carbidopentadecacarbonylhexarhodate dianion ($\mathrm{Rh_6(CO)_{15}C)^{2-}}$[10] with 90 valence electrons and therefore nine skeletal electron pairs could have been anticipated (see above) on the basis of the polyhedron skeletal electron pair theory (PSEPT).

The polyhedron skeletal electron pair theory allows a clear prediction of the stereochemistries of the several remaining osmium cluster complexes isolated by Eady, *et al.*[1] $\mathrm{Os_7(CO)_{21}}$ and $\mathrm{Os_8(CO)_{23}}$ each have seven skeletal electron pairs and therefore are consistent with capped octahedral geometries.[11]

Acknowledgment. We are grateful to the Science Research Council for their support of these studies.

(10) V. G. Albano, M. Sansori, and P. Chini, Abstract VI-12, International Union of Crystallography Congress, Kyoto, Japan, 1972.

(11) Note Added in Proof. After much experimental difficulty, Professor Lewis provided us with one suitable crystal of $\mathrm{Os_7(CO)_{21}}$. As predicted above, an X-ray analysis shows the seven osmium atoms in a capped octahedral arrangement.

R. Mason,* K. M. Thomas
School of Molecular Sciences, University of Sussex
Brighton, England

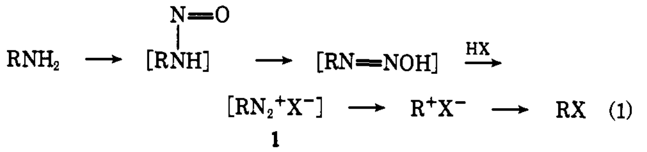
D. M. P. Mingos
Department of Chemistry, Queen Mary College
London, England

Received January 12, 1973

A Comparison of Intermediates from the Deamination of *N*-Nitrosohydroxylamines and the Reaction of Alkyl Azides with Nitrosonium Tetrafluoroborate

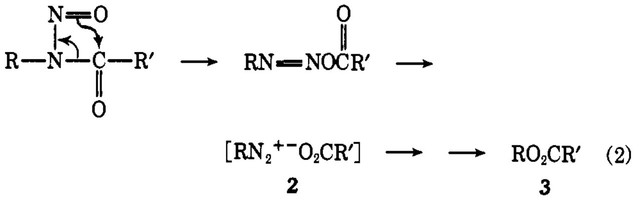
Sir:

In the nitrous acid deamination of aliphatic amines, alkyl diazonium ions **1** can be written, formally, as reaction intermediates

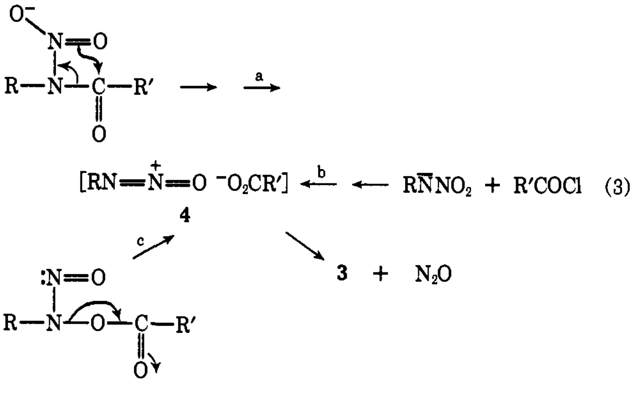


$$\mathrm{RNH_2} \longrightarrow [\mathrm{R}\overset{\mathrm{N{=}O}}{\mathrm{N}}\mathrm{H}] \longrightarrow [\mathrm{RN{=}NOH}] \xrightarrow{\mathrm{HX}} \underset{\mathbf{1}}{[\mathrm{RN_2{}^+X^-}]} \longrightarrow \mathrm{R^+X^-} \longrightarrow \mathrm{RX} \quad (1)$$

Similar species (**2** and **4**) can be written for the decomposition of *N*-nitrosoamides (eq 2), *N*-nitroamides (eq 3, path a), and *N*-nitrosohydroxylamines (eq 3, path c). Species **4** is relatively unstable since infrared spectra of reactions 3, path b, and 3, path c, at Dry Ice temperature gave no evidence for its presence, but showed instead the instantaneous formation of nitrous oxide.[1] No reaction of **4** other than loss of nitrous oxide has ever been detected in our studies.[2]

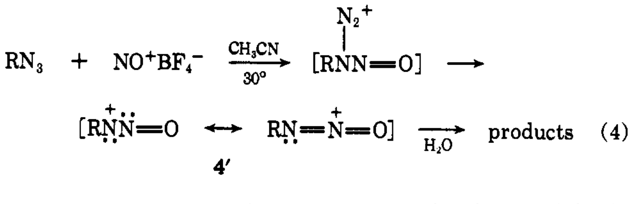


(2)



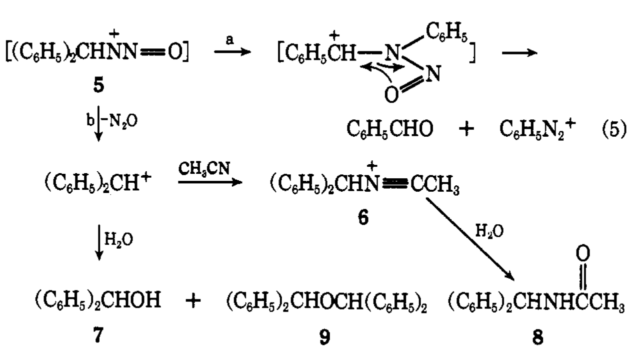
(3)

The same cation, **4′**, has been proposed recently as an interceptible intermediate in the reaction of alkyl azides with nitrosonium tetrafluoroborate (eq 4).[3]



$$\mathrm{RN_3} + \mathrm{NO^+BF_4{}^-} \xrightarrow[30^\circ]{\mathrm{CH_3CN}} [\mathrm{R}\overset{\mathrm{N_2{}^+}}{\mathrm{N}}\mathrm{N{=}O}] \longrightarrow \underset{\mathbf{4'}}{[\mathrm{R}\overset{+}{\ddot{\mathrm{N}}}\ddot{\mathrm{N}}{=}\mathrm{O} \longleftrightarrow \mathrm{R}\ddot{\mathrm{N}}{=}\overset{+}{\mathrm{N}}{=}\mathrm{O}]} \xrightarrow[\mathrm{H_2O}]{} \text{products} \quad (4)$$

For R = benzhydryl, it was reported that benzaldehyde, a phenyl diazonium compound, and benzophenone were formed in addition to the major products, benzhydrol **7** and *N*-(benzhydryl)acetamide (**8**), the latter being formed, presumably, during the quenching of the reaction with water. The authors proposed that the first two of the minor products originated in a 1,2-phenyl migration in species **5** = **4′** (eq 5). Such a migration, in principle, could lead to information concerning the lifetime of **4** and related ions. We now report investigations of the azide reaction (eq 4 and 5) which show that the minor products are not formed by reaction 5, but by a pathway related to the Schmidt reaction of azides.[4]



(5)

We first treated *N*-benzhydryl-*O*-benzoylhydroxylamine with $\mathrm{NO^+BF_4{}^-}$ in acetonitrile under the same conditions used by Doyle and Wierenga for reaction 4. The intermediate *N*-nitroso compound **10** decomposed spontaneously to cleanly yield benzhydryl benzoate (**11**, 20%), benzoyl fluoride (**12**, 20%), and *N*-benzhydrylacetamide (**8**, 60%) in 91% overall yield, but no benzaldehyde (<0.5%), one of the expected products if reaction 5a were operating.[5] Reactions 4 and 6 have

---

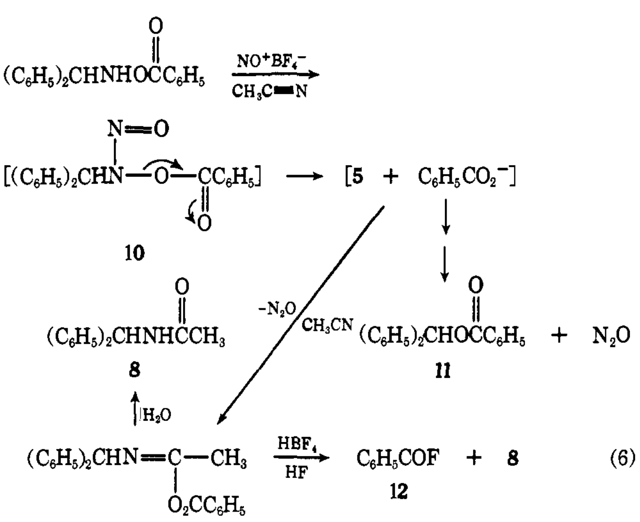
(1) (a) E. H. White, H. P. Tiwari, and M. J. Todd, *J. Amer. Chem. Soc.*, **90**, 4734 (1968); (b) E. H. White, M. J. Todd, M. Ribi, T. J. Ryan, A. A. F. Sieber, R. E. Dickerson, and J. Bordner, *Tetrahedron Lett.*, 4467 (1970).

(2) E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, pp 440–483.

(3) M. P. Doyle and W. Wierenga, *J. Amer. Chem. Soc.*, **92**, 4999 (1970); **94**, 3896 3901 (1972).

(4) For examples, see P. A. S. Smith in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 457.

(5) The products were identified by their ir and nmr spectra and glpc retention times on 3% SE-30 and 5% QF-1 columns. Authentic samples were either commercially available or they were synthesized by well-established procedures.

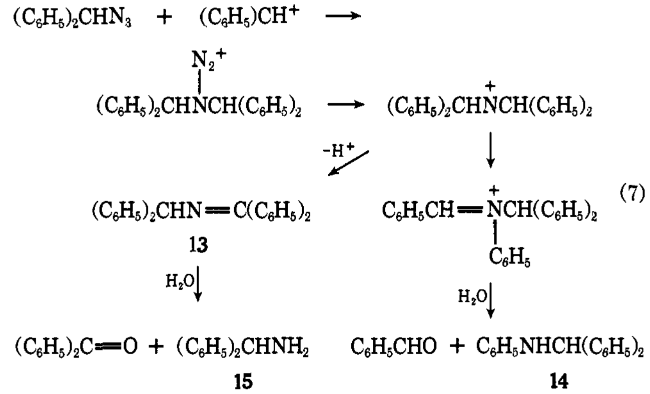


(6)

different counterions. The negative result for phenyl migration just cited is still valid, however, since the counterions can alter the lifetime of species **5**, but they should not alter the ratio of the rates of phenyl migration to loss of nitrous oxide (eq 5, paths a and b).

In view of these results, we examined reaction 5 in some detail to determine the source of benzaldehyde. When benzhydryl azide and $NO^+BF_4^-$ were allowed to react in a 1:1 molar ratio and hydrolyzed with 10 equiv of water as described by Doyle and Wierenga,[3] several previously undetected compounds were isolated and identified:[5] benzhydryl ether (**9**), *N*-benzhydrylbenzophenonimine (**13**), *N*-benzhydrylaniline (**14**), and small amounts of benzhydrylamine (**15**). The formation of these products suggested to us that the benzhydryl cation[6] (or some other electrophile)[7] was responsible for the benzaldehyde by initiating a Schmidt reaction (eq 7).

To determine the role if any of the benzhydryl cation, we added 0.5 molar equiv of nitrosonium tetrafluoroborate to 1 mol of benzhydryl azide to see whether we could favor reaction 7. After a reaction time of 30



(7)

min, water was added and the products were analyzed by glpc. The same products were formed as in the reaction carried out with a 1:1 ratio of reactants except that benzhydrol **7** and benzhydryl ether **9** were not formed. Further, the yields of benzaldehyde, *N*-benzhydrylbenzophenonimine (**13**), and *N*-benzhydrylaniline (**14**) were greater than in the 1:1 experiment (Table I), confirming the validity of eq 7.

Table I. Products from the Reaction of Benzhydryl Azide with Nitrosonium Tetrafluoroborate[a]

Compound	Products, %[b,c] Azide:NO+ 1:1	1:0.5[d]
Benzhydrol (**7**)	15	
N-Benzhydrylacetamide (**8**)	28	15
Dibenzhydryl ether (**9**)	2[e]	
Benzaldehyde	20	33
Benzophenone	8	6
N-Benzhydrylbenzophenonimine (**13**)[f]	10	10
N-Benzhydrylaniline (**14**)[f]	17	36

[a] According to the procedure described in ref 3, solid $NO^+BF_4^-$ was added to the azide being stirred at 26° in CH_3CN followed by rapid quenching with 10 equiv of water after 30 min had elapsed. Inverse addition made little difference. [b] Product ratios were determined by glpc. The absolute yields, determined by nmr, were 87% in the 1:1 case and 97% in the 1:0.5 case. [c] Average of duplicate runs. Variation was ±2%. [d] Benzhydryl azide (25%) was also present at the end of the reaction. Benzhydrylamine (1.5%) and aniline (0.5%) were also detected. [e] 23% was detected on one occasion involving slow addition of 10 equiv of water. [f] Slowly decomposes under hydrolysis conditions.

We also generated the benzhydryl cation from benzhydryl chloride in the presence of benzhydryl azide to demonstrate that the cation will react with benzhydryl azide. When the solvent was dichloromethane, addition of $AgBF_4$ to a 1:1 mixture of benzhydryl chloride and benzhydryl azide produced vigorous nitrogen evolution.[8] After 30 min, the mixture was hydrolyzed with water to yield benzaldehyde (51%), **13** (4%), and **14** (45%) in 73% overall yield. The addition of benzhydryl chloride (1 mmol) to a solution of benzhydryl azide (1.2 mmol) and $AgBF_4$ (1 mmol) in 7 ml of acetonitrile led to the slow evolution of nitrogen. After 30 min, 7% of benzhydryl azide was converted to benzaldehyde and amine **14**, and, after 4 hr, the conversion was 32%.

Finally, the mechanism proposed by Doyle and Wierenga (eq 5) predicts the formation of benzaldehyde prior to water addition. Using ir, glpc, and nmr techniques, we scrutinized the reaction for benzaldehyde before adding water but failed to detect any (<1%). However, addition of water to the sample produced benzaldehyde immediately.

The latter facts, the formation of compounds **13**, **14**, and **15**, and the failure of reaction 6 to yield benzaldehyde, strongly support reaction 7 (proceeding more slowly than reaction 4) as the source of the benzaldehyde formed. Thus, to date, species **4** remains noninterceptible.

Acknowledgment. We thank the National Science Foundation for its support of this work (GP-8993X4) and Martha Umbreit for doing some of the preliminary work.

Richard H. McGirk, Emil H. White*
Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218

Received December 27, 1972

---

(6) One report in the literature describing the reaction of alkyl azides with alkyl cations was found; Schiff bases were observed as products (W. Pritzkow and G. Pohl, *J. Prakt. Chem.*, **20**, 132 (1963)).

(7) Possible sources of aniline and several of the other products are Schmidt reactions of the azide with protic acids (from adventitious water), benzaldehyde, imines, and iminium ions.

(8) For a discussion on the reaction of silver salts with alkyl halides, see N. Kornblum and D. E. Hardies, *J. Amer. Chem. Soc.*, **88**, 1707 (1966).