interaction force constant should be reduced, because an asymmetric displacement is no longer energetically favored over a symmetric displacement. In the symmetric mode, the terminal atom repulsions that tend to raise the energy are counteracted by the central atom positive charge.

In view of these considerations, we feel that a more educated guess of the force constants for HeF_2 is possible. In the last row of Table I, we propose a more likely potential function (and an appropriately shortened bond length) together with the implied frequencies.

Though the two sets of predicted frequencies are discordant, they show that the infrared absorptions should fall in a readily accessible region. A search for this species, HeF_2, is in progress here.

(14) A prototype effect is noted in the successively shorter bond lengths of ClO_2^- (1.64 Å.), ClO_3^- (1.57 Å.) and ClO_4^- (1.50 Å.), which also can be associated with the accumulating formal charge on the central atom.

DEPARTMENT OF CHEMISTRY GEORGE C. PIMENTEL
UNIVERSITY OF CALIFORNIA RICHARD D. SPRATLEY
BERKELEY, CALIFORNIA

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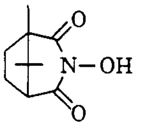
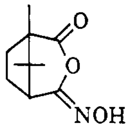
AN UNUSUAL NEF REACTION. THE REARRANGEMENT OF 3-NITROCAMPHOR

Sir:

We wish to report the rearrangement of 3-nitrocamphor to N-hydroxycamphorimide (I) by acid catalysis. The reaction illustrates a variation of the direct Nef reaction[1] by acid catalyzed hydrolysis. The product of the isomerization was formulated as an oximino compound (II) by Lowry,[2] who rejected the alternative structure. Synthesis of the N-hydroxyimide establishes I as the structure for the product of the rearrangement.



I

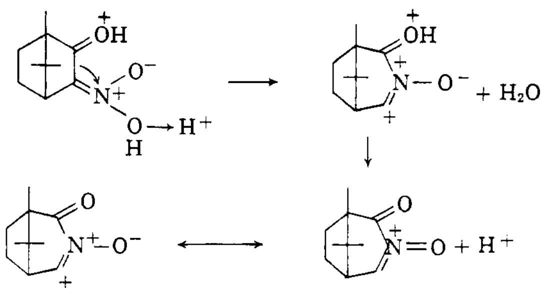


II

Camphoric anhydride was treated with N-benzyloxyamine according to the method of Ames and Grey[3] to form N-benzylcamphorimide (III), m.p. 80–81°; $[\alpha]^{23}D$ +19.2° ($CHCl_3$). (*Anal.* Calcd. for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.37; N, 4.87. Found C, 70.99; H, 7.38; N, 4.97.) Hydrogenolysis of III gave the N-hydroxyimide (I) in 51% yield, m.p. 229–230°, $[\alpha]^{23}D$ +7.29° (*Anal.* Calcd. for $C_{10}H_{15}NO_3$: C, 60.89; H, 7.67; N, 7.10. Found: C, 60.60; H, 7.65; N, 7.20). Absorption in the infrared spectrum characteristic of the N-hydroxyimide group[3] occurred at 3.0, 5.74, and 5.95 μ.

The rearrangement of 3-nitrocamphor with concentrated hydrochloric acid gave N-hydroxycamphorimide in 94% yield, m.p. 229–230°; $[\alpha]^{23}D$ +7.46° ($CHCl_3$). (*Anal.* Found: C, 60.76; H, 7.58; N, 7.18.) The infrared spectra of the N-hydroxyimides formed by rearrangement and by synthesis were identical.

The unusual course of the Nef reaction, in contrast to the normal Nef reaction, must be effected by protonation of the carbonyl group in 3-nitrocamphor to facilitate the cleavage of the C–C bond and the migration of the carbonyl carbon atom with the electrons to form the C–N bond which occurs concertedly with the acid catalyzed dehydration of the nitronic acid. Loss of a proton forms the carbonyl group. Protonation and hydration of the resulting intermediate would lead to I with the development of a carbonyl group by elimination of the catalyst. The rearrangement involves a 1,2-shift with ring expansion.



The rearrangement of 3-nitrocamphor with sodium hydroxide and benzoyl chloride forms the benzoate of I in a yield of 46%, m.p. 136–137°; $[\alpha]^{23}D$ +9.73° ($CHCl_3$). (*Anal.* Calcd. for $C_{17}H_{19}NO_4$: C, 67.75; H, 6.35; N, 4.65. Found: C, 67.76; H, 6.20; N, 4.76.) The benzoyl derivative of N-hydroxycamphorimide was prepared in the usual way, m.p. 136–137°; $[\alpha]^{23}D$ +9.76° (*Anal.* Found: C, 68.01; H, 6.65; N, 4.93.) The infrared spectra of the benzoyl derivatives were identical. Similar rearrangements of α-nitro ketones have not been reported. The product of the rearrangement was previously formulated as a derivative of II.

Treatment of 3-nitrocamphor with acetic anhydride forms N-acetoxycamphorimide in 45% yield, m.p. 116–117°; $[\alpha]^{24}D$ +6.43° ($CHCl_3$) (*Anal.* Calcd. for $C_{12}H_{17}NO_4$: C, 60.24; H, 7.16; N, 5.85. Found: C, 60.22; H, 7.22; N, 5.82.) The acetate was prepared from I, m.p. 116–117°, $[\alpha]^{24}D$ +6.69°. (*Anal.* Found: C, 60.53; H, 7.01; N, 6.07.) The infrared spectra were identical.

Further work is in progress on the rearrangements of α-nitro ketones.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF HAWAII H. O. LARSON
HONOLULU, HAWAII EDWARD K. W. WAT

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(1) H. Feuer and A. T. Nielsen, *J. Am. Chem. Soc.*, **84**, 688 (1962).

(2) T. M. Lowry, *J. Chem. Soc.*, 986 (1898).

(3) D. E. Ames and T. F. Grey, *ibid.*, 631 (1955).

PRIMARY PHOTOPRODUCT OF 2,6-DIMETHYL-4-AMINOPYRIMIDINE

Sir:

During the course of a systematic study of the photochemical (2537 Å.) behavior of a number of 4-aminopyrimidines,[1] one of these, 2,6-dimethyl-4-aminopyrimidine (I), was found to give rise in slightly alkaline medium (0.02 *M* phosphate buffer, pH 8–9) to a single primary photoproduct (II) which, because of its low solubility, crystallized spontaneously during irradiation. The importance of identifying II stems in part from the fact that the photochemical reaction involved appears to be typical of those undergone by other 4-aminopyrimidines[1]; it also bears some resemblance to the reactions exhibited by the 5-substituted cytosine residues found in the DNA of the T-even bacteriophages.[1,2]

Large scale preparation of II was achieved in better than 50% yield by irradiation of I in specially constructed preparative equipment elsewhere described.[3] Its molecular weight and elementary composition were similar to those for I, suggesting an intramolecular rearrangement. In the ultraviolet the long wave

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(1) K. L. Wierzchowski and D. Shugar, 4th Intern. Cong. Photobiol., Copenhagen, 1960 (in "Progress in Photobiology," Elsevier, Amsterdam, 1961, pp. 606–608).

(2) K. L. Wierzchowski and D. Shugar, *Acta Biochim. Polon.*, **7**, 63 (1960).

(3) D. Shugar, in "The Nucleic Acids" (E. Chargaff and J. N. Davidson, ed.), Vol. III, Chapt. 30, Academic Press, Inc., New York, N. Y., 1960.