among phenyl groups in PST is expected to be inefficient and has been discounted (cf. ref 7). In a similar study of the TMD/DBA system Turro et al. (cf. *J. Am. Chem. Soc.*, **100**, 3170 (1978)) obtained experimental quenching radii ($R_c \sim 30$ Å) which were in good agreement with the theoretical values as calculated by the Förster and Perrin models.

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Rearrangement of Cycloheptatrienylidenes in Solution

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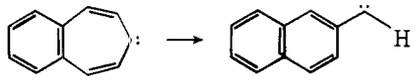
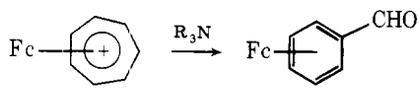
Factors that could promote the rearrangement of cycloheptatrienylidene to phenylcarbene in solution were studied. Simple dilution and increase of the temperature to 240 °C were not sufficient for the rearrangement of the parent cycloheptatrienylidene to be competitive with dimerization to heptafulvalene. Rearrangement did appear when dimerization was retarded by 2,7-disubstitution. 2,7-Diphenylcycloheptatrienylidene was thermally and photolytically generated from the corresponding tosylhydrazone salt and gave exclusively 9-phenylfluorene, the product expected from carbene–carbene rearrangement. 2,7-Dimethyltropone was synthesized next, but could not be converted to its tosylhydrazone. 2,7-Dimethylcycloheptatrienylidene was therefore generated by dehydrochlorination of 2-chloro-1,3-dimethylcycloheptatriene. At 100 °C, tetramethylheptafulvalene was exclusively formed, but at 150–160 °C, in addition to 37% of dimer, 31% of *o*-methylstyrene (from the rearrangement) was isolated. Finally, attempts were made to generate 2,7-diethylcycloheptatrienylidene by dehydrochlorination of 2-chloro-1,3-diethylcycloheptatriene. Conditions could not be found in which base-induced elimination was competitive with thermal aromatization.

The conversion of aromatic carbenes to aryl carbenes has been found in the gas phase,[1] but in solution confirmed examples[2] have been limited to the rearrangement of benzannelated cycloheptatrienylidenes such as **1**.



1 **2**

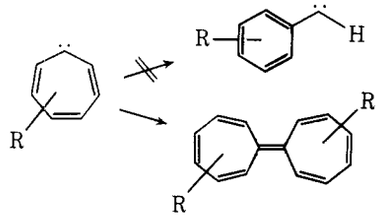
The first reported example of a reaction that might involve this type of rearrangement in solution is the base-induced contraction of the ferrocenyl substituted tropylium salt **3** to



3 **4**

give benzaldehyde products.[3] Carbene involvement in this reaction remains to be confirmed.

In the absence of reactive substrates either the parent or simple substituted cycloheptatrienylidenes[4] give only heptafulvalenes.[1] If it is assumed that the heptafulvalenes arise



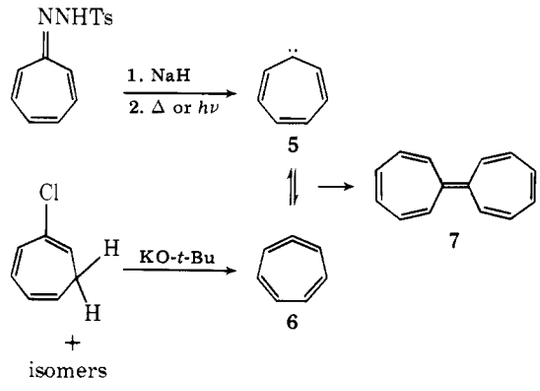
from simple dimerization of the aromatic carbenes (or allenes) by a mechanism of low activation energy, then it should be possible to promote the rearrangement over the dimerization by: (a) reducing the concentration of the reactive intermediate (and probably also by increasing the temperature); and (b) substituting the cycloheptatrienylidene with groups that would retard dimerization.

In view of the ease of detection of rearrangement from the known reaction of phenylcarbene with solvent,[1c,5] we undertook a study of the chemistry of cycloheptatrienylidene in solution under the conditions of (a). A series of 2,7-disubstituted tropone tosylhydrazones were also prepared in order to study aromatic carbenes under the conditions of (b).

Results and Discussion

(1) Effect of Concentration and Temperature on the Carbene–Carbene Rearrangement of Cycloheptatrienylidene. Initially cycloheptatrienylidene (**5**) was generated at low concentration by slowly adding solid tropone tosylhydrazone salt to refluxing dioxane. Careful analysis of the reaction mixture showed only heptafulvalene (**7**). Since the sodium salt is only slightly soluble in dioxane, a Soxhlet thimble was charged with the salt and extracted over a 48-h period. During this time only a fraction of the salt was extracted, but again only the dimer was formed (11% isolated); no dioxane–phenylcarbene insertion product could be detected.

As the rates of dimerization and rearrangement could have different temperature dependencies, the effect of increasing the temperature of the reaction was studied. At 150–160 °C, generation of cycloheptatrienylidene either by slowly adding a mixutre of 1-, 2-, and 3-chlorocycloheptatrienes to potassium *tert*-butoxide in refluxing diglyme[6] or by the Bamford–Stevens reaction[7] led exclusively to the formation of heptafulvalene (**7**).



5 **6** **7**

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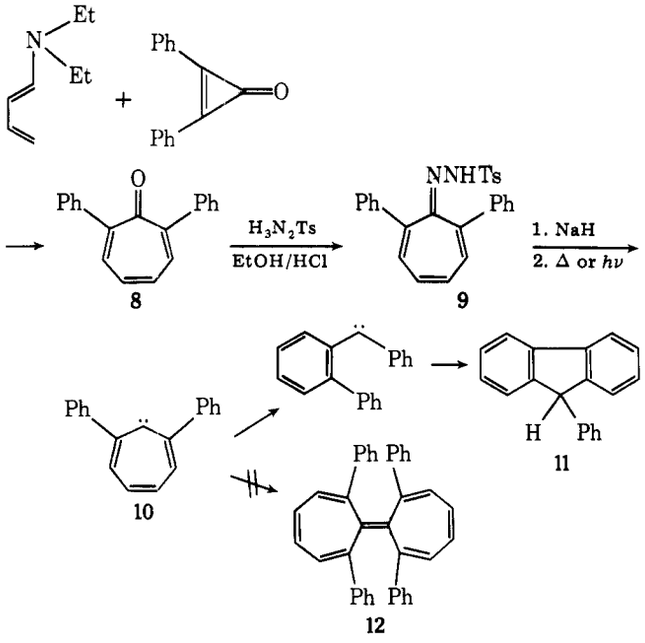
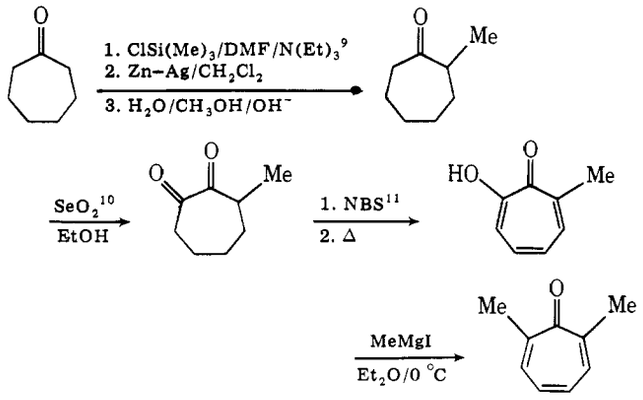
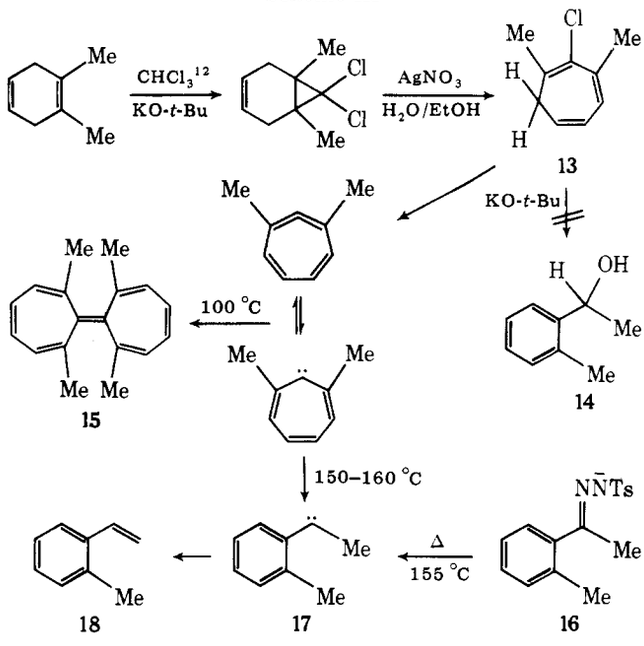
Scheme I



Scheme II



Scheme III



The dehydrochlorination reaction at 230–240 °C gave some aromatic product. However, this probably arose from benzyl chloride which was independently found to be quantitatively formed from heating the starting material in the absence of base under the reaction conditions. Generation of the intermediate at 230–240 °C by slow addition of the tosylhydrazone salt to hot tetraglyme again gave only heptafulvalene (83% isolated).

(2) Effect of 2,7 Disubstitution. As a second approach to promoting rearrangement relative to dimerization, we undertook the generation of a series of 2,7-disubstituted cycloheptatrienylidenes.

2,7-Diphenyltropone (8) was synthesized by the known method[8] outlined in Scheme I. Conversion to the tosylhydrazone was effected by refluxing for 48 h with tosyl hydrazide in ethanolic HCl. Pyrolysis of the salt at 145 °C in diglyme gave 60% of 9-phenylfluorene (1), the product expected of carbene–carbene rearrangement, with no trace of dimer **12**.

2,7-Diphenylcycloheptatrienylidene (**10**) was also generated at lower temperature by photolysis of the tosylhydrazone salt. The decomposition was surprisingly slow, but after 9 h at 10 °C using a 500-W lamp, most of the sodium salt color had disappeared and again 9-phenylfluorene (**11**) was isolated as the exclusive product, albeit in this case in much lower yield (30%).

Thus it is clear that if cycloheptatrienylidene is perturbed by phenyl substitution in the 2 and 7 positions, carbene–carbene rearrangement becomes not only competitive with, but occurs to the exclusion of dimerization.

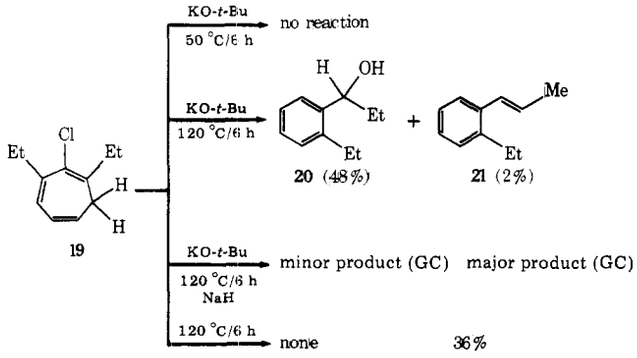
As it is conceivable that two aryl rings could promote the rearrangement as well as retard the dimerization, the effects of less electronically perturbing (and smaller) substituents were then studied. 2,7-Dimethyltropone was synthesized as outlined in Scheme II. However, it was not possible to convert the ketone to its tosylhydrazone. We therefore turned to Untch's elegant dehydrochlorination reaction as a route to the substituted cycloheptatrienylidene.[6] The required 2-chloro-1,3-dimethylcycloheptatriene (**13**) was synthesized as shown in Scheme III.

Reaction of **13** with potassium *tert*-butoxide in monoglyme at 25 °C was much slower (<50% in 1 h) than the parent chlorocycloheptatriene, but dehydrochlorination did occur, yielding exclusively tetramethylheptafulvalene (**15**). At 100 °C, again only the dimer was observed (up to 92%). However, at 150–160 °C, in addition to 37% of the dimer **15**, 31% of *o*-methylstyrene (**18**) was isolated. This is the product expected of carbene–carbene rearrangement as shown independently by generating **17** from the pyrolysis of the *o*-methylacetophenone tosylhydrazone salt (**16**). This result is somewhat clouded by the fact that **13** slowly aromatizes on simple heating in diglyme (~10% under the reaction conditions). However, the significantly larger amount (three times more) of *o*-methylstyrene obtained from the reaction with the base is a strong argument for carbene–carbene rearrangement as the primary source of **18** at 150 °C. It can also be pointed out that aromatization in the presence of potassium *tert*-butoxide and *tert*-butyl alcohol (from the elimination) would probably give as the primary product the alcohol **14** (vide infra; no trace was detected) rather than the olefin **18**.

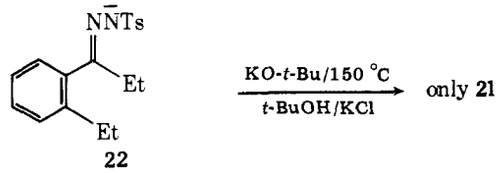
Generation of diethylcycloheptatrienylidene was attempted next to evaluate the effect of substituents whose steric bulk is intermediate to that of phenyl and methyl.[13] 2-Chloro-1,3-diethylcycloheptatriene (**19**) was synthesized by the same method used for **13**. Unfortunately, little could be learned about carbene–carbene rearrangements from attempted dehydrochlorination of this system because conditions could not be found where base-induced elimination was competitive with thermal aromatization (Scheme IV).

In the first place **19** was much less reactive with base than

Scheme IV



13, which may simply reflect a steric retardation of proton abstraction. No reaction was observed up to 90 °C and at 120 °C 6 h were required for complete reaction, yielding the alcohol **20** as the principal product. That **20** did not arise from the rearranged carbene was shown by decomposing the corresponding tosylhydrazone salt **22** under the conditions of the dehydrohalogenation (i.e., at 150 °C in the presence of *tert*-butyl alcohol, potassium *tert*-butoxide, and potassium chloride in diglyme solvent); only the expected hydrocarbon **21** was detected.



The origin of the alcohol **20** is unknown, but it was found that reaction in the presence of sodium hydride significantly increases the yield of styrene **21** at the expense of the alcohol. This suggests *tert*-butyl alcohol may be a necessary reagent. As far as thermal aromatization of **19** is concerned, its mechanism was not studied in detail. However, the rate is not exceptional if the rate-determining step is 1,5-hydrogen migration (e.g., $t_{1/2}$ for rearrangement of 7-methyl-[14] and 7-phenylcycloheptatriene[15] is about 12 and 2 h, respectively, rearrangement of the parent being considerably slower).

From these results, one interesting and possibly important conclusion did emerge. Although the thermal aromatization of **19** in the absence of base gave only the styrene **21**, in the presence of *tert*-butoxide very little (2%) of the olefin was formed; in its place the alcohol **20** appeared. If this empirical result is extrapolated to 1,3-dimethyl-2-chlorocycloheptatriene (**13**), its thermal aromatization in the presence of potassium *tert*-butoxide (and a trace of *tert*-butyl alcohol) would be expected to give 1-(*o*-methylphenyl)ethanol. As mentioned above, the fact that none was observed augers well for carbene–carbene rearrangement of 2,7-dimethylcycloheptatrienylidene at 150 °C.

Conclusion

From these results it would appear that, even at modest temperatures, carbene–carbene rearrangement is accessible in solution to cycloheptatrienylidenes in which the π system is relatively unperturbed. However, in order to be observed a very rapid competitive dimerization reaction must be suppressed.

Simple dilution and increase of the temperature up to 240 °C are not sufficient for rearrangement of the parent cycloheptatrienylidene to be competitive. The rearrangement does appear when dimerization is retarded by 2,7 disubstitution. Furthermore, as the size of the groups are increased from methyl to phenyl, dimer formation drops off and the temperature at which rearrangement is observed appears to decrease. Although there is little question that steric hindrance to dimerization is the major effect of the methyl substituents,[16] one cannot exclude the possibility that the phenyl rings might promote rearrangement as well as retard dimerization.

Experimental Section

General. Melting points were taken in a Thomas–Hoover Unimelt apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia. Accurate mass measurements were performed on an AEI NS 30 with a DS 30 data system.

Chemical shifts are reported in δ values from internal tetramethylsilane standard. Low-resolution mass spectra were determined on a Hitachi Model RMU-6E mass spectrometer.

Analytical thin-layer chromatography (TLC) was accomplished on 2 × 8 in. plates coated with 0.25-mm layers of E. Merck HF-254 silica gel. Components were visualized by their quenching of fluorescence under UV light.

MCB and Baker silica gel (60–200 mesh) or Merck silica gel 60 (particle size 0.063–0.200 mm; 70–230 mesh) were used for column chromatography.

All chemicals were reagent grade used as supplied unless otherwise stated. Dioxane, tetrahydrofuran, and diglyme were dried by (1) distillation from lithium aluminium hydride, (2) refluxing over sodium wires (benzophenone test), and (3) passage over activity grade I Woelm basic alumina just before use.

All reactions were conducted under argon.

2,7-Diphenyltropone. This ketone was synthesized in 79% yield from diphenylcyclopropenone according to the method of Ciabattoni and Berchtold:[8] mp 134–135 °C; reported mp 132–133 °C.

2,7-Diphenyltropone Tosylhydrazone and Salt. A solution of 1.5 g (5.8 mmol) of 2,7-diphenyltropone and 1.1 g (5.8 mmol) of tosyl hydrazide in 30 mL of anhydrous ethanol containing 1% HCl was refluxed for 48 h through a Soxhlet extractor charged with 2 g of magnesium sulfate. After 5 h yellow crystals began to precipitate. The mixture was cooled to room temperature and filtered. The residue was stirred vigorously in a mixture of 15 mL of 10% aqueous sodium bicarbonate and 15 mL of dichloromethane. After 20 min the organic layer was separated and dried over magnesium sulfate and the solvent was evaporated. The resulting crude solid was recrystallized from ethanol to yield 1.2 g (46%) of yellow crystals: mp 190–191 °C; NMR (Me_4Si, $CDCl_3$) δ 7.8–6.5 (m, 18), 2.5 (s, 3); *m/e* 426.1415 (calcd 426.1401).

Anal. Calcd for $C_{26}H_{22}N_2SO_2$: C, 73.21; H, 5.20; N, 6.57. Found: C, 73.18; H, 5.20; N, 6.57.

The sodium salt was prepared by dissolving 600 mg (1.4 mmol) of tosylhydrazone in 20 mL of dry THF and adding 80 mg (1.4 mmol) of a 50% suspension of sodium hydride in oil with stirring. After 1 h 10 mL of pentane was added and the resulting yellow crystals were collected on a frit.

2,7-Dimethyltropone. This ketone was synthesized by both the method of Closs and Closs[18] and the reaction of methyltropolone (synthesized as indicated in Scheme II) with methylmagnesium iodide. In a typical reaction, to a large excess (ca. fourfold) of methylmagnesium iodide in 12 mL of ether (cooled in an ice bath) was added 0.9 g of methyltropolone (mixed with ~25% tropolone). The mixture was stirred 3 h at ice temperature and 3 h at room temperature. The mixture was treated with 15% H_2SO_4 and the aqueous phase was extracted with $CHCl_3$. The organic phase was washed with 10% NaOH (recover 500 mg of tropolones) and water and dried over $MgSO_4$. Evaporation of solvent gave 100 mg of a mixture of tropones with 2,7-dimethyltropone as the predominant product. The same reaction with methyllithium gave predominantly 2,3-dimethyltropone. The mixture of tropones was separated by chromatography over neutral alumina (benzene) with the 2,7 isomer eluting first. Its NMR was identical with that of the ketone synthesized by the known method: NMR (Me_4Si, $CDCl_3$) δ 7.5–6.7 (m, 4 H), 2.3 (s, 6 H); *m/e* 134.

All attempts to convert the ketone to its tosylhydrazone failed.

1,3-Dimethyl-2-chloro-1,3,5-cycloheptatriene. 7,7-Dichloro-1,6-dimethylbicyclo[4.1.0]-3-heptene was synthesized from 1,2-dimethyl-1,4-cyclohexadiene by the method of Vogel et al.[12] This, in turn, was converted to 1,3-dimethyl-2-chloro-1,3,5-cycloheptatriene as follows.

A mixture of 8.5 g (44.5 mmol) of 7,7-dichloro-1,6-dimethylbicyclo[4.1.0]heptene and 11.2 g (64.7 mmol) of silver nitrate in 225 mL of ethanol and 90 mL of water was refluxed for 48 h in the dark with stirring. At the end of this period the silver chloride was removed by filtration on a frit and the filtrate was diluted with water to 800 mL. The resulting mixture was extracted with dichloromethane and the

combined organic extracts were washed with 10% aqueous sodium bicarbonate and water and dried over magnesium sulfate. Removal of solvent gave 6.8 g of brown oil that was purified by distillation [74–78 °C (11 Torr)] to give 5.7 g of the desired product: NMR (Me_4Si, $CDCl_3$) δ 6.5–5.3 (m, 3 H), 2.4 (d, 2 H), 2.15 (br s, 3 H), 2.1 (s, 3 H); *m/e* 154.0050 (calcd 154.0549).

1,2-Diethyl-1,4-cyclohexadiene. A mixture of 25 g (0.2 mol) of *o*-diethylbenzene (Aldrich), 17.8 g (0.6 mol) of methanol, and 37 mL of ether was slowly added to a solution of 10.6 g (0.5 g atom) of sodium in 200 mL of liquid ammonia at −67 °C. The addition was completed in 1.5 h and the mixture was stirred 2 h more at this temperature. The ammonia was removed by evaporation overnight and the residue was hydrolyzed with 600 mL of water. The resulting solution was extracted three times with pentane and the combined organic extracts were washed with water and dried over sodium sulfate. Elimination of solvent left 22.3 g of colorless oil which was a mixture of starting material and the desired product (42.9% based on NMR): NMR (Me_4Si, $CDCl_3$) δ 5.8–5.65 (m), 2.65 (bd s), 2.61 (q), 1.0 (t). This mixture was used for the next step without further purification.

7,7-Dichloro-1,6-diethylbicyclo[4.1.0]-3-heptene. A mixture of 20 g (63 mmol) of the above mixture and 7.8 g (70 mmol) of potassium *tert*-butoxide in 10 mL of pentane was cooled to −5 °C. The mixture was vigorously stirred and 7.5 g (63 mmol) of chloroform was added over 1.5 h. The resulting mixture was hydrolyzed with 100 mL of water and extracted three times with pentane. After usual workup, elimination of solvent gave 21 g of yellow oil. This oil was purified by distillation. Following a first fraction [68–70 °C (13 Torr), mixture of *o*-diethylbenzene and dihydrodiethylbenzene] the desired product distilled at 118–120 °C (13 Torr) as a pale yellow oil: 7.8 g (22.5%); NMR (Me_4Si, $CDCl_3$) δ 5.45–5.60 (m, vinyl), 2.25 (bd s, allylic), 1.7 (q), 1.0 (t); *m/e* 218.

1,3-Diethyl-2-chloro-1,3,5-cycloheptatriene. To 1.4 g (6.4 mmol) of the carbene adduct dissolved in 40 mL of ethanol was added 1% water and 1.5 g (6.9 mmol) of silver perchlorate. The mixture was refluxed for 72 h in the dark with stirring. The precipitated silver chloride was removed by filtration and the filtrate was diluted with water. The resulting mixture was extracted with methylene chloride and the organic layers were washed with 10% aqueous sodium bicarbonate and water and finally dried over $MgSO_4$. Removal of solvent gave 946.4 mg of yellow oil. The product was purified by preparative GC (8 ft × 0.5 in. 5% Carbowax 20 M on Chromosorb P) at 150 °C to give 842 mg (72%) of the desired product. Although the NMR spectrum is complex, the pattern in the vinyl region is strikingly similar to the dimethyl analogue, leaving little doubt of the structure: NMR (Me_4Si, $CDCl_3$) δ 5.2–6.5 (complex vinyl multiplets), 2.2–2.75 (m), 1.1 (t); *m/e* 182.0859 (calcd 182.0862).

***o*-Methylacetophenone Tosylhydrazone and Salt.** A mixture of 15 g (0.1 mol) of *o*-methylacetophenone (Aldrich) and 20.6 g (0.1 mol) of tosylhydrazide in 100 mL of anhydrous ethanol was stirred at room temperature for 1 h. After 15 min white crystals began to appear. The crystals were collected and purified by recrystallization from methanol to give 20 g (60%) of colorless crystals: mp 138–140 °C; NMR (Me_4Si, $CDCl_3$) δ 7.1–7.95 (A_2B_2, tosylphenyl), 7.1 (s, 4 H), 2.4 (s, 3 H), 2.1 (s, 6 H). The sodium salt was prepared by dissolving the ketone in THF and adding 15% excess NaH as a 50% suspension in oil. After stirring 30 min at room temperature, pentane was added to precipitate the salt.

Anal. Calcd for $C_{16}H_{18}N_2SO_2$: C, 63.55; H, 6.00; N, 9.26. Found: C, 63.52; H, 6.02; N, 9.24.

***o*-Ethylpropiophenone Tosylhydrazone and Salt.** The ketone was synthesized according to the method of Caubere[19] and purified by preparative GLC (20 ft × 0.5 in. 25% SE 30 on Chromosorb W, 30–60 mesh at 200 °C). The tosylhydrazone was synthesized by refluxing a mixture of 773.1 mg (4.7 mmol) of the ketone and 888.3 mg (4.7 mmol) of tosylhydrazide in anhydrous ethanol for 2 h. The resulting mixture was cooled to 0 °C and the crystals were collected. Recrystallization from methanol gave 0.8 g (53%) of pure product: mp 122–123 °C; NMR (Me_4Si, $CDCl_3$) δ 7.1–7.9 (A_2B_2, tosyl), 6.5–7.3 (m), 2.1–2.7 (m: s overlapping quartets, 7 H), 1.2 (t, 6 H); *m/e* 330.1379 (calcd 330.1401). The sodium salt was prepared as described above except it is soluble in THF and did not precipitate even with addition of pentane. The solvent was therefore evaporated and the residue was washed with pentane.

1-(*o*-Ethylphenyl)-1-propanol. A solution of 300 mg (1.8 mmol) of *o*-ethylpropiophenone in 2 mL of ether was slowly added to a suspension of 43.6 mg (1.1 mmol) of lithium aluminum hydride in 5 mL of ether. Addition was completed at a rate that maintained gentle reflux (~10 min) and the mixture was then refluxed for 1 h. The resulting mixture was then hydrolyzed with 10% H_2SO_4 followed by extraction of the aqueous phase three times with ether. Combined ether extracts were washed with 10% sodium bicarbonate and water and dried over $MgSO_4$. Removal of solvent gave 327.6 mg of colorless oil: NMR (Me_4Si, $CDCl_3$) δ 7.0–7.6 (m, 4 H), 4.9 (t, 1 H), 2.7 (q, 2 H), 2.05 (s, 1 H), 1.7 (q, 2 H), 1.2 (t, 3 H), 1.0 (t, 3 H); *m/e* 164.

Thermolysis of the Sodium Salt of Tropone Tosylhydrazone in Dioxane and Tetraglyme. From a solid addition tube, 164 mg (0.5 mmol) of tropone tosylhydrazone was slowly added to 20 mL of gently refluxing anhydrous dioxane. The addition was completed in about 1 h and the resulting mixture then poured into 100 mL of water and extracted three times with pentane. The combined pentane extracts were washed with water and dried over $MgSO_4$. Removel of solvent gave a quantitative yield of heptafulvalene. The reaction was repeated in diglyme at 150–160 °C and in tetraglyme at 230–240 °C (30 min). In both cases only heptafulvalene was observed.

Thermolysis of the Sodium Salt of Tropone Tosylhydrazone by Continuous Extraction with Dioxane. A Soxhlet thimble was charged with 250 mg of the sodium salt of tropone tosylhydrazone and extracted continuously with 150 mL of dioxane over 48 h. At the end of this period the yellow dioxane solution was poured into 250 mL of water and extracted three times with pentane. The combined pentane extracts were washed with water and dried and solvent was removed to give a brown oil. Chromatography over silica gel gave only heptafulvalene (11%). The residue remaining in the thimble was primarily the unreacted sodium salt of tropone tosylhydrazone.

Reaction of a Mixture of 1-, 2-, and 3-Chlorocycloheptatrienes with Potassium *tert*-Butoxide at 150 and 250 °C. To a solution of 113 mg (1 mmol) of KO-*t*-Bu in 25 mL of diglyme at 150–160 °C was slowly added a solution of 126.5 mg (1 mmol) of a mixture of the title compounds dissolved in 10 mL of diglyme. The mixture was stirred for 20 min at this temperature, cooled to room temperature, and poured into 250 mL of water. Extraction with pentane followed by washing, drying, and evaporation gave 283 mg of brown residue. Purification by chromatography through silica gel gave 82% heptafulvalene.

Thermolysis of a Mixture of 1-, 2-, and 3-Chlorocycloheptatriene at 230–240 °C. A solution of 100 mg of the title mixture in 5 mL of tetraglyme was heated for 45 min at 230–240 °C with stirring. The mixture was cooled and poured into 50 mL of water. Extraction with pentane followed by washing with water and drying over magnesium sulfate gave 52 mg of a yellow oil whose NMR was identical with that of authentic benzyl chloride.

Thermolysis of the Salt of *o*-Methylacetophenone Tosylhydrazone. To 10 mL of dry diglyme at 150 °C was slowly added (solid addition tube) 500 mg (1.5 mmol) of the sodium salt of *o*-methylacetophenone tosylhydrazone. The addition was completed in 15 min and the reaction mixture was stirred at this temperature for 20 min more. Workup gave 78% *o*-methylstyrene, identified by comparison with authentic (Fluka) material.

Reaction of 1,3-Dimethyl-2-chloro-1,3,5-cycloheptatriene with Potassium *tert*-Butoxide; Tetramethylheptafulvalene. To a solution of 2 g (12.92 mmol) of the title compound dissolved in 30 mL of dry diglyme at 100 °C (argon atmosphere) was slowly added 1.65 g (12.92 mmol) of potassium *tert*-butoxide from a solid addition tube. The mixture was maintained at 100 °C for 3 h more with stirring. The resulting mixture was worked up by cooling, diluting with water, and extracting three times with pentane. After washing the pentane extracts with water and drying over $MgSO_4$, the solvent was removed and the resulting product was purified by chromatography (silica/pentane) to give 2.2 g (92%) of yellow crystals, mp 121–123 °C. Recrystallization from MeOH gave pure product: mp 120.5–121.5 °C; NMR (Me_4Si, $CDCl_3$) δ 6.0–6.5 (complex m, 8 H), 2.0 (s, 12 H); *m/e* 236.15658 (calcd 236.15650). The dimer is relatively stable for short periods of time, even in the crystalline state. However, it decomposes slowly and attempts to obtain C,H analyses were not successful.

The above reaction was also carried out at 25 °C (1 h) to give 33% of the heptafulvalene along with unreacted starting material and at 150–160 °C (3 h). At the higher temperature, 200 mg of the chlorocycloheptatriene gave 57.3 mg (37%) of tetramethylheptafulvalene and 48.7 mg (32%) of *o*-methylstyrene (identified by comparison with authentic material from Fluka).

Thermal Stability of 1,3-Dimethyl-2-chloro-1,3,5-cycloheptatriene. A solution of 200 mg of the title compound was heated in dry diglyme for 1 h at 150–160 °C. After usual workup, the isolated oil was checked by NMR. No aromatization could be detected. The same experiment was repeated with 350 mg of the title compound which was heated for 3 h. Usual workup gave 246 mg of brown oil. NMR and GC showed primarily starting material contaminated with about 10% *o*-methylstyrene (identified by GC separation at 120 °C on a 3 m × 0.5 in. column packed with 10% SE 30 on Chromosorb W and comparison with the NMR of authentic material from Fluka) and a small amount of material that is probably an isomer of the title compound.

Thermal Stability of Tetramethylheptafulvalene in Diglyme at 150–160 °C. A suspension of 61 mg of dimer in 10 mL of diglyme was heated for 1 h at 150 °C. Workup gave 95.5% recovered starting material; no other product could be detected.

Attempted Base-Induced Decomposition of 1,3-Diethyl-2-chloro-1,3,5-cycloheptatriene. To a solution of 32.7 mg (0.2 mmol) of the title compound in 5 mL of dry glyme at 50 °C was slowly added by solid addition tube 23 mg (0.2 mmol) of KO-*t*-Bu. The mixture was stirred for 2 h at 50 °C, after which it was poured into 50 mL of water and worked up in the usual manner. Evaporation of pentane left 15.8 mg of starting material. No other reaction product could be detected.

The above was repeated using 350 mg (1.9 mmol) of title compound and 213 mg (1.9 mmol) of KO-*t*-Bu for 6 h at 120 °C. Workup as above gave 161 mg of yellow oil. Chromatography on silica gel gave (pentane) 5.6 mg (2%) of β-methyl-*o*-ethylstyrene and (ether) 150 mg of 1-(*o*-ethylphenyl)-1-propanol. When this experiment was repeated in the presence of 1 equiv of NaH, the alcohol was formed as a minor product; in this case NMR and GC indicated β-methyl-*o*-ethylstyrene to be the primary product.

Thermal Stability of 1,3-Diethyl-2-chloro-1,3,5-cycloheptatriene in Diglyme at 120 °C. A solution of 500 mg of title compound in 25 mL of dry diglyme was heated at 120 °C for 6 h. Workup as described above (chromatography on silica gel) gave 36% β-methyl-*o*-ethylstyrene.

β-Methyl-*o*-ethylstyrene. The title compound was synthesized by thermolysis of *o*-ethylpropiophenone tosylhydrazone salt. A solution of 100 mg (0.3 mmol) of freshly prepared sodium salt was heated at 150 °C for 20 min. After dilution with 100 mL of water, the solution was extracted three times with pentane. Workup as described above gave 17.6 mg (40.2%) of β-methyl-*o*-ethylstyrene (mixture of isomers). The predominant isomer showed the following: NMR (Me_4Si, $CDCl_3$) δ 7.0–7.5 (m, 4 H), 6.65 (d of d, 1 H), 5.7–6.3 (pair of quartets, 1 H), 2.7 (q, 2 H), 2.1 (d of d, 3 H), 1.2 (t, 3 H). Areas were not exact because superimposed on this spectrum was a small amount of what appears to be the other stereoisomer.

Thermolysis of 2,7-Diphenyltropone Tosylhydrazone Salt. In a typical experiment, 100 mg (0.2 mmol) of the title compound was slowly added (solid addition tube) over a 30-min period to 10 mL of dry diglyme at 150 °C. After 20 min of additional stirring, the reaction mixture was cooled and poured into 75 mL of water. Extraction with pentane followed by workup and chromatography over silica gel with pentane as eluent gave 32 mg (60%) of 9-phenylfluorene: mp 142–143 °C; reported[20] mp 146–147 °C. Both NMR and *m/e* were consistent with this assignment.

Photolysis of 2,7-Diphenyltropone Tosylhydrazone Salt. A solution of 50 mg (0.1 mmol) of the title compound in 100 mL of dry diglyme was photolyzed under argon for 9 h at 10 °C with a 500-W Hanovia pressure mercury lamp. At the end of that time the yellow color of the starting solution had been almost completely dispelled. After dilution with 200 mL of water, extraction with pentane, and workup, the residual oil was chromatographed over silica gel to give 8.1 mg (30%) of 9-phenylfluorene: mp 141–142 °C; reported[20] mp 146–147 °C. The NMR was identical with that obtained in the previous experiment.

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Registry No.—**8,** 1154-38-7; **9,** 67541-77-9; **9** Na salt, 67541-78-0; **11,** 789-24-2; **13,** 67541-79-1; **15,** 67541-80-4; **18,** 611-15-4; **19,** 67541-81-5; tosyl hydrazide, 1576-35-8; 2,7-dimethyltropone, 49747-09-3; methyltropolone, 67541-82-6; 2,3-dimethyltropone, 53951-51-2; 7,7-dichloro-1,6-dimethylbicyclo[4.1.0]-3-heptene, 38749-42-7; 1,2-diethyl-1,4-cyclohexadiene, 67541-83-7; *o*-diethylbenzene, 135-01-3; 7,7-dichloro-1,6-diethylbicyclo[4.1.0]-3-heptene, 67541-84-8; *o*-methylacetophenone tosylhydrazone, 67541-85-9; *o*-methylacetophenone tosylhydrazone Na salt, 67541-86-0; *o*-methylacetophenone, 577-16-2; *o*-ethylpropiophenone, 16819-79-7; *o*-ethylpropiophenone tosylhydrazone, 67541-87-1; *o*-ethylpropiophenone tosylhydrazone Na salt, 67541-88-2; 1-(*o*-ethylphenyl)-1-propanol, 67541-89-3; heptafulvalene, 531-45-3; tropone tosylhydrazone Na salt, 18870-24-1; 1-chloro-1,3,5-cycloheptatriene, 32743-66-1; 2-chloro-1,3,5-cycloheptatriene, 34896-79-2; 3-chloro-1,3,5-cycloheptatriene, 55619-05-1; benzyl chloride, 100-44-7; (*E*)-β-methyl-*o*-ethylstyrene, 67541-90-6; (*Z*)-β-methyl-*o*-ethylstyrene, 67541-91-7.

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