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PREPARATION AND REACTIONS OF 1,5-POLYMETHYLENE-BRIDGED 3,7-DIMETHYLENEBICYCLO[3.3.1]NONAN-9-ONES

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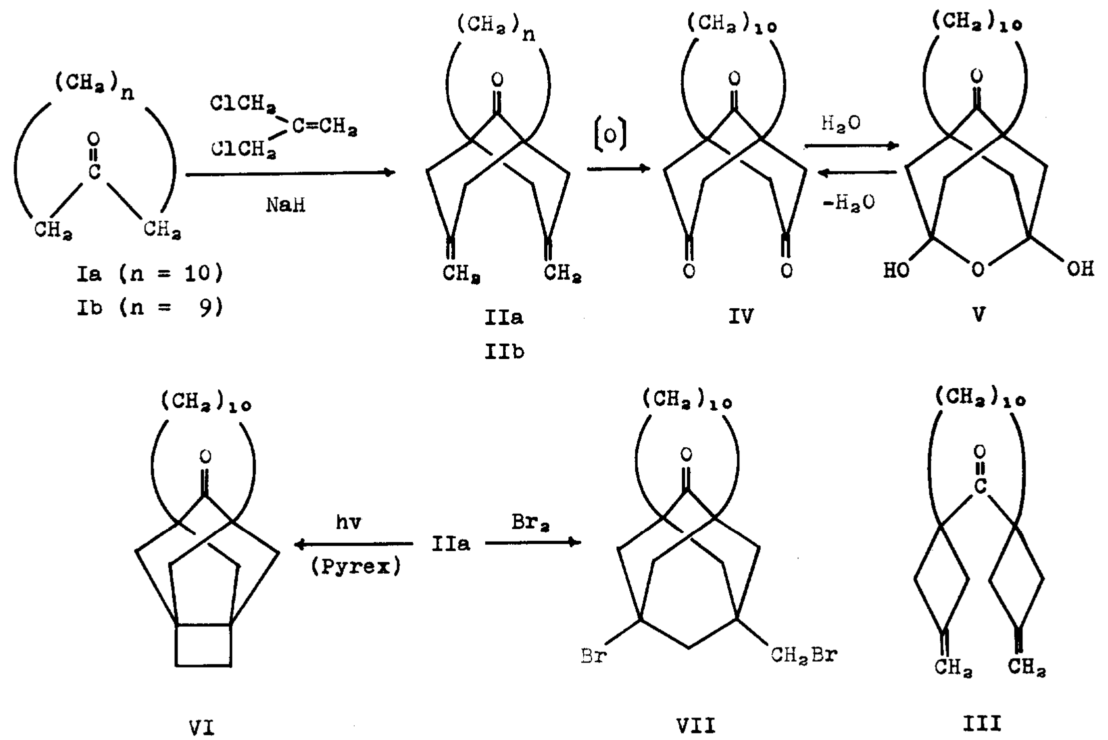
During a synthetic work on dl-muscone (1), we have investigated the condensation reaction of cycloalkanones I and α,α'-dichloroisobutylene to find out that this reaction provides substantial amounts of the title compounds II in addition to the desired bicyclic products. The current interest in bicyclo-[3.3.1]nonane system (2) prompts us to record our preliminary results including some reactions of II.

Condensation of cyclotridecanone (Ia) (3) with two moles of α,α'-dichloroisobutylene (4) was carried out in the presence of excess sodium hydride in toluene at 90-100° for 40-50 hrs to afford IIa, m.p. 69.5-70°, in a 26% yield. This structure followed from an elemental analysis (5) and spectral results; IR (Nujol): 1710 (C=O), 3080, 1650, 880 cm^{-1} ($=CH_2$); NMR (CCl_4): δ 4.67 s (4 H, olefinic protons), 2.47 distorted AB-quartet (8 H, cyclohexane ring protons, $\delta_A-\delta_B$ = ca. 0.14, J = ca. 15 Hz), 1.8-0.7 m (20 H, decamethylene protons); UV (n-hexane): ε(220 nm) = 2800, ε_{min}(268 nm) = 8, ε_{max}(305 nm) = 32.

The possible existence of methylenecyclobutane moieties such as in III was ruled out by the oxidative cleavage of exo-double bonds. Thus, hydroxylation with $KMnO_4$ followed by treatment with $Pb(OAc)_4$ gave IV (5) in a 13% yield; m.p. 176-178°; IR (Nujol): 1730, 1710 cm^{-1} (C=O, no cyclobutanone); NMR ($CDCl_3$): δ 2.70 AB-quartet (8 H, $\delta_A-\delta_B$ = 0.31, J = 15 Hz), 2.1-1.0 m (20 H). Upon periodate-permanganate oxidation (6), the diene IIa afforded an oxaadamantane V (5) in a 78% yield; m.p. 174-175° (dec.); IR (Nujol): 3250 (OH), 1710 (C=O), 1110, 980 cm^{-1} (C-O). Dehydration of V into IV was effected by means of p-toluenesulphonic acid and molecular sieves in tetrahydrofuran, whereas IV was reconverted into V on



treatment with aq. Na_2CO_3.

Similarly, cyclododecanone (Ib) afforded IIb (5), m.p. 94-95°, in a 15% yield (7). IR (Nujol): 1710 (C=O), 3080, 1650, 885, 880 cm^{-1} (=CH_2); NMR (CCl_4): δ 4.68 s̲ (4 H), 3.3-2.1 m̲ (8 H), 2.0-0.6 m̲ (18 H).

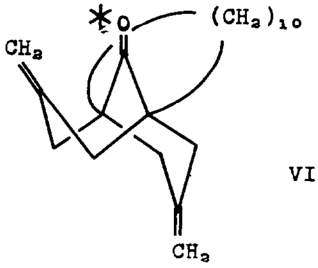
The success in constructing the bicyclo[3.3.1]nonane system would possibly be rationalized on the basis of so-called <u>O-inside conformation</u> (8) of large ring ketones. Throughout the alkylation steps of the ring ketones I, this conformation allows the successive C-alkylation to give II. In contrast, both acetone and acetonedicarboxylic ester lacking this prerequisite failed to give the bicyclo[3.3.1]nonane system due to ready O-alkylation under similar conditions.

UV-irradiation of IIa in cyclohexane solution (9) caused smooth intramolecular cycloaddition giving a novel type of cage compound VI (5), m.p. 99-100°, in a 73% yield. IR (Nujol): 1705 cm^{-1} (C=O); NMR (CCl_4): δ 2.05 s̲ (4 H, cyclobutane ring protons), 1.87 broad s̲ (8 H, noradamantane ring protons), 1.8-0.9 m̲ (20 H, decamethylene protons). The equivalency of cyclobutane ring protons as well as the thermal and chemical stability (10) of the product would be incompatible with an alternative reaction pattern, viz., a cross addition of the two double bonds.

In accord with Stetter's observation on 3,7-dimethylenebicyclo[3.3.1]nonane (11), our diolefin IIa reacted with only one mole of bromine under construction of a polymethylene-bridged adamantane VII (5), m.p. 105-106°, in an 85% yield. IR (Nujol): 1710 cm^{-1} (C=O); NMR (CCl_4): δ 3.22 s (2 H), 2.9-1.8 m (10 H), 1.8-0.9 m (20 H).

The formation of the cage molecules V and VII would probably be assisted to some extent by the flipping action of the mobile decamethylene chain, which should favour the twin-chair form in the conformational equilibrium of bicyclo[3.3.1]-nonane system (12).

The smoothly proceeding photochemical ring closure of IIa to VI merits further discussion. On the basis of aforementioned UV absorption data of IIa this photoreaction must be initiated by $n-\pi^*$ excitation of the carbonyl group followed by intersystem crossing to triplet state. The cycloaddition should proceed through intramolecular energy transfer (13) from the carbonyl group to olefinic bond, as the carbonyl group is situated under too much crowded environment to deliver its triplet excitation energy to another molecule. The transfer of $n-\pi^*$ excitation energy of carbonyl to a simple olefin demands the approach of each chromophore (14), which may be attained in this case as follows. Upon the excitation of O-inside carbonyl group, the expanded π-electron cloud expels the decamethylene chain to one side so as to result in a transient boat-chair conformation (VIII) of the bicyclic system, in which the energy transfer occurs from carbonyl to the nearer olefinic bond intramolecularly through transannular interaction. This is followed by conformational change into the twin-chair form and the final ring closure.



VIII

REFERENCES AND NOTES

1. H. Nozaki, H. Yamamoto and T. Mori, Can. J. Chem. 47, 1107 (1969).
2. See, for example, T. Sasaki, S. Eguchi and T. Kiriyama, J. Am. Chem. Soc. 91, 212 (1969); A. R. Gagneux and R. Meier, Tetrahedron Letters, 1365 (1969); A. C. Udding, H. Wynberg and J. Straiting, ibid. 5719 (1968); J. P. Schaefer and C. A. Flegal, J. Am. Chem. Soc. 89, 5729 (1967); refs. cited therein.
3. H. Nozaki, S. Kato and R. Noyori, Can. J. Chem. 44, 1021 (1966); W. Kirchhof, W. Stumpf and W. Franke, Ann. Chem. 681, 32 (1965); M. Mühlstädt and J. Graefe, Chem. Ber. 100, 223 (1967); W. E. Parham and R. J. Sperley, J. Org. Chem. 32, 926 (1967).
4. L. F. Hatch, J. J. Russ and L. B. Gordon, J. Am. Chem. Soc. 69, 2614 (1947).
5. All new compounds gave correct analyses.
6. R. U. Lemiuex and E. von Rudloff, Can. J. Chem. 33, 1701 (1955).
7. An attempted synthesis of II (n = 8) from cycloundecanone failed in one run, but further investigation would be necessary on the reaction conditions.
8. T. Ledaal, Tetrahedron Letters, 651 (1968); and refs. cited therein.
9. Photolysis of IIa (5 mmole/l) was effected in a Pyrex tube with 200 W high pressure mercury arc for 6 hrs.
10. No change was observed on heating VI at 270°. Treatment with H_2SO_4/AcOH at reflux temperature also failed in ring opening.
11. H. Stetter and J. Gärtner, Chem. Ber. 99, 925 (1966).
12. W. A. C. Brown, J. Martin and G. A. Sim, J. Chem. Soc. 1844 (1965).
13. P. A. Leermaker, G. W. Byers, A. A. Lamola and G. S. Hammond, J. Am. Chem. Soc. 85, 2670 (1963); H. Morrison, ibid. 87, 932 (1965); W. Herz and M. G. Nair, ibid. 89, 5474 (1967); H. Morrison, R. Bainard and D. Richardson, Chem. Comm. 1653 (1968).
14. G. Porter and F. Wilkinson, Proc. Roy. Soc. A264, 1 (1961); N. C. Yang, J. I. Cohen and A. Shani, J. Am. Chem. Soc. 90, 3264 (1968).

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