based on the full kinetic isotopic criterion, *i.e.*, the variation of k_H/k_D with temperature.[18]

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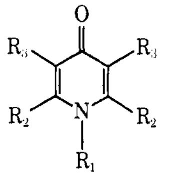
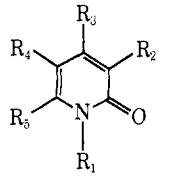
Photochemical Rearrangement of 4-Pyridones

Sir:

The photochemistry of 2-pyridones has been extensively studied and the 4 + 4 adducts[1] or bicyclic isomer[2,3] was obtained. On the other hand, relatively little attention has been given to the photochemical reaction of the isomeric 4-pyridones. Sugiyama and his group reported that irradiation of Ic resulted in the recovery of the starting material.[4] We wish to report a novel photorearrangement of hindered 4-pyridones (Ia and Ib) leading to their isomers, 2-pyridones (IIa and IIb).



Ia, $R_1 = R_2 = Me$; $R_3 = Ph$
b, $R_1 = Et$; $R_2 = Me$; $R_3 = Ph$
c, $R_1 = Me$; $R_2 = Ph$; $R_3 = H$
d, $R_1 = n\text{-Pr}$; $R_2 = Me$; $R_3 = Ph$
e, $R_1 = Me$; $R_2 = R_3 = Ph$



IIa, $R_1 = R_3 = R_5 = Me$; $R_2 = R_4 = Ph$
b, $R_1 = Et$; $R_3 = R_5 = Me$; $R_2 = R_4 = Ph$
c, $R_1 = R_3 = R_4 = Me$; $R_2 = R_5 = Ph$
d, $R_1 = R_4 = R_5 = Me$; $R_2 = R_3 = Ph$

Irradiation[5] of Ia[6] in acetonitrile, followed by column chromatography of the reaction mixture on silica gel, resulted in the isolation of IIa[7] (mp 179.5–181.0°; ir 1630 cm^{-1} (C=O); nmr (CCl$_4$) δ 1.62 (s, 3 H), 2.06 (s, 3 H), 3.51 (s, 3 H), 7.1–7.4 (m, 10 H); mass spectrum (70 eV) at *m/e* (relative intensity) 289 (M$^+$ 78), 288 (100), 261 (44), 260 (39), 115 (27), 77 (39), 56 (37)) and IIc[7] (mp 203.0–203.5°; ir 1625 cm^{-1} (C=O); nmr (CCl$_4$) δ 1.72 (s, 3 H), 1.97 (s, 3 H), 3.10 (s, 3 H), 7.1–7.5 (m, 10 H); mass spectrum (70 eV) at *m/e* (relative intensity) 289 (M$^+$ 98), 288 (100), 261 (26), 260 (31), 115 (36), 105 (20), 77 (72), 51 (28)) in 35 and 2.5% yields, respectively. Photolysis[5] of Ib in acetonitrile gave IIb[7] in 31% yield (mp 159.5–160.5°; ir 1635 cm^{-1} (C=O); nmr (CCl$_4$) δ 1.32 (t, 3 H, J = 6.0 Hz), 1.61 (s, 3 H), 2.11 (s, 3 H), 4.16 (q, 2 H, J = 5.5 Hz), 7.1–7.5 (m, 10 H); mass spectrum (70 eV) at *m/e* (relative intensity) 303 (M$^+$ 99), 302 (71), 275 (50), 274 (100), 246 (12), 230 (10), 203 (14), 202 (17), 189 (11), 115 (12), 77 (10)). Irradiation[5] of Id[6] or Ie[6] in acetonitrile did not affect the starting materials.

In the mass spectra of photoproducts the presence of the intense peak corresponding to the expulsion of carbon monoxide from the parent peak (*m/e* 261 for IIa and IIc and 275 for IIb) clearly indicates that the photoproducts have the structure of 2-pyridone.[8] IIc was identical (melting point, ir and nmr spectra) with an authentic sample prepared from the condensation of 3,6-diphenyl-4,5-dimethyl-2-pyrone[9] with methylamine. The appearance of an intense peak at *m/e* 56 in the mass spectrum of IIa suggests the presence of a methyl group at C-6 in II.[10] The change of the nmr signals of the *C*-methyl protons by addition of Eu(fod)$_3$ suggests[11] that the other methyl group should be at C-4 or C-5, not at C-3. Confirmation of the structure of IIa was obtained by comparison with the melting point and the nmr spectrum of an authentic sample prepared by N-methylation of 4,6-dimethyl-3,5-diphenyl-2-pyridone.[12,13]

The accelerating effect of the phenyl groups on the photochemical rearrangement of the hindered 4-pyridones to 2-pyridones is reminiscent of similar substituent effects on the photoisomerization of the hindered 4-pyrones to 2-pyrones[9] and the photoconversion of the hindered 4-thiopyrones to cyclopentadienones.[15] A striking difference in the behavior of the hindered 4-pyridones upon ultraviolet irradiation from that of the hindered 4-pyrones is the position of the substituents in the photoproducts. Photolysis of Ia or Ib gave IIa or IIb, respectively, as the major product, whereas

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(1) L. A. Paquette and G. Slomp, *J. Amer. Chem. Soc.*, **85**, 765 (1963); E. C. Taylor and R. Kan, *ibid.*, **85**, 776 (1963); W. A. Ayer, R. Hayatsu, P. de Mayo, S. T. Reid, and J. B. Stothers, *Tetrahedron Lett.*, 648 (1961).

(2) E. J. Corey and J. Streith, *J. Amer. Chem. Soc.*, **86**, 950 (1964); R. C. Deselms and W. R. Schleigh, *Tetrahedron Lett.*, 3563 (1972); H. Furrer, *Chem. Ber.*, **105**, 2780 (1972).

(3) We thank a referee for calling our attention to the recent papers on the photochemistry of 2-pyridones.

(4) C. Kashima, M. Yamamoto, Y. Sato, and N. Sugiyama, *Bull. Chem. Soc. Jap.*, **42**, 3596 (1969).

(5) All irradiations were carried out with a 500-W medium-pressure mercury lamp in a Vycor immersion-well apparatus filled with nitrogen. Irradiation of Ia filtered by Pyrex instead of Vycor produced no reaction.

(6) The hindered 4-pyridones,[7] Ia (mp 278.5–279.0°), Ib (mp 242.5–243.5°), Id (mp 231.0–232.0°), and Ie (mp 317.0–318°), were obtained by heating a mixture of the corresponding 4-pyrones and alkylamines in a sealed tube.

(7) Satisfactory elemental analyses were obtained for all new compounds reported here.

(8) H. Budzikiewicz, C. Djerassi, and D. W. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 359.

(9) N. Ishibe, M. Odani, and M. Sunami, *Chem. Commun.*, 1034 (1971); N. Ishibe, M. Sunami, and M. Odani, *J. Amer. Chem. Soc.*, **95**, 463 (1973).

(10) R. Lawrence and E. S. Waight, *J. Chem. Soc. B*, 1 (1968).

(11) When the chemical shifts of the *C*-methyl protons of IIa and IIc were plotted as a function of added shift reagent, the following slopes (the lowest slope arbitrarily chosen as 1.0) were obtained: 1.1 and 1.9 for IIa and 1.0 and 2.1 for IIc. The comparison of these values with those of 3-methyl-, 4-methyl-, 5-methyl-, and 6-methyl-2-pyridones (8.0, 1.0, 1.8, and 2.0) clearly indicates that a methyl group of IIa is not at C-3 of 2-pyridone.

(12) J. F. M. Wajon and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **76**, 65 (1957).

(13) IId (mp 174.0–175.0°) prepared by condensation, with methylamine, of 5,6-dimethyl-3,4-diphenyl-2-pyrone, which was synthesized by the reaction[14] of diphenylcyclopropenone with α-methylacetonylpyridinium ylide, was ruled out as the structure of the photoproduct from comparison of its ir and nmr spectra with those of IIa.

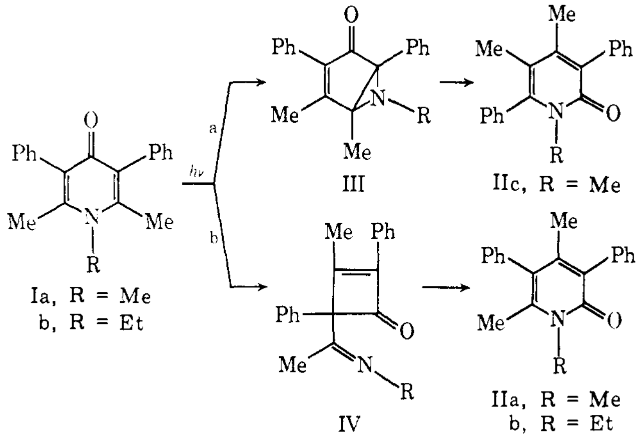
(14) T. Eicher, E. v. Angerer, and A. M. Hansen, *Justus Liebigs Ann. Chem.*, **746**, 102 (1971).

(15) N. Ishibe and M. Odani, *Chem. Commun.*, 702 (1971); N. Ishibe, M. Odani, and R. Tanuma, *J. Chem. Soc., Perkin Trans. 1*, 1203 (1972).

photolysis of 2,6-dimethyl-3,5-diphenyl-4-pyrone afforded 3,6-diphenyl-4,5-dimethyl-2-pyrone as the sole product.[9] Neither IIa nor IIc is a precursor for the other in the formation of IIc or IIa, independent thermolysis and irradiation of IIa or IIc having no effect. These results suggest the predominance of a distinctly different mechanism for the rearrangement of hindered 4-pyridones.

A tentative mechanism to account for the formation of 2-pyridones (II) from 4-pyridones (I) is presented in Scheme I. We believe that photolysis of the hindered 4-pyridones leads initially to the 6-azabicyclo[3.1.0]hexenone (III)[16] which is converted, in either a photochemical or thermal process, to the pyridone IIc as a minor product (path a). This photoconversion is analogous to photoisomerization of the hindered 4- to 2-pyrones.[9] For the formation of the major product, photolysis of I may initially proceed by isomerization to the cyclobutenone derivative IV,[17] which is converted to II (path b). The entirely different nature of the photochemical primary reactions of furans and pyrroles was recently demonstrated by trapping of the transient species.[18,19] Stability of Id and Ie against light might be explained in terms of the steric effect of the substituents,[20] since molecular models show that C–N bond cleavage in Id and Ie would lead to the formation of intermediate III or IV in which there was appreciable steric hindrance.

Scheme I



The proposed mechanism, while it rationalizes the experimental observation presented, may not constitute a unique explanation for the results. An investigation of the factors influencing reactivity in the 4-pyridones is currently in progress.

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Gas-Phase Isopropylation of Toluene. On the Question of the Positional Selectivity in Gas-Phase Aromatic Substitutions

Sir:

From experiments carried out during the past five years in this laboratory with different gaseous electrophiles, including HeT^+ ions from the β decay of molecular tritium,[1-3] $^{80}Br^+$ ions from the isomeric transition of CH_3–^{80m}Br,[4] and radiolytically formed D_2T^+ [5] and alkyl[6] ions, we conclude that the gas-phase electrophilic attack on the aromatic ring is characterized by a significant *positional* selectivity.

In a recent paper the isomeric distribution of isopropyltoluenes from the gas-phase attack of radiolytically formed i-$C_3H_7^+$ ions on C_7H_8 was reported to be *statistical* (*i.e.*, 44.2% ortho, 40.4% meta, and 15.4% para) at low pressures of toluene, going to a *thermodynamically controlled* distribution (*i.e.*, 28.2% ortho, 59.2% meta, and 12.6% para) at higher pressures of toluene.

The formation of large amounts of the meta isomer was regarded as a typical feature of the gas-phase isopropylation, and the *statistical* distribution observed at low C_7H_8 pressures was ascribed to the inherent lack of selectivity of the gaseous i-$C_3H_7^+$ cation.

Since the behavior of the i-$C_3H_7^+$ ion described in ref 7 represented a conspicuous and disturbing departure from the selectivity established for other gaseous electrophiles, further investigation was undertaken in the hope of accounting for the discrepancy.

The isopropylation described in ref 7 was carried out with gaseous i-$C_3H_7^+$ ions obtained according to a general technique introduced by Ausloos and coworkers,[8] based on the γ radiolysis of a gaseous alkane, in this case C_3H_8, containing a radical scavanger and a low concentration of the aromatic substrate.

The well established radiation-induced decomposition of C_3H_8 and the subsequent ion–molecule reactions

$$C_3H_8 \rightsquigarrow C_3H_7^+ + H + e \qquad (1)$$

$$C_3H_8 \longrightarrow C_2H_5^+ + CH_3 + e \qquad (2)$$

$$C_2H_5^+ + C_3H_8 \longrightarrow C_2H_6 + C_3H_7^+, \text{ etc.} \qquad (3)$$

of the charged fragments lead to the predominant formation of the secondary propyl ion, whose attack on toluene gives isomeric arenonium ions and eventually the isomeric isopropyltoluenes, following the loss of a

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(16) The synthetic method of the 6-azabicyclo[3.1.0]hexenyl system was recently reported: L. Kaplan, J. W. Pavlik, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, **94**, 3283 (1972); A. Mishra, S. N. Rice, and W. Lwowski, *J. Org. Chem.*, **33**, 481 (1968).

(17) An isolation of vinylcyclobutenone from photolysis of 4-hydroxy-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone was reported: D. A. Plank, J. C. Floyd, and W. H. Starnes, Jr., *Chem. Commun.*, **1003** (1969).

(18) H. Hiraoka, *ibid.*, 1610 (1971).

(19) A preliminary attempt to trap the intermediate III or IV by methanol was unsuccessful and photolysis of Ia in methanol gave only IIa and IIc.

(20) Comparison of the absorption and emission (fluorescence and phosphorescence) spectra of Id and Ie with those of Ia and Ib did not give distinct evidence to distinguish their photoreactivity. Analysis of the absorption and emission spectra of 4-pyridones, 4-thiopyrones, and 4-pyrones will be published elsewhere.

(1) F. Cacace and S. Caronna, *J. Amer. Chem. Soc.*, **89**, 6848 (1967).

(2) F. Cacace and G. Perez, *J. Chem. Soc. B*, 2086 (1971).

(3) F. Cacace, R. Cipollini, and G. Ciranni, *ibid.*, 2089 (1971).

(4) F. Cacace and G. Stöcklin, *J. Amer. Chem. Soc.*, **94**, 2518 (1972).

(5) F. Cacace, R. Cipollini, and G. Occhiucci, *J. Chem. Soc., Perkin Trans. 2*, **84** (1972).

(6) F. Cacace, *et al.*, unpublished data.

(7) S. Takamuku, K. Iseda, and H. Sakurai, *J. Amer. Chem. Soc.*, **93**, 2420 (1971).

(8) For an exhaustive review, *cf.* P. Ausloos, "Ion-Molecule Reactions," J. L. Franklin, Ed., Plenum Press, New York, N. Y., 1970.