

PYRYLIUM SALTS FORMED BY DIACYLATION OF OLEFINS. XVIII.¹ DIACETYLATION OF CYCLODODECENE

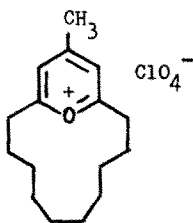
A.T. Balaban

Institute of Atomic Physics, Bucharest, Roumania (Present address: I.A.E.A., Vienna, Austria)

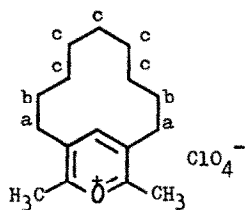
(Received in UK 11 July 1968; accepted for publication 6 August 1968)

Electrophilic monoacylation of olefins possessing at least three carbon atoms leads to a mixture of α,β - and β,γ -unsaturated ketones. The latter (or, less probably, their enolic forms) are able to afford by a second acylation step unsaturated 1,5-diketones. Intramolecular dehydration of these diketones under the prevailing acidic reaction conditions gives pyrylium cations, when the two carbonyl groups can approach one another closely enough.² This is not the case of 3- to 8-membered cycloolefins without side-chains. However, large-ring cycloolefins should be able to afford on diacylation pyrylium salts with a bridge between positions 3 and 5. The only bridged pyrylium salt so far known (I) had the bridge between positions 2 and 6 and was prepared by intramolecular diacylation of isobutene with dodecanedicarboxylic acid dichloride.³

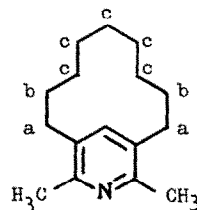
Diacetylation of cyclododecene was accomplished by gradual addition of 70% perchloric acid (1 mole) into a stirred mixture of the olefin (1 mole) and excess acetic anhydride (5 moles) without cooling. Refluxing was caused by the exothermal reaction. After cooling, a double volume of diethyl ether was added, the upper layer was discarded, and the lower viscous black layer was extracted several times with boiling water. In the aqueous filtrates, straw-coloured needles of the diacetylation product of cyclododecene, 2,6-dimethyl-3,5-nonamethylene-pyrylium perchlorate (II), crystallised. They were purified by recrystallisation from 1% perchloric acid and had m.p. 170°. (Found: C,57.4; H,7.6; $C_{16}H_{24}ClO_5$ requires C,57.9; H,7.3%).



I



II



III

The infrared spectrum in KBr-pellet presents CH stretching bands at 3027 (m), 2900 - 2950 (vs), and 2865 (s) cm^{-1} , a band due to the ν_{8a} vibration⁴ at 1614 (s) cm^{-1} and bands due to vibrations of the perchlorate anion and to deformation vibrations. In the NMR spectrum (trifluoroacetic acid solution) the six methyl protons appear as a singlet at τ 7.10, the four methylene protons (a) adjacent to the pyrylium ring as a triplet centered at τ 7.00 (coupling constant 6 cps), the next four methylene protons (b) as a symmetrical multiplet centered at τ 8.05, the other ten methylene protons (c) as a non-symmetrical multiplet at τ ca. 8.75, and the pyrylium proton as a singlet at τ 1.26. These values are consistent with those obtained for other pyrylium salts⁵ and thus serve as a reliable structural proof.

Treatment of the pyrylium salt (II) afforded a liquid pyridine (III) which was extracted with ether and distilled in vacuum. Its NMR spectrum presents in CCl_4 singlet peaks at τ 2.82 (one pyridine proton) and 7.62 (six methyl protons), a triplet ($J=6.5$ cps) centered at τ 7.32 (4 methylene protons of type a) and multiplets at τ 8.33 (4 methylene protons b) and 8.93 (ten methylene protons c).

Attempts to dibenzoylate cyclododecene with benzoyl chloride and aluminium chloride or stannic chloride were unsuccessful.

Acknowledgements. Thanks are expressed to Chemische Werke Huls A.G. for a gift of cyclododecene, to Dr. W. Silhan for recording the NMR spectra, to Mrs. E. Romaş for recording the infrared spectrum, and to Mrs. M. Roman for the elementary analysis.

R E F E R E N C E S

1. D. FĂRCAŞTU, C. UNCUŢA and A.T. BALABAN, Rev. Roumaine Chim., 12, 899 (1967), preceding part.
2. A.T. BALABAN, W. SCHROTH and G. FISCHER, Advances in Heterocyclic Chemistry (A.R. Katritzky and A.J. Boulton, editors), volume 10, Academic Press, in press.
3. A.T. BALABAN, M. GAVĂT and C.D. NENITZESCU, Tetrahedron, 18, 1079 (1962).
4. A.T. BALABAN, G.D. MATEESCU and M. ELIAN, ibid., 18, 1083 (1962).
5. A.T. BALABAN, G.R. BEDFORD and A.P. KATRITZKY, J. Chem. Soc. 1646 (1964).