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PHOTOISOMERIZATION OF 6-METHYLENETRICYCLO[3.2.1.$0^{2,7}$]OCT-3-EN-8-OLS : A CONVENIENT SYNTHESIS OF 3-METHYLENETETRACYCLO[3.3.0.0.^{4,6} $0^{2,8}$]OCTAN-7-OLS AND RELATED KETONES

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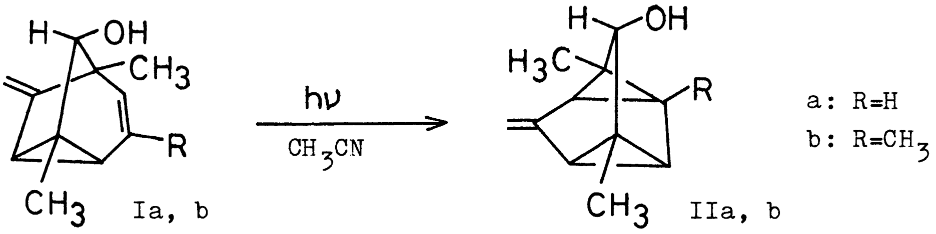
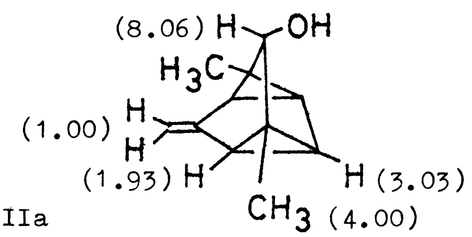
Ultraviolet irradiation of 6-methylenetricyclo[3.2.1.$0^{2,7}$]-oct-3-en-8-ols (Ia) and (Ib) afforded 3-methylenetetracyclo[3.3.0.0.$^{4,6}0^{2,8}$]octan-7-ols (IIa) and (IIb) in fairly good yields. This photorearrangement is considered to be a di-π-methane rearrangement. Oxidation of the photoproducts gave the ketones retaining the carbon skeleton of IIa and IIb

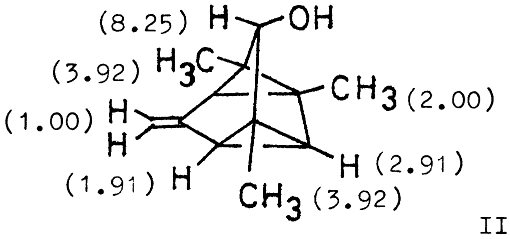
The valence bond formalism for a di-π-methane rearrangement has been developed by Zimmerman et. al.[1] and evidence have been presented for the existence of both cisoid and transoid diradicals as intermediates in the rearrangement.[2] On photolysis, 1,3,4,5,7,8,8-heptamethyl-6-methylenetricyclo[3.2.1.$0^{2,7}$]oct-3-ene (VI), which possesses a di-π-methane system, isomerizes to 2-methylenetetracyclo-[3.3.0.0.$^{4,6}0^{3,8}$]octane derivative (IX).[3] In this paper we will describe a novel type of photorearrangement of 1,5-dimethyl-6-methylenetricyclo[3.2.1.$0^{2,7}$]oct-3-en-8-ol (Ia) and its 1,3,5-trimethyl derivative (Ib), both of which possess a transoid di-π-methane system, leading to 3-methylenetetracyclo[3.3.0.0.$^{4,6}0^{2,8}$]octan-7-ol derivatives (IIa) and (IIb).



Photolysis of Ia[4] in acetonitrile (0.5 M) was carried out using a Rayonet photoreactor (MGR-100, 254 nm, quartz vessel). Purification of the photolysate was achieved by an alumina chromatography to afford IIa,[5] mp 76-78° in 88 % yield. In the similar manner, Ib afforded IIb in 87 % yield. The structures of IIa and IIb were deduced from the following spectral data and the chemical transformation: IIa, ν (KBr), 3320, 1635, 865 cm^{-1}; δ (CCl_4), 1.14 (6H, s), 1.60 (2H, d, J=6.0 Hz), 1.89 (2H, d, J=6.0 Hz), 3.51 (1H, s), 4.78 (2H, s); IIb, ν (neat), 3300, 1635, 850 cm^{-1}; δ (CCl_4), 1.08 (3H, s), 1.12 (3H, s), 1.22 (1H, d, J=3.0 Hz), 1.34 (3H, s), 1.60 (1H, dd, J=3.0, 7.0 Hz), 1.71 (1H, d, J=7.0 Hz), 3.56 (1H, s), 4.66 (1H, s), 4.70 (1H, s). The nmr spectrum of IIa suggests a symmetric structure and is consistent with the proposed structure IIa. In the case of IIb, the existence of W-shape coupling(J=3.0 Hz) between the protons at δ 1.22 and δ 1.60 also supports the proposed structure. The configuration of hydroxy groups of IIa and IIb was assigned to be exo to the methylene group, according to the relative down field shifts (ppm/mol) of δ in the presence of $Eu(fod)_3$, which are given in parentheses on the following structural formulae IIa and IIb.[6]

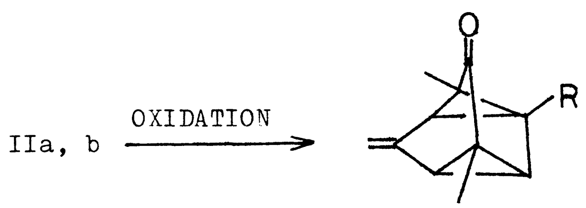


IIa

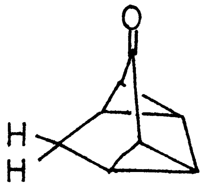


IIb

IIa and IIb, thus obtained, were submitted to oxidation using pyridinium chlorochromate,[8] and the corresponding ketones IIIa and IIIb were obtained in 71 % and 57 % yields, respectively. The structures of IIIa and IIIb were characterized by the following spectral properties: IIIa, ν (neat), 1710, 875 cm^{-1}; δ (CCl_4), 1.12 (6H, s), 2.00 (2H, d, J=6.0 Hz), 2.44 (2H, d, J=6.0 Hz), 5.04 (2H, s); IIIb, ν (neat), 1695, 875 cm^{-1}; δ (CCl_4), 1.10 (3H, s), 1.14 (3H, s), 1.45 (3H, s), 1.68 (1H, d, J=3.0 Hz), 2.01 (1H, dd, J=3.0, 6.0 Hz), 2.25 (1H, d, J=6.0 Hz), 5.01 (1H, s), 5.06 (1H, s).



IIIa: R=H
IIIb: $R=CH_3$

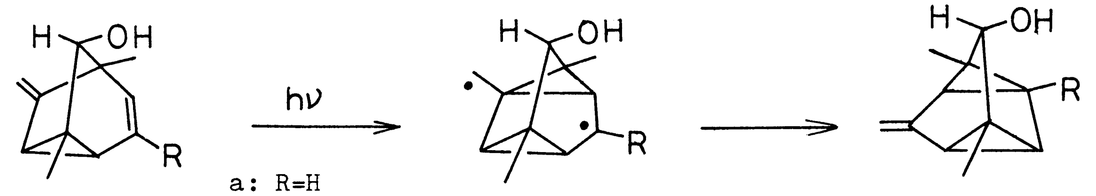


IV

The low frequency of the absorption due to the carbonyl band at 1710 cm^{-1} and 1695

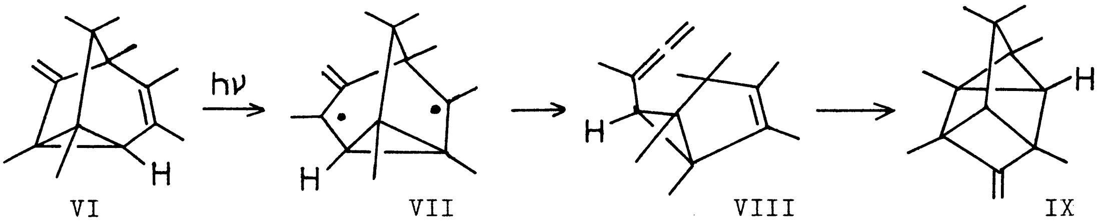
cm^{-1} for IIIa and IIIb, as compared to compound IV (1720 cm^{-1}),[9] should be ascribed to the conjugative effect of the methylene group and the substituent effect of the methyl groups on the cyclopropane rings. IIa and IIIa were stable to heat and the starting materials were recovered after heating at 180° for 3 hr.

To rationalize the formation of the photoproducts IIa and IIb, a plausible mechanism is proposed as follows. Since Ia and Ib contain a di-π-methane system, the formation of IIa and IIb can be ascribed to a kind of di-π-methane rearrangement via a transoid cyclopropyldicarbinyl diradical (V) as depicted in the scheme. This photorearrangement was not sensitized by either acetone, acetophenone and benzophenone,[7] and hence it probably proceeds via a singlet excited state. The triplet excited state must dissipate its energy by a free rotor effect.[1,10] It is remarkable that 1,3,4,5,7,8,8-heptamethyl-6-methylenetricyclo[3.2.1.$0^{2,7}$]oct-3-ene VI undergoes the photoreorganization leading to the framework of IX via the allene intermediate VIII[3] but Ia and Ib undergo a kind of di-π-methane rearrangement. Evidence have been presented that a hydroxy group affects the regioselectivity of a di-π-methane rearrangement by a kind of through space interaction.[11] It is not clear at present stage whether this kind of effect is operative for the selective transformation of I into II.



a: R=H

Ia, b b: R=CH_3 Va, b IIa, b



VI VII VIII IX

Since the ketone, from which Ia is derived by hydride reduction, is known to undergo the photorearrangement leading to 1,4-dimethylindan-2-one via ketene intermediate,[12] the photorearrangement described here is a very convenient method for making the tetracyclo[3.3.0.$0^{4,6}0^{2,8}$]octane ring system bearing a methylene group and the functions of hydroxy or carbonyl group. The chemistry of those compounds and the mechanistic aspect of the present photorearrangement involving the substituent effects are in progress.

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References and Notes

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    We also tried the photolysis of 1,3,5-trimethyl-6-methylenetricyclo[3.2.1.$0^{2,7}$]oct-3-en-8-one at 77K, and observed the ketene band at 2105 cm^{-1} in low temperature ir spectrum.

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