

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.

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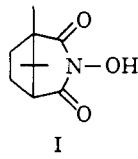
GEORGE C. PIMENTEL
RICHARD D. SPRATLEY

RECEIVED FEBRUARY 11, 1963

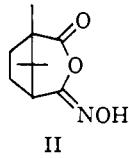
AN UNUSUAL NEF REACTION. THE REARRANGEMENT OF 3-NITROCAMPHOR

Sir:

We wish to report the rearrangement of 3-nitroc�푸 to N-hydroxycamphorimide (I) by acid catalysis. The reaction illustrates a variation of the direct Nef reaction¹ 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

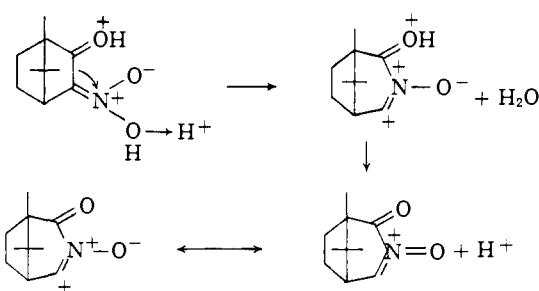


II

Camphoric anhydride was treated with N-benzyl-oxyamine according to the method of Ames and Grey³ to form N-benzylcamphorimide (III), m.p. 80–81°; $[\alpha]^{23}\text{D} + 19.2^\circ$ (CHCl_3). (Anal. Calcd. for $\text{C}_{17}\text{H}_{21}\text{NO}_3$: 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°, $[\alpha]^{23}\text{D} + 7.29^\circ$ (Anal. Calcd. for $\text{C}_{10}\text{H}_{15}\text{NO}_3$: 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 group³ occurred at 3.0, 5.74, and 5.95 μ .

The rearrangement of 3-nitroc�푸 with concentrated hydrochloric acid gave N-hydroxycamphorimide in 94% yield, m.p. 229–230°; $[\alpha]^{23}\text{D} + 7.46^\circ$ (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-nitroc�푸 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-nitroc�푸 with sodium hydroxide and benzoyl chloride forms the benzoate of I in a yield of 46%, m.p. 136–137°; $[\alpha]^{23}\text{D} + 9.73^\circ$ (CHCl_3). (Anal. Calcd. for $\text{C}_{17}\text{H}_{19}\text{NO}_4$: 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°; $[\alpha]^{23}\text{D} + 9.76^\circ$ (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-nitroc�푸 with acetic anhydride forms N-acetoxycamphorimide in 45% yield, m.p. 116–117°; $[\alpha]^{24}\text{D} + 6.43^\circ$ (CHCl_3) (Anal. Calcd. for $\text{C}_{12}\text{H}_{17}\text{NO}_4$: 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°, $[\alpha]^{24}\text{D} + 6.69^\circ$. (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.

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RECEIVED NOVEMBER 19, 1962

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-aminopyrimidines¹; 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

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

(2) K. L. Wierchowski 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.

(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).

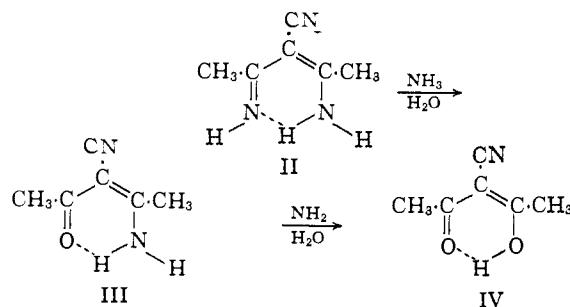
length maximum of I, λ_{\max} 2640 Å. (ϵ_{\max} 3,800) is shifted in II to λ_{\max} 2920 Å. (ϵ_{\max} 11,800), for the neutral forms.

In aqueous medium, at room temperature, II underwent deamination at pH below 4 or above 9 with loss of one nitrogen to give, quantitatively, III, λ_{\max} 2900 Å. (ϵ_{\max} 14,700). The latter, in dilute alkali at room temperature, was further deaminated with loss of one nitrogen to give, quantitatively, IV⁴ which, on crystallization from dilute acid, m.p. 52.5–53.0°, had a molecular weight and elementary analysis corresponding to $C_8H_7NO_2$ and λ_{\max} 2760 Å. (ϵ_{\max} 10,300) for the neutral form.

Compound IV exhibits an acid function, $pK = 3.5$, but the infrared spectrum shows neither the carbonyl nor the OH stretching frequencies typical for a normal carboxyl group. There is, instead, a broad, weak, band in the region 2850–2450 cm.⁻¹ (attributable to a strongly bonded OH group, and a strong, broad, band centered at 1598 cm.⁻¹ which may be due to the C=O stretching vibration in either a strongly internally hydrogen-bonded carboxyl group or an enolic β -diketone. There is also a strong, sharp, band at 2220 cm.⁻¹, present also in II and III, but absent in I, indicative of the presence of either a cumulative double bond or a nitrile group. The latter possibility was at first disregarded because of the remarkable stability of IV in acid and alkali. For the same reason the similarity in melting point and elementary composition of IV to the cyanoacetylacetone described by Traube⁵ was initially regarded as coincidental.

Recourse was then had to n.m.r. In carbon tetrachloride IV exhibits a sharp peak at 7.62 (all values in p.p.m., SiMe₄ measured at 40 Mc.) ascribed to methyl groups and a broad peak at –6.80 assigned to OH groups, the low field position for the latter being characteristic for a β -diketone, e.g., for acetylacetone the absorption is at about –6. In addition both the methyl groups of I were found in II and appeared to be equivalent; the presence of two methyl groups in II was further substantiated by an examination of III (see below).

The foregoing findings, together with the infrared evidence, led us to prepare Traube's acetylacetone, the properties of which proved indeed to be identical with those of IV. Furthermore the dissociated form of IV exhibits a bathochromic shift in λ_{\max} to 2800 Å. (ϵ_{\max} 18,000) which finds its counterpart in the dissociated form of II, λ_{\max} 2980 Å. (ϵ_{\max} 22,000). The locations of these maxima and, in particular, their high extinction coefficients, indicate a common skeletal structure differing from I and in line with that for acetylacetone derivatives. The formula of IV, and its formation from II, is therefore as follows



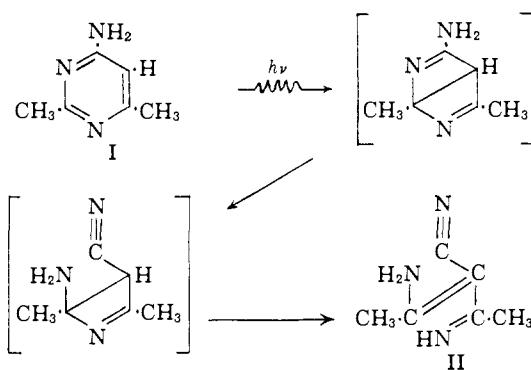
From the foregoing it is clear why the methyl groups in II (2-amino-3-cyano-2-ene-4-imine) and IV (3-cyano-2-en-2-ol-4-one) appear to be equivalent on time average by n.m.r. In III (2-amino-3-cyano-

(4) Deaminations were carried out at 100° for preparative purposes.

(5) W. Traube, *Ber.*, **31**, 2938 (1898).

pent-2-en-4-one), on the other hand, there is a singlet at 7.66 assigned to CH₃CO; the other methyl peak, at 7.67, is split by the amino protons. Additional ultraviolet, infrared and n.m.r. data are in accord with the above and will be presented in full detail elsewhere. The stability of the nitrile group in II, III and IV toward acid and alkali at elevated temperatures can now be understood in terms of the resonance stabilization resulting from "conjugate chelation."⁶

A tentative mechanism for formation of II from I is



While there is no direct evidence for the unstable Dewar-like intermediates, a radical path not involving bridging would require that the reaction proceed *via* at least two steps. We consider this unlikely in view of the first-order course of the reaction and the formation of only one primary photoproduct (II). This is being investigated further.

The elucidation of this photochemical reaction is expected to be of considerable assistance in clarifying the nature of the photochemical transformations of other 4-aminopyrimidines and, particularly, of the various cytosine analogs^{1,2} which are of current importance in the photochemistry of nucleic acids.

(6) R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1068 (1949); J. Weinstein and G. M. Wyman, *J. Org. Chem.*, **23**, 1618 (1958).

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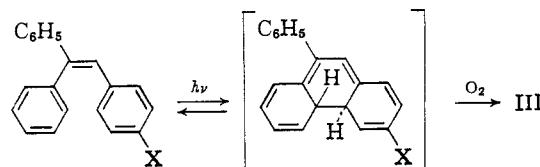
K. L. WIERZCHOWSKI
D. SHUGAR
A. R. KATRITSKY

RECEIVED NOVEMBER 10, 1962

PHOTOCHEMISTRY OF STILBENES. II. SUBSTITUENT EFFECTS ON THE RATES OF PHENANTHRENE FORMATION

Sir:

In further studies¹ of the photochemical conversion of stilbenes to phenanthrenes we have determined the effects of substituents on the rates of conversion of the substituted triphenylethylenes (I) *via* the presumed intermediate dihydrophenanthrenes (II) to the corresponding 3-X-9-phenylphenanthrenes (III) where X = H, CH₃, CH₃O, or Cl.



Magnetically stirred cyclohexane solutions, ca. 4 × 10⁻⁵ M in triphenylethylene and saturated either with air or with oxygen at 30°, were irradiated in a quartz cell with filtered light of wave lengths 312.5–313.1 m μ from a mercury arc.¹ The reactions were fol-

(1) F. B. Mallory, C. S. Wood, J. T. Gordon, L. C. Lindquist and M. L. Savitz, *J. Am. Chem. Soc.*, **84**, 4361 (1962).