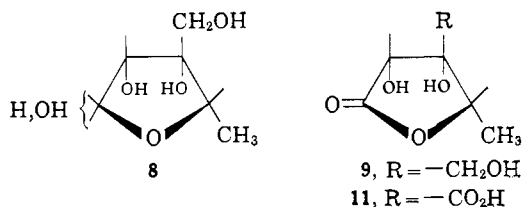


ysis of **6**, followed by direct reduction with sodium borohydride, gave 1,2-O-isopropylidene-3-C-hydroxy-methyl-5-deoxy- $\beta$ -L-lyxofuranose (**7**), m.p. 104–106°,  $[\alpha]_D +7.6^\circ$ . Deacetonation of **7** was accomplished by stirring an aqueous solution of **7** with Dowex-50 ( $H^+$ ) at room temperature for 2 days. This produced, after chromatography over carbon, L-dihydrostreptose (**8**),<sup>15, 18</sup> a sirupy mixture of anomeric C-4<sup>19</sup> furanoses,  $[\alpha]_D -24^\circ$ , whose n.m.r. spectrum in deuterium oxide showed absorptions of two isomers. The  $\beta^{20}$  anomer comprised 74% of the mixture and showed absorptions at  $\tau$  8.76 (3 H, doublet,  $J = 6.6$  c.p.s.), 6.38 (2 H, singlet), 5.85 (1 H, doublet,  $J = 3.8$  c.p.s.), 5.65 (1 H, quartet,  $J = 6.6$  c.p.s.), and 4.72 (1 H, doublet,  $J = 3.8$  c.p.s.). The  $\alpha$  anomer showed absorptions at  $\tau$  8.71 (3 H, doublet,  $J = 6.6$  c.p.s.), 6.38 (2 H, singlet), 5.91 (1 H, quartet,  $J = 6.6$  c.p.s.), 5.82 (1 H, doublet,  $J = 5.1$  c.p.s.), and 4.76 (1 H, doublet,  $J = 5.1$  c.p.s.). The yield of dihydrostreptose from **4** was 23%. Synthetic dihydrostreptose gave, in poor yield, a tosylhydrazone, m.p. 133–137° (lit.<sup>16</sup> m.p. 137.5–138°). Bromine water oxidation converted synthetic dihydrostreptose, in 60% yield, to dihydrostreptosonic acid lactone (**9**), m.p. 140.5–142.5°,  $[\alpha]_D -32^\circ$  (lit.<sup>22</sup> m.p. 143–144°,  $[\alpha]_D -32^\circ$ ). Synthetic **9** showed the expected infrared<sup>22</sup> and n.m.r. absorptions.



Catalytic hydrogenation of the ozonide of **6** gave 1,2-O-isopropylidene-3-C-formyl-5-deoxy- $\beta$ -L-lyxofuranose (**10**) which, on reduction with sodium borohydride, gave **7** in 55% yield. Deacetonation of **10** by stirring with water-dioxane and Dowex-50 ( $H^+$ ) at room temperature for 2 days furnished, after chromatography on carbon, L-streptose (**2**),<sup>18</sup>  $[\alpha]_D -18^\circ$ , a glass. The n.m.r. spectrum of streptose in deuterium oxide showed absorptions assigned to two

(15) Wang and co-workers<sup>15</sup> obtained, by partial reduction of naturally derived dihydrostreptosonic acid lactone, a mixture of substances, one of which was claimed to be dihydrostreptose. The sirupy dihydrostreptose obtained (no rotation given) was characterized by a crystalline tosylhydrazone, m.p. 137.5–138°. McGilveray and Stenlake<sup>17</sup> have recently claimed the isolation of dihydrostreptose by mild acid hydrolysis of methyl N-acetyldihydrostreptobiosaminide (m.p. 140°,  $[\alpha]_D -125^\circ$ ). They reported that their product was a hygroscopic solid that had m.p. 135–140° and  $[\alpha]_D -70^\circ$ ; the product was characterized as a monoacetyl derivative, m.p. 173°. We suggest that this preparation was composed of some dihydrostreptose (or some decomposition product of dihydrostreptose) and the starting material. The constitution of the acetyl derivative reported is obscure.

(16) Y. Wang, H.-Y. Loh, W.-T. Lin, and C.-H. Chang, *Acta chim. Sinica*, **25**, 257 (1959).

(17) I. J. McGilveray and J. B. Stenlake, *Chem. Ind.* (London), 238 (1964).

(18) Dihydrostreptose and streptose were each chromatographically homogeneous.

(19) That no significant amount of C<sub>branch</sub> furanose isomer was present is shown by the fact that the C<sub>branch</sub> methylene group protons absorb (n.m.r.) at  $\tau$  6.38, the same value as the corresponding protons in **7** and **9**.

(20) The anomer present in larger amount is tentatively assigned the  $\beta$  configuration. Detailed examination of the n.m.r. spectra of these and related compounds and optical activity calculations using the method of Brewster<sup>21</sup> support this assignment.

(21) J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5483 (1959).

(22) F. A. Kuehl, Jr., R. L. Clark, M. N. Bishop, E. H. Flynn, and K. Folkers, *ibid.*, **71**, 1445 (1949).

anomeric C-4 furanose aldehyde hydrates corresponding to structure **2**. The  $\beta^{20}$  anomer, which comprised 79% of the mixture, showed absorptions at  $\tau$  8.73 (3 H, doublet,  $J = 6.5$  c.p.s.), 5.81 (1 H, doublet,  $J = 4.1$  c.p.s.), 5.55 (1 H, quartet,  $J = 6.5$  c.p.s.), 4.97 (1 H, singlet), and 4.77 (1 H, doublet,  $J = 4.1$  c.p.s.). The  $\alpha$  anomer showed absorptions at  $\tau$  8.68 (3 H, doublet,  $J = 6.6$  c.p.s.), 5.75 (1 H, quartet,  $J = 6.6$  c.p.s.), 5.64 (1 H, doublet,  $J = 5.1$  c.p.s.), 4.97 (1 H, singlet), and 4.73 (1 H, doublet,  $J = 5.1$  c.p.s.). The over-all yield of streptose from **4** was 36%. Synthetic streptose, when oxidized by bromine water, gave streptosonic acid monolactone (**11**), m.p. 154–156°,  $[\alpha]_D -41^\circ$  (lit.<sup>23</sup> m.p. 146–148°,  $[\alpha]_D -37^\circ$ )<sup>24</sup> in 50% yield. The infrared (KBr pellets) and n.m.r. spectra of synthetic and authentic<sup>10</sup> streptosonic acid monolactone (**11**) were identical.

Because N-methyl-L-glucosamine<sup>25</sup> and streptidine<sup>26</sup> have been synthesized and the asymmetry of the streptidine ring carbons has been established,<sup>1</sup> the results reported complete the synthetic proof of the structure of streptomycin and the stereochemistry assigned to all the asymmetric centers except the glycosidic linkages.

*Acknowledgment.* This investigation was supported in part by research Grant No. GP-258 from the National Science Foundation.

(23) F. A. Kuehl, Jr., E. H. Flynn, N. G. Brink, and K. Folkers, *ibid.*, **68**, 2679 (1946).

(24) Our authentic sample<sup>10</sup> of streptosonic acid monolactone showed m.p. 154.5–156.6° and  $[\alpha]_D -41^\circ$ . The mixture melting point of authentic and synthetic samples was 153.5–155.5°.

(25) F. A. Kuehl, Jr., E. H. Flynn, F. W. Holly, R. Mazingo, and K. Folkers, *J. Am. Chem. Soc.*, **69**, 3032 (1947).

(26) M. L. Wolfrom, S. M. Olin, and W. J. Polglase, *ibid.*, **72**, 1724 (1950).

(27) National Institutes of Health Predoctoral Fellow, 1962–1964.

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## A Stable Dianion of Naphthalene

Sir:

Aromatic hydrocarbons react with alkali metals in suitable solvents, such as tetrahydrofuran, forming mono- or dinegative ions.<sup>1, 2</sup> The mononegative radical-ions proved to be paramagnetic, since they possess an extra electron in the lowest unoccupied  $\pi$ -orbital,<sup>3</sup> whereas the dinegative ions, e.g., anthracene-<sup>22</sup>Na<sup>+</sup>, are diamagnetic and may be represented as species possessing two coupled electrons in that orbital. The driving force leading to the formation of such ions is determined by the electron affinity of the parent aromatic hydrocarbon and by the solvation of the resulting ions or ion pairs. The total free energy of their formation is measured by the reduction potential of the respective hydrocarbon,<sup>4, 5</sup> which is usually larger for the first step (formation of the mononegative ions) than

(1) W. Schlenk and E. Bergmann, *Ann.*, **463**, 1 (1928).

(2) N. D. Scott, J. F. Walker, and V. L. Hansley, *J. Am. Chem. Soc.*, **58**, 2442 (1936).

(3) D. E. Paul, D. Lipkin, and S. I. Weissman, *ibid.*, **78**, 116 (1956).

(4) J. Hoijtink, E. de Boer, P. H. van der Meij, and W. P. Weyland, *Rec. trav. chim.*, **75**, 487 (1956).

(5) J. Jagur-Grodzinski, M. Feld, S. L. Yang, and M. Szwarc, *J. Phys. Chem.*, in press.

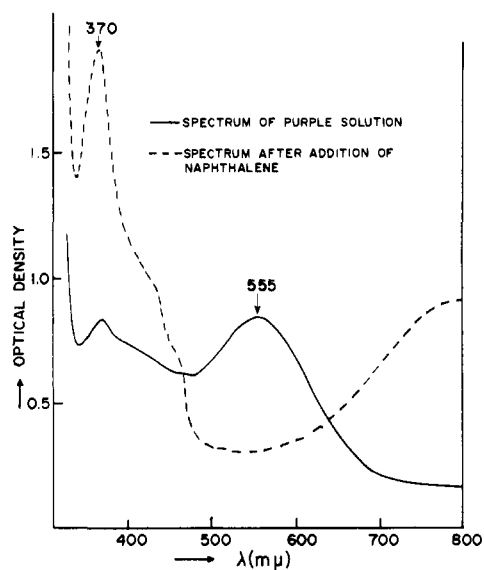
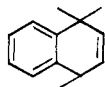


Figure 1.

for the second (reduction of the monoanion to the dianion). Since the first reduction potential of naphthalene in THF is lower than the standard potential of sodium,<sup>4</sup> it is not surprising that this hydrocarbon is not reduced further to the dianion by this metal.

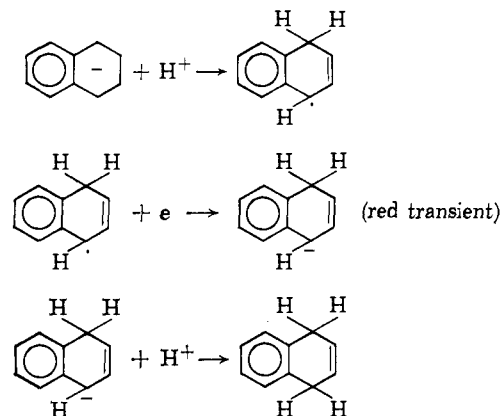
However, a dianion of naphthalene is formed when lithium is used as the reducing agent in THF. A deaerated tetrahydrofuran solution of naphthalene reacts with this metal forming first a green solution of the mononegative ion of naphthalene, and then, as the stirring continues, the green color slowly changes to a deep purple, the reaction being completed after about 15–30 min. The solution slowly decomposes at room temperature but is stable for many hours at  $-80^{\circ}$ .

The visible spectrum of the purple solution is depicted in Figure 1 and shows a broad maximum at  $550\text{ m}\mu$ . On addition of a slight excess of naphthalene the color changes immediately to green, the resulting spectrum being identical with that of the mononegative naphthalene ion (see Figure 1). Similarly, on addition of a slight excess of biphenyl to the purple solution, the color changes instantly, the resulting spectrum being a superposition of the spectra of the naphthalene and biphenyl radical ions. These reactions prove that one does not deal here with a half-reduced anion of naphthalene, *i.e.*



which is expected to be red, but with the dianion of naphthalene,  $N^{2-}Li^{+}$ . This is also confirmed by titration of the purple solution with acid or methyl iodide. The dianion seems to be a powerful reducing agent capable of transferring one electron either to a naphthalene or to a biphenyl molecule.

The reduction of naphthalene to dihydronaphthalene by metallic sodium was reported in ether and in liquid ammonia.<sup>1</sup> It seems that such a reaction does not proceed through the naphthalene dianion. Most probably the final product arises from the following sequence<sup>3,4</sup>



Finally, the difference between sodium and lithium reduction should be discussed. The standard potential of lithium in water is lower<sup>6</sup> than that of sodium by 0.3 v., and a similar relation may be expected in THF. On the other hand, the work function and the ionization potential of sodium are lower than those of lithium. The reason for this anomaly is found in the high solvating energy of the  $Li^{+}$  ion which is greater than that of the  $Na^{+}$  ion.<sup>7</sup>

This fact was also confirmed recently<sup>8</sup> by our observation that, at room temperature, the sodium salt of the naphthalene radical ion in THF is a contact ion pair, whereas the corresponding lithium compound exists almost completely as a solvent separated ion pair. The energy gained in ion-pair solvation is apparently sufficient to overcome the potential difference between the first and second reduction steps of naphthalene, which amounts to about 0.2 to 0.3 e.v.<sup>5,9</sup>

The reduction of phenanthrene was found to proceed in a similar way. Again, a dianion is formed, with lithium as reducing agent, although the reaction appears to be slower. The phenanthrene dianion shows a sharp absorption peak at  $415\text{ m}\mu$  and a broad maximum at  $580\text{ m}\mu$ . Addition of biphenyl to the solution yields instantly the mononegative ions of phenanthrene and biphenyl, as identified by their absorption spectra.

*Acknowledgment.* The author is indebted to the National Science Foundation for financial assistance of this work and to Dr. Michael Szwarc for his interest and encouragement.

(6) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, New York, N. Y., 1952.

(7) C. L. Lee, D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, in press.

(8) T. E. Hogen-Esch and J. Smid, to be published.

(9) NOTE ADDED IN PROOF. After completion of this communication, we noticed a recent paper by Buschow and Hoijtink [*J. Chem. Phys.*, **40**, 2501 (1964)] mentioning the formation of naphthalene $^{2-}Li^{+}$  in methyltetrahydrofuran at  $-80^{\circ}$ . They stress that the feasibility of the lithium reduction at this temperature is due to the complete dissociation of the mononegative ion for this metal, while the dinegative ion is still associated with two counterions. Our findings indicate almost complete dianion formation in THF even at room temperature and at concentrations of naphthalene of about  $10^{-2}\text{ M}$ . Conductivity measurements<sup>8</sup> show that under these conditions the fraction of free ions in a solution of naphthalene $^{-}Li^{+}$  is very small ( $K_D \approx 1.0 \times 10^{-6}\text{ M}$ ). It seems therefore unlikely that in MeTHF with its considerably lower dielectric constant ( $\epsilon = 4.63$  as compared to  $\epsilon = 7.39$  for THF at  $25^{\circ}$ ) any appreciable dissociation occurs, even at  $-80^{\circ}$ .

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