CHEMISTRY LETTERS, pp. 1357-1360, 1982.

FUNCTIONALIZATION OF UNACTIVATED CARBON INVOLVING PHOTOCHEMICAL INTRAMOLECULAR REARRANGEMENT OF NITRO GROUP ATTACHED TO TETRAHEDRAL CARBON TO NITROSOOXY GROUP1)

Hiroshi SUGINOME*, Kyohei TAKAKUWA, and Kazuhiko ORITO
Organic Synthesis Division, Department of Chemical Process Engineering,
Faculty of Engineering, Hokkaido University, Sapporo 060

Photolysis of both 6β-nitrocholest-4-ene and 4β-nitrocholest-6-ene gave a mixture of (*E*)-19-hydroxyiminocholest-4-en-6β-ol and (*E*)-19-hydroxyiminocholest-5-en-4β-ol; this mixture arose in both cases from a photochemical nitro-nitrosooxy rearrangement followed by the Barton reaction. The structures of the products were established by their synthesis.

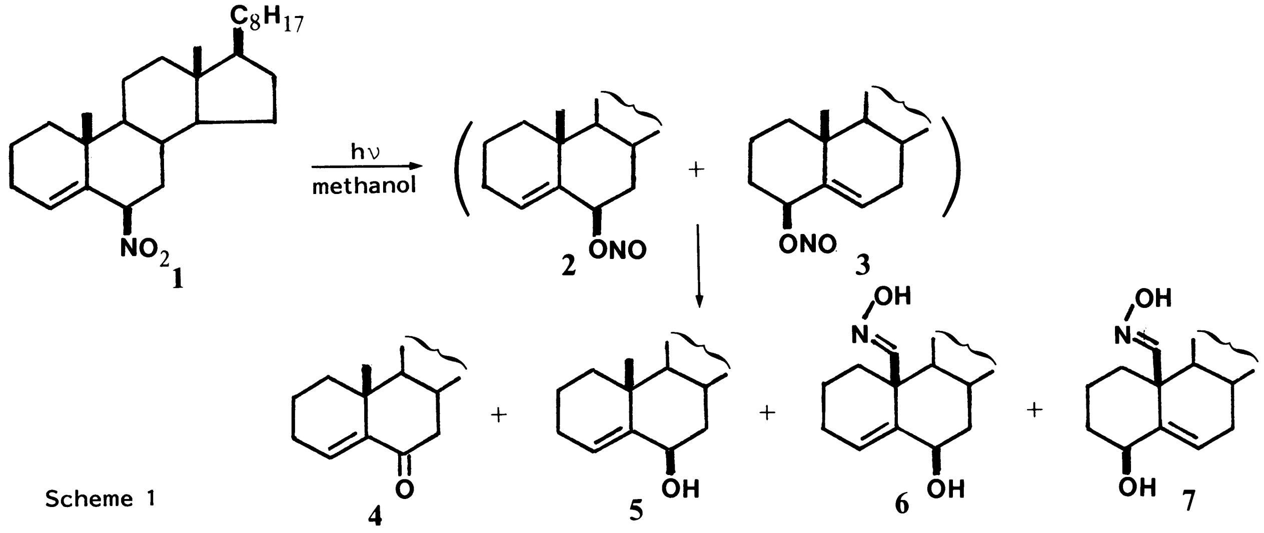
We wish to report the first recorded example of the functionalization of unactivated carbon involving an intramolecular photochemical nitro-nitrosooxy rearrangement. The nitro-nitrosooxy rearrangement has been reported in the photolysis of nitroalkenes in solution2) and in the photolysis of nitroalkanes in a gas phase and in a solid argon matrix.3-6) The rearrangement found is, however, believed to be the first example of the unambiguous photochemical rearrangement of a nitro group attached to a tetrahedral carbon to the corresponding nitrosooxy group in a solution.

Thus, photolysis of 6β-nitrocholest-4-ene(1)7) [λ_{max} (methanol) 286 nm (100)] in methanol with a low pressure mercury arc generated by a Rayonet RPR 208 photochemical reactor under a nitrogen atmosphere for 3 h resulted in an 81% conversion of 1 and gave cholest-4-en-6-one(4)8-10) (7%), cholest-4-en-6β-ol(5)11) (11%), and two products, (6) (24%) and (7) (7%). The products 6 and 7 were assignable to either (*E*)-19-hydroxyiminocholest-4-en-6β-ol or (*E*)-19-hydroxyiminocholest-5-en-4β-ol on the basis of their spectroscopic data (Scheme 1).12)

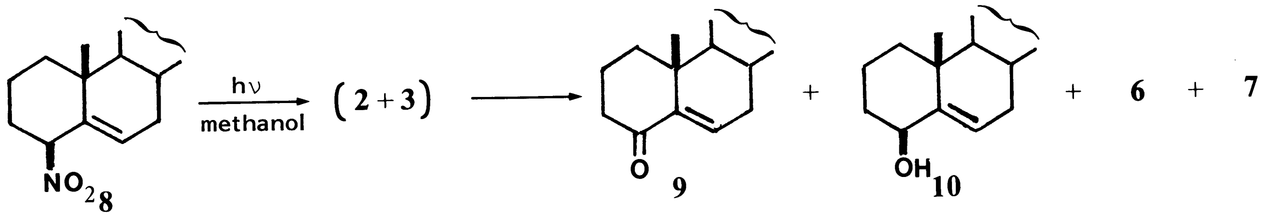
Photolysis of 4β-nitrocholest-5-ene(8)7) [λ_{max} (methanol) 292 nm (102)] for 3 h under the conditions similar to the photolysis of 1 proceeded in an entirely parallel manner and gave cholest-5-en-4-one(9)9,13) (1%), cholest-5-en-4β-ol(10)11) (13.5%), and two (*E*)-19-hydroxyiminocholestenes, 6 (6%), and 7 (25%), (Scheme 2).14)

It was immediately clear that oximes 6 and 7 are the products which arise from the Barton reaction15) of cholest-4-en-6β-ol nitrite(2) and cholest-5-en-4β-ol nitrite (3) generated by the photochemical nitro-nitrosooxy rearrangement and that all the other products are those which are usually formed in the Barton reaction.

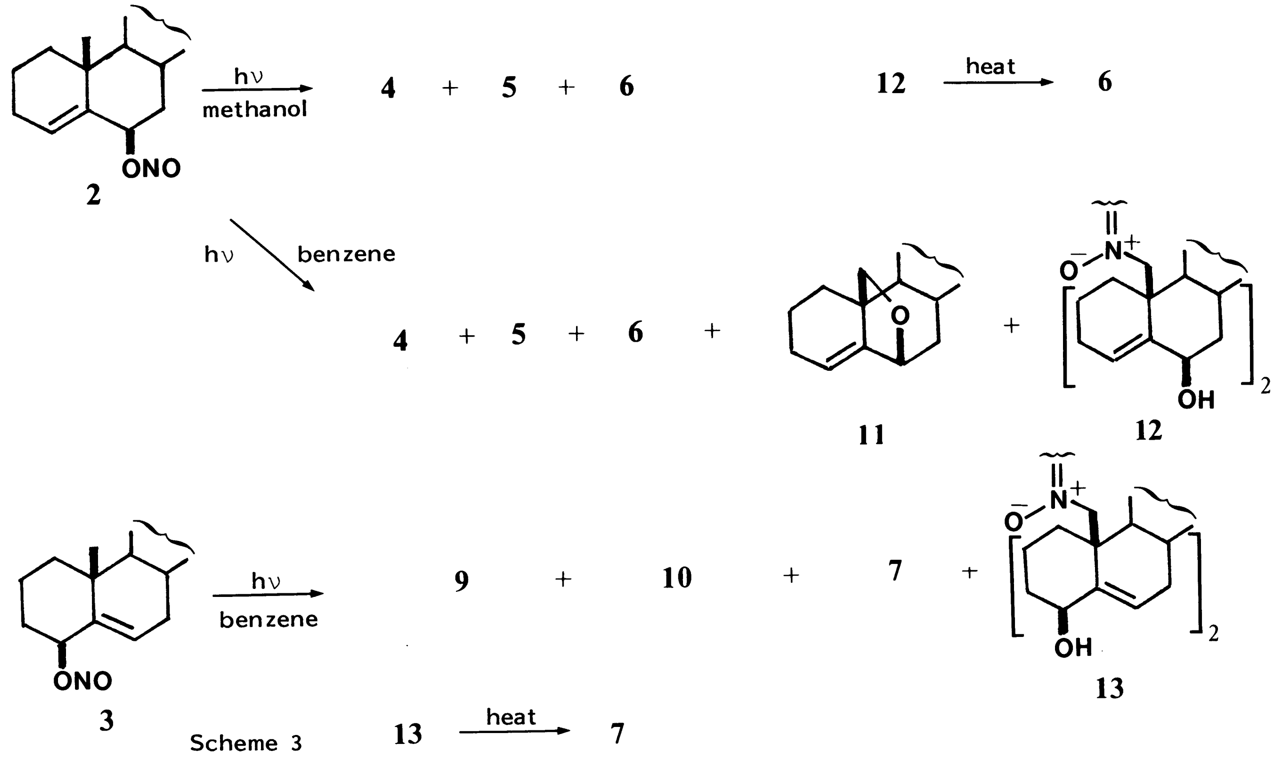
The intermediacy of nitrites 2 and 3 as well as the structures of 6 and 7 were established by the photolysis of nitrites 216) and 317) which were newly prepared by nitrosation of 6β-ol10,11) 5 and 4β-ol11) 10 respectively. Thus, photolysis of 2 in a 1 : 3 benzene-methanol with a low pressure mercury arc generated by a Rayonet photochemical chamber reactor for 4 h gave 4 (6%), 5 (30%), and 618) (30%); this



Scheme 1



Scheme 2



Scheme 3

final product was identical with the product 6 obtained in the photolysis of 1. Photolysis of 2 in benzene with a 100-W high pressure mercury arc through Pyrex-filter gave 6β,19-epoxycholest-4-ene(11)19) (4%), 4 (12%), 5 (12%), 6 (10%) as well as a dimer (12)20) of 19-nitrosocholest-4-en-6β-ol(52%). The nitroso-dimer 12 was transformed into 6 in an 87% yield by refluxing its isopropyl alcohol solution for 30 min (Scheme 3). On the other hand, similar photolysis of 3 in benzene gave 9 (6%), 10 (10%), 721) (20%), and a dimer (13) (mp 162-163°C) of 19-nitrosocholest-5-en-4β-ol (34%). The nitroso-dimer(13) was transformed into 7, identical with the oxime 7 obtained by the photolysis of 8, by warming it in DMSO-chloroform (Scheme 3).

It should be noted that no products bearing an α-hydroxy group were found in this rearrangement and all the isolated products except the ketones were those bearing a β-hydroxy group.

The foregoing results can be accounted for by assuming that the nitro-nitrite rearrangement is taking place via the C-N bond dissociation and a β-axial coupling of nitryl radical with the resulting stabilized allyl radical intermediates.22)

The significant feature of the present rearrangement is the regioselectivities found in the recombination of NO_2 to the allyl radical intermediate. Thus, in both of the rearrangements, a hydroxyimino-compound which carries the hydroxy group at the carbon center where the nitro group was originally attached, is predominantly formed. This may imply that the present nitro-nitrite rearrangement is taking place largely intramolecularly through the formation of a radical pair in a solvent cage since if the rearrangement is an intermolecular one, NO_2 generated from 1 could combine predominantly with the less hindered C-4 of the resulting allyl radical intermediate rather than with the C-6 where the nitro group was originally attached and we ought to have observed a predominant formation of 7 instead of 6 in the photolysis of 1 but didn't.

Another noteworthy feature of the present reaction is that no product arising from the abstraction of a hydrogen of the 10β-methyl by the 6β-nitro group of 1 or 8, which requires the 7-membered transition state, is found in the products. This result is in agreement with a previous report that no evidence was found for the formation of any product derived by intramolecular hydrogen abstraction similar to that of alkoxy radicals in the photolysis of 2-nitropentane and 2-nitrooctane.23)

References

1) Photoinduced Transformations. Part 65. Part 64: H. Suginome and A. Osada, J. Chem. Soc. Perkin 1, in the press.
2) O. L. Chapman, D. C. Heckert, J. W. Reasoner, and S. P. Thackaberry, J. Am. Chem. Soc., 88, 5550 (1966); H. E. Zimmerman, L. C. Roberts, and R. Arnold, J. Org. Chem., 42, 621 (1977); J. S. Cridland, P. J. Moles, S. T. Reid, and K. T. Taylor, Tetrahedron Lett., 1976, 4497.
3) H. W. Brown and G. C. Pimental, J. Chem. Phys., 29, 883 (1958).
4) A. J. C. Nicholson, Nature (London), 190, 143 (1961).
5) R. E. Rebbert and W. Slagg, Bull. Soc. Chem. Belges, 71, 709 (1962).
6) S. Paszyc, Photochem. Photobiol., 4, 841 (1965).
7) J. R. Bull, E. R. H. Jones, and G. D. Meakins, J. Chem. Soc., 1965, 2601.

8) H. Reich, R. E. Walker, and R. W. Collins, J. Org. Chem., 16, 1753 (1951).

9) E. J. Becker and E. S. Wallis, J. Org. Chem., 20, 353 (1955).

10) All the separations of the products described in this paper were made by preparative TLC. All the new compounds gave correct analytical results by combustion or high resolution mass spectral analysis and sound IR spectra.

11) D. N. Jones, J. R. Lewis, C. W. Shoppee, and G. H. R. Summers, J. Chem. Soc., 1955, 2876.

12) Ketone 9 and alcohol 10, which arose from intermediate nitrite 2, were only detected in the ^{1}H NMR of the crude TLC fractions of 4 and 5.

13) A. Butenandt and A. Bolff, Chem. Ber., 68, 2091 (1935).

14) The formation of isomeric ketone 4 and alcohol 5, which arose from intermediate nitrite 3, was only proved by examining the ^{1}H NMR of the crude TLC fractions of 9 and 10.

15) D. H. R. Barton, J. M. Beaton, L. E. Geller, and M. M. Pechet, J. Am. Chem. Soc., 82, 2640 (1960). R. H. Hesse, "Adv. Free Radical Chem." 3, 83 (1969).

16) Mp 87-89°C, ^{1}H NMR (90 MHz-$CDCl_3$), δ=0.67 (3H, s, 18-H), 0.97 (3H, s, 19-H), 5.79 (2H, superimposed br.t, J=4 Hz, 4- and 6α-H).

17) Mp 68-70°C, ^{1}H NMR (100 MHz-$CDCl_3$), δ=0.68 (3H, s, 18-H), 1.02 (3H, s, 19-H), and 5.83 (2H, br.s, 4α-H and 6-H).

18) Mp 184-188°C (acetone), ^{1}H NMR (400 MHz-$CDCl_3$), δ=0.64 (3H, s, 18-H), 4.18 (1H, br.t, J=5 Hz, 6α-H), 5.82 (1H, br.t, J=7 Hz, 4-H), and 7.43 (1H, s, 19-H); Mass, m/z (rel intensity), 415 (M^+, 21.4), 398 (M^+-OH, 60.6), and 380 (M^+-H_2O-OH, 61.9%).

19) ^{1}H NMR (90 MHz-$CDCl_3$), δ=0.75 (3H, s, 18-H), 3.33 and 4.11 (each 1H, d, J=8.0 Hz, 19-H), 4.46 (1H, d, J=4.0 Hz, 6α-H), and 5.51 (1H, t, J=3.6 Hz, 4-H); Mass, m/z (rel intensity), 384 (M^+-HOCO, 59.50, and 122 (100%).

20) Mp 190-193°C, (dichloromethane-diethyl ether), ^{1}H NMR (100 MHz-$CDCl_3$), δ=0.68 (6H, s, 18- and 18'-H), 4.33 (1H, br.s, 6α- and 6α'-H), 4.71 and 5.08 (each 2H, d, J=12 Hz, 19- and 19'-H), 5.79 (2H, br.s, 4- and 4'-H).

21) Mp 166-168°C (acetone), ^{1}H NMR (400 MHz-$CDCl_3$), δ=0.64 (3H, s, 18-H), 4.17 (1H, broad s, 4α-H), 5.84 (1H, dd, J=5 and 7 Hz, 6-H), and 7.55 (1H, s, 19-H); Mass, m/z (rel intensity), 415 (M^+, 46.5), 398 (M^+-OH, 49.4), and 380 (M^+-OH-H_2O, 19.6%).

22) The dissociation-recombination mechanism has been proposed for the photochemical rearrangements of nitromethane and nitroethane to methyl nitrite and ethyl nitrite in both gas and liquid phases and in a solid argon matrix.[3-6)]

23) S. T. Reid, J. N. Tucker, and E. J. Wilcox, J. Chem. Soc., Perkin Trans. 1, 1974, 1359.

(Received June 4, 1982)