

## ION RADICALS XIX. REACTIONS OF TRI-1-NAPHTHYLBORANE WITH SODIUM AND WATER\*

H. J. SHINE, L. D. HUGHES\*\* AND P. GESTING\*\*\*

*Department of Chemistry, Texas Tech University, Lubbock, Texas 79409 (U.S.A.)*

(Received February 26th, 1970)

### SUMMARY

Tri-1-naphthylborane (TNB) has been reduced to the anion radical ( $\text{TNB}^{\bullet-}$ ) by 1.5% sodium amalgam in dimethoxyethane (DME). The ESR spectrum consists of 14 poorly-resolved lines based on an  $^{11}\text{B}$  quartet of 7.2 G.  $\text{TNB}^{\bullet-}$  is stable in DME but not in hexamethylphosphoramide. Reduction of TNB by 40% amalgam and sodium metal proceeds to the dianion, and the dianion decomposes to produce, ultimately, the naphthalene anion radical. Reduction of TNB may be complicated by reactions of TNB with water and oxygen. TNB forms a complex with water, and the complex is not reduced by 1.5% amalgam. Therefore, attempts to prepare  $\text{TNB}^{\bullet-}$  in dilute solutions with this amalgam may be unsuccessful if the solvent is not well dried. TNB undergoes light-catalyzed reaction with oxygen and two of the products are 1,1'-binaphthyl and naphthalene. Consequently, reduction of TNB solutions which have been left standing in air may give the anion radical of 1,1'-binaphthyl ( $\text{BN}^{\bullet-}$ ) instead of  $\text{TNB}^{\bullet-}$ .  $\text{BN}^{\bullet-}$  is stable in DME solution, except in the presence of excess sodium, in which case decomposition (presumably via the dianion) occurs and the naphthalene anion radical is formed.

---

### INTRODUCTION

It has been well recognized that triarylboranes should be able to accept one or two electrons from a metal donor. Chemical, conductometric, and magnetic techniques have been employed in investigating these possibilities at infrequent intervals over the last 40 years. Early work by Krause<sup>2</sup> on the reactions of the alkali-metal adducts of triphenylborane with oxygen, iodine, and triphenylmethyl indicated that the adducts had the general formula  $\text{Ar}_3\text{BM}$ . During the period 1932–1935 Bent and Dorfman<sup>3,4</sup> used chemical and conductometric methods with triphenyl- and tri-1-naphthylborane (TNB). They found<sup>3</sup> that TNB formed a black disodium salt,  $\text{TNBNa}_2$ , which reacted with TNB to form the anion-radical salt,  $\text{TNBNa}$ .

---

\* For Part XVIII see ref. 1.

\*\* Post-doctoral fellow, 1968–1969.

\*\*\* Undergraduate research fellow, 1969.

These systems are well suited to study by magnetic techniques. Magnetic measurements were first made by Chu<sup>5</sup> on the sodium salt of triphenylborane (TPB), and later by Chu and Weismann<sup>6</sup> on the salts of trimesitylborane (TMB) and tris-[1-(2-methylnaphthyl)]borane (TMNB). Chu<sup>5</sup> used mostly magnetic susceptibility measurements, although ESR was used in the earliest stage of the work with TPB. Chu found that solutions of TPBNa were diamagnetic, and that solutions of TMBNa and TMNBNa were either paramagnetic or diamagnetic, depending on the solvent. The paramagnetic solutions were not characterized by ESR spectroscopy.

More recently, Moeller and Wilmarth<sup>7</sup> have investigated the reaction of sodium with TNB. Magnetic susceptibility measurements were made in this work, too. It was found that reaction with one equivalent of sodium gave paramagnetic TNBNa in green solutions, while an excess of sodium gave black solutions of diamagnetic TNBNa<sub>2</sub>. The solvent was tetrahydrofuran (THF). The UV and visible absorption maxima of TNBNa in THF were also reported.

There appear to be no reports in the published literature on the use of ESR in the present context other than those on TMBNa<sup>8-10</sup>. Van Willigen's dissertation<sup>11</sup>\* contains reports on TMBNa, TNBNa and similar salts of tri-2,4-xylenylborane and tri-*o*-biphenylborane. The ESR spectrum of TNB<sup>•-</sup> was reported to consist of four partly resolved broad lines, with a splitting of 8 G. Van Willigen also noted that prolonged contact of sodium with TNB gave the naphthalene anion radical<sup>11</sup>.

We have studied the reactions of sodium and sodium amalgam with TNB in dimethoxyethane (DME), THF, and hexamethylphosphoramide (HMPA). In the course of these studies it was also necessary to investigate the reaction of TNB with water, oxygen, and light.

## RESULTS

### *Reaction of TNB with sodium amalgam in DME*

Two amalgams were used. One of them contained 1.5% sodium, which gave a conveniently barely-mobile solid. The other contained 40% sodium, which was chosen to correspond with earlier usage<sup>3,4</sup>. Reactions were carried out in a sealed, all-glass apparatus after degassing.

Contact of the TNB solution with 1.5% amalgam slowly gave a green solution whose ESR spectrum (Fig. 1) consisted of 14 lines. The best resolution was obtained in the temperature range -35 to -50°. Use of lower concentrations did not improve the resolution. The spectrum had a *g*-value of 2.0028. The ESR spectrum is poorly resolved and is not amenable to complete analysis. The hyperfine pattern overlays a quartet of 7.2 G. We are confident that this is the spectrum of the TNB anion radical. Prolonged contact of the solution with 1.5% amalgam did not alter the spectrum, and the solution was stable indefinitely. The visible spectrum of TNB<sup>•-</sup> had maxima at 440, 470 and 630 nm, which correspond with those quoted by Moeller and Wilmarth<sup>7</sup>. After the conversion of TNB into TNB<sup>•-</sup> was complete, the addition of a second equivalent of sodium as a 1.5% amalgam caused no further change in the UV spectrum. Therefore, the anion radical appears to be stable toward 1.5% amalgam at room temperature.

\* We are grateful to Dr. Van Willigen for a gift of a copy of the dissertation.

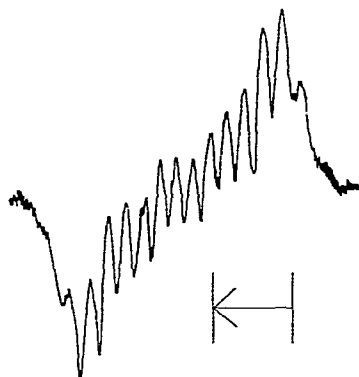


Fig. 1. ESR spectrum of the TNB anion radical in DME. The scale mark is 10 G and indicates the direction of increasing field.

Removal of the solvent from a green solution of TNBNa *in vacuo* left a dark brown solid. Replacement of the solvent regenerated the green solution.

Admission of dry air into a solution of TNBNa caused decolorization. Examination of the colorless solution by TLC showed only TNB to be present. When de-aerated water was added to a solution of TNBNa in an attempt to recover the TNB, and the solvent was evaporated, an oil was obtained which contained very little TNB. This result led to a study of the reaction of TNB with water whose results are given later.

When TNB in solution is brought into contact with amalgam the green color of TNBNa is seen immediately on the surface of the amalgam. The color disappears into the body of the solution and persists only after a period of time. A persistent color was obtained more quickly with 40% than with 1.5% amalgam. In further contrast also, prolonged contact with 40% amalgam caused the eventual disappearance of  $\text{TNB}^{\cdot-}$  and the formation of the naphthalene anion radical. The changes could be followed by ESR spectroscopy. Initially,  $\text{TNB}^{\cdot-}$  was formed in increasing concentrations over a period of about 4 h, after which the  $\text{TNB}^{\cdot-}$  spectrum became distorted and after 5 h completely replaced by that of the naphthalene anion radical. The latter remained unchanged indefinitely.

#### Reaction of TNB with sodium in DME

Contact between TNB in DME solution and a film of sodium led to the same sequence of results, but much more quickly, as those obtained with 40% amalgam. The initially formed TNBNa was stable provided it was kept out of contact with the sodium. Prolonged contact caused the formation of the naphthalene anion radical. When a solution of TNBNa was prepared with 1.5% amalgam and next placed over a sodium film the naphthalene anion radical was formed quickly. It is clear that the formation of the naphthalene anion radical occurs after the  $\text{TNB}^{\cdot-}$  has been formed, and most likely from the decomposition of  $\text{TNB}^{2-}$ . A solution which contains only the naphthalene anion radical is dark green. A DME solution of TNB which had been in long contact with sodium and which contained the naphthalene anion radical was dark grey. Admission of dry air to such a solution caused the disappearance of radicals. TLC examination showed at least 8 compounds, among which were TNB and naphthalene.

### *Reaction between TNB and sodium in THF*

TNB $\cdot^-$  formation was detected within 30 sec of contact time, and was complete within 2 min. Four min of contact caused the complete disappearance of the ESR signal, and the formation of a black suspension. The black suspension has been characterized<sup>7</sup> as TNBNa<sub>2</sub>. The black suspension appeared to be stable if left out of contact with sodium. However, when the suspension was left in contact for 24 h, a new spectrum was formed having 28 lines and appearance like that of the naphthalene anion radical-sodium ion pair<sup>12</sup>.

### *Reactions in HMPA solution*

Attempts to prepare TNBNa in HMPA solution were carried out with the hope of obtaining a minimum of ion pairing<sup>13</sup>. To our surprise we found that TNB $\cdot^-$  is quite unstable in HMPA. Sodium dissolves in HMPA, and after going through a sequence of color changes (yellow, gold, yellow-green), gives a blue solution whose single ESR line has been attributed to the solvated electron<sup>14</sup>. If the blue solution remains out of contact with sodium for several hours it becomes red and loses its ESR signal. Renewed contact with sodium regenerates the blue color and ESR signal.

When a solution of TNB in HMPA was similarly treated essentially the same sequence of color changes was observed except that the final color of the solution was green and the ESR spectrum was of the naphthalene anion radical. This solution was stable for several days. Further contact with sodium caused the disappearance of the anion radical and the formation of a blue solution. At no stage of the experiment was the TNB $\cdot^-$  detectable.

TNBNa was prepared in DME with the use of 1.5% amalgam. The DME was distilled off at room temperature and replaced by HMPA, to give a solution in which a fleeting green color gave way to brown. The brown solution was not paramagnetic.

### *Reaction of TNB with water*

TNB reacts with water in solvents that are thought to be dry. The reaction can be complicated because TNB will also react with oxygen and the reaction is affected by light. Consequently, if TNB is dissolved in a wet solvent without prior removal of air, and if the solution is exposed to the light, changes occur which can be followed by UV spectroscopy. The absorption maximum of TNB at 351 nm disappears and new bands appear in the region 260–300 nm. Until we were aware of the effect of light and oxygen, changes in this region varied with each experiment. A consistent pattern for the reaction of TNB with only water was obtained by using thoroughly degassed wet DME. The UV spectrum is shown in Fig. 2, and resembles closely the UV spectrum of the TNB $\cdot$ NH<sub>3</sub> complex prepared by other workers<sup>15</sup>. We believe that the spectrum in Fig. 2 is of the complex TNB $\cdot$ H<sub>2</sub>O. Once such a complex was formed in solution it would not give ESR signals when shaken with 1.5% amalgam.

Removal of DME solvent from the TNB $\cdot$ H<sub>2</sub>O complex *in vacuo* left a brown oil. The UV spectrum of a solution of the oil in degassed carbon tetrachloride had a strong TNB band at 351 nm. Further, TLC of the brown oil gave a TNB spot extending in a streak to the origin. These results suggest that the complex dissociated in dry solvent and also became dehydrated on the silica plate.

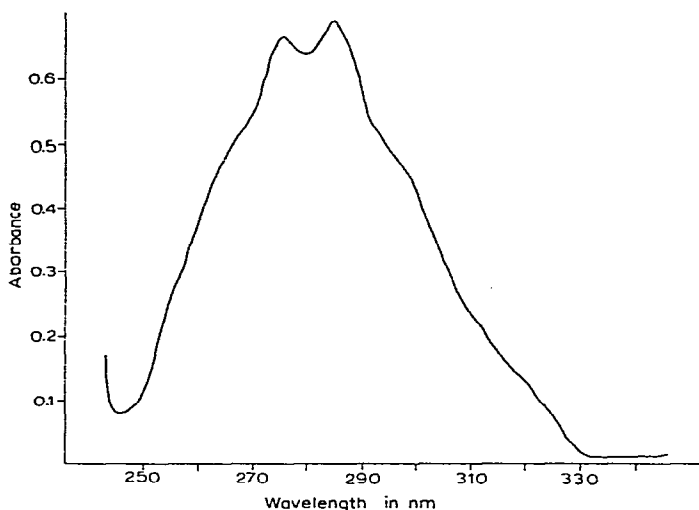


Fig. 2. UV spectrum of product of reaction of TNB in wet, degassed DME.

#### *Reaction of TNB with oxygen*

A solution of TNB in dry, degassed DME was irradiated *in vacuo* for 6 h at 350 nm. The solution remained colorless and was shown by TLC to contain only TNB. Naphthalene and 1,1'-binaphthyl were not present. A similar solution was left under oxygen but *in the dark* for 52 h. Removal of the solvent left a light brown solid, and TLC showed this to contain no naphthalene, no 1,1'-binaphthyl, a small amount of 1-naphthol and a large amount of TNB. Irradiation of a solution of TNB in dry DME under oxygen for 2 h at 350 nm was next carried out. Removal of the solvent *in vacuo* left a light brown oil, and TLC showed this to contain not only TNB but also naphthalene, and 1,1'-binaphthyl. Several other spots were obtained in the thin-layer chromatogram but were not identified.

#### EXPERIMENTAL

##### *Spectroscopy and irradiations*

ESR spectra were recorded with a Varian Associates V-4502 Spectrometer equipped with "Fieldial" and low temperature accessories. Calibrations and *g*-value measurements were made with the help of a dual-sample cavity, conventional frequency-measuring equipment and Fremy's salt as a standard, as described earlier<sup>16</sup>.

Absorption spectra were recorded with either a Cary Model 14 or a Beckman Model DK2-A Spectrophotometer.

Irradiations with monochromatic light were carried out with a Bausch and Lomb Monochromator, Model 33-86-07. Cells of fused silica were used.

##### *Materials*

Tri-1-naphthylborane was made by the method of Brown and Sujishi<sup>17</sup>, and had m.p. 203.5–204°. 1,1'-Binaphthyl was prepared by the method of Kovachic and Koch<sup>18</sup> and had m.p. 143.5–144°<sup>19</sup>. All ethereal solvents were dried over lithium aluminum hydride (LAH), distilled over LAH, and stored over LAH before use.

Hexamethylphosphoramide (HMPA) was dried over calcium hydride before distillation. Sodium amalgam was made by weight and stored under nitrogen. The mercury was cleaned with dilute nitric acid before use.

### Manipulative techniques

A variety of all-glass apparatus was built to suit particular experiments. For a reduction of TNB by sodium amalgam or sodium, the apparatus (Fig. 3) consisted

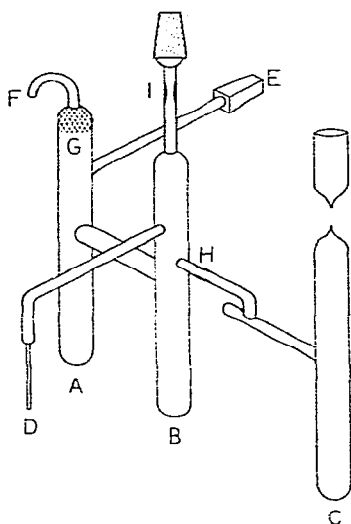


Fig. 3. Apparatus used, in general, in preparing solutions of TNB ions.

in general of separate chambers containing: (A) the metal, (B) TNB, and (C) the solvent stored over a drying agent (LAH, molecular sieve, or calcium hydride). A trap to prevent carry-over of solid particles was inserted between (B) and (C). Where necessary the several chambers were separated by break seals. A capillary (D) for ESR measurements and a 1 cm silica cell (E) for optical measurements were sealed into the apparatus. If reduction was to be carried out by sodium rather than amalgam, the sodium was distilled from a small side chamber (F), attached to (A) through a break-seal, so as to coat the upper portion (G) of (A) with a film of metal. If more than one solvent was to be used the appropriate number of solvent chambers and break seals were used.

The solvent was degassed by repeated freeze-thaw cycles and distilled *in vacuo* into chamber (B). The apparatus was then sealed by flame at point (H) and (C) was removed. The apparatus was next sealed at point (I). The solution of TNB was poured periodically between (A) and (B) for intermittent contact with metal.

When reactions were carried out with wet solvents and under oxygen atmosphere appropriate changes were made.

### Reduction of TNB with 1.5% amalgam

In a typical procedure 42.5 mg (108  $\mu$ moles) of TNB, 165 mg of amalgam (containing 2.5 mg, 108  $\mu$ g-atoms of sodium), and 10 ml of DME were used. The

TNB solution was shaken with the amalgam on a mechanical shaker and kept out of contact of the amalgam when necessary by being returned to chamber (B). ESR spectra were recorded at timed intervals. A typical spectrum is given in Fig. 1.

#### *Reduction of TNB with sodium*

The amount of sodium used was several-fold larger than 1/1 equivalence. A green solution was formed on immediate contact between the TNB solution and the metal film. When DME was the solvent the green color gave way to grey after overnight shaking, and the ESR spectrum of  $\text{TNB}^{\bullet-}$  gave way to that of the naphthalene anion radical<sup>12</sup>. By recording the ESR spectrum at timed intervals it was possible to see the overlapping of the two spectra before one was replaced completely by the other. When THF was the solvent the  $\text{TNB}^{\bullet-}$  spectrum disappeared within 4 min of contact and a black suspension of  $\text{TNBNa}_2$  was formed<sup>7</sup>. Contact between this suspension and sodium film overnight gave a 28-line ESR spectrum similar to that for the naphthalene anion radical-sodium ion pair<sup>12</sup>.

#### *Reaction of TNBNa with sodium*

A solution of TNBNa in DME was prepared with 1.5% amalgam as described above. The solution was transferred to a separate chamber containing a film of sodium and shaken for several hours. The naphthalene anion radical was formed over a period of several hours, during which time the  $\text{TNB}^{\bullet-}$  disappeared.

#### *Reaction of TNB with water*

(a). *In degassed solution.* Three drops of water were added to 10 ml of DME. The solvent was degassed in the usual way and added to 10 mg of TNB *in vacuo*. After 10 min the UV spectrum of TNB had disappeared. The new spectrum (Fig. 2) had a broad band centered on 280 nm and containing some fine structure. The solvent was pumped off and the oily residue was kept under high vacuum for 2 h. The oil was dissolved in  $\text{P}_2\text{O}_5$ -dried carbon tetrachloride, and its UV spectrum contained the 351 nm peak of TNB. Spotting the oil on a silica TLC plate had developing with dry carbon tetrachloride gave a TNB spot linked to the origin with a continuous streak.

(b). *In the presence of oxygen.* Many experiments were performed in which the amount of water in DME solvent was varied and in which either an air or oxygen atmosphere was used. In all cases both 1,1'-binaphthyl and naphthalene were formed. The binaphthyl appeared first. The rate at which these compounds were formed appeared to depend on the amount of water present, but since the experiments were carried out on the bench top they must have been affected, as was found subsequently, by light also. In a simple experiment, 100 mg of TNB was dissolved in dry DME saturated with oxygen and containing 0.5 ml of water. After 48 h both binaphthyl and naphthalene were detected by TLC, using 20% benzene in n-hexane for development.

#### *Reaction of TNB with oxygen*

(a). *In the absence of light.* A solution of 200 mg of TNB in dry, degassed DME was prepared in the usual way. Oxygen, dried with phosphorous pentoxide, was allowed into the apparatus which was then kept in the dark for 52 h. Removal of the solvent left a light brown solid. TLC showed this to be TNB, but there was a trace of 1-naphthol at the origin.

(b). *In the presence of light.* The solution of TNB was made as in (a), transferred to the 1 cm cell and irradiated at 350 nm for 2 h. The solution was found by TLC to contain TNB, 1,1'-binaphthyl, and naphthalene. Other spots were present in the chromatogram but were not identified.

#### *Irradiation of TNB in absence of oxygen*

A solution of TNB in dry, degassed DME was irradiated at 350 nm for 6 h. The colorless solution was examined by TLC and found to contain only TNB.

#### *Reaction of sodium with the TNB·water complex*

A solution of 50 mg of TNB in 10 ml of DME containing one drop of water was allowed to stand for 1 h at which time the 351 nm peak of TNB was no longer present in the UV spectrum. The solvent was removed in the usual apparatus (Fig. 3), and dry DME was distilled onto the remaining light brown oil. The solution was shaken over a sodium film. No change was apparent until 25 h at which time a weak single-line ESR spectrum was obtained. Intermittent contact with the film during the next 23 h produced a purple solution with the ESR spectrum of the 1,1'-binaphthyl anion radical. Further intermittent contact with sodium over a period of some days caused the 1,1'-binaphthyl anion radical spectrum to disappear and be replaced by that of the naphthalene anion radical.

#### *Reaction of the 1,1'-binaphthyl anion radical with sodium*

The anion radical was prepared by shaking a solution of 1,1'-binaphthyl in dry, degassed DME over a sodium film overnight. The ESR spectrum remained unchanged for 3 weeks while the purple solution was out of contact with sodium. Subsequent shaking over sodium for 30 h produced the ESR spectrum of the naphthalene anion radical.

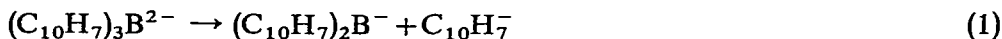
## DISCUSSION

The pattern of behavior of TNB on reduction is now reasonably clear. Reduction does not go beyond the one-electron stage when 1.5% sodium amalgam is used. The green solution of  $\text{TNB}^{\cdot-}$  was stable for several weeks until used, and is presumably stable indefinitely. The ESR spectrum of  $\text{TNB}^{\cdot-}$  (Fig. 1) is not well resolved. Its general shape corresponds with that of the spectrum of  $\text{TMB}^{\cdot-}$  in methyltetrahydrofuran<sup>1</sup> although the number of hyperfine lines in the  $\text{TNB}^{\cdot-}$  spectrum is greater. The only known well-resolved spectrum of an anion radical of the type  $\text{Ar}_3\text{B}^{\cdot-}$  is that of  $\text{TMB}^{\cdot-}$  in liquid ammonia, and analysis of the spectrum has not been made<sup>10,11</sup>. It seems that in ethereal solvents anion radicals of the type  $\text{Ar}_3\text{B}^{\cdot-}$  are likely to give poorly resolved quartets due to  $^{11}\text{B}$ , affected, however, by contributions from  $^{10}\text{B}$ -splittings.

In the presence of excess of sodium, either as 40% amalgam or pure metal,  $\text{TNB}^{\cdot-}$  accepts another electron. The dianion does not appear to be stable.  $\text{TNBNa}_2$  is more soluble in DME than in THF. When formed in THF,  $\text{TNBNa}_2$  precipitates as a black solid. Nevertheless, decomposition occurs in both solvents, faster in DME than in THF, and eventually the naphthalene anion radical is formed. Most likely, decomposition first gives the  $\text{C}_{10}\text{H}_7$  anion [eqn. (1)] which must remove a proton



from the solvent and then become reduced to  $C_{10}H_8^{\cdot-}$ . The fate of the boron-containing fragments is not known.



TNB $\cdot^-$  is not stable in HMPA. Our feeling is that disproportionation occurs rapidly in this solvent [eqn. (2)], followed by decomposition of TNB $^{2-}$ .



The behavior of TNB on reduction is affected and complicated by its reactions with water and oxygen. TNB forms a complex with water, whose UV spectrum is similar to that of the TNB $\cdot$ -NH $_3$  complex<sup>15</sup>. Brown and Dodson have reported that TNB is unaffected by prolonged contact with cold water, but is decomposed by boiling with water. The difference between our result and theirs must be attributed to their having used solid TNB. Reaction with water *in solution* proceeded smoothly but did not lead to decomposition.

We understand now why occasionally we were unable to convert dilute solutions of TNB into TNB $\cdot^-$  with 1.5% sodium amalgam. If sufficient water remains in the solvent to complex with TNB before contact with 1.5% amalgam is made, the complex remains inert to reaction with 1.5% amalgam. This does not apply to 40% amalgam and sodium metal.

Reactions of TNB with metal are further complicated by the effects of oxygen and light. At one time our attempted reductions of TNB produced the anion radical of 1,1'-binaphthyl. The source of this compound was traced to the decomposition of TNB by oxygen *and* light. TNB is stable to light in dry, degassed solution. If an undegassed solution is allowed to stand on the bench, or if a solution saturated in oxygen is irradiated with 350 nm light, 1,1'-binaphthyl and naphthalene are formed. The binaphthyl is formed sooner than the naphthalene.

Brown and Dodson<sup>20</sup> have reported that TNB reacts with dry oxygen gas, and presume the reaction to be as in eqn. (3). Our experience is that the photochemical



reaction seems more related to the decomposition of tetraarylborates by light in an air atmosphere<sup>21</sup>. Williams and co-workers have pointed out that the boron atom needs to be in a tetrahedral configuration in order to give hydrocarbon products on photolysis<sup>22</sup>. We presume that a TNB-oxygen complex is formed initially, and that this, in its tetrahedral configuration, is the reactant in the light-catalyzed formation of 1,1'-binaphthyl. Work-up of products gave both binaphthyl and naphthalene. We did not pursue the fate of the boron-containing fragments.

A final note needs to be added to the side issues which accompany investigations of TNB chemistry. We have found that the directly-prepared anion radical of 1,1'-binaphthyl is stable for weeks in DME solution. If such a solution is shaken with sodium the anion radical of naphthalene is formed. Presumably, the binaphthyl dianion is formed first and then decomposes into naphthalene, with solvent as the proton donor. Shaking with sodium causes the disappearance of the 21-line ESR spectrum<sup>23,\*</sup> and the appearance of the naphthalene anion radical spectrum. Solo-

\* We wish to thank Dr. K. C. Lin for translating the original article.

dozovnikov and co-workers have noted that when 1,1'-binaphthyl is treated with butyllithium or -potassium the anion radical is formed, followed by the dianion, followed during one day by hydrogen gas and perylene<sup>24</sup>. We did not observe the formation of perylene in reactions of 1,1'-binaphthyl with sodium.

#### ACKNOWLEDGEMENT

This work was supported by the Directorate of Chemical Sciences Air Force Office of Scientific Research, Grant Nos. 69-1635 and 70-1855.

#### REFERENCES

- 1 Y. MURATA AND H. J. SHINE, *J. Org. Chem.*, 34 (1969) 3368.
- 2 E. KRAUSE AND H. POLAK, *Ber.*, 59 (1926) 777.
- 3 H. E. BENT AND M. DORFMAN, *J. Amer. Chem. Soc.*, 57 (1935) 1259.
- 4 H. E. BENT AND M. DORFMAN, *J. Amer. Chem. Soc.*, 57 (1935) 1924.
- 5 T. L. CHU, *J. Amer. Chem. Soc.*, 75 (1953) 1730.
- 6 T. L. CHU AND T. J. WEISMANN, *J. Amer. Chem. Soc.*, 78 (1956) 3610.
- 7 C. W. MOELLER AND W. K. WILMARTH, *J. Amer. Chem. Soc.*, 81 (1959) 2638.
- 8 S. I. WEISMAN, J. TOWNSEND, D. E. PAUL AND G. E. PAKE, *J. Chem. Phys.*, 21 (1953) 2227.
- 9 J. E. LEFFLER, E. DOLAN AND T. TANIGAKI, *J. Amer. Chem. Soc.*, 87 (1965) 927.
- 10 S. I. WEISMAN AND H. VAN WILLIGEN, *J. Amer. Chem. Soc.*, 87 (1965) 2285.
- 11 H. VAN WILLIGEN, *Biradical and Ion Cluster Formation of Some Aromatic Negative Ions*, Ph. D. thesis, University of Amsterdam, 1965.
- 12 C. L. DODSON AND A. H. REDDOCH, *J. Chem. Phys.*, 48 (1968) 3226.
- 13 A. CSERHEGYI, J. CHAUDHURI, E. FRANTA, J. JAGUR-GRODZINSKI AND M. SZWARC, *J. Amer. Chem. Soc.*, 89 (1967) 7129.
- 14 G. FRAENKEL, S. H. ELLIS AND D. T. DIX, *J. Amer. Chem. Soc.*, 87 (1965) 1406; H. NORMANT, T. CUVIGNY AND J. NORMANT, *Bull. Soc. Chim. Fr.*, (1965) 3441.
- 15 B. RAMSEY, M. ASHRAF EL-BAYOUMI AND M. KASHA, *J. Chem. Phys.*, 35 (1961) 1502.
- 16 H. J. SHINE, C. F. DAIS AND R. J. SMALL, *J. Org. Chem.*, 29 (1964) 21.
- 17 A. C. BROWN AND S. SUJISHI, *J. Amer. Chem. Soc.*, 70 (1948) 2793.
- 18 P. KOVACHIC AND F. W. KOCH, *J. Org. Chem.*, 30 (1965) 3176.
- 19 Y. BADAR, C. C. K. LING, A. S. COOKE AND M. M. HARRIS, *J. Chem. Soc.*, (1965) 1543.
- 20 H. C. BROWN AND V. H. DODSON, *J. Amer. Chem. Soc.*, 79 (1957) 2302.
- 21 P. J. GRISDALE, B. E. BABB, J. C. DOTY, T. H. REGAN, D. P. MAIER AND J. L. R. WILLIAMS, *J. Organometal. Chem.*, 14 (1968) 53 and references therein.
- 22 J. L. R. WILLIAMS, P. J. GRISDALE AND J. C. DOTY, *J. Amer. Chem. Soc.*, 89 (1967) 4538.
- 23 K.-H. FU, H.-Y. SHENG AND C.-L. P'AN, *K'o Hsueh Tung Pao*, (1965) 540; *Chem Abstr.*, 64 (1966) 18747.
- 24 S. P. SOLODOVNIKOV, S. T. IOFFE, YU. B. ZAKS AND M. I. KABACHNIK, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1968) 442.

*J. Organometal. Chem.*, 24 (1970) 53-62