Table I
Bro-assays by the Ansbacher Procedure

| Substance (In 1 cc peanut oil) | No. of birds | 5 |  | $\begin{aligned} & \mathrm{g} \text { times, } \\ & 10-20 \end{aligned}$ | $\min _{20-30}$ |  | $\begin{aligned} & \% \underset{\text { birds }}{10-\mathrm{min}} . \\ & \hline \end{aligned}$ | Remarks |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Controls (1st series) | 20 | 2 | 4 | 6 | . | 8 | 30 |  |
| Peanut oil (1 cc.) | 10 | - | 3 | -• | . | 7 | 30 |  |
| Alfalfa (100 mg.) | 10 | 5 | 3 | 1 | 1 | . | 80 |  |
| Alfalfa (50 mg.) | 9 | 2 | 5 | 1 | 1 | . | 77 |  |
| Alfalfa ( 25 mg .) | 10 | 1 | 4 | 2 | 1 | 2 | 50 |  |
| Alfalfa (10 mg.) | 10 | 1 | 3 | 2 | 2 | 2 | 40 |  |
| 2- $\alpha$-Heptenyl-3-hydroxy-1,4-naphthoquinone (0.2 mg.) | 10 | 3 | 4 | 2 | . | 1 | 70 | Some activity |
| $2-n$-Heptyl-3-hydroxy-1,4-naphthoquinone (0.2 mg.) | 10 | 2 | 6 | 2 | . | . | 80 | Some activity |
| 2-Allyl-1,4-naphthoquinone ( 0.2 mg .) | 10 | 10 | $\cdots$ | - | $\cdots$ | . | 100 | Very active |
| Controls (2nd series) | 11 | $\cdots$ | . | $\ldots$ | . | 11 | 0 | All over 60 min |
| Alfalfa (150 mg.) | 10 | 7 | 3 | . | . | . | 100 |  |
| 2,3-Diallyl-1,4-naphthohydroquinone diacetate ( 0.2 mg.) | 10 | . | 1 | 1 | 5 | 3 | 10 | Inactive |
| 2,6-Dimethyl-1,4-naphthoquinone (0.2 mg.) | 10 | $\cdots$ | 4 | - | $\cdots$ | 6 | 40 | Very sl. act. |
| 2,7-Dimethyl-1,4-naphthoquinone (0.2 mg.) | 10 | 3 | 3 | 2 | $\cdots$ | 2 | 60 | Active |

Table II
Absorption Maxima
In ethanol, except as noted; $\log \epsilon$ values given in parentheses

Vitamin $\mathrm{K}_{1}$ (Doisy, et al.)
(Dam, Karrer, et al.)
Vitamin $\mathrm{K}_{2}$ (Doisy, et al.)
2,3-Dimethyl-1,4-naphthoquinone (T. J. Webb)
(D. M. B., new reading)

6,7-Dimethyl-2,3-diallyl-1,4-naphthoquinone
(In hexane)
2-Allyl-1,4-naphthoquinone
(In hexane)
2-Methyl-1,4-naphthoquinone (T. J. Webb)
2,6-Dimethyl-1,4-naphthoquinone (T. J. Webb)
2,6-Dimethyl-3-allyl-1,4-naphthoquinone ${ }^{a}$
none, m. p. $118-119^{\circ}$ (Found: C, 77.43 ; H, 5.61), was similarly prepared from the known diene addition product. (3) Monobutadiene-1,4-benzoquinone with allyl bromide and potassium carbonate in acetone gave 5,8 -dihydro-1,4-naphthohydroquinone diallyl ether, m. p. 64-65 (Found: $\mathrm{C}, 79.51 ; \mathrm{H}, 7.55$ ), and when heated in kerosene this rearranged smoothly to 5,8 -dihydro- 2,3 -diallyl-1,4-naphthohydroquinone, m. p. 108-109 ${ }^{\circ}$ (Found: C, 79.36; H, 7.78). Chromic acid oxidation in acetic acid gave 2,3-diallyl-1,4naphthoquinone, m. p. $29-30^{\circ}$ (Found: C, $80.53 ; \mathrm{H}, 6.02$ ). The substance (m. p. $130^{\circ}$ ) obtained previously by the action of ethyl or $n$-butylmagnesium bromide on 2,3-diallyl-1,4naphthohydroquinone diacetate is a naphthoquinone (spectrum) having two hydrogen atoms more than the expected diallyl compound (Calcd. for $\mathrm{C}_{16} \mathrm{H}_{16} \mathrm{O}_{2}$ : $\mathrm{C}, 79.97 ; \mathrm{H}, 6.71$. Found: C , 80.06, 79.93; $\mathrm{H}, 6.78,6.76$ ). More gentle cleavage with methylmagnesium bromide and

| Maxima (in $\mathrm{m} \mu)$ |  |  |
| :---: | :--- | :--- |
| 243,248 | 261,270 | 323 |
| 248 | 261,270 | 328 |
| 249 | 261,269 | 320 |
| $244,249(4.29)$ | $264,270(4.27)$ | $332(3.39)$ |
| $243,249(4.26)$ | $262,267(4.24)$ | $330(3.38)$ |
| $253,260(4.40)$ | $273,278(4.12)$ | $343(3.45$ |
| $253,260(4.41)$ | $271,276(4.14)$ | $338(3.46)$ |
| $246,251(4.31)$ | Shoulder | $332(3.43)$ |
| $243,251(4.1)$ | $260(3.9)$ | Not measured |
| $250(4.29)$ | $263(4.24)$ | $334(3.38)$ |
| $256(4.33)$ |  | $340(3.47)$ |
| $249(4.30) 256(4.35) 266,272(4.17)$ | $335(3.39)$ |  |

silver oxide oxidation gave 2,3 -diallyl-1,4-naphthoquinone, m. p. $28.5-29.5^{\circ}$, identical with the above sample.

In the Dam-Karrer color test with sodium ethylate in ethanol, regarded by some as characteristic of vitamin $\mathrm{K}_{1}$ (Almquist and Klose, This Journal, 61, 1610 (1939); see, however, Fernholz, et al., ibid., 61, 1613 (1939)), our synthetic naphthoquinones having at least one allyl group in the quinonoid ring all give intense and transient blue or purple colors and contrast sharply with the 2,3 -dimethyl compound (weak, purplish color). ${ }^{a}$
${ }^{a}$ Received June 26, 1939.
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Harvard University Douglas M. Bowen Cambridge, Massachusetts William P. Campbell Edward M. Fry
Marshall D. Gates, Jr.
Received June 23, 1939

## THE STEREOCHEMISTRY OF TERVALENT NITROGEN

## Sir:

Jackson and Kenner [J. Chem. Soc., 573 (1928)] briefly reviewed the existing evidence bearing
on the spatial configuration of tervalent nitrogen compounds in which three separate groups are attached to the nitrogen atom. They pointed out that "the search for isomerides demanded by a non-planar configuration has been (almost completely) unsuccessful, and it would therefore appear that, in general, the non-planar readily passes into a planar form, from which the original or its enantiomorph may be regenerated; or else the normal configuration is plane [compare Meisenheimer, Ber., 57, 1747 (1924)].
"Before, however, such conclusions can be accepted, it is desirable that the negative results on which they rest should be supplemented by positive evidence. This would be supplied by the preparation of a compound in the molecule of which a nitrogen atom is common to two ring structures which are at the same time plane and co-planar. Since . . . there is no evidence available which renders doubtful the plane configuration of five-membered ring structures, it would appear that these conditions would be fulfilled by a structure of type I, if Kekule's formula for benzene and its derivatives be accepted.'


I

Jackson and Kenner were unable to report the preparation of a compound of this type. However, there had been recorded just previously some experiments by Manjunath [ $J$. Indian Chem. Soc., 4, 271 (1927)] in which it was shown that treatment of a glacial acetic acid solution of 9 -nitroso-hexahydro-carbazole (II, $R, R=H$ ) containing cyclohexanone with zinc dust, and then warming, led to formation of a crystalline substance $\mathrm{C}_{18} \mathrm{H}_{21} \mathrm{~N}$, which he described as " $8,9-(1,2-$ cyclohexyl)-tetrahydro-carbazole." His structural formula for this substance is obviously incorrect as it represents a substance of formula $\mathrm{C}_{19} \mathrm{H}_{23} \mathrm{~N}$. Every analogy suggests that Manjunath's compound should be formulated as III $(\mathrm{R}=\mathrm{H})$, that is, as a normal product of a Fischer indole


ring closure, and as a substance fulfiling the requirements of Jackson and Kenner's test.

We have now confirmed Manjunath's result, and his further observation that a similar substance (III, $\mathrm{R}=\mathrm{CH}_{3}$ ) can be obtained in a similar manner from 9-nitroso-6-methyl-hexahydro-carbazole (II, $\mathrm{R}=\mathrm{CH}_{3}, \mathrm{R}^{\prime}=\mathrm{H}$ ). On the other hand, we have been unable to prepare a substance of similar structure from 9 -nitroso- 8 -methyl-hexa-hydro-carbazole ( $\mathrm{II}, \mathrm{R}=\mathrm{H}, \mathrm{R}^{\prime}=\mathrm{CH}_{3}$ ) because the ortho position essential for indole ring closure has been "blocked" by the methyl group.

That the substances III have the structures assigned to them is strongly supported by the fact that addition of zinc dust to an acetic acid solution of 1 -nitroso-indoline containing cyclohexanone, followed by warming, leads to formation of a colorless crystalline neutral substance, $\mathrm{C}_{14} \mathrm{H}_{15} \mathrm{~N}$, melting at $154^{\circ}$. There can be no doubt that this must be formulated as IV, so that it, also, must be regarded as fulfilling the requirements of Jackson and Kenner's test.


There is thus no doubt that substances can be prepared containing a tervalent nitrogen atom with three separate atoms attached to the nitrogen, in which the three nitrogen valences must be regarded as definitely co-planar.
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## ON THE CONSTITUTION OF VITAMIN $\mathrm{K}_{1}$

 Sir:In a previous communication [This Journal, 61,1295 (1939)] we suggested that vitamins $\mathrm{K}_{1}$ and $\mathrm{K}_{2}$ contain the quinone structure, and subsequently [ibid., 61, 1612 (1939)] we confirmed this by preparation of the diacetates by reductive acetylation. The pure yellow color of the vitamins suggests that they belong to the 1,4 series of quinones and this conclusion is supported by the discovery that 1,4 -naphthoquinone has vitamin K activity whereas 1,2 -naphthoquinone does not. Investigation of a considerable number of quinones has revealed only the derivatives of $1,4-$ naphthoquinone as having vitamin K activity.

