

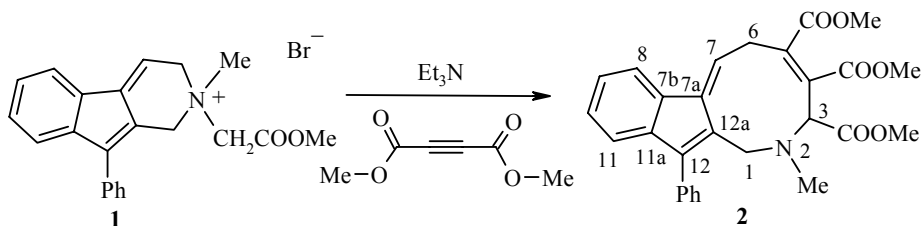
SYNTHESIS OF THE FIRST EXAMPLE OF A TETRAHYDROINDENO[2,1-*c*]AZONINE SYSTEM BY THE REACTION OF 2,3-DIHYDRO-1H-INDENO[2,1-*c*]PYRIDINIUM METHYLIDE WITH METHYL ACETYLENE DICARBOXYLATE

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N-Ethoxycarbonylmethylides of 1,2,3,6-tetrahydropyridines undergo a variety of reactions, the direction of which depends on the nature of the substituents on the heterocycle. Six-membered heterocycles may decyclize into pentadienamides [1], recyclize with constriction of the ring to derivatives of pyrrolidine [2], or recyclization with expansion of a seven-membered azacycle [3]. When the anhydrobase is generated in the presence of methyl acetylenedicarboxylate (MADC) the latter readily reacts with the carbanion center to give addition products [4] or products of cyclization of the indolizine type [5-7].

However when a solution of an equimolar mixture of MADC, 2-methoxycarbonylmethyl-2-methyl-9-phenyl-2,3-dihydro-1H-indeno[2,1-*c*]pyridinium bromide (**1**) and triethylamine in methylene chloride was kept at $\sim 20^\circ\text{C}$ for 3 h the indenoazonine **2** was unexpectedly formed and was isolated in 47% yield by column chromatography.



In its ^1H NMR spectrum two three proton singlets (at 3.19 ppm, NMe and 3.30 ppm, 3-COOMe) and one six proton singlet at 3.71 (two COOMe groups) were observed. At strong field (3.04-4.60 ppm), four double signals were observed from protons of two CH_2 groups with large geminal coupling constants ($^2J = 14.6\text{-}16.3$ Hz). A broad singlet was observed at 6.31 ppm, which can be assigned to the methyne proton H-3, under the descreening influence of the nitrogen atom and the COOMe group. Finally in the same region (7.62 ppm) there is a slightly broadened singlet signal which is evidently assignable to the proton H-7 of the vinyl group. These results in combination with the presence in the mass spectrum of a molecular ion peak at $[\text{M}]^+$ with m/z 473 confirm the structure of the indenoazonine derivative **2**.

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Evidently the tetrahydroindenoazonine **2** can be formed by electrophilic addition of MADC to the intermediate N-ylid, which arises from the corresponding 1,4-zwitterion and recyclization of the latter with expansion of the six-membered piperidene unit into the nine-membered azacycle. Thus a new direction of recyclization of an N-ylid system is observed on interaction of a quaternary tetrahydroindenopyridium salt with a base in the presence of MADC. The 2-methyl-9-phenyl-2,3-dihydro-1H-indeno[2,1-*c*]pyridine was prepared by method [8].

¹H NMR spectra of CDCl₃ solutions with TMS as internal standard were recorded on a Bruker WM-400 (400 MHz) machine. Mass spectra were recorded on a MAT-112 spectrometer with direct input of the sample into the ion source with an ionizing current of 70 eV. IR spectra of KBr disks were recorded on an IR-75 spectrometer. Silufol UV-254 strips (developed with iodine vapor) were used for TLC. Column chromatography was carried out on silica gel (Silicagel L 32/63).

2-Methoxycarbonylmethyl-2-methyl-9-phenyl-2,3-dihydro-1H-indeno[2,1-*c*]pyridinium Bromide (1). Methyl bromoacetate (6.11 g, 0.04 mol) was added with stirring to a solution of 2-methyl-9-phenyl-2,3-dihydro-1H-indeno[2,1-*c*] pyridine (10 g, 0.4 mol) in THF. The mixture was boiled for 1 h in an atmosphere of argon. The precipitate of the quaternary salt was filtered off, washed with ether, and dried in air to give yellow crystals of salt **1** (16 g, 97%); mp 178-180°C. Found, %: N 3.45. C₂₂H₂₂NO₂Br. Calculated, %: N 3.40.

2-Methyl-3,4,5-trimethoxycarbonyl-1,2,3,6-tetrahydroindeno[2,1-*c*]azonine [2]. Triethylamine (0.7 ml, 0.5 g, 5.8 mmol) and methyl acetylenedicarboxylate (0.61 ml, 0.71 g, 5.8 mmol) were added dropwise to a suspension of salt **1** (2.06 g, 5.8 mmol) in dichloromethane. The mixture was stirred at 20°C for 3h. the solvent was evaporated and compound **3** (1.27 g, 47%); mp 89-90°C, was isolated from the residue as brownish red crystals by chromatography. IR spectrum, ν , cm⁻¹: 1731 (C=O). ¹H NMR spectrum, δ , ppm (*J*, Hz): 3.04 (1H, d, *J* = 14.5, H-1); 3.19 (3H, s, NCH₃); 3.30 (3H, s, OCH₃); 3.71 (6H, s, OCH₃); 3.73 (1H, d, *J* = 14.5, H-1); 3.88 (1H, d, *J* = 16.2, H-6); 4.60 (1H, d, *J* = 16.2, H-6); 6.31 (1H, s, H-3); 7.09 (1H, d, *J* = 6.9 (H-11)); 7.23-7.51 (5H, m, H_{arom}); 7.58 (1H, d, *J* = 6.9, H-9); 7.62 (1H, s, H-7). Mass spectrum, *m/z*: 473 [M]⁺ (57), 442 (7), 414 (100), 357 (33), 294 (28), 281 (29), 239 (78), 216 (76), 202 (78), 77 (16), 59 (100). Found, %: C 70.81; H 5.73; N 2.88. C₂₈H₂₇NO₆. Calculated, %: C 70.95; H 5.70; N 2.95.

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