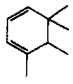
shift has recently been reported: E. E. Waali and W. M. Jones, *J. Org. Chem.*, **38**, 2573 (1973).
(40) J. A. Berson and R. G. Salomon, *J. Am. Chem. Soc.*, **93**, 4620 (1971); R. A. Baylouny, *ibid.*, **93**, 4621 (1971).
(41) P. Schiess and P. Fünfschilling, *Tetrahedron Lett.*, 5191, 5195 (1972).
(42) L. L. Miller, R. Greisinger, and R. F. Boyer, *J. Am. Chem. Soc.*, **91**, 1578 (1969).
(43) E. Ciganek, *J. Am. Chem. Soc.*, **89**, 1458 (1967).
(44) J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Wilcott, III, *J. Am. Chem. Soc.*, **89**, 4076 (1967); V. A. Mironov, V. S. Pashegorova, T. M. Fadeeva, and A. A. Akhren, *Tetrahedron Lett.*, 3397 (1968); R. Grigg, A. W. Johnson, K. Richardson, and K. W. Shelton, *Chem. Commun.*, 1192 (1967); V. Boekelheide and E. Sturm, *J. Am. Chem. Soc.*, **91**, 902 (1969).
(45) R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, *Chem. Soc. Spec. Publ.*, **No. 19**, 3 (1965).
(46) G. Scholes, C. R. Graham, and M. Brookhart, *J. Am. Chem. Soc.*, **96**, 5665 (1974).
(47) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968; E. N. Cain and R. K. Solly, *Aust. J. Chem.*, **25**, 1443 (1972); *J. Am. Chem. Soc.*, **95**, 4791 (1973).
(48) For a review, see G. Maier, "Valenzisomerisierungen", Verlag Chemie, Weinheim/Bergstr., 1972.
(49) C. W. Spangler, T. P. Jondahl, and B. Spangler, *J. Org. Chem.*, **38**, 2478 (1973).
(50) J. M. Photis, unpublished observations in this laboratory.
(51) In this connection, we note a fifth mechanistic alternative not considered specifically earlier, viz., 1,5 shift of the angular substituent followed by a 1,5 return of hydrogen to the 9- or 10-position. If the assumption is made that suprafacial patterns of migration prevail, then the trans 1,9 isomer would be first formed to be followed by the 1,5 and 1,4 isomers. That no 1,4 material is formed in detectable amounts mitigates against this reaction course. Also, the intermediate first formed would be expected to give rise rapidly to a 1-phenylbutadiene derivative, but such have not been uncovered. These facts in addition to the observed features of the 1,9 isomers permit rejection of this option.
(52) E. F. Bradbrook and R. P. Linstead, *J. Chem. Soc.*, 1739 (1936).
(53) We thank Professor M. S. Newman for the authentic sample.
(54) G. Snatzke and G. Zanati, *Justus Liebigs Ann. Chem.*, **684**, 62 (1965).
(55) At 100 MHz, the splitting pattern exhibited by the olefinic protons is identical with that of α-pyronene (ii, 220-MHz spectrum): S. G. Traynor, Ph.D. Thesis, Trinity College, Dublin, 1974.



ii

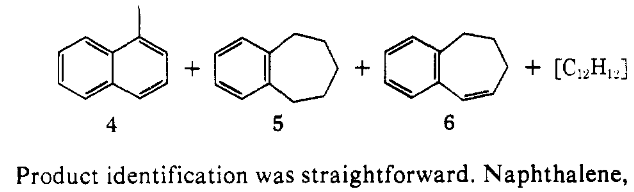
Benzotropyl + Benzene ⇌ Tropyl + Naphthalene[1]

Martin Pomerantz*[2a] and Alan S. Ross[2b]

Contribution from the Department of Chemistry, Belfer Graduate School of Science, Yeshiva University, New York, New York 10033. *Received March 10, 1975*

Abstract: Pyrolysis (400°) of 1,2-benzotropilidene (**1**) has been shown to produce naphthalene (**2**), 2-methylnaphthalene (**3**), 1-methylnaphthalene (**4**), benzocycloheptene (**5**), and benzocycloheptadiene (**6**). The formation of naphthalene was shown not to involve extrusion of methylene, even though in the presence of benzene toluene was produced, but did involve free radicals. Initiation by di-*tert*-butyl nitroxide at 300° produced naphthalene and, in the presence of benzene, toluene. It was also shown that the thermal rearrangement of tropilidene (**11**) to produce benzene gives methylnaphthalene when naphthalene is present. Di-*tert*-butyl nitroxide also was a good initiator for this free radical reaction and, when it was run at 300°, 1,2-benzotropilidene was a product. The observation that bitropyl produced products similar to tropilidene or tropilidene plus nitroxide suggests the tropyl radical is involved. By analogy, the benzotropyl radical is implicated in the benzotropilidene reaction. The free radicals (**9** and **10**) produced by the addition of the benzyl radical to naphthalene and by the α-naphthylmethyl radical to benzene were shown not to be intermediates in the reaction of benzotropilidene with benzene to produce naphthalene and toluene. As a result of these data the mechanism shown in Scheme I is postulated for the above reactions. The central feature of this mechanistic pathway is the reversible reaction shown in reaction 1.

Our interest in the thermal hydrogen rearrangement reactions of benzotropilidenes[3,4] has led us to discover a heretofore unrecognized reaction of 1,2-benzotropilidene. As we recently reported[5] the pyrolysis (gas phase, evacuated Pyrex ampoule) of 1,2-benzotropilidene (**1**) at 410° results in the formation of naphthalene (**2**, 14% relative, 12% absolute), 2-methylnaphthalene (**3**, 18% relative), 1-methylnaphthalene (**4**, 50% relative), benzocycloheptene (**5**, ca. 1% relative), and 1,2-benzocyclohepta-1,3-diene (**6**, 17% relative).[6] In addition, low voltage mass spectroscopic analysis of the crude pyrolysate indicated an ion at *m/e* 156 corresponding to $C_{12}H_{12}$.

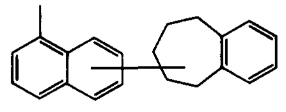


Product identification was straightforward. Naphthalene, the methylnaphthalenes, and benzocycloheptene were compared spectrally to authentic samples. The low voltage mass spectrum of **6**[7] showed the parent at *m/e* 144 and the NMR spectrum showed the following resonances which were consistent with **6**: τ 8.11 (m, 2, CH_2), 7.75 (m, 2, CH_2), 7.24 (m, 2, CH_2), 4.16 (dt, 1, J = 12.5 and 4 Hz, $-CH{=}CHCH_2-$), 3.50 (dt, 1, J = 12.5 and 2 Hz, Ar-$CH{=}CH$), and 2.82 (m, 4, ArH). In addition, the reduction of benzotropylium fluoborate with lithium aluminum hydride produced some **6** among the products.[8,9]

Control experiments demonstrated that the methylnaphthalenes were not converted to naphthalene under the reaction conditions.

We also looked for dimers among the products by heating a 200 mg sample at 360° for 2 hr and chromatographing the pyrolysate over alumina. A yellow oil (34 mg) was obtained (after the monomeric fraction had been eluted) which could not be crystallized. The NMR spectrum of this material was consistent with a "dimer", more properly a dihydrodimer or mixture of isomeric dihydrodimers of methylnaphthalene and benzocycloheptene: τ 2.1–3.1 (m, 10, Ar-H), 6.9–8.8 (m, 9, CH_2 and CH), and 7.4 ppm (s, 3, CH_3Ar). In addition the uv spectrum resembled that of naphthalene: uv max [$(C_2H_5)_2O$] 222 (log ε 4.08), 258

(3.52), 264 (3.51), 284 (3.37), 295 (3.25), and 345 nm (2.83). The mass spectrum showed a small parent at *m/e* 286 consistent with $C_{22}H_{22}$. A general structure for the dihydrodimer or mixture of dihydrodimers is shown below.



When **1** was heated in the presence of a fivefold excess of benzene at 400° there was formed, in addition to compounds **2–6**, a small amount (ca. 0.2% total, 1.5% of the naphthalene) of toluene.[10] In a high-pressure gas-phase reaction at 360° for 24 hr using a fivefold molar excess of benzene (evacuated, heavy-walled Pyrex ampoule, where the initial liquid volume was one-third of the total available volume) the distribution of major products was **2**, 17%; **3**, 16%; **4**, 17%; and **5**, 51%. Significantly, the amount of toluene formed was increased to 0.6 and 4% of the naphthalene produced. When common free-radical inhibitors such as diphenylamine and 2,6-di-*tert*-butyl-4-hydroxymethylphenol were used there was no apparent change in the quantities of naphthalene or toluene produced.

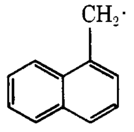
Since the effectiveness of these inhibitors at 400° is questionable, there remain the possibilities that the conversion of **1** to **2** is either a methylene extrusion reaction or a free-radical reaction. The extrusion of free methylene was eliminated by the following observations. When heated (420°) in the presence of excess cyclohexane, **1** produced no (less than 0.005% under conditions where the toluene yield was 0.2%) methylcyclohexane. Control experiments demonstrated the stability of methylcyclohexane under the reaction conditions. In addition, when **1** was heated (high pressure; Pyrex ampoule; 360° for 24 hr) with a fivefold molar excess of benzene-d_6 the major toluene product was toluene-d_5 as determined by VLC and low-voltage mass spectroscopy. Free methylene transfer to benzene-d_6 would have given toluene-d_6 either directly by C–H insertion or by rearrangement of the intermediate tropilidene-d_6.[10] A control experiment, heating toluene-α,α,α-d_3 under the reaction conditions, indicated that no deuterium was lost from the molecule and none rearranged into the aromatic ring.

The free-radical nature of the rearrangement was supported by the observation that when the pyrolysis was carried out with increasing pressures of **1** the amount of hydrogenated benzotropilidenes (**5** and **6**) increased while the yield of methylnaphthalenes (**3** and **4**) decreased accordingly. Hydrogenated products are well known in static pyrolyses[12] and these products are usually free radical in origin. In addition, the formation of naphthalene closely paralleled the production of the hydrogenerated products.

The generalized formula for the dihydrodimer presented above is also consistent with free-radical intermediates in that, since **4** and **5** are the major products, it is not unreasonable to speculate that a benzocycloheptenyl radical could attack α-methylnaphthalene. The resulting product would be the indicated dihydrodimer.

When the pyrolysis of **1** was carried out in the presence of di-*tert*-butyl nitroxide,[13] a compound which presumably is a source of initiating radicals at elevated temperatures,[14] the amount of naphthalene formed increased substantially, while the methylnaphthalene production was essentially unaltered. More significantly, when the reaction was carried out in excess benzene at 300°, toluene was formed to the extent of 0.67% (6% of the naphthalene produced) compared to no toluene formation (i.e., less than 0.005%) under the same conditions without added nitroxide. Thus the mechanism of the conversion of 1,2-benzotropilidene (**1**) to naphthalene (**2**) is free radical in character.

Of the many free-radical mechanisms which can be postulated we were able to rule out those involving 1-naphthylmethyl (**7**) and benzyl (**8**) radicals along with radicals **9** and **10**. This will be discussed later.



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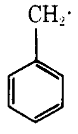

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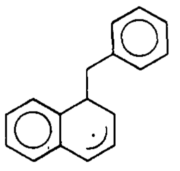

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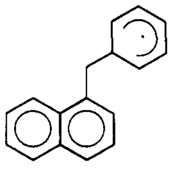

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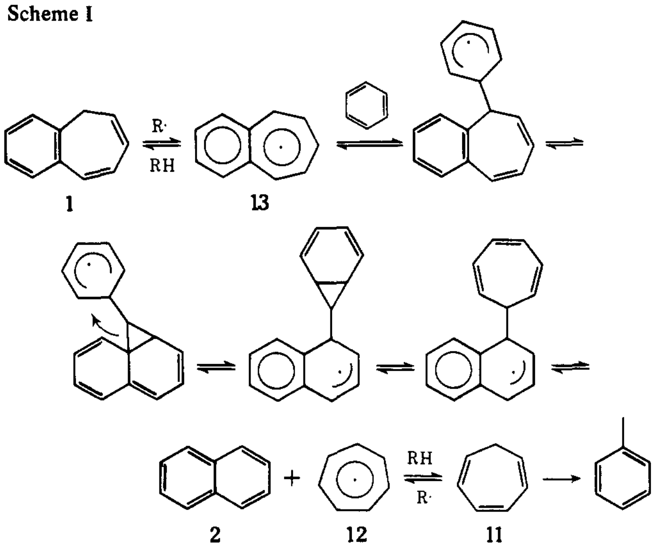
The mechanism we wish to postulate for the reaction is shown in Scheme I. The reversible nature of the reaction follows from the observation that tropilidene **11** behaves very similar to benzotropilidene upon heating. At 405° tropilidene (**11**) produced the expected toluene[11,15] (89%), 8% of recovered starting material, and 3% of benzene. A control experiment showed that the source of benzene was not toluene. This result is very similar to that observed by Woods[11] who postulated a dimerization–fragmentation sequence to explain the benzene.[16]

Scheme I



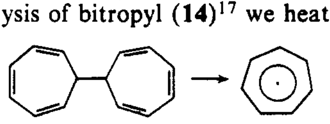
To see if benzene formation here was similar to naphthalene production from **1** the pyrolysis (390°, 2 hr) was conducted in the presence of naphthalene in an attempt to trap the "CH_2" fragment. One of the products was shown to be α-methylnaphthalene by its VLC retention time on three different columns. In addition, mass spectroscopic analysis of the crude pyrolysate showed no ions corresponding to benzylnaphthalene (*m/e* 218) or dinaphthylmethane (*m/e* 268), thus ruling out radicals **7**, **8**, **9**, and **10** as possible intermediates (vide infra).

The similarity between the thermal conversion of tropilidene (**11**) to benzene and of benzotropilidene (**1**) to naphthalene was further substantiated by heating **11** at 295° for 2 hr along with naphthalene both with and without added di-*tert*-butyl nitroxide. The sample without nitroxide revealed no product formation other than a small amount of toluene, whereas the sample with nitroxide showed some (ca. 1% of the initial tropilidene) 1,2-benzotropilidene by VLC and NMR analysis. Only trace amounts of the methylnaphthalenes were observed. Thus it appears as though the primary product of the reaction of tropilidene and naphthalene in the presence of nitroxide is benzotropilidene and this in turn produces the methylnaphthalenes at higher temperatures.[3] An appropriate control experiment demonstrated that naphthalene and di-*tert*-butyl nitroxide, when heated together, do not produce 1,2-benzotropilidene or the methylnaphthalenes.

It should also be pointed out that a mass spectrum of the 390° pyrolysate revealed no ions corresponding to benzylnaphthalene (*m/e* 218) or dinaphthylmethane (*m/e* 268). Thus, in this reaction also, benzyl (**8**) and α-naphthylmethyl radicals (**7**) are eliminated as intermediates.

From the above data it can be seen that the benzotropilidene plus benzene reaction and the tropilidene plus naphthalene reaction are the reverse of one another. One problem is that we have not been able to obtain the seven-membered ring product, tropilidene, from the benzotropilidene plus benzene reaction. Even at 300° toluene is the only C_7 product observed. It is known, however, that tropilidene rearranges to toluene at 300°.[11]

To further elucidate and prove the mechanism in Scheme I we were able to show that the tropyl radical **12** is indeed involved and that, by analogy, the benzotropyl radical **13** is implicated. Since the tropyl radical (**12**) is very readily produced by pyrolysis of bitropyl (**14**)[17] we heated bitropyl by itself at 410° for 1 hr. VLC analysis showed the volatile products (up to C_8) were toluene (72% relative), benzene (19%), and xylene (9%) in addition to a trace of ethylbenzene. There was also a substantial amount of bibenzyl produced.[17] When bitropyl (**14**) was heated for 1 hr at 410° in excess naphthalene, 1- and 2-methylnaphthalene were detected among the products by VLC on three different columns. In addition, a mass spectrum of this pyrolystate showed no ions corresponding to either benzylnaphthalene or dinaphthylmethane which, once again, rules out the intermediacy of benzyl and naphthylmethyl radicals.



14 **12**

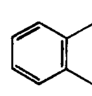
When the above reaction was conducted at 300° for 3 hr, 1,2-benzotropilidene was formed at the expense of the methylnaphthalenes. Thus, once again, the primary product appears to be benzotropilidene which, at 400°, is converted to the more thermodynamically stable methylnaphthalenes.

Since bitropyl (**14**) decomposition is an unambiguous source of tropyl radicals and **14** gives the same reaction as tropilidene it therefore seems reasonable that tropyl radicals are involved in the "methylene transfer" reaction. Thus the reaction of tropilidene with di-*tert*-butyl nitroxide to produce benzene involves the conversion of **11** to the radical **12**.

As a further mechanistic proof we attempted to prepare the benzotropyl radical **13**. This of course was independent of its preparation (by analogy) from 1,2-benzotropilidene and di-*tert*-butyl nitroxide. We first attempted to prepare bis(1,2-benzotropyl) in a manner similar to that which was done for bitropyl.[17] Reaction of benzotropylium fluoborate with zinc dust failed to produce the expected dimer. The only observable product of this reaction was a small yield (ca. 10%) of the reduction product 1,2-benzotropilidene. The tarry residue was shown by TLC not to contain any dimers.

A second synthetic attempt was based on the formation of bitropyl by the reaction of manganese pentacarbonyl anion with tropylium fluoborate.[18] Reaction of benzotropylium fluoborate with sodium pentacarbonylmanganate (−I) produced ca. 25% yield of 1,2-benzotropilidine along with 85% of dimanganese decacarbonyl. The residue was shown by TLC not to contain any dimers.

A further attempt to prepare the benzotropyl radical by disrotatory ring opening of 2,3-benzonorcaradien-7-yl radical (**15**) also did not prove successful.[19,20]



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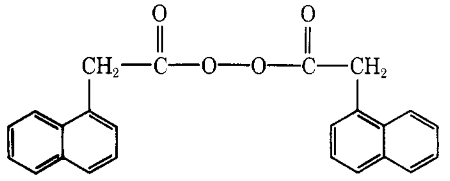
Thus, since we were unable to prepare **13** by a route other than by reaction of **1** with di-*tert*-butyl nitroxide or by pyrolysis of **1**, our conclusion about the mechanism relies upon the analogous tropyl-tropilidene system.

As proof for the assertion that radicals **7**, **8**, **9**, and **10** are not involved in the benzotropilidene plus benzene reaction we prepared them independently and showed that they gave different products. When bis(1-naphthylacetyl) peroxide (**16**) was heated at 300° for 1.25 hr in benzene neither toluene nor naphthalene were produced. The major product was α-methylnaphthalene; there was no β-methylnaphthalene. Analysis of the reaction mixture by VLC showed the presence of some 1-benzylnaphthalene. The trapping efficiency of the radical is low since benzene is not a very efficient radical trap and **7** is a relatively stable radical. We also used the azo compound **17**[21] as a precursor for radical **7**. This azo compound (**17**) was prepared from the azine **18**[22] by partial hydrogenation in acetic acid using Adam's catalyst at 3 atm H_2 pressure. Identification of **17** rests on its NMR and mass spectra. NMR ($CDCl_3$) τ 1.8–2.8 (m, 14, Ar*H*) and 4.5 ppm (s, 4, ArC*H*$_2$). The mass spectrum showed the parent at *m/e* 310 ($C_{22}H_{18}N_2$) and the base peak at *m/e* 141 corresponding to the α-naphthylmethyl cation, $C_{11}H_9$. In addition there was a significant peak (13.8% of the base peak) at *m/e* 282 corresponding to P − 28 (P − N_2).



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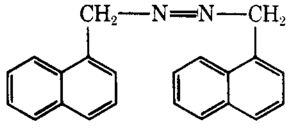

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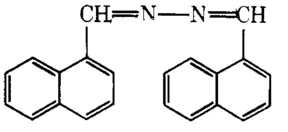

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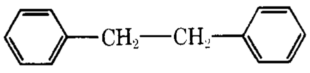
The results of the thermal decomposition of **17** were essentially the same as from **16**, namely some benzylnaphthalene was produced when benzene was present. The major product was α-methylnaphthalene and there was a small amount of the dimer of **7** as indicated by the mass spectrum (*m/e* 282). No toluene was produced from benzene but VLC showed a trace of naphthalene.

Since α-benzylnaphthalene was not observed as a product from benzotropilidene (**1**) pyrolyses in the presence of benzene, radicals **7** and **10** are eliminated as possible intermediates. In addition, careful analysis of the pyrolysate indicated no trace of diphenylmethane. This observation coupled with the absence of benzylnaphthalene argues against the benzyl radical as the precursor of toluene. We also decomposed bis(phenylacetyl) peroxide (**19**)[23] in the presence of naphthalene and obtained bibenzyl (**20**) (ca. 10% yield) and 1- and 2-benzylnaphthalene (ca. 3% yield) in a 2:1 ratio. There was no benzene, tropilidene, or methylnaphthalenes



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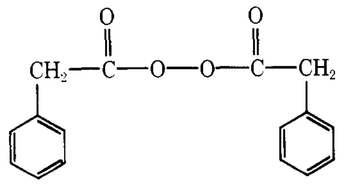

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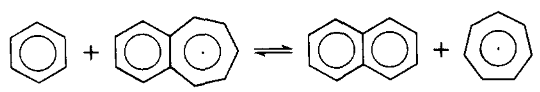
formed in this reaction and thus radical **9** (along with **8**) is eliminated as an intermediate.

One final observation which would also tend to rule out simple methylene extrusion is the mass spectrum. It is well known that many mass spectral fragmentation reactions have analogy in thermal and photochemical reactions. The spectrum of VLC purified 1,2-benzotropilidene (**1**) showed no peak (<1% of the parent ion) at the parent minus CH_2 (P − CH_2) at *m/e* 128.

In conclusion, the evidence favors the mechanism shown in Scheme I for the reaction of benzotropilidene with benzene to produce toluene and naphthalene and for the reaction of tropilidene with naphthalene to produce benzene and benzotropilidene. The central feature of the mechanism can be formulated as



(1)

which, it should be pointed out, is a C–H group transfer rather than the originally postulated CH_2 group transfer.

Experimental Section

General. Melting and boiling points are uncorrected. Relative yields based on VLC peak areas are not corrected for thermal conductivity differences. Vapor phase chromatography was done with either a Varian 1200 flame ionization instrument or a Matronic 500 dual column, thermal conductivity instrument using the following columns: (A) 15 ft × 0.25 in. column packed with 20% Carbowax, 20 *M* on 60–80 mesh Chromosorb P; (B) 5 ft × 0.25 in. column packed with 10% Carbowax, 20 *M* on 60–80 Chromosorb P; (C) 7 ft × 0.25 in. column packed with 10% DC 710 silicone oil on 45–60 Chromosorb P; (D) 7 ft. × 0.125 in. column packed with 15% DC 710 silicone oil on 60–80 mesh Chromosorb P; (E) 7 ft × 0.125 in. column packed with 10% Morflex 510 (triisodecyl trimellitate) on 45–60 mesh Chromosorb P; (F) 5 ft × 0.25 in. column packed with 20% SE-30 silicone rubber on 60–80 mesh Chromosorb P; (G) 5 ft × 0.25 in. column packed with 10% Apiezon L on 60–80 mesh Chromosorb P.

Nuclear magnetic resonance spectra were obtained on a Varian A-60-A high-resolution spectrometer with 5–25% solutions in CCl_4 containing tetramethylsilane as internal standard. Infrared spectra were obtained on either a Perkin-Elmer 700 or 467 spectrometer. Ultraviolet spectra were recorded on either a Cary 15 or Perkin-Elmer 402 spectrometer. Mass spectra were obtained on either a Du Pont 21-492 or a JEOL-07 mass spectrometer.

General Procedure for Static Pyrolysis Reactions. Two basic types of reaction vessels were used. Gas-phase reactions were carried out in Pyrex ampoules of wall thickness 1 mm, inside diameter 6 mm, and volumes of ca. 5 ml, except where otherwise noted. High-pressure gas-phase pyrolyses were performed in sealed Pyrex capillary tubes of wall thickness 3.5 mm, inside diameter 2 mm, and volumes of ca. 0.75 ml, except where otherwise noted. The vessels were washed with ammonium hydroxide, rinsed with water, and oven dried. After addition of the sample the ampoules were cooled in Dry Ice, evacuated to 10–25 Torr of pressure with an aspirator, and sealed. Pyrolyses were carried out in a combustion furnace and temperatures were monitored with a thermometer. After addition of the sample and an initial equilibration period of 5–10 min, the temperature could be maintained within 3–5°. After heating for the required amount of time, the ampoule was removed from the oven and cooled in Dry Ice so that the sample condensed in one end. After complete cooling the ampoule was opened and the sample removed.

Extended Pyrolysis of 1,2-Benzotropilidene (1). In a typical reaction 0.5 g of 1,2-benzotropilidene[24] was sealed in a 30-ml ampoule and heated at 410° for 1 hr. The products and their relative yields were: naphthalene (**2**, 14%), 2-methylnaphthalene (**3**, 18%), 1-methylnaphthalene (**4**, 50%), benzocycloheptene (**5**, ca. 1%), and 1,2-benzocyclohepta-1,3-diene (**6**, 17%). The products were collected by preparative VLC (column A). Naphthalene and the methylnaphthalenes were identified by comparison of their VLC retention times and NMR spectra with those of authentic material. Benzocycloheptene was identified by comparison with its known[8] NMR spectrum: τ 8.25 (m, 6), 7.20 (m, 4), and 3.15 ppm (m, 4). 1,2-Benzo-1,3-cycloheptadiene was identified by its NMR spectrum: τ 8.11 (m, 2), 7.75 (m, 2), 7.24 (m, 2), 4.16 (dt, 1, J = 12.5 and 4 Hz), 3.50 (dt, 1, J = 12.5 and 2 Hz), and 2.82 ppm (m, 4). The assignment was confirmed when identical material was obtained as a minor product in the lithium aluminum hydride reduction of benzocycloheptatrienyl tetrafluoborate.[9]

A 200-mg sample of **1** was pyrolyzed in the gas phase at 360° for 2 hr. The pyrolysate was chromatographed on a 6 in. column of neutral alumina using a 3:1 mixture of petroleum ether to ether as the solvent. Analysis was by TLC and VLC (column B). The first fraction (66 mg) contained monomeric products, mostly methylnaphthalenes and benzocycloheptene. The second fraction (34 mg) consisted of a yellow oil. Further purification through recrystallization was unsuccessful. An NMR spectrum of this material was consistent with a dimer or a mixture of isomeric dimers of methylnaphthalene-benzocycloheptene: τ 2.1–3.1 (m, 10, ArH), 6.9–8.8 (m, 9, -CH_2-), and 7.4 ppm (s, 3, CH_3); uv max [$(C_2H_5)_2O$] 222 (log ϵ 4.08), 258 (3.52), 264 (3.51), 284 (3.37), 295 (3.25), and 345 nm (2.83). A mass spectrum of this fraction introduced through the solid inlet probe of the mass spectrometer (probe temperature 350°) indicated a small ion at *m/e* 286 corresponding to the dimer parent.

The third and final chromatography fraction of the pyrolysate (ca. 100 mg) consisted of tars and polymers.

Pyrolysis of 1,2-Benzotropilidene (1) in the Presence of Benzene. A sample of 50 mg of 1,2-benzotropilidene and 140 mg of benzene which had been purified by preparative VLC (column C) was sealed in a 50-ml ampoule and heated at 400° for 1 hr. Analysis by VLC (columns A, C, and D) revealed the presence of toluene in addition to the above-mentioned products. The toluene was identified by its VLC retention time (columns A, C, and D), its low-voltage mass spectrum (molecular ion at *m/e* 92), and comparison of its infrared spectrum with authentic toluene.

The above reaction was repeated on a smaller scale using 5-ml ampoules and varying the initial ratio of benzene to 1,2-benzotropilidene. No significant effect on the naphthalene formation was observed (VLC column A). Analysis of the low-boiling components (VLC column D) revealed that optimum toluene formation occurs with a 5 *M* excess of benzene.

High-Pressure Pyrolysis of 1,2-Benzotropilidene (1) with Benzene. In a Pyrex capillary ampoule (0.75 ml) was placed 0.20 ml of benzene and 0.05 ml of **1**. The sample was evacuated, sealed, and heated at 360° for 24 hr. Analysis by VLC (column A) revealed the following products: naphthalene (17%), benzocycloheptene (51%), 1-methylnaphthalene (17%), and 2-methylnaphthalene (16%). Further analysis (VLC column D) showed toluene formed in a total yield of 0.6%, representing 4.0% of the naphthalene produced.

Pyrolysis of 1,2-Benzotropilidene (1) and Benzene in the Presence of Radical Inhibitors. The previous reaction was repeated with the addition of a few milligrams of either diphenylamine or 2,6-di-*tert*-butyl-5-hydroxymethylphenol to the sample. Analysis (VLC columns A and D) revealed no change in the relative yields of naphthalene (15%) or toluene (0.6%).

Pyrolysis of 1,2-Benzotropilidene (1) with Cyclohexane. In a control run cyclohexane was sealed in a Pyrex ampoule and heated at 425° for 2 hr. Analysis (VLC column E) revealed no change in the starting material and no formation of methylcyclohexane. Methylcyclohexane was shown to be similarly stable under these conditions.

To a 300-ml Pyrex ampoule was added 0.20 g of 1,2-benzotropilidene (**1**) and 1.0 g of freshly distilled cyclohexane. The sample was heated for 3 hr at 420°. Analysis (VLC column E) revealed no methylcyclohexane. The limits of detection were calculated using a standardized solution of methylcyclohexane to be 0.005% or 50 ppm.

Pyrolysis of 1,2-Benzotropilidene (1) with Benzene-d_6. Three Pyrex capillary ampoules (vol. 1.65 ml each) were each filled with 0.45 ml of benzene-d_6 and 0.15 ml of 1,2-benzotropilidene (**1**). The samples were heated at 360° for 24 hr. The toluene peak on the VLC (column C) was collected as part of the tail of the benzene peak. Collections from all three pyrolyses were combined. They were shown by VLC to contain an approximately equal mixture of benzene and toluene. Mass spectral analysis at low voltage revealed the major toluene isomer to be toluene-d_5 (*m/e* 97). The relative abundance of deuterated isomers was d_0, 0%; d_1, 2%; d_2, 2%; d_3, 4%; d_4, 13%; d_5, 100%; and d_6, 15%.

In a 1-ml Pyrex capillary ampoule was placed 0.080 ml of **1** and 0.250 ml of benzene-d_6. The sample was heated at 360° for 21 hr. The following products were individually collected by VLC (column B); benzocycloheptene (**5**), naphthalene (**2**), and the methylnaphthalenes (**3** and **4**). Authentic samples of the above compounds were obtained and their mass spectra taken. The mass spectra of the pyrolysis products were similarly obtained. Comparison of intensities of P + 1 peaks with authentic samples yielded the following amounts of deuteration in the pyrolysis products: **5** (2% d_1), **2** (5% d_1), **3** and **4** (3% d_1).

Pyrolysis of Toluene-α,α,α-d_3. A 0.150-ml sample of VLC-purified toluene-α,α,α-d_3 (92% d_3)[25] was sealed in a Pyrex ampoule and heated at 400° for 2 hr. Analysis by NMR showed no scrambling (92% d_3) within experimental limits. A capillary tube of volume 2 ml was filled with 0.500 ml of benzene-d_6, 0.170 ml of 1,2-benzotropilidene (**1**), and 0.010 ml of pure toluene-α,α,α-d_3. The evacuated tube was heated at 360° for 24 hr and the VLC purified (column C) toluene was shown to be 89% d_3 by NMR analysis.

Pyrolysis of 1,2-Benzotropilidene (1) with Di-*tert*-butyl Nitroxide. A series of pyrolyses were carried out in Pyrex ampoules using varying amounts of 1,2-benzotropilidene (**1**) and di-*tert*-butyl nitroxide.[13] The samples were heated at 400° for 1 hr. Analysis was by VLC using column B. The optimum naphthalene formation was obtained using a fivefold excess of nitroxide.

Two Pyrex capillary ampoules were filled with 0.20 ml of benzene and 0.02 ml of 1,2-benzotropilidene (**1**) each. In addition, to one of the ampoules was added 0.10 ml of di-*tert*-butyl nitroxide. The samples were evacuated (15 Torr), sealed, and heated at 300° for 1.2 hr. Analysis by VLC (column D) revealed that the sample without the added nitroxide showed no toluene formation (i.e., less than 0.005%), but the nitroxide-containing sample formed toluene to the extent of 1200 ppm of the benzene or 0.67% of the starting material and 6% of the naphthalene formed. VLC analysis (column B) showed that without nitroxide 40% of the starting material (**1**) had disappeared while 95% of the benzotropilidene (**1**) had reacted in the presence of added nitroxide. The addition of nitroxide increased the naphthalene yield from 0 to 11%.

Control Pyrolyses with Di-*tert*-butyl Nitroxide. A sample of toluene was heated with di-*tert*-butyl nitroxide[13] at 400° for 1 hr. No benzene, xylene, or cycloheptatriene was observed (i.e., less than 0.005%) using VLC column D. A sample of purified 1-methylnaphthalene was heated with the nitroxide at 310° for 1 hr. No 2-methylnaphthalene or 1,2-benzotropilidene was observed as products (VLC column B) to a limit of 0.01%. A sample of benzene was heated with excess 1-methylnaphthalene and nitroxide at 400° for 1 hr. No toluene or cycloheptatriene was observed (VLC column D).

Pyrolysis of Cycloheptatriene (11). VLC purified (column C) cycloheptatriene (**11**) (0.15 ml) was heated in a Pyrex ampoule at 310° for 1 hr. VLC analysis (column C) revealed that less than 2% of the cycloheptatriene (**11**) had reacted. The products, formed in trace amounts, were toluene and benzene. A Pyrex ampoule containing 0.15 ml of **11** and 0.05 ml of di-*tert*-butyl nitroxide was heated at 310° for 0.75 hr. The product formation was as follows (VLC column D): 88% cycloheptatriene, 5% toluene, 7% benzene, and a trace amount of what is most likely a cycloheptadiene isomer.

To monitor absolute yields, the previous pyrolysis was carried out using cyclododecane[26] as an internal standard. After heating at 310° for 1 hr the reaction was 53% complete. The absolute yield of toluene was 0.3 mol % while that of benzene was 2.0 mol %. A trace amount of a compound whose VLC retention time (column F) matched that of bibenzyl was also found in the pyrolysate.

Pyrolysis of Cycloheptatriene with Naphthalene. A sample of cycloheptatriene (0.10 ml) was sealed in an ampoule with 200 mg of naphthalene and heated at 390° for 2 hr. The presence of 1-methylnaphthalene among the products was substantiated by its VLC retention time comparison with that of authentic material on three columns (B, C, and F). A mass spectrum of the pyrolysate revealed no ions corresponding to benzylnaphthalene (*m/e* 218) or dinaphthylmethane (*m/e* 268).

Two ampoules were each charged with 0.150 ml of cycloheptatriene (**11**) and 200 mg of naphthalene. In addition, 0.050 ml of di-*tert*-butyl nitroxide was added to one of the ampoules. The samples were sealed and heated at 295° for 2 hr. The sample without the added nitroxide showed no product formation other than some toluene. However, the nitroxide-containing sample was shown (VLC columns B, C, and F) to contain 1,2-benzotropilidene (ca. 1% of initial cycloheptatriene). A VLC collection of this peak and subsequent NMR analysis substantiated the presence of 1,2-benzotropilidene. Only trace amounts of methylnaphthalenes were observed in the VLC of the pyrolysate.

Pyrolysis of Bitropyl (14). A 20-mg sample of bitropyl prepared by the method of Dauben[17] was sealed in an ampoule and heated at 410° for 1 hr. Analysis of the lower molecular weight components (C_8 and less) was by VLC using column D. Products and their relative yields were: benzene (19%), toluene (72%), and xylenes (9%). The higher molecular weight products consisted mainly of bibenzyl.

When the above reaction was repeated in the presence of excess toluene, the benzene to xylene ratio in the product mixture remained the same. When the pyrolysis of bitropyl was performed in excess benzene, no diphenylmethane was observed as a product. When the reaction was carried out at 410° for 1 hr in excess (200 mg) naphthalene, the relative yields of the lower molecular weight products remained the same as they were without naphthalene. In addition, two small peaks (ca. 1% of the initial bitropyl) with the retention times of 1- and 2-methylnaphthalene were detected on columns B, C, and F. A mass spectrum of the crude product mixture revealed a small ion at *m/e* 141 corresponding to the benzotropyl cation produced from the methylnaphthalenes. No ions corresponding to either benzylnaphthalene (*m/e* 218) or dinaphthylmethane (*m/e* 268) were observed.

A 20-mg sample of bitropyl was heated at 300° for 3 hr in 200 mg of naphthalene. VLC analysis (columns B, C, and F) revealed a peak whose retention time matched that of 1,2-benzotropilidene (**1**). Collection of this peak and analysis by NMR substantiated that it was 1,2-benzotropilidene.

Attempted Preparation of 7,7′-Bis(1,2-benzotropyl). Dauben's synthesis of bitropyl[17] was followed in an attempt to prepare 7,7′-bis(1,2-benzotropyl) from benzotropylium tetrafluoborate.[27] A yellow oil was extracted from the zinc dust. Chromatography was over neutral alumina (6 in. column) with ether as the solvent. The first fraction contained 1,2-benzotropilidene (ca. 10%, VLC column B). Further elution did not result in any dimeric products. A tarry residue remained on the column. Anaysis of this material by TLC (alumina, with ether solvent) revealed that no dimers of R_f value similar to the dihydrodimer formed from pyrolysis of **1** were present.

A second attempt to prepare the bisbenzotropyl was based upon Whitesides' synthesis of bitropyl.[18] Benzotropylium tetrafluoborate[27] (0.45 g, 2 mmol) was dissolved in 25 ml of freshly distilled (from $LiAlH_4$) THF. The solution was cooled to −78° (acetone–Dry Ice bath) and 4 mmol of sodium pentacarbonylmanganate (−I)[28] in 10 ml of cold (−78°) THF was added. The mixture was stirred at −78° for 30 min. It was warmed to room temperature, concentrated under reduced pressure (rotary evaporator), and diluted with 150 ml of water. The solution was extracted with hexane (3 × 100 ml), dried ($MgSO_4$), and concentrated by rotary evaporator at reduced pressure to leave a yellow oil along with some yellow crystals. The crystals were separated and identified as manganese decacarbonyl (ca. 85%) by their melting and mixture melting points. The yellow oil was chromatographed over neutral alumina. The major organic material was 1,2-benzotropilidene (ca. 25%, VLC column B). No dimers were eluted. A brown-yellow residue remained on the column. It was shown by TLC (alumina, with ether as solvent) not to contain any dimers of R_f value similar to the dihydrodimer formed from pyrolysis of **1**.

Pyrolysis of Phenylacetylperoxide (19) in the Presence of Naphthalene. In a Pyrex capillary tube were placed 50 mg of naphthalene and 0.25 ml of a solution of phenylacetyl peroxide (**19**) in toluene prepared by the method of Bartlett.[23] Temperatures were kept below −20°. The tube was sealed and heated for 2 hr at 300°. Analysis of the pyrolysate by VLC (columns C, D, and F) revealed no formation of benzene, cycloheptatriene, xylene, or methylnaphthalenes. The major combination product was found to be bibenzyl (ca. 10% absolute). A significant amount (ca. 3% absolute) of 1- and 2-benzylnaphthalene in a 67:33 ratio was also formed.

An authentic sample of 1-benzylnaphthalene (50 mg) was heated in an evacuated Pyrex ampoule at 360° for 24 hr. VLC analysis showed only ca. 10% formation of 2-benzylnaphthalene. A sample of 1-benzylnaphthalene (50 mg) was heated at 300° for 24 hr in the presence of 0.10 ml of di-*tert*-butyl nitroxide. Analysis by VLC (columns C, D, and F) revealed no formation of benzene, toluene, or methylnaphthalene. Naphthalene was formed in less than 1% yield. Isomerization to 2-benzylnaphthalene (ca. 10%) was observed.

Bis(1-naphthylacetyl) Peroxide (16). In a 250-ml round-bottomed flask equipped with a magnetic stirrer and a reflux condenser with drying tube was placed 25 g (0.15 mol) of 1-naphthylacetic acid dissolved in 150 ml of benzene. To this was added 20 ml of thionyl chloride and six drops of pyridine. The mixture was stirred at 45° for 5 hr. Low-boiling materials were removed by reduced pressure distillation (aspirator) through a Dry Ice-2-propanol trap. The residue was distilled at 0.2 Torr through a 6 in. Vigreux column to afford 20.1 g (91% of theoretical) of 1-naphthylacetyl chloride: bp 116° (0.2 Torr) (lit.[29] bp 167° (10 Torr)); ir (neat film) 1780 cm^{-1} ($C{=}O$); NMR (CCl_4) τ 2.6 (m, 7, ArH) and 5.8 ppm (s, 2, CH_2).

To a 125-ml Erlenmeyer flask immersed in an ice-salt bath and equipped with a magnetic stirrer was added 12.6 g (0.034 mol) of the above acid chloride. To this was added 7.5 ml of 30% hydrogen peroxide followed by a cold solution of 7.0 g (0.17 mol) of NaOH in 50 ml of water. The mixture was stirred and shaken for a few minutes while kept in the bath. Cold benzene (40 ml) was added and the stirring was continued for ca. 5 min while in the bath. The liquid mixture was allowed to settle, and the benzene layer (yellow-green) was decanted and cooled in Dry Ice.

Pyrolysis of Bis(1-naphthylacetyl) Peroxide (16). A Pyrex capillary tube containing 0.25 ml of the benzene solution of the peroxide, **16**, was heated at 300° for 1.25 hr. Analysis by VLC (columns C, D, and E) showed benzene and 1-methylnaphthalene as the only low molecular weight components present. Analysis for higher molecular weight substances (columns F and G) revealed the presence of a trace amount of 1-benzylnaphthalene by comparison with the retention time of an authentic sample. No other components were observed. When a sample of **16** in benzene was allowed to decompose at room temperature overnight a white precipitate was formed. Filtration and spectral analysis showed this to be the 1-methylnaphthyl ester of α-naphthylacetic acid: mp 98-101°; ir (CCl_4) 1720 cm^{-1} ($C{=}O$); NMR (CCl_4) τ 2.8 (m, 14, ArH), 4.9 (s, 2, CH_2O), and 6.4 ppm (s, 2, CH_2CO).

Azobis(1-naphthylmethane) (17).[21] 1-Naphthaldazine (**18**)[22] was prepared by the method of Cohen and Wang[30] as a yellow powder, mp 151-153°. To a solution of **18** (8 g, 0.026 mol) in 100 ml of glacial acetic acid was added platinum oxide (ca. 0.1 g) and the mixture was hydrogenated in a Parr shaker at 3.06 atm for 2 hr. Hydrogen uptake was 0.024 mol, 92% of theoretical, and the solution had turned colorless. Acetic acid was removed by reduced pressure distillation. The residue was washed with water, taken up in hexane, and recrystallized to yield a tan powder, mp 122-125°. Further recrystallization from petroleum ether afforded white crystals: mp 124-125° dec; yield 0.3 g, 1 mmol (4% of theoretical). The infrared spectrum showed a complete absence of absorption in the 3400-3500 cm^{-1} region indicating that none of the hydrazine was present. The NMR spectrum ($CDCl_3$) 1.8-2.8 (m, 14, ArH) and 4.5 ppm (s, 4, $ArCH_2N{=}$) was consistent with the bisazo structure. In addition when the NMR sample was shaken with a few milliliters of D_2O, the signal at 4.5 ppm disappeared indicating a facile exchange of the 1-methylnaphthyl protons. The major ions in the mass spectrum (70 eV) were: *m/e* (rel intensity) 312 (0.3), 311 (2.0), 310 (6.8), 282 (13.8), 142 (15.8), 141 (100.0), and 28 (1.4); P + 1 (24.5), P + 2 (4.5), calculated values 24.8 and 2.95, respectively.

Pyrolysis of Azobis(1-naphthylmethane) (17). A 20-mg sample of the azo compound (**17**) and 0.20 ml of benzene were sealed in a Pyrex ampoule and heated at 300° for 24 hr. Analysis by VLC showed no toluene (column D) to the limits of detection, ca. 0.005%. The major product, 1-methylnaphthalene (**4**), and a trace amount of naphthalene (**2**) were detected on column B. A small amount (ca. 1% of the 1-methylnaphthalene) of benzylnaphthalene was detected on column G.

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References and Notes

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(2) (a) Alfred P. Sloan Foundation Research Fellow: (b) this work was taken from the Ph.D. Thesis of A. S. Ross, Yeshiva University, New York, N.Y., 1974; NSF Trainee 1969–1970; NDEA Graduate Fellow, 1971–1972.

(3) M. Pomerantz and G. W. Gruber, *J. Org. Chem.*, **33,** 4501 (1968).

(4) G. W. Gruber and M. Pomerantz, *Tetrahedron Lett.*, 3755 (1970).

(5) M. Pomerantz, A. S. Ross, and G. W. Gruber, *J. Am. Chem. Soc.*, **94,** 1403 (1972).

(6) In one run a compound tentatively identified as 1,2-benzocyclohepta-1,4-diene was isolated.

(7) R. Huisgen and G. Seidl, *Chem. Ber.*, **97,** 2730 (1963).

(8) G. W. Gruber, Ph.D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1970.

(9) M. Pomerantz and A. S. Ross, unpublished observations.

(10) If tropilidene were a product it would be expected to be rapidly converted to toluene under the reaction conditions.[11]

(11) W. G. Woods, *J. Org. Chem.*, **23,** 110 (1958).

(12) S. W. Benson and A. Shaw, *J. Am. Chem. Soc.*, **89,** 5351 (1967).

(13) R. Briere and A. Rassat, *Bull. Soc. Chim. Fr.*, 378 (1965).

(14) Di-*tert*-butyl nitroxide disproportionates above 125°: A. K. Hoffmann, A. Feldman, E. Gelblum, and W. Hodgson, *J. Am. Chem. Soc.*, **86,** 639, 646 (1964).

(15) W. C. Herndon and L. L. Lowry, *J. Am. Chem. Soc.*, **86,** 1922 (1964), and references cited therein.

(16) Other reports of benzene or derivatives produced in small amounts from tropilidene pyrolyses are: K. W. Egger, *J. Am. Chem. Soc.*, **90,** 6 (1968); O. Nefedow, N. Nowizkaja, and A. I. Waschenko, *Justus Liebigs Ann. Chem.*, **707,** 217 (1967); A. P. TerBorg, E. Razenberg, and K. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **85,** 774 (1966).

(17) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82,** 5593 (1960).

(18) T. H. Whitesides and R. A. Budnik, *Chem. Commun.*, 1514 (1971); T. H. Whitesides, private communication.

(19) Studies on the 2,3-benzonorcaradien-7-yl radical (**15**) will be reported in a subsequent publication; M. Pomerantz, A. S. Ross, and S. Lichtiger, unpublished results.

(20) For a similar system see: A. Barmetler, C. Rüchardt, R. Sustmann, S. Sustmann, and R. Verhülsdonk, *Tetrahedron Lett.*, 4389 (1974).

(21) We wish to thank Mr. Rakesh Jain for the preparation of compound **9**.

(22) M. L. Rousset, *Bull. Soc. Chim. Fr.*, **17,** 304 (1897).

(23) P. D. Bartlett and J. E. Leffler, *J. Am. Chem. Soc.*, **72,** 3030 (1950).

(24) For the preparation of 1,2-benzotropilidene see: M. Pomerantz and G. W. Gruber, *Org. Photochem. Synth.*, **1,** 23 (1971).

(25) C. Renaud and J. Leitch, *Can. J. Chem.*, **34,** 98 (1956).

(26) A control experiment demonstrated that cyclododecane is stable under the reaction conditions.

(27) D. J. Bertelli and W. J. Rossiter, *Tetrahedron*, **24,** 609 (1968).

(28) R. B. King, *Organomet. Syn.*, **1,** 149 (1965).

(29) D. Libermann, J. Himbert, and L. Hengl, *Bull. Soc. Chim. Fr.*, 486 (1950).

(30) S. Cohen and C. Wang, *J. Am. Chem. Soc.*, **77,** 2457 (1955).