386. *Addition Reactions of Heterocyclic Compounds. Part XV.* Tetramethyl 9a-Methyl-9aH-quinolizine-1,2,3,4-tetracarboxylate.*

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Diels and Pistor [1] obtained red and yellow 1 : 2 molar adducts from α-picoline and dimethyl acetylenedicarboxylate, and subsequently converted the yellow compound into an orange isomer whereas Jackman, Johnson, and Tebby [2] from the same reaction isolated only the orange isomer. The ultraviolet and infrared [2,3] absorption spectra of this orange compound show it to be tetramethyl 6-methyl-4*H*-quinolizine-1,2,3,4-tetracarboxylate. We have repeated the reaction and so far have succeeded in isolating only the yellow adduct.

The nuclear magnetic resonance spectrum of the yellow adduct, kindly measured by Dr. E. O. Bishop at 29·92 Mc./sec. for a chloroform solution, showed *ester*-methyl groups at τ 6·04, 6·21 (two) and 6·28 and an additional isolated methyl group at τ 8·81. This last value is similar to that (τ 8·48) observed [4] for the isolated methyl group of tetramethyl 11a-methyl-11a*H*-benzo[*c*]quinolizine-1,2,3,4-tetracarboxylate and is much higher than those recorded [2,5] for the methyl groups of several methyl-4*H*- and -9a*H*-quinolizines where the methyl groups are attached to a double-bond system. The conclusion, that the yellow adduct is tetramethyl 9a-methyl-9a*H*-quinolizine-1,2,3,4-tetracarboxylate, is in agreement with its infrared and ultraviolet absorption spectra which are similar to those of related 9a*H*-quinolizines.[3,5]

Heating the adduct with dimethyl acetylenedicarboxylate gave dimethyl phthalate and tetramethyl 2-methylpyridine-3,4.5,6-tetracarboxylate. Presumably addition of the acetylene across the 6,9-positions gives a product which decomposes to the more stable

* Part XIV, *J.*, 1963, 1907.

[1] Diels and Pistor, *Annalen*, 1937, **530**, 87.
[2] Jackman, Johnson, and Tebby, *J.*, 1960, 1579.
[3] Acheson and Hole, *J.*, 1962, 748.
[4] van Tamelen, Aldrich, Bender, and Miller, *Proc. Chem. Soc.*, 1959, 309.
[5] Acheson and Taylor, *J.*, 1960, 1691.

aromatic structures; a similar reaction occurs between the acetylenic ester and tetramethyl 3a,7a-dihydro-1-methylindole-2,3,3a,4-tetracarboxylate.[6]

Experimental.—Tetramethyl 9a-*methyl*-9aH-*quinolizine*-1,2,3,4-*tetracarboxylate*. α-Picoline (5 ml.), previously refluxed with calcium hydride for 1 hr. and distilled, was added to dimethyl acetylenedicarboxylate (13 ml.) in cold dry ether (70 ml.) and the mixture left in an open flask for 3 weeks. During this time, as the solvent evaporated, methanol–ether (1 : 1 by vol.) was added occasionally. The solid product after recrystallisation from methanol gave the *quinolizine* (2·6 g.) as yellow plates, m. p. 139° (Found: C, 57·6; H, 5·1; OMe, 33·0. $C_{17}H_{19}NO_8$ requires C, 57·3; H, 5·1; 4OMe, 32·9%) (lit.,[1] gives m. p. 138° and another structure). $\lambda_{max.}$ 4200 (ε 6100), 3380 (ε 5200), and 2810 Å (ε 12,400) for methanol, and $\nu_{max.}$ 5·76, 5·87 (inflexion), 6·03, 6·22, 6·56, and 6·99 μ for chloroform. The compound was recovered unchanged after being refluxed with α-picoline for 2 hr. or with glacial acetic acid for 8 hr.

Reaction with dimethyl acetylenedicarboxylate. The quinolizine (1·50 g.) and the ester (1·15 g.) were heated at 100° for 18 hr. and the resulting orange oil chromatographed on alumina (Spence, grade " H "; 40 g.; deactivated with 2 ml. of aqueous 10% acetic acid). Elution with light petroleum (b. p. 40—60°) (250 ml.) followed by ether (250 ml.) gave colourless oils tal 0·51 g.) which smelt strongly of the acetylenic ester and contained a compound ring the same characteristics as dimethyl phthalate on vapour-phase chromatography e argon chromatograph with apiezon L as stationary phase). Elution with ether (250 ml.) containing 5% of methanol gave an orange oil (1·20 g.) which was partially solid after 7 days; crystallisation of the solid from light petroleum (b. p. 40—60°)–ether (1 : 5 v/v) gave tetramethyl 2-methylpyridine-3,4,5,6-tetracarboxylate as yellow rhombs (0·68 g.). It had m. p. and mixed m. p. 72° with a specimen prepared as described [7]; its conversion [7] into α-picoline picrate has been confirmed.

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[6] Acheson, Hands, and Vernon, *Proc. Chem. Soc.*, 1961, 164; Acheson and Vernon, *J.*, 1962, 1148.
[7] Diels, Alder, Winckler, and Petersen, *Annalen*, 1932, **498**, 1.