium salts (Figure 1). When poly(4-vinylpyridine) was used, the reaction rate was markedly lower than that observed for the corresponding low molecular weight analogue (4-methylpyridine) (Figure 2) as previously observed in PAN monoalkylation.[5] This is perhaps obvious because of steric reasons and/or heterogeneity of the reaction medium. The effect of the former factor on rate control is confirmed by the fact that a longer reaction time is required to obtain 50% theoretical yields of 2-ethyl- and 2-butyl-2-phenylhexanonitriles than for 2-ethyl-2-phenylbutanonitrile.

This differentiated reactivity and the reproducibility of the investigated systems, in spite of the complexity of the reaction

Table I. Dialkylation of Phenylacetonitrile[d] (PAN) in Alkaline Aqueous Organic Medium[a]

Amine or quaternary ammonium salt	Registry no.	Alkyl bromide, alkyl =	Registry no.	Time for total disappearance of PAN, min	Time for 50% dialkylation, min	Dialkylated product after 325 min, mol %
Poly(4-vinylpyridine)	25232-41-1	C_2H_5	74-96-4	245	450	19
4-Methylpyridine	108-89-4	C_2H_5		155	160	85
Tri-n-butylamine	102-82-9	C_2H_5		95	190	100
		C_4H_9	109-65-9	125	355	40
		C_4H_9, C_2H_5[b]		90	255	94[c]
Tetra-n-butylammonium bromide	1643-19-2	C_2H_5		45	125	100

[a] Runs carried out at 70 °C under stirring. Molar ratios: alkyl bromide/PAN = 5, NaOH/PAN = 37.5, and catalyst/PAN = 0.167. [b] Run carried out in two steps. Alkylation with n-C_4H_9Br until 98% PAN conversion (90% monoalkylation and 10% dialkylation) then after removal of excess 1-bromobutane C_2H_5Br was added and the reaction carried out again as in footnote a. [c] Constituted by 10% of 2-butyl-2-phenylhexane nitrile and 90% of 2-ethyl-2-phenylhexanenitrile. [d] Registry no. 140-29-4.

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