of the more basic compound is always more intense than its parent species. Reactions 1 and 2 both show a negative dk/dE_{ion},[11] with the change being much greater for the latter reaction. Charge transfer (eq 4)

$$R_2NNO\cdot^+ + R_2'NNO \longrightarrow R_2NNO + R_2'NNO\cdot^+ \qquad (4)$$

proceeds irreversibly from the less basic to the more basic compound. This is in agreement with the expected decrease in ionization potential with increasing length or branching of the alkyl chain.

(11) J. Beauchamp and S. Buttrill, *J. Chem. Phys.*, **48**, 1783 (1968).
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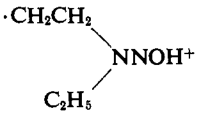
Electrical Effect of Free-Radical Groups[1]

Sir:

In the course of a study of dialkyl-*N*-nitrosamines by ion cyclotron resonance we have found a way to estimate the electrical (substituent) effect of groups like $\cdot CH_2CH_2$–.

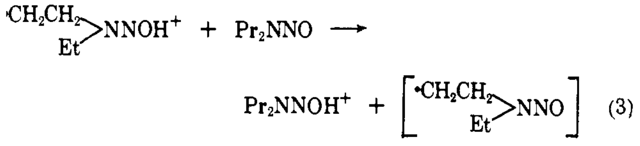
In a previous communication[2] we have shown that the order of base strengths in the gas phase of a series of compounds R_2NNO is R = Me < Et < *n*-Pr < *n*-Bu ≈ *i*-Pr. We have also shown that a rearrangement occurs in the parent ions of these compounds, leading to ions of the structure



and that these ions undergo proton transfer with free nitrosamines. For diethyl-*N*-nitrosamine reactions 1–3

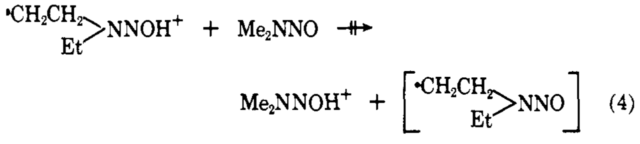
$$Me_2NNOH^+ + \underset{\mathbf{2}}{Et_2NNO} \mathrel{\substack{\rightarrow\\ \not\leftarrow}} \underset{\mathbf{1}}{Me_2NNO} + Et_2NNOH^+ \qquad (1)$$

$$Et_2NNOH^+ + \underset{\mathbf{3}}{Pr_2NNO} \mathrel{\substack{\rightarrow\\ \not\leftarrow}} \underset{\mathbf{2}}{Et_2NNO} + Pr_2NNOH^+ \qquad (2)$$



$$\cdot CH_2CH_2(Et)NNOH^+ + Pr_2NNO \longrightarrow Pr_2NNOH^+ + \underset{\mathbf{4}}{\left[\cdot CH_2CH_2(Et)NNO\right]} \qquad (3)$$

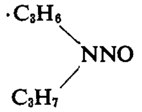
were observed, among others, but the reverse of reactions 1 and 2 and reaction 4 were shown not to occur.



$$\cdot CH_2CH_2(Et)NNOH^+ + Me_2NNO \not\longrightarrow Me_2NNOH^+ + \underset{\mathbf{4}}{\left[\cdot CH_2CH_2(Et)NNO\right]} \qquad (4)$$

Reactions 1 and 2 and their reverse show that the basicity sequence is **1** < **2** < **3**, as previously indicated. Reactions 3 and 4 further show that another basicity sequence is **1** < **4** < **3**. In other words, replacement of $-C_2H_5$ in **2** by $\cdot CH_2CH_2$– to give **4** does not alter the basicity by more than the difference of the basicities between **1** and **2** or **2** and **3**.

The same arrangement can be made for the sequence **2**, **3**, Bu_2NNO (**5**), and **6**, where $-C_3H_6\cdot$ is *probably*



6

$CH_3\dot{C}HCH_2$–, since this is the species formed by a δ hydrogen abstraction. The basicity sequences then are **2** < **3** < **5** and **2** < **6** < **5**. This shows that the electrical effects of $-C_2H_4\cdot$ and $-C_3H_6\cdot$ lie, respectively, between those of Me and Pr and Et and Bu. Since the difference between Me and Pr is small and that between Et and Bu even smaller, it may be concluded that the effects of $-C_2H_6\cdot$ and Et are very nearly the same, as are those of $-C_3H_7\cdot$ and Pr.

Similar information on $-CH_2\cdot$, $-C_4H_8\cdot$ (presumably $CH_3CH_2\dot{C}HCH_2$–), and i-$C_3H_6\cdot$ (presumably $H_2\dot{C}(CH_3)CH$) is not as complete. The reactions observed show that $\cdot CH_2$– is less electron releasing than Et, but not how much less, and that the other two radical groups are more electron releasing than Pr, but not how much more. However, the conclusion suggests itself that each radical group has an electrical effect very nearly the same as that of the corresponding alkyl group.

Unfortunately, no information is available on the detailed structure of the free-radical groups. Although it was assumed that the radical site is β to the amino group, there is no way, at this time, to assure that no internal rearrangement shifting the site has occurred.

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(1) This work was performed under NSF Grant No. GP 7551.

(2) S. Billets, H. H. Jaffé, and F. Kaplan, *J. Amer. Chem. Soc.*, **92**, 6964 (1970).

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Borohydride Reduction of σ-Bonded Organopalladium Complexes in the Norbornenyl–Nortricyclenyl System. Evidence against a Radical Mechanism

Sir:

Reductive cleavage of d^8 or d^{10} metal–carbon bonds by borohydride is well known, particularly among compounds of palladium, platinum, and mercury. We now report that in the norbornenyl–nortricyclenyl system, σ-bonded organopalladium complexes Ia and IIa are reduced by sodium borodeuteride with complete retention of stereochemistry, and with little rearrangement. By contrast, the mercury analogs of Ia and IIa are known to afford rearranged products from borohydride reduction, apparently *via* radical intermediates.[1]

In order to determine the stereochemistry and extent of deuterium substitution in the products by nmr, it was necessary to devise conditions for reduction which avoid hydrogenation of double bonds[2] and hydrogen-

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(1) (a) D. J. Pasto and J. A. Gontarz, *J. Amer. Chem. Soc.*, **91**, 719 (1969); (b) G. A. Gray and W. R. Jackson, *ibid.*, **91**, 6205 (1969).

(2) (a) H. Takahashi and J. Tsuji, *ibid.*, **90**, 2387 (1968); (b) R. Palumbo, A. DeRenzi, A. Panunzi, and G. Paiaro, *ibid.*, **91**, 3874 (1969); (c) M. Green and R. I. Hancock, *J. Chem. Soc. A*, 2054 (1967).