The above data clearly show that branched-chain alkynes exhibit much less complicated fragmentation behavior than their straight-chain isomers. The major decomposition modes are processes of low activation energy, such as the McLafferty rearrangement and β fission. The *tert*-butyl group in particular exerts an anchoring effect suppressing isomerization of the molecular ion to a high degree.

Experimental Section

The mass spectra were determined on a AEI MS-9 instrument using the heated inlet system with a source temperature of 200°. All ionizing voltages quoted are nominal values. The repeller voltages ranged between +3 to 5 V and the accelerating voltage amounted to 8000 V.

The alkynes[23] and their deuterated analogs were prepared in 70–95% yield by reacting the appropriate terminal acetylene (Farchan Research Laboratories, Willoughby, Ohio) with an alkyl halide. A typical detailed procedure follows.

To an ice-cold solution of hept-1-yne (0.1 mol) in hexamethylphosphoramide (0.75 ml, distilled from 13X molecular sieves) was added dropwise a solution of *n*-butyllithium in hexane (0.35 ml of 2.67 *M* solution). The ice bath was removed and the mixture was stirred for 5 min at ambient temperature. The ice bath was then replaced, and *n*-propyl bromide (0.077 ml) was added. After stirring at room temperature for 30 min, the mixture was poured into 1 *N* HCl (20 ml). Pentane (5 ml) was added, and the organic layer separated, washed with aqueous $NaHCO_3$ and water, and dried. Removal of the solvent was followed by vpc purification (20% Apiezon or 15% SE 30 on Chromosorb W) to give dec-4-yne.

---

(23) We thank Dr. Michele Rudler for the preparation of the unlabeled straight-chain compounds.

Reactions of *N*-Phenyl-2-naphthylamino Radicals[1]

R. F. Bridger

Contribution from the Mobil Research and Development Corporation,
Central Research Division Laboratory, Princeton, New Jersey 08540.
Received May 7, 1971

Abstract: The thermal decomposition of 1,4-diphenyl-1,4-(2-naphthyl)-2-tetrazene (**1**) ($\Delta H^{\ddagger}$ = 24.8 kcal/mol, $\Delta S^{\ddagger}$ = 0.7 eu in benzene) produces *N*-phenyl-2-naphthylamino radicals (A·). The major products are the carbon–carbon (**3**) and carbon–nitrogen (**4**) dimers of A·, with *N*-phenyl-2-naphthylamine (**2**) and 7-phenyldibenzo[*c,g*]carbazole (**5**) formed as minor products. No stable diarylamino radicals are detectable in the reaction mixture by electron resonance spectroscopy. Surprisingly facile hydrogen transfer reactions occur between A· and a variety of hydrocarbons. Hydrogen transfer reactions of A· with hydroperoxides, hindered phenols, thiols, phosphines, amines, and aldehydes are also described. The data show *N*-phenyl-2-naphthylamino radicals to be considerably more reactive than generally believed. The results are discussed in the context of amine inhibition of hydrocarbon autoxidations.

Diarylamino radicals are of significant historical interest to organic chemistry. The diphenylamino radical was erroneously reported[2] as one of the earliest examples of a stable organic free radical. This claim stood unchallenged for nearly 50 years. Musso[3] demonstrated that diphenylamino radicals disproportionate rapidly at 90° to a mixture of oligomers and diphenylamine. Neugebauer and Fischer[4] showed that the diphenylamino radical could not be observed by esr during decomposition of the hydrazine over a range of temperatures. Stable diarylamino radicals could be observed, however, if the reactive para positions were blocked by electron donating substituents, in agreement with the classic series of papers by Wieland and coworkers.[5]

Despite the voluminous literature on carbon-centered radicals, knowledge of nitrogen-centered radicals is surprisingly meager, and even the most rudimentary reactions of diarylamino radicals have been attended by a good deal of confusion. Various reports[6-10] of hydrogen transfer reactions by the diphenylamino radical are of questionable significance because earlier workers assumed the amino radicals to be stable in solution or were unaware of the extensive disproportionation reaction, which produces about 50% yield of the apparent hydrogen abstraction product, diphenylamine.[11]

The absence of a comprehensive study of diarylamino radicals has prompted us to investigate the reactions of the *N*-phenyl-2-naphthylamino radical. This radical is uniquely suited for such a study because of its low degree of disproportionation and its well-defined coupling products.[12,13]

---

(1) Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March–April, 1971.

(2) H. Wieland, *Justus Liebigs Ann. Chem.*, 381, 200 (1911).

(3) H. Musso, *Chem. Ber.*, **92**, 2881 (1959).

(4) (a) F. A. Neugebauer and P. H. H. Fischer, *ibid.*, **98**, 844 (1965). (b) The spectrum of the short-lived diphenylamino radical was recently resolved during photolysis of the hydrazine in a flow system: F. A. Neugebauer and S. Bamberger, *Angew. Chem.*, 83, 47 (1971).

(5) An excellent review is given by A. R. Forrester, J. M. Hay, and R. H. Thompson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968, Chapter 3.

(6) T. J. Wallace, J. J. Mahon, and J. M. Kelliher, *Nature* (*London*), **206**, 709 (1965).

(7) R. A. Jackson and W. A. Waters, *J. Chem. Soc.*, 4632 (1958).

(8) P. F. Holt and B. P. Hughes, *ibid.*, 1320 (1955).

(9) H. Low and P. Tavs, *Tetrahedron Lett.*, 1357 (1966).

(10) V. D. Pokhodenko and V. A. Bidzilya, *Teor. Eksp. Khim.*, **2**, 234 (1966).

(11) For more recent studies of the disproportionation of diarylamino radicals confirming the results of ref 3, see (a) P. Welzel, *Chem. Ber.*, 103, 1318 (1970); (b) K. M. Johnston, G. H. Williams, and H. J. Williams, *J. Chem. Soc., B*, 1114 (1966); (c) F. A. Neugebauer and H. Fischer, *Chem. Ber.*, 104, 886 (1971).

(12) R. F. Bridger, D. A. Law, D. F. Bowman, B. S. Middleton, and K. U. Ingold, *J. Org. Chem.*, 33, 4329 (1968).

(13) R. F. Bridger, *ibid.*, **35**, 1746 (1970).

Because of the importance of the *N*-arylnaphthylamines as antioxidants,[14] many of the results will be interpreted in the context of reactions involved in the inhibition of hydrocarbon autoxidation[15]

$$\text{initiator} \xrightarrow{2ek_1} 2R\cdot \qquad (1)$$

$$R\cdot + O_2 \xrightarrow{k_2} RO_2\cdot \qquad (2)$$

$$RO_2\cdot + RH \xrightarrow{k_3} RO_2H + R\cdot \qquad (3)$$

$$2RO_2\cdot \xrightarrow{k_4} O_2 + \text{inert products} \qquad (4)$$

$$RO_2\cdot + AH \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} RO_2H + A\cdot \qquad (5)$$

$$A\cdot + RO_2\cdot \xrightarrow{k_6} \text{inert products} \qquad (6)$$

$$2A\cdot \xrightarrow{k_7} \text{inert products} \qquad (7)$$

$$A\cdot + RH \xrightarrow{k_8} AH + R\cdot \qquad (8)$$

where RH is hydrocarbon, RO_2H is hydroperoxide, and AH is the inhibitor, *N*-phenyl-2-naphthylamine.

Results and Discussion

Kinetics and Products of the Thermal Decomposition of 1,4-Diphenyl-1,4-di(2-naphthyl)-2-tetrazene (1). Rates of nitrogen evolution from the tetrazene were determined manometrically. Specific rate constants, *k*, were taken from the slopes of ln $[V_\infty/(V_\infty - V)]$ *vs.* time. All runs gave good first-order plots, and *k* was independent of the initial tetrazene concentration as seen in Table I, which summarizes data obtained in benzene. There was no evidence of induced decomposition in the concentration range 0.01–0.08 *M*. The tetrazene does, however, undergo an acid-catalyzed decomposition which has not yet been studied in detail. For this reason solvents for decomposition studies, which might have acidic impurities, were treated with base and distilled prior to use.

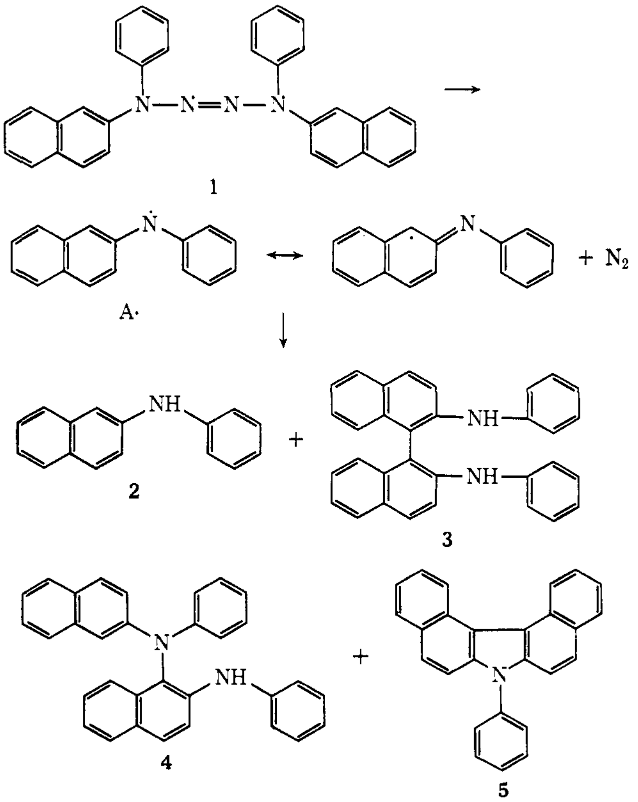
Table I. Kinetics of Thermal Decomposition of 1,4-Diphenyl-1,4-di(2-naphthyl)-2-tetrazene in Benzene

Concn, *M*	Temp, °C	$k \times 10^5$ sec^{-1}	Concn, *M*	Temp, °C	$k \times 10^5$ sec^{-1}
0.01	60	58.3	(Av)	60	57.4
0.02	60	57.7	0.05	40	4.70
0.03	60	57.5	0.05	50	17.3
0.05	60	54.3	0.05	70	170
0.08	60	59.3			

Activation parameters for the homolysis were determined from an Eyring plot, resulting in $\Delta H^{\ddagger}$ of 24.8 kcal/mol and $\Delta S^{\ddagger}$ of 0.7 eu. Comparable data for other tetrazene decompositions are surprisingly sparse. Nelsen and Heath[16] recently reported kinetic data for 1,4-diphenyl-1,4-dimethyl-2-tetrazene, which yielded 34 kcal/mol for $\Delta H^{\ddagger}$ and 10 eu for $\Delta S^{\ddagger}$. Comparison of the two systems indicates a lowering of $\Delta H^{\ddagger}$ by about 9 kcal/mol is effected by replacement of the two methyl groups by 2-naphthyl groups, but this is attended by a decrease of 9 eu in $\Delta S^{\ddagger}$. This suggests that weakening of the nitrogen–nitrogen bond by 2-naphthyl participation requires a relatively high degree of order in the transition state for homolysis. This is consistent with a required conformation in which the nitrogen–nitrogen bond being broken is approximately perpendicular to the naphthyl system, providing maximum overlap between the incipient unpaired electron and the aromatic system. Nelsen and Heath[16] have discussed this aspect of tetrazene decomposition in detail, and have presented substituent effects illustrating the importance of lone pair *vs.* single electron delocalization on $\Delta S^{\ddagger}$. The effects of increased aromatic substitution of tetrazenes are qualitatively similar to those obtained for thermal decompositions of substituted azomethanes, but the lowering of $\Delta H^{\ddagger}$ in the present instance is surprisingly small, and the decrease in $\Delta S^{\ddagger}$ with increased aromatic participation is greater than expected. Nelsen and Bartlett[17] have shown that symmetrical replacement of two methyl groups in azo compounds by phenyl groups lowers $\Delta H^{\ddagger}$ by 13–15 kcal/mol and $\Delta S^{\ddagger}$ by 5–7 eu. Although our results in part reflect the diminishing effect of introducing a second aromatic substituent,[18] they agree with Nelsen's observation[16] that aromatic substitution is less effective in tetrazenes than in azo compounds.

The products of the thermal decomposition of tetrazene **1** are *N*-phenyl-2-naphthylamine (**2**), 1,1′-bis(*N*-phenyl-2-naphthylamine) (**3**), *N*-(2-naphthyl)-*N*,*N*′-diphenyl-1,2-naphthylenediamine (**4**), and 7-phenyldibenzo[*c*,*g*]carbazole (**5**), as shown in Scheme I. The

Scheme I



---

[14] G. Scott, "Atmospheric Oxidation and Antioxidants," Elsevier, New York, N. Y., 1965.

[15] L. R. Mahoney, *Angew. Chem., Int. Ed. Engl.*, 8, 547 (1969).

[16] S. F. Nelsen and D. H. Heath, *J. Amer. Chem. Soc.*, 91, 6452 (1969).

[17] S. F. Nelsen and P. D. Bartlett, *ibid.*, 88, 137 (1966).

[18] (a) H. Zollinger, "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds," Interscience, New York, N. Y., 1961, Chapter 12; (b) G. C. Overberger, J.-P. Anselme, and J. G. Lombardino, "Organic Compounds with Nitrogen–Nitrogen Bonds," Ronald Press, New York, N. Y., 1966, pp 32 ff.

same products have been isolated from the coupling of *N*-phenyl-2-naphthylamino radicals generated by reactions of **2** with potassium permanganate[12,13] or peroxy radicals.[19] Compounds **2**, **3**, and **4** were isolated and identified by comparison with authentic specimens.[12] Carbazole **5** was identified by its R_f value on the thin-layer chromatogram (tlc) and its highly characteristic ultraviolet spectrum.[20] No stable free radicals were detected by electron spin resonance spectroscopy of freshly decomposed solutions of **1** or of solutions heated in the esr cavity.

There was no evidence for the formation of a stable tetrasubstituted hydrazine. The infrared spectra[21] of freshly decomposed solutions of **1** gave N–H absorptions which agreed well with tlc analyses of decompositions which were carried out at 60° for 5 and 10 half-lives. This agrees with recently published results[13] which compared the permanganate oxidation of **2** with the photolysis of **1** at 0–5°. In neither case was there any evidence for a stable tetraarylhydrazine. Welzel[22] recently published similar findings for di-2-naphthylamino radicals derived from thermolysis of the nitrosamine. These results contrast strongly with the well-known chemistry of tetraphenylhydrazine, which is not only isolable,[2,23] but has an extrapolated[24] half-life of 8.6 hr at 60°. If a hydrazine of comparable stability were formed from the thermolysis of **1** it should be readily detectable.

The yields of the products arising from decomposition of **1** in benzene under various conditions are summarized in Table II. Yields were independent of temperature and initial concentration of **1**. The ratio (**3**:**4**) of the major coupling products was constant at 1.20 for all reaction conditions. The minor products were constant with **2** being formed in 6% yield, while **5** was about 1% in all experiments. The invariance of yields with temperature suggests that the overall activation energies for product formation are nearly equal in all cases. Nelsen and Bartlett[17] have reported the activation energies for disproportionation and combination of the cumyl radical to be similar, and have pointed out that this observation is generally true for most alkyl radicals.

Table II. Effects of Temperature and Concentration on Products of Thermal Decomposition of 1,4-Diphenyl-1,4-di(2-naphthyl)-2-tetrazene in Benzene

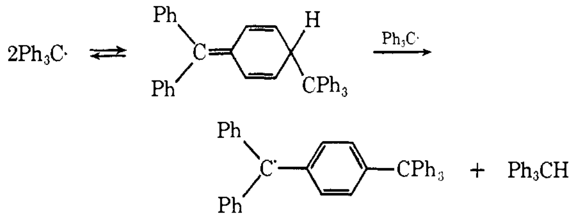
Concn, *M*	Temp, °C	% yield **2**[a]	**3**[b]	**4**[b]	**5**[b]
0.01	60	6.1	42.9	36.1	1.0
0.02	60	5.9	44.7	37.2	1.6
0.05	60	6.2	43.3	37.1	1.3
0.08	60	6.0	43.6	34.8	1.3
0.05	40	5.7	46.1	39.4	1.2
0.05	50	6.2	43.1	36.0	1.0
0.05	70	6.1	41.5	34.3	1.0

[a] Mol per 50 mol of **1**. [b] Mol per 100 mol of **1**.

The formation of **3** and **4** may be regarded as arising from carbon–carbon and carbon–nitrogen coupling of the *N*-phenyl-2-naphthylamino radicals produced upon thermolysis of tetrazene **1**. The sources of **2** and **5** are not as obvious, however. While **2** is regarded as a disproportionation product, **5** is not, because its formation does not parallel that of **2**. The origins of these products are discussed in the next section.

Effects of Solvent and Oxygen on the Decomposition of 1. Decompositions of tetrazene **1** in various solvents are summarized in Table III. During most runs, the rate of nitrogen evolution was monitored to ensure that the decomposition was first order and that no induced or catalytic decomposition was taking place. The ratio of yields of coupling products (**3**:**4**) was the same in all hydrocarbon solvents. In polar solvents the relative yields of **3** were slightly enhanced, raising the ratio of **3**:**4** to 1.3–1.6. Carbazole **5** formation was slightly enhanced in polar solvents, but the increase in **5** was dramatic in polyhalomethanes and ethers. Polar solvents which are poor hydrogen donors gave increased yields of **2**. This is not due to hydrogen transfer reactions with the solvents. It was shown earlier[13] by experiments with acetone and acetone-d_6 that **2** did not arise by hydrogen abstraction from the acetone. A similar run with acetonitrile-d_3 is included in Table III. Control experiments showed that **2** was not formed by reaction of A· with the products. Both **3** and **4** are hindered and undergo hydrogen transfer with free radicals an order of magnitude more slowly than **2** or other aromatic amines.[25]

The reactions leading to **2** are representative of disproportionation reactions occurring with a variety of radicals which are delocalized into an aromatic group. It has been known for some time that the triphenylmethyl radical disproportionates extensively to triphenylmethane.[26] More recently it was shown[27] that the dimer of the triphenylmethyl radical exists as 1-diphenylmethylene-4-tritylcyclohexa-2,5-diene. Such hydroaromatic intermediates are extremely reactive,[26b] and the hydrogen transfer reaction leading to the disproportionation product competes well with other reactions. Spectral evidence has been reported for an analogous quinoid dicumyl which is formed reversibly during photolysis of azocumene.[17]



(9)

The formation of **2** is attributed to hydrogen abstraction by A· from the initial coupling products (**6**, **8**) prior to aromatization as summarized in Scheme II. The effects of solvents on the formation of **2** are believed due to their net influence on the complex dis-

---

(19) D. F. Bowman, B. S. Middleton, and K. U. Ingold, *J. Org. Chem.*, 34, 3456 (1969).

(20) J. Rehner, Jr., F. W. Banes, and S. B. Robison, *J. Amer. Chem. Soc.*, 67, 605 (1945).

(21) See ref 12 for discussion of the infrared method.

(22) P. Welzel, *Chem. Ber.*, 104, 808 (1971).

(23) H. Wieland and S. Gambarjan, *ibid.*, 39, 1499 (1906).

(24) Calculated from the data of C. K. Cain and F. Y. Wiselogle, *J. Amer. Chem. Soc.*, 62, 1163 (1940).

(25) R. F. Bridger, *J. Org. Chem.*, 36, 1214 (1971).

(26) (a) D. H. Hey and J. Peters, *J. Chem. Soc.*, 79 (1960); (b) J. A. Kampmeier, R. P. Geer, A. J. Meskin, and R. M. D'Silva, *J. Amer. Chem. Soc.*, 88, 1257 (1966).

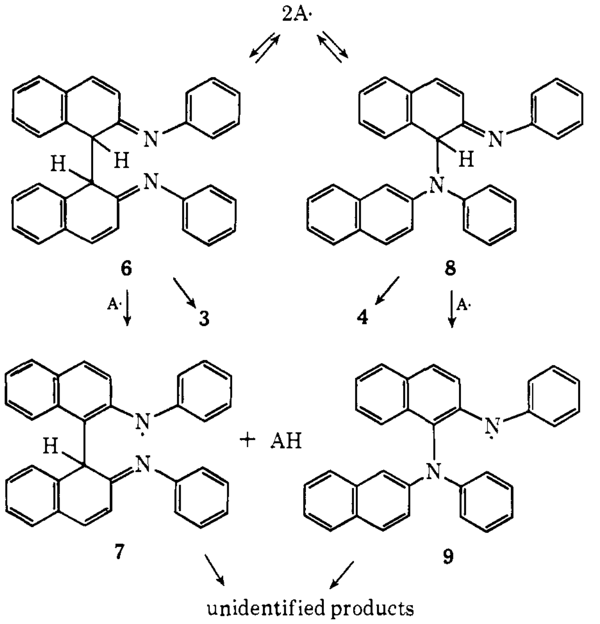
(27) (a) H. Lankamp, W. Th. Nauta, and C. MacLean, *Tetrahedron Lett.*, 249 (1968); (b) R. D. Guthrie and G. R. Weisman, *J. Chem. Soc. D*, 1316 (1969); (c) H. A. Staab, H. Brettschneider, and H. Brunner, *Chem. Ber.*, 103, 1101 (1970).

Table III. Effects of Solvents on Coupling of *N*-Phenyl-2-naphthylamino Radicals

Solvent	Temp, °C	k(solvent)[a]/ k(benzene)	Products, % yield[b] 2	3	4	5
Benzene	60	(1)	5.9	44.7	37.2	1.6
Styrene	60	1.02	5.6	40.8	37.8	1.3
Heptane	60	0.91	4.1	40.0	34.8	Trace
Acetonitrile	60	1.55	11.6	35.6	23.2	2.5
Acetonitrile-d_3	60		16.0	35.2	27.1	1.6
Acetone	40	1.10	15.2	33.3	25.4	2.8
Ethanol	60	1.19	9.3	33.8	24.4	1.7
Carbon tetrachloride	60	0.96	9.4	18.6	29.8	20.8
Chloroform	40	1.84	13.8	21.4	26.0	17.1
Methylene chloride	40		7.3	35.5	21.0	1.8
Carbon disulfide	40		5.9	23.7	27.7	4.5
Triethylamine	60	0.91	17.2	35.1	29.7	None
1,2-Dimethoxyethane	60	0.96	10.0	20.2	23.2	15.6[c]
1,2-Dimethoxyethane[d]	60		20.0	30.3	13.8	0.6
Tetrahydrofuran	60	0.91	11.2	21.5	29.7	13.2
N-Methylmorpholine	60		12.3	26.4	37.2	8.8
Methyl sulfide	60		8.5	25.8	35.5	5.4
Methyl disulfide	60		12.3	34.3	35.0	2.3

[a] Relative rates of nitrogen evolution, based on values in benzene at 40° ($4.70 \times 10^{-5}\ M^{-1}\ \text{sec}^{-1}$) and 60° ($57.4 \times 10^{-5}\ M^{-1}\ \text{sec}^{-1}$). [b] Yields of **2** are mol/50 mol of **1**; yields of **3-5** are mol/100 mol of **1**. [c] Aniline (10% yield) was detected by gas chromatography. [d] Contained adventitious hydroperoxide from autoxidation on storage; all other solvents were freshly distilled.

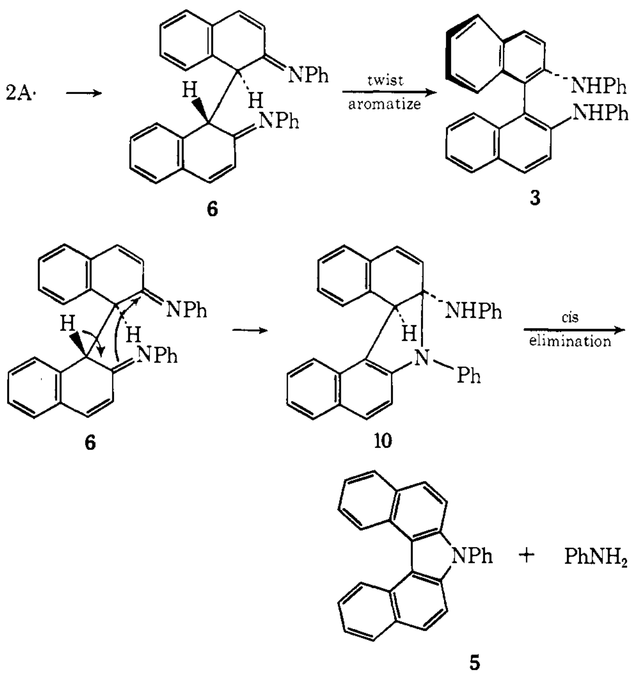
Scheme II



proportionation process which includes competitive reactions of coupling, decoupling, aromatization, and hydrogen abstraction. Hydrogen transfer reactions of A·, discussed below, show that reactions with compounds similar to the hydroaromatic intermediates occur with surprising ease. The fates of **7** and **9** are unknown, but it is likely they could further disproportionate *via* the benzene ring[3] or combine with other radicals. In general, increased production of **2** leads to decreased overall yields, as seen in Table III. Although **7** has the proper skeletal arrangement to be a precursor to **5**, it is difficult to conceive a reasonable mechanism for this conversion. Upon aromatization, **7** becomes an oxidation product of **3**. Control experiments[19] show that **5** cannot be produced by oxidation or hydrogen abstraction from **3**. The yields of **5** do not parallel those of **2** and are much smaller. Furthermore, the solvent effects enhancing **2** are fairly general to all polar solvents while solvents promoting **5** are quite specific.

These observations lead to the conclusion that the reactions leading to **5** are unrelated to the disproportionation. There is a close analogy for the formation of **5** in the thermal benzidine rearrangement of 2,2′-hydrazonaphthalene, which was studied in detail by Shine and Trisler.[28] As seen in Table III, enhancement of carbazole **5** occurs at the expense of **3**, suggesting that both have a common mechanistic precursor. Scheme III shows the initially formed hydroaromatic dimer **6** which can either aromatize to give **3**, or can undergo an internal displacement followed by extrusion of aniline to give **5**. The factors governing this competition are not well understood. Two classes of solvents, however (polyhalocarbons and ethers), strongly promoted formation of carbazole

Scheme III



---

(28) H. J. Shine and J. C. Trisler, *J. Amer. Chem. Soc.*, 82, 4054 (1960).

5. Decomposition of **1** in carbon tetrachloride or chloroform produced greatly enhanced yields of **5** and diminished amounts of **3**. This effect is independent of the source of A·, as shown by comparison of the potassium permanganate oxidation[29] of **2** in acetone and in acetone containing 2 *M* carbon tetrachloride. Addition of carbon tetrachloride to the permanganate oxidation raised the yield of **5** from 0.4 to 10.6%.

A rationale for the highly specific influence of the halocarbons may be offered by their ability to charge transfer with nitrogen compounds. Both chloroform and carbon tetrachloride readily form charge transfer complexes with amines.[30] Such interaction could assist in the elimination of the anilino moiety from intermediate **10** to give **5**.

The reasons for the high yields of **5** in ether solvents are not apparent. Their action cannot be similar to that of the halocarbons, as ethers are donors and the polyhalomethanes are acceptors.[31] Curiously the presence of hydroperoxides inhibits the formation of **5**, as shown with the experiment using aged 1,2-dimethoxymethane which had autoxidized on storage. The enhanced yield of **2** in this run is due to hydrogen transfer with hydroperoxide, which is discussed in a later section. Aliphatic amines suppress **5** formation entirely. This may reflect the tendency of bases to catalyze aromatization[27b] of **6**, but in the bifunctional solvent *N*-methylmorpholine the ether function was predominant, and a substantial quantity of carbazole **5** was formed (Table III).

One of the requirements for the kinetics treatment of inhibited autoxidations is that the radicals arising from the inhibitor be inert toward oxygen.[15] The data summarized in Table IV show that both the products and the kinetics of nitrogen evolution are unaffected when **1** is decomposed in the presence of oxygen, showing that the *N*-phenyl-2-naphthylamino radical does not react with molecular oxygen.

Table IV. Effect of Oxygen on Coupling of *N*-Phenyl-2-naphthylamino Radicals

Conditions[a] Temp, °C	Conditions[a] Atmosphere	Nitrogen evolution, $k \times 10^6$ sec^{-1}	Products, % yield: 2	3	4	5	Total
60	N_2	57.4	6.2	43.3	37.1	1.3	87.9
60	O_2	59.8	5.7	41.9	32.6	1.3	81.5
40	N_2	4.70	5.7	46.1	39.4	1.2	92.4
40	O_2	4.56	6.3	43.0	35.4	1.0	85.7

[a] 0.02 *M* **1** in benzene.

Hydrogen Transfer Reactions of *N*-Phenyl-2-naphthylamino Radicals with Hydrocarbons. The low degree of disproportionation and the absence of solvent effects in hydrocarbon solvents enables the use of **1** as a source of *N*-phenyl-2-naphthylamino radicals (A·) for a study of hydrogen transfer reactions with hydrocarbons. The reactions of interest are

$$A\cdot + RH \longrightarrow AH\ (\mathbf{2}) + R\cdot \qquad (8)$$

$$2A\cdot \longrightarrow \text{dimers}\ (\mathbf{3} + \mathbf{4}) \qquad (7)$$

$$2R\cdot \longrightarrow R\text{–}R \qquad (10)$$

$$R\cdot + A\cdot \longrightarrow R\text{–}A \qquad (11)$$

where RH is a hydrocarbon or other hydrogen donor.

In the presence of a large excess of RH the reversibility of reaction 8 can be neglected and the competition between reactions 7 and 8 should offer a measure of the reactivity of RH toward A·. Since these reactions are of different order in A·, however, a difficulty arises with the kinetics. In principle it is possible to obtain the ratio $k_8/k_7^{1/2}$ if the rates of reactions 7 and 8 can be measured as a function of time. This could not be accomplished because the presence of unreacted tetrazene interfered with the available analytical techniques. Only the yields after complete decomposition could be measured. The ratio of hydrogen transfer product to coupling products, **2**/(**3** + **4**), provides a semiquantitative measure of reactivity, however. This ratio will be considered a reactivity parameter in this discussion and the following sections, bearing in mind that it is not a legitimate kinetic parameter.

In Table V are summarized representative data for three olefins which represent high, low, and medium ranges of reactivity. Material balances range from about 80% for the less reactive olefins to about 100% for the highly reactive 1,4-cyclohexadiene. There was no evidence for cross-coupling (eq 11) with 1,4-cyclohexadiene. In the reaction with 1,4-pentadiene, tlc revealed an extra product with a uv spectrum similar to that of **2**. It seems likely that this is a product derived from reaction 11. The rates of nitrogen evolution from **1** were measured in 1,4-cyclohexadiene and several other hydrocarbons of varying reactivity. In all cases the decomposition of **1** was first order with no indications of induced decomposition.

Complete analyses were not feasible for all experiments because of the difficulties of removing excess hydrocarbon which interfered with the tlc determinations. In most cases the yield of **2** serves as a measure of reactivity, since the sum of **3** and **4** is approximately fixed by the material balance. The contribution of reaction 8 will be the difference between the observed yield and the background **2** formed in benzene.[32]

The yields of **2** are summarized in Table VI for a variety of hydrocarbons with bond dissociation energies ranging from 85 (toluene) to 74 kcal/mol (1,4-cyclohexadiene).[33] Unfortunately thermodynamic data are not available for most of the compounds in Table VI. Accurate kinetic data are available, however, for the propagation rate constant (k_3) for most hydrocarbons.[34] The comparisons of the yields of **2** with the values of k_3 which are made in Table VI show parallel trends in reactivity. Two notable exceptions are allylbenzene and cyclohexene, which are conspicuous in their low reactivity toward A·.

The first group of aralkyl hydrocarbons, with the exception of diphenylmethane, have negligible reac-

---

[29] It was shown in ref 13 that this reaction produces free *N*-phenyl-2-naphthylamino radicals.

[30] D. P. Stevenson and G. M. Coppinger, *J. Amer. Chem. Soc.*, **84**, 149 (1962).

[31] L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964.

[32] The background, or disproportionation **2**, may well not be constant. It should decrease as the hydrocarbon solvent becomes more reactive, as is apparent from the high overall yields for 1,4-cyclohexadiene in Table V.

[33] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

[34] J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **44**, 1113 (1966); (b) *ibid.*, **44**, 1119 (1966); (c) *ibid.*, **45**, 785 (1967); (d) *ibid.*, **45**, 793 (1967); (e) *ibid.*, **46**, 2661 (1968).

Table V. Decomposition of 1,4-Diphenyl-1,4-di(2-naphthyl)-2-tetrazene in Olefins

Olefin	Olefin concn, M	Temp, °C	% yield			Reactivity parameter
			2	**3**	**4**	**2**/(**3** + **4**)
1,4-Cyclohexadiene	10.6^a	40	89.1	2.2	6.3	10.5
1,4-Cyclohexadiene	10.6^a	60	90.0	2.2	7.8	9.0
1,4-Cyclohexadiene	6.36^b	60	90.3	2.4	7.7	8.9
1,4-Cyclohexadiene	2.12^b	60	82.6	4.9	10.7	5.3
1,4-Pentadiene	20.2^a	40	53.5	6.3	13.6^c	2.7
1,4-Pentadiene	20.2^a	60	46.6	11.9	10.6^c	2.1
1,4-Pentadiene	8.16^b	60	26.2	18.6	22.3	0.64
1,3-Pentadiene	*a*	60	11.7	31.6	36.1	0.17

[a] Neat; 0.02 M **1**. [b] Diluted with benzene. [c] An unidentified product of R_f 1.10 that of **4** was estimated to be in 5–7% yield, assuming an ϵ equal to that of **2**.

Table VI. Hydrogen Transfer Reactions of *N*-Phenyl-2-naphthylamino Radicals with Hydrocarbons at 60°

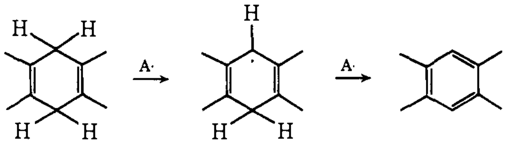
RH^a	**2** Yield^b	k_3,[c] M^{-1} sec^{-1}
Benzene	5.9	
Toluene	4.7	0.1^d
Ethylbenzene	6.4	0.5^d
Cumene	4.5	0.5^d
Diphenylmethane	13.9	2.1^d
Triphenylmethane (0.82 M)	5.5	
Indan	21.6	4.8^e
Tetralin	56.3	6.3^d
1,2-Dihydronaphthalene	60.3	104^e
1,4-Dihydronaphthalene	90.3	900^f
9,10-Dihydroanthracene (2.0 M)[i]	81.6	$240–350^d$
Indene	68.0	14^g
Allylbenzene	19.6	10^h
Cyclohexene	12.9	6.1^h
Cyclopentene	12.2	
1,3-Cyclohexadiene	68.5	220^e
1,3-Pentadiene (*cis–trans*)	11.7	
1,4-Cyclohexadiene	90.0	1400^f
1,4-Pentadiene	46.6	14^e
Cycloheptatriene	53.9	

[a] The pure hydrocarbon was used as solvent unless otherwise specified; concentrations indicate solution in benzene. [b] Mol per 50 mol of **1**; initial tetrazene concentration was 0.02 M. [c] Absolute rate constant at 30° for reaction 3; data of Howard and Ingold from references indicated. [d] Reference 34e. [e] Reference 34d. [f] Reference 34c. [g] Reference 34a. [h] Reference 34b. [i] Anthracene was formed in 41% yield.

tivities toward A· and values of k_3 of 0.5 M^{-1} sec^{-1} or less. Diphenylmethane gave a yield of **2** significantly greater than the background obtained in benzene. Triphenylmethane, despite its low bond dissociation energy (75 kcal/mol),[33] was unreactive for obvious steric reasons.

Aromatic hydrocarbons with fused cyclic alkyl substituents were considerably more reactive. This is presumably due to the locked conformation of the benzylic carbon–hydrogen bond, which makes it more readily accessible to the bulky *N*-phenyl-2-naphthylamino radical, and provides for maximum overlap of the incipient radical.[35] The requirement that the reacting carbon–hydrogen bond be nearly perpendicular to the benzene ring seems most important in hydrogen abstraction reactions of A·, and suggests a high degree of bond breaking in the transition state. Conformational requirements are not fulfilled in allylbenzene, which accounts for the low reactivity of its doubly activated methylene group.

The most reactive hydrocarbons are the derivatives of 1,4-cyclohexadiene which have doubly activated carbon–hydrogen bonds locked into the preferred conformation. Steric considerations appear to be of overwhelming importance in reactions of A·, as indicated by the negligible difference in temperature coefficients for 1,4-cyclohexadiene and 1,4-pentadiene (Table V). The difference in reactivity of these two olefins must be ascribed primarily to entropy factors. The driving force toward aromaticity also provides further activation for the hydroaromatic hydrocarbons, and in some cases the highly reactive intermediate radical may be contributing to the observed yield of **2**.



(12)

This does not occur to a major extent with 9,10-dihydroanthracene, which gave a yield of only 41% anthracene.

The results in Table VI reveal the *N*-phenyl-2-naphthylamino radical to be considerably more reactive than previously believed. While reaction 8 is recognized as a general problem with phenolic inhibitors,[15] it has been considered not to occur with naphthylamine inhibitors. Apparently many such hydrogen transfer reactions have remained undetected in inhibited autoxidations because of the subtleties of the kinetics. Bickel and Kooyman were the first to demonstrate kinetically the general occurrence of reaction 8 in phenolic inhibited hydrocarbon autoxidations.[36a] Their kinetic study of the inhibition of 9,10-dihydroanthracene autoxidation by **2**, however, indicated that reactions −5 and 8 did not occur with this inhibitor.[36b] Our results show that reaction 8 occurs extensively and competes well with the coupling reaction (eq 7). Since reaction 7 is the major termination event during inhibition by **2**,[19] reaction 8 must be significant for inhibited autoxidations of hydrocarbons which show definite reactivity in Table VI. For hydrocarbons less reactive than diphenylmethane it seems unlikely that reaction 8 occurs with diarylamine inhibitors.

While this manuscript was in preparation, Emanuel[37] and coworkers published an elegant kinetic anal-

---

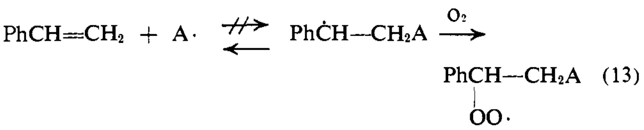
(35) J. A. Meyer, V. Stannet, and M. Szwarc, *J. Amer. Chem. Soc.*, **83**, 25 (1961).

(36) (a) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 2215 (1956); (b) *ibid.*, 2217 (1957).

(37) G. V. Karpuzhina, Z. K. Maizus, N. Ya. Meskina, and N. M. Emanuel, *Zh. Fiz. Khim.*, **44**, 1377 (1970).

ysis which suggests that reaction 8 is significant during inhibition of ethylbenzene by **2** at 60°. Unfortunately that work was done before product studies[19] showed the major termination event to be reaction 7 under the usual experimental conditions of kinetic experiments. In the ethylbenzene kinetics[37] termination was assumed to be exclusively *via* reaction 6, and reaction −5 was neglected.

Styrene is of special interest because the most extensive kinetic studies of amine inhibitors have been conducted with that hydrocarbon.[38] From the material balance of the decomposition of **1** in styrene shown in Table III it is apparent that no *N*-phenyl-2-naphthylamino radicals are lost through addition to the olefin. On the possibility that the addition was not observed because of a high degree of reversibility, decompositions of **1** in styrene were compared in nitrogen and oxygen. No significant difference was



$$PhCH{=}CH_2 + A\cdot \underset{\longleftarrow}{\not\longrightarrow} Ph\dot{C}H{-}CH_2A \xrightarrow{O_2} \begin{array}{l}PhCH{-}CH_2A \quad (13)\\ \;|\\ OO\cdot\end{array}$$

observed in either the products or kinetics of nitrogen evolution, indicating that no reaction occurred between A· and styrene. In both experiments all the styrene was removed unchanged by vacuum distillation at room temperature, and there was no evidence of polymer or polyperoxide. These results are in agreement with the kinetic experiments,[38] and confirm that initiation of autoxidation by diarylamino radicals does not occur with styrene.

Reactions with Hydroperoxides. Hydrogen transfer reactions from hydroperoxide to phenoxy radicals (reaction −5) are recognized as kinetically significant[15,39,40] during inhibited autoxidations and have been observed directly.[41] The occurrence of reaction −5 during autoxidations inhibited by **2** has been considered negligible by some experienced investigators,[36b,37] while others[38] have found its inclusion necessary to adequately describe the kinetics. It seemed desirable to demonstrate the hydrogen transfer from hydroperoxide to A· directly by a method independent of autoxidation kinetics.

Table VII. Reactions of *N*-Phenyl-2-naphthylamino Radicals with Tetralin Hydroperoxide at 60°

	Yield[a]			
Product	0.04 *M* ROOH	0.08 *M* ROOH	0.08 *M* ROOH[b] + H_2O	0.08 *M* ROOH[b] + D_2O
2	45.1	46.9	43.7	39.5
3	4.9	2.5	2.8	4.1
4	6.5	3.5	3.6	5.3
5	1.4	1.7	1.7	1.7
11	9.2	11.0	12.6	12.7
12	1.9	1.4	3.7	4.5
13	12.2	10.9	8.5	8.3
2/(**3** + **4**)	4.0	7.8	6.8	4.2

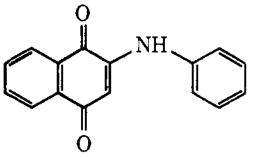
[a] Mol per 50 mol of **1** for **2** and **11**; mol per 100 mol for **3**, **4**, **5**, **12**, and **13**; initial concentration 0.02 *M* **1** in benzene. [b] Stirred reactor, 1 ml of D_2O or H_2O per 10 ml of benzene solution.

Table VIII. Reactions of *N*-Phenyl-2-naphthylamino Radicals with Cumene Hydroperoxide at 60°

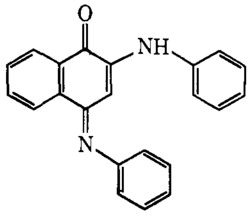
	Yield[a]			
Product	0.04 *M* ROOH	0.08 *M* ROOH	0.04 *M* ROOH[b] + H_2O	0.04 *M* ROOH[b] + D_2O
2	35.2	41.1	38.3	31.0
3	10.4	4.6	8.4	12.1
4	8.0	4.2	7.1	10.0
5	None	None	0.3	0.8
11	10.7	16.0	9.8	7.1
12	7.3	9.5	9.1	10.5
13	20.9	20.1	20.4	18.3
2/(**3** + **4**)	1.9	4.7	2.5	1.4

[a] Mol per 50 mol of **1** for **2** and **11**; mol per 100 mol for **3**, **4**, **5**, **12**, and **13**; initial concentration 0.02 *M* **1** in benzene. [b] Stirred reactor, 1 ml of D_2O or H_2O per 10 ml of benzene solution.

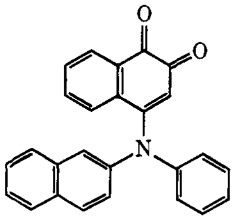
The products from the decomposition of **1** in benzene solutions of tetralin hydroperoxide and cumene hydroperoxide are shown in Tables VII and VIII. Control experiments confirmed that no reaction took place between **2** and either hydroperoxide. In addition to products **2–5** the quinoid products **11–13** were formed. These are termination products of A· which are formed in the presence of excess hydroperoxide, as first reported by Ingold and coworkers.[19]



11



12



13

The results in Tables VII and VIII demonstrate unambiguously that hydrogen abstraction reactions between *N*-phenyl-2-naphthylamino radicals and both hydroperoxides occur extensively. The ratio **2**/(**3** + **4**) is approximately twice as large for tetralin hydroperoxide as for cumene hydroperoxide. This is consistent with the observation of Mahoney and DaRooge[41] that k_{-5} for the 2,4,6-tri-*tert*-butylphenoxy radical is dependent upon the size of the hydrocarbon moiety of the hydroperoxide. In the present work this difference is probably reinforced by some induced decomposition[42] of the cumene hydroperoxide.

Brownlie and Ingold[38a] have determined from inhibition kinetics that reaction 5 exhibits a deuterium isotope effect of 3.0 when the inhibitor is **2**. Comparisons of runs in H_2O and D_2O in Tables VII and VIII

---

[38] (a) I. T. Brownlie and K. U. Ingold, *Can. J. Chem.*, **44**, 861 (1966); (b) *ibid.*, **45**, 2419, 2427 (1967).

[39] J. R. Thomas, *J. Amer. Chem. Soc.*, **85**, 2166 (1963); **86**, 4807 (1964).

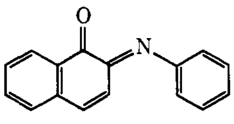
[40] J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **42**, 2324, 2724 (1964).

[41] L. R. Mahoney and M. A. DaRooge, *J. Amer. Chem. Soc.*, **92**, 4063 (1970).

[42] R. Hiatt, T. Mill, and F. R. Mayo, *J. Org. Chem.*, **33**, 1416 (1968), and references contained therein.

indicate a primary deuterium isotope effect in reaction −5, as required by the principle of microscopic reversibility. In both cases the ratio **2**/(**3** + **4**) is decreased by a factor of about 1.7 upon the introduction of deuterium.

Bowman, Middleton, and Ingold[19] isolated quinoid products **11–13** from the reaction of **2** with peroxy radicals from the cobalt-induced decomposition of a large excess of *tert*-butyl hydroperoxide. They postulated a mechanism involving initial formation of 1,2-naphthoquinone-2-anil (**14**) *via* attack of peroxy radicals at the α position of A·. Quinoid product **11** is formed by reaction of **14** with either hydroperoxide or peroxy radical. Products **12** and **13** were described[19] as mechanistically related, depending on several subsequent reactions with peroxy radicals. This predicts that the formation of **12** and **13** should exhibit an apparent kinetic order in peroxy radicals greater than that of **11**. Such a difference should be reflected in the change of relative yields of these products in going from tetralin hydroperoxide to cumene hydroperoxide, the tertiary hydroperoxide providing a larger effective concentration of peroxy radicals because of induced decomposition.[42] Comparison of Tables VII and VIII confirms that the relative yields of **12** and **13** increase substantially upon changing from a secondary to a tertiary hydroperoxide, in agreement with the mechanism postulated by Ingold and coworkers. The observation that the yield of **11** increases upon increasing hydroperoxide concentration, but not upon changing from secondary to tertiary hydroperoxide, indicates that **11** is formed by the reaction of **14** with hydroperoxide and not peroxy radicals.



14

Reactions with Various Hydrogen Donors. *N*-Phenyl-2-naphthylamino radicals were found to be reactive toward most common hydrogen donors. The results in Table IX summarize hydrogen transfer reactions with aromatic amines, hydrazines, thiols, and phosphines. In the reaction of A· with 1,2-diphenylhydrazine, an equivalent amount of azobenzene was formed.

$$2\mathrm{A}\cdot + \mathrm{PhNHNHPh} \longrightarrow 2\mathrm{AH} + \mathrm{PhN{=}NPh} \qquad (14)$$

Hexanal is considerably more reactive toward A· than benzaldehyde, as anticipated from the behavior of these aldehydes in other radical reactions.[43] The reaction with hexanal was accompanied by extensive decarbonylation as measured by the volume of gas evolution and confirmed by the mass spectrum of the evolved gas. Unidentified spots on the tlc indicated that some cross coupling took place. No decarbonylation occurred with benzaldehyde.

Table IX. Reactions of *N*-Phenyl-2-naphthylamino Radicals with Hydrogen Donors at 60°

Reactant[a]	AH, yield[b]
Aniline	65.9
Phenylhydrazine	70.9
Phenylhydroxylamine, 1 *M*	81.4
1,2-Diphenylhydrazine, 1 *M*	73.5[c]
Thiophenol	75.0
Methanethiol	58.2
Diphenylphosphine, 0.05 *M*	52.9
Diphenylphosphine, 0.5 *M*	77.8
Hexanal	61.6[d]
Benzaldehyde	27.4[e]
2,6-Di-*tert*-butyl-4-methylphenol, 1 *M*	93.1
2,4,6-Tri-*tert*-butylphenol, 1 *M* (inert atm)[f]	44.0
2,4,6-Tri-*tert*-butylphenol, 1 *M* (O_2 atm)[f,g]	80.4
Diphenylsilane	9.2
Triphenylsilane, 2 *M*	9.4
Diethylsilane	11.5
Triethylsilane	9.4

[a] Neat unless otherwise specified; concentrations indicate solution in benzene; 0.02 *M* **1**. [b] Mol per 50 mol of **1**. [c] Approximately 80% azobenzene was detected by tlc. [d] Carbon monoxide (62 mol per 50 mol of **1**) equivalent to the quantity of AH was evolved. [e] No decarbonylation was observed. [f] See text. [g] A molecule of oxygen was absorbed for each two phenoxy radicals formed.

The low reactivity of the substituted silanes in Table IX is noteworthy because it contrasts drastically with high reactivity of silanes toward carbon-centered radicals.[44,45] This cannot be attributed to steric hindrance because diphenylsilane is less reactive than its carbon analog (Table VI). Similarly, the steric requirements for diethylsilane and 1,4-pentadiene are equivalent, yet the silane is much less reactive. In the absence of a steric explanation, the results with silanes suggest that reactions of A· involve a substantial polar effect which creates an unfavorable partial positive charge on the silicon atom in the transition state for hydrogen abstraction.[46]

While phenol could not be investigated because of a direct reaction with the tetrazene, highly hindered phenols were found not to interfere with the kinetics of nitrogen evolution from the tetrazene thermolysis. The 2,6-di-*tert*-butylphenols were extremely reactive toward A·. This is consistent with the strain energy associated with the steric interaction of the *tert*-butyl groups with the hydroxyl function of 2,6-di-*tert*-butylphenol systems. This strain energy has been calculated from thermodynamic data to be 8 ± 2 kcal/mol.[47] The reaction of 0.02 *M* tetrazene with 1 *M* 2,6-di-*tert*-butyl-4-methylphenol at 60° yielded 93.1% AH.

The reactivity of 2,4,6-tri-*tert*-butylphenol appeared to be much lower in experiments done in an inert atmosphere (Table IX). This results from the reversibility of the hydrogen transfer reaction, and the great difference in the disproportionation rates of the two phenoxy radicals.[48] After 10 half-lives of the tetrazene at 60°, the 2,4,6-tri-*tert*-butylphenoxy radical was still present in substantial concentration as evi-

---

(43) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1963, pp 273–279.

(44) R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, **85**, 3754 (1963).

(45) J. Curtice, H. Gilman, and G. S. Hammond, *ibid.*, **79**, 4754 (1957).

(46) G. A. Russell, *ibid.*, 78, 1047 (1956).

(47) L. R. Mahoney, F. C. Ferris, and M. A. DaRooge, *ibid.*, **91**, 3883 (1969).

(48) (a) R. Stebbins and F. Sicilio, *Tetrahedron*, **26**, 291 (1970); (b) C. D. Cook and B. E. Norcross, *J. Amer. Chem. Soc.*, **81**, 1176 (1959); **78**, 3797 (1956); (c) E. Müller, R. Mayer, U. Heilmann, and K. Scheffler, *Justus Liebigs Ann. Chem.*, **645**, 66 (1961); (d) R. H. Bauer and G. M. Coppinger, *Tetrahedron*, **19**, 1202 (1963); (e) L. R. Mahoney and M. A. DaRooge, *J. Amer. Chem. Soc.*, **89**, 22 (1967).

denced by its visible spectrum. The color gradually faded as the phenoxy radical reacted with *N*-phenyl-2-naphthylamine. On the other hand, the 2,4-di-*tert*-butyl-4-methylphenoxy radical disproportionates[48] rapidly, and reversibility is not detected. From the second-order rate constant of Stebbins and Sicilio,[48a] the estimated half-life at 24° of a 10^{-3} *M* solution would be about 2 sec. In the presence of oxygen, the yield of AH from 2,4,6-tri-*tert*-butylphenol is nearly doubled as the reverse reaction is prevented by rapid scavenging of the phenoxy radicals by oxygen to form the peroxide which is stable at 60°.[49] As discussed earlier, A· is stable toward oxygen. The result in oxygen indicates that 2,4,6-tri-*tert*-butylphenol is only slightly less reactive than 2,6-di-*tert*-butyl-4-methylphenol, in agreement with kinetic data for reactions of peroxy radicals with these two phenols.[36a,50]

Experimental Section

Preparations of compounds **1–5** have been described.[12,13] Products **11–13** were gifts of K. U. Ingold of the National Research Council of Canada.[19] Analytical procedures have been published.[13,19] For the determination of small amounts of **3** in the presence of excess **2**, it was necessary to develop the thin layer chromatogram in a tank saturated with water vapor.

Acknowledgment. The author is grateful to Dr. K. U. Ingold for helpful discussions and for the disclosure of experimental results prior to publication.

---

(49) C. D. Cook and M. Fraser, *J. Org. Chem.*, **29**, 3716 (1964).

(50) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 2800 (1963).

Acid-Catalyzed Isomerization of 1,2-Bis(trimethylsilyl)benzene and Related Compounds

Dietmar Seyferth* and David L. White

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received July 24, 1971*

Abstract: When heated to about 152° in the presence of a few mole per cent of trifluoroacetic acid, 1,2-bis(trimethylsilyl)benzene isomerizes rapidly to a mixture containing mostly 1,3-bis(trimethylsilyl)benzene and a small amount of the 1,4 isomer. 1-Dimethylsilyl-2-trimethylsilylbenzene and 1,2-bis(dimethylsilyl)benzene undergo this isomerization as well, but to a much lesser extent. With 1-trimethylsilyl-2-trimethylgermylbenzene only 5% isomerization occurs, and 1,2-bis(trimethylgermyl)benzene isomerizes hardly at all. The rapid isomerization of 1,2-bis(trimethylsilyl)benzene is attributed to acceleration due to the steric strain resulting from nonbonded interactions between the two vicinal Me$_3$Si groups. The lack of isomerization of 1,2-bis(trimethylgermyl)benzene apparently is due to the consumption of the acidic catalyst in Ge–C bond cleavage at a rate faster than that of the isomerization reaction. A mechanism for the isomerization process is proposed which involves protonation of the benzene ring, silyl group migration in the protonated intermediate, and finally deprotonation. This appears to be an equilibrium process, but the isomerization rates of the 1,3 and 1,4 isomers are very much slower.

In previous work, we demonstrated that the formation of 1,3-bis(trimethylsilyl)benzene in the Diels–Alder reaction of α-pyrone with bis(trimethylsilyl)acetylene in bromobenzene in a sealed tube was due to isomerization of the initially formed 1,2-bis(trimethylsilyl)benzene by acidic impurities present in the reaction mixture.[1] The acids most likely involved were HBr (from bromobenzene pyrolysis during sealing of the tube) or H$_2$SO$_4$ (from an α-pyrone preparation step). Addition of triethylamine to the reaction mixture prevented the isomerization, and 1,2-bis(trimethylsilyl)benzene then was the sole product. Other experiments showed that catalytic amounts of trifluoroacetic or *p*-toluenesulfonic acids catalyzed the isomerization of 1,2-bis(trimethylsilyl)benzene as well. Since 1,2 shifts of silyl substituents on aromatic rings had not been described previously, we felt that reactions of this type merited further study.

Results and Discussion

The acid-catalyzed isomerization of 1,2-bis(trimethylsilyl)benzene was studied using 0.5 *M* benzene solutions of the silicon compound containing 2.3 or 5.0 mol % of trifluoroacetic acid. The samples were heated in sealed tubes for measured periods of time and then analyzed by gas–liquid partition chromatography (glc). Relative amounts of each isomer, as well as of trimethylphenylsilane (the product of acid desilylation), were determined. In addition, random samples were subjected to quantitative glc analysis to check the stoichiometry of the reaction. At room temperature the rate of isomerization was extremely slow (1% isomerization after 240 hr in the presence of 5 mol % CF$_3$COOH), and these isomerization experiments therefore were carried out at 152 ± 2°.

When 1,2-bis(trimethylsilyl)benzene was heated in benzene at 152° in the presence of 2.3 mol % CF$_3$COOH, its relative concentration fell exponentially to 2% in 48 hr. At the same time, the concentration of the 1,3 and 1,4 isomers rose to 93 and 5%, respectively. There was little further change with time (Figure 1). The effect of small amounts of trifluoroacetic acid on 1,3- and 1,4-bis(trimethylsilyl)benzene also was examined. The 1,3 isomer, under these conditions, rearranged only gradually to give (after 96 hr) a mixture containing 97% of the starting 1,3 compound and 3%

---

(1) D. Seyferth and D. L. White, *J. Organometal. Chem.*, **34**, 119 (1972).