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A PHOTOREARRANGEMENT OF 6-METHYLENETRICYCLO[3.2.1.0^{2,7}]OCT-3-EN-8-ONE OXIME DERIVATIVES : DI-π-METHANE TYPE REARRANGEMENT INVOLVING AN OXIME MOIETY

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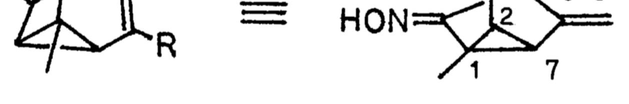
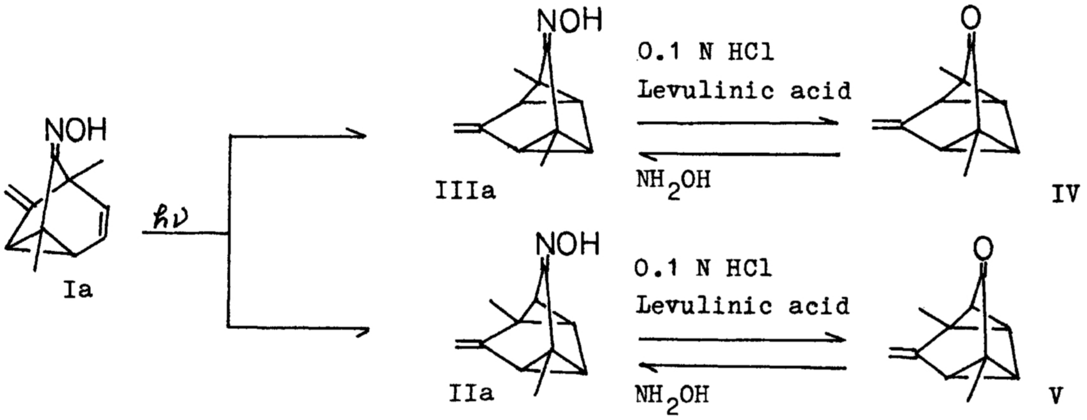
6-Methylenetricyclo[3.2.1.0^{2,7}]oct-3-en-8-one oxime derivatives (Ia) and (Ib), upon irradiation, afforded 3-methylenetetracyclo-[3.3.0.0.^{2,8}0^{4,6}]octan-8-one oxime derivatives (IIa), (IIIa) and (IIb), respectively. The photorearrangement leading to IIa and IIb were ascribed to a novel di-π-methane type rearrangement involving the oxime moiety.

Previously we have described that 6-methylenetricyclo[3.2.1.0^{2,7}]oct-3-en-8-ols undergo a photochemical di-π-methane rearrangement leading to 3-methylenetetracyclo-[3.3.0.0.^{2,8}0^{4,6}]octan-8-ols.[1] Although a di-π-methane rearrangement and an oxa-di-π-methane rearrangement have been investigated in various systems,[2] this type of photoreaction has not been found in the system containing a carbon-nitrogen double bond. Oximes undergo the photoreaction leading to oxaziridines,[3] or nitriles.[4] From these points of view, we investigated the photoreaction of the compounds (Ia) and (Ib) in the title.[5] These compounds possess two transoid di-π-methane systems,[6] C_3-C_4-C_5-C_6-$C_{6'}$ moiety and C_3-C_4-C_5-C_8-$C_{8'}$ moiety (aza-di-π-methane system), both systems exist in the same stereochemical situation. Another aza-di-π-methane system ($C_{6'}$-C_6-C_5-C_8-$C_{8'}$) exists as well. We would like to report the preliminary results in this paper.



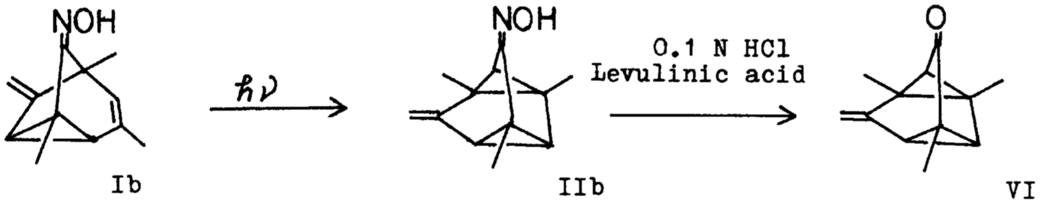
Ia : R=H
Ib : R=CH_3

A degassed solution of Ia (5 mmol) in acetonitrile (100 ml) was photolyzed (Rayonet photoreactor, 254 nm, quartz vessel) for 3.5 hr. Separation of the photolysate was achieved by silica-gel chromatography to afford IIa, mp 177-180° and IIIa, mp 151-152° in 55 % and 24 % yields respectively, in addition to 11 % of the starting material. The spectral properties of IIa and IIIa are as follows : IIa, m/e, 175 (10 %, M^+), 158 (100 %); ν (KBr), 3200, 1645, 895 cm^{-1}; δ ($CDCl_3$), 1.20 (3H, s), 1.28 (3H, s), 2.02 (1H, d, J=6.0 Hz), 2.30 (1H, t, J=6.0 Hz), 2.42 (1H, t, J=6.0 Hz), 2.58 (1H, d, J=6.0 Hz), 4.96 (1H, s), 5.16 (1H, s), 8.94 (1H, s); IIIa, m/e, 175 (10 %, M^+), 160 (100 %); ν (KBr), 3300, 1680, 875 cm^{-1}; δ ($CDCl_3$), 1.12 (3H, s), 1.42 (3H, s), 1.64-1.85 (2H, m), 1.85-2.24 (2H, m), 4.73 (1H, s), 4.75 (1H, s), 8.22 (1H, s).



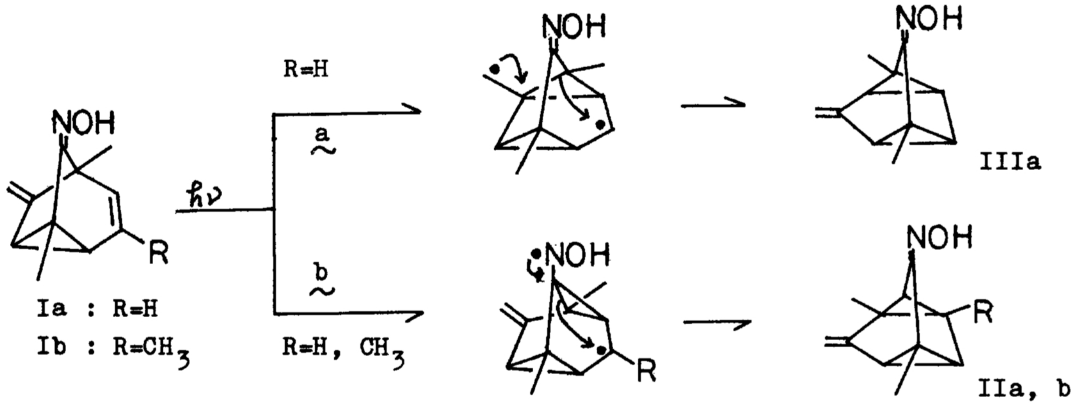
Treatment of IIIa with 0.1 N hydrochloric acid in levulinic acid at room temperature afforded the known ketone IV[1] in 69 % yield and the ketone regenerated IIIa in 57 % yield by treatment with hydroxylamine in the usual manner, hence the structure for IIIa was settled. Exactly the same chemical transformations are realized for IIa as in the case of IIIa and ketone V thus obtained gave the following spectral characteristics : V, m/e, 160 (3 %, M^+), 132 (99 %), 117 (100 %); ν (neat), 1710, 870 cm^{-1}; δ (CCl_4), 1.06 (3H, s), 1.25 (3H, s), 1.59 (1H, m), 2.06 (1H, m), 2.44 (2H, m), 5.00 (1H, s), 5.20 (1H, s). The chemical shifts and the coupling patterns of nmr spectrum of IIa suggest the existence of two cyclopropane rings and exo-methylene group in IIa, and carbonyl absorption band at 1710 cm^{-1} of V[1,7] is consistent with the proposed skeleton for V, hence the structures were deduced for IIa and V.[8]

The photoreaction of the closely related trimethyl analogue Ib was also studied in order to asses the generality and substituent effect of the above photorearrangement. Direct irradiation of Ib in the similar manner afforded only one product IIb, mp 150-152° in 54 % yield, in addition to 25 % of the starting material. IIb exhibited the following spectral properties : m/e, 189 (11 %, M^+), 176 (100 %0; ν (KBr), 3300, 1635, 860 cm^{-1}; δ ($CDCl_3$), 1.20 (6H, s), 1.37 (3H, s), 1.94 (1H, d, J=6.0 Hz), 2.06 (1H, d, J=6.0 Hz), 2.20 (1H, s), 4.85 (1H, s), 5.01 (1H, s), 8.48 (1H, s). Similarly the treatment of IIb with 0.1 N hydrochloric acid in levulinic acid afforded ketone VI : m/e, 174 (3 %, M^+), 146 (100 %); ν (neat), 1700, 870 cm^{-1}; δ (CCl_4), 1.06 (3H, s), 1.16 (3H, s), 1.38 (3H, s), 1.94 (1H, d, J=5.0 Hz), 2.14 (1H, d, J=5.0 Hz), 2.42 (1H, s), 4.86 (1H, s), 4.98 (1H, s). These spectral characteristics are consistent with the structures IIb and VI.[1] The stereochemistry of oxime groups of the photoproducts IIa and IIb are unknown at present stage.



In order to assign the excited state responsible for the present photorearrangement, Ia was irradiated in acetone, and in acetonitrile containing benzophenone, xanthone and acetophenone respectively. No di-π-methane rearrangement took place under these conditions.[9] This result might suggest that Ia undergoes the photorearrangement via a singlet state.

The formal reaction consequences to give IIa, IIb and IIIa are shown below in order to explain the present photoreaction. The di-π-methane rearrangement shown by



path a should lead IIIa as seen in the case of 6-methylenetricyclo[3.2.1.$0^{2,7}$]oct-3-en-8-ols.[1] The formation of IIa and IIb seemingly follows path b (aza-di-π-methane type rearrangement). The photorearrangement of Ia follows path a and path b, while that of Ib follows only path b , and hence the methyl group on C_3 seems to affect the reaction pathway. Available evidence do not allow us to distinguish two mechanisms, stepwise or concerted, for the formation of IIa, IIIa and IIb.

Since the ketone corresponding to Ia and Ib are known to afford 2-indanones upon irradiation,[10] the present photoreaction might have a synthetic utility to prevent the reaction arising from an $n-\pi^*$ excitation of carbonyl group. Scope and limitation of the present photoreactions as well as the mechanistic aspects are under investigation.

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5. Ia and Ib were prepared by treatment of the corresponding ketones (J. Zsindely, H. Schmid, Helv., 51, 1510, 1968) with hydroxylamine in the usual manner. The stereochemistry of hydroxy group of Ia and Ib could not be determined. Mass spectral data and elemental analyses are satisfactory for all new compounds in this paper.
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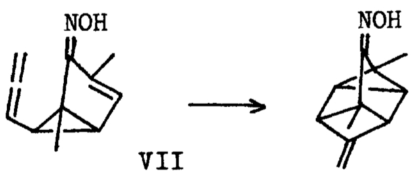
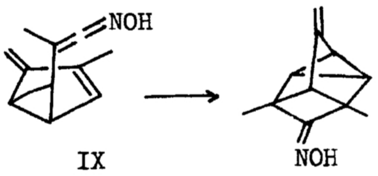
8. Other structural possibility for IIa is VIII and X, which possibly arise from allene VII and ketene imine IX. However these structures were easily eliminated on the basis of the spectral properties of IIa and V.



VII VIII



IX X

9. In the presence of benzophenone, the photocycloadducts of Ia and benzophenone were obtained. See, M. Nitta, H. Sugiyama, Y. Sekine, Chem. Lett., 55 (1977).
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