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)

$$R_2 NNO^{+} + R_2' NNO \longrightarrow R_2 NNO + R_2' NNO^{+}$$
(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). * Address correspondence to this author.

> Stephen Billets, H. H. Jaffé,* Fred Kaplan Department of Chemistry, University of Cincinnati Cincinnati, Ohio 45221 Received June 23, 1970

Electrical Effect of Free-Radical Groups¹

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 communication² 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 \approx *i*-Pr. We have also shown that a rearrangement occurs in the parent ions of these compounds, leading to ions of the structure

·CH₂CH₂ NNOH+

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

$$Me_2NNOH^+ + Et_2NNO \implies Me_2NNO + Et_2NNOH^+ (1)$$

$$2 \qquad 1$$

$$Et_2NNOH^+ + D_2NNO \implies D_2NNO + D_2NNOH^+ (1)$$

$$\begin{array}{c} \text{Et}_{2}\text{NNOH} + \text{Pr}_{2}\text{NNOH} & (2)\\ 3 & 2\\ \text{CHCH} \end{array}$$

$$\begin{array}{rcl} & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & &$$

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

4

$$\begin{array}{rcl} & \overset{\circ CH_2 CH_2}{\underset{Et}{\sim}} & & \\$$

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 $-C_3H_6$ is probably



CH₃CHCH₂-, 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 $-C_2H_6$ and Et are very nearly the same, as are those of $-C_{\$}H_{7}$ · and Pr.

Similar information on $-CH_2$, $-C_4H_8$ (presumably $CH_3CH_2CHCH_2$, and $i-C_3H_6$ (presumably $H_2\dot{C}(CH_3)CH)$ is not as complete. The reactions observed show that 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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Borohydride Reduction of σ -Bonded Organopalladium Complexes in the Norbornenyl-Nortricyclenyl System. Evidence against a Radical Mechanism

Sir:

Reductive cleavage of d⁸ or d¹⁰ 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 bonds² and hydrogen-

⁽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).

 ^{(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);
 (b) G. G. Gray, and G. Paiaro, *ibid.*, 91, 3874 (1969); (c) M. Green and R. I. Hancock, J. Chem. Soc. A, 2054 (1967).

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Starting complex	Trap (moles)	Overall yield, ^b %	Products (rel yield, %)
Ia	Norbornene (20)	70	IIIa (84), dihydro-IIIa (5), IVa (11)
Ia	Norbornene (2)	80	IIIa (34), dihydro-IIIa (64), IVa (2)
Ia	2,3-Dicarbomethoxy-	76	IIIa (37), dihydro-IIIa (57.5),
	norborn-5-ene (20)		IVa (2), norbornene (2), norbor- nane (1), norbornadiene (0.5)
Ib	Norbornene (20)	64	IIIb (89), dihydro-IIIb (8), IVb (3)
IIb	Norbornene (20)	85	IIIb (2), dihydro-IIIb (1), IVb (97)
IIa	Norbornene (20)	80	IVa (100)
IIc	Norbornene (20)	82	IIIa (1), dihydro-IIIa (1), IVa (98)
CIPd	Norbornene (20)	67	CH,O (98), dicyclopentadiene (1), dihydrodicyclopentadiene (1)

^a 3 hr at -40° ; 1:1 NaBH₄ (NaBD₄): Pd. ^b Yields by glpc; hydrocarbon products could not be determined from I or II in experiments using norbornene. Reference 2c.

olysis of oxygen substituents.³ We have found that both of these side reactions can be suppressed by excess norbornene in monoglyme at -40° . The function of norbornene is most likely to trap diborane,⁴ produced in situ by the reaction RPdCl + NaBH₄ \rightarrow RPdH + $NaCl + [BH_3]$. While saturated hydrocarbons are major products in the absence of norbornene, our conditions permit specific reduction at palladium-carbon σ bonds in a variety of palladium complexes (Table I). Thus, acetoxy complexes Ia⁵ and IIa⁶ are reduced to the corresponding acetates IIIa and IVa in good yield.

The small proportion of rearranged product IVa from reduction of Ia is probably the result of conversion of Ia to IId by norbornene. Other coordinating agents such as pyridine,6 bis(diphenylphosphino)ethane,^{7a} and carbon monoxide^{7b} are known to induce closure of Ia or Ib to the corresponding tricyclic structures. In the present case, norbornene may induce some closure of Ia prior to reduction. A decrease in the norbornene: Ia ratio from 20:1 to 2:1 causes a decrease in the relative yield of rearranged acetate IVa from 11 to 2%, but diborane is no longer trapped as effectively and overreduction products predominate (Table I, entry 2). The minor rearranged products

(3) (a) J. K. Stille and R. A. Morgan, J. Amer. Chem. Soc., 88, 5135 (1966); (b) C. B. Anderson and B. J. Burreson, J. Organometal. Chem., 7, 181 (1967).

(4) We have found that reduction of palladium complexes with diborane in THF produces hydrocarbons directly, presumably via palladium hydrides. The mechanism of deoxygenation remains obscure; acid-catalyzed deoxymetalation has been suggested as a possible first step.3a

(5) Ia was prepared by the method of Anderson and Burreson:^{3b} pale yellow crystals from benzene-hexane; 140-180° dec (sealed capil-lary); mol wt (benzene) 603 (calcd 586). The bicyclic structure is indicated by the presence of two olefinic protons at δ 6.0-6.2 in the nmr spectrum (CDCl₃).

(6) IIa was prepared by the method of Coulson⁷a: mp 245, 165° dec; nmr (CDCl₃) δ 0.62 (1 H, t, J = 5 H2), 0.7–2.9 (10 H, m), 1.92 (3 H, s), 5.08 (1 H, br s), 7.25–8.15 (20 H, m). IIb has been prepared previously by Green and Hancock ²⁰ but the structure was assigned incorrectly as bicyclic $C_7H_8(OCH_3)Pd(C_5H_5N)_2+Cl^-$. The nmr spectrum of IIb (or IIc, prepared similarly) requires the tricyclic structure: IIb, mp 123.5–124.5° dec; mol wt (benzene) 428, calcd 423; nmr (CDCl₃ + 10% pyridine); δ 0.35 (1 H, t, J = 5 Hz), 0.9-1.7 (5 H, m), 2.08 (1 H, br s), 3.16 (3 H, s),4.49 (1 H, br s), 7.35 (4 H, m), 7.78 (2 H, m), 8.92 (4 H, m). In CDCl₃ without added pyridine, the above signals accounted for 85% of the spectrum, and new signals appeared at δ 5.8–6.2 (m), 3.3 (s), 4.15 (br s), and 8.5 (m), indicating 15% bicyclic complex and free pyridine in equilibrium with IIb. Similarly IIc was prepared from Ia and pyridine: mp 116-118° dec; mol wt (benzene) 477, calcd 451. The nmr spectrum of IIc is analogous to that of IIb, and also indicates 15% bicyclic com-(7) (a) D. R. Coulson, J. Amer. Chem. Soc., 91, 200 (1969); (b)

J. K. Stille and L. F. Hines, ibid., 92, 1798 (1970).

(<3%) from reduction of IIb or IIc can be explained similarly since the equilibrium between IIb or IIc and bicyclic complex + pyridine can be observed by nmr.⁶ This equilibrium is not operative with the strongly co-



ordinated complex IIa,6 and acetoxynortricyclene (IVa) is the sole reduction product.

The stereochemistry of deuterium in exo-2-acetoxynorborn-5-ene (IIIa) was proved by comparison of spectra with IIIa as prepared by Berson and Nelson.8 Partial overlapping of the nmr signals from H₃ endo and H₇ prevented an accurate analysis of deuterium content, so the acetate IIIa was converted to exo-2norbornenol with lithium aluminum hydride. The necessary nmr signals of exo-2-norbornenol can be resolved cleanly in the presence of tris(dipivaloylmethanato)europium, Eu(DPM)3,9 and the spectrum is reproduced in Figure 1, trace A. Careful integration reveals that all of the deuterium, within limits of integral accuracy, is located at the 3-endo position of the exo-2norbornenol derived from IIIa.

Similarly, IVa was converted to Va by known methods and the nmr spectrum of the latter was examined in the presence of Eu(DPM)₃. At a ratio of 0.22 mol of europium/mol of V, the chemical shifts of H_b and H_c become identical, and the complex cyclopropyl signals collapse to a broad singlet. Integration

⁽⁸⁾ J. A. Berson, Accounts Chem. Res., 1, 152 (1968); J. A. Berson and G. L. Nelson, J. Amer. Chem. Soc., 89, 5503 (1967).

⁽⁹⁾ J. K. M. Sanders and D. H. Williams, Chem. Commun., 422 (1970).



Figure 1. exo-Norbornenol: trace A, R = D; 22 mol % Eu(DPM)₃-CCl₄; B, R = H; 22 mol % Eu(DPM)₃-CCl₄; C, R = H; CCl₄. Nortricyclenone: trace D (Vb), R¹ = D; R = H; 22 mol % Eu(DPM)₃-CCl₄; E (Va), R¹ = H; R = D; 22 mol % Eu(DPM)₃-CCl₄; F, R¹ = R = H; 22 mol % Eu(DPM)₃-CCl₄; G, R¹ = R = H; CCl₄.

of the resulting spectrum (Figure 1, trace E) shows that deuterium in Va is located exclusively at the 5-endo position. The isomeric 5-exo deuterated ketone Vb was prepared from the known acetate IVc, 10 and comparison of the spectra of Va and Vb confirms our spec-



tral and stereochemical assignments.11

(10) S. J. Cristol, T. C. Morill, and R. A. Sanchez, J. Org. Chem., 31, 2719 (1966), and references therein.

(11) Mass spectral analysis indicates the following distribution of deuterium, confirmed by nmr integration: IIIa, $7\% d_0$, $92\% d_1$, $1\% d_2$; Va, $9.5\% d_0$, $90\% d_1$, $0.5\% d_2$; Vb, $6.5\% d_0$, $92\% d_1$, $1.5\% d_2$. The

Both Ia and IIa are reduced by sodium borodeuteride with >97% retention of stereochemistry¹² and structure. The high specificity of reduction is inconsistent with a mechanism involving long-lived radical intermediates, as proposed for reduction of the mercury analogs of I and II.¹ Our results are consistent with an alternate interpretation involving initial formation of RPdH followed by concerted collapse to RH and palladium metal.13

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per cent d_0 species corresponds to the isotopic distribution of the commercial deuterated reagents NaBD4 and DOAc used in our work.

(12) Predominant retention of stereochemistry (per cent unspecified) has also been observed in the reduction of methoxydicyclopentadienylpalladium chloride dimer by Stille and Morgan.3a

(13) A nonradical bimolecular mechanism is also conceivable, and has some analogy: G. M. Whitesides, J. San Filippo, Jr., E. R. Stred-ronsky, and C. P. Casey, J. Amer. Chem. Soc., 91, 6542 (1969). Address correspondence to this author.

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Exchange of Olefins with Oxymercurials

Sir:

We have found that oxymercurial ions (abbreviated Hg(O1)OH⁺), formed by reactions of olefins with mer-