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SYNTHESIS OF ETHYL 2-ACETYLBICYCLO-(3.3.0)OCT-1(2)-ENE-5-CARBOXYLATE

W. F. KEIR
Chemistry Department, Paisley College of Technology

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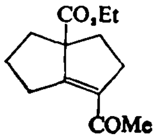
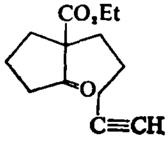
Abstract—The structure of ethyl 2-acetylbicyclo(3:3:0)oct-1(2)-ene-5-carboxylate has been confirmed by synthesis.

IN THE course of investigations into methods of synthesizing bicyclo(3.3.1)nonane ring systems[1] a liquid ketonic by-product was isolated, which from chemical and spectroscopic evidence was believed to be ethyl 2-acetylbicyclo(3.3.0)oct-1(2)-ene-5-carboxylate (I). A synthesis of I by an unambiguous route was undertaken, so that a direct comparison with the ketonic by-product could be made.

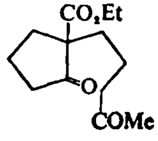
Pent-4-yn-1-ol was prepared by the dehydrohalogenation of tetrahydrofurfuryl chloride.[2] The corresponding bromide was prepared via the tosylate since it is known that direct conversion of such alcohols into the bromides gives poor yields.[3] Alkylation of 2-ethoxycarbonylcyclopentanone gave 2-(pent-4′-ynyl)-2-ethoxycarbonylcyclopentanone (II). The bromide and the tosylate were compared as alkylating agents.[4,5] The tosylate gave a better yield and since a stage is also eliminated, it is a superior alkylating agent in this reaction.



I



II



III

Hydration of II in the usual way gave 2-(4′-oxo-pentyl)-2-ethoxycarbonylcyclopentanone (III). Cyclization of III to I was accomplished with cold conc sulphuric acid, this proving to be a more effective condensing agent than sodium ethoxide.

The IR spectrum of I was found to be identical with an authentic sample of the liquid ketonic by-product aforementioned. Gas chromatographic retention times were also identical and a mixed m.p. of the semicarbazones showed no depression.

EXPERIMENTAL

The m.ps and b.ps are uncorrected. UV and IR spectra were measured on Unicam SP 500 and SP 100 spectrophotometers respectively, the NMR spectra were measured on a Perkin–Elmer 60 m/c instrument.

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[1] R. D. H. Murray, W. Parker, R. A. Raphael and (in part) D. B. Jhaveri, *Tetrahedron* **18**, 55 (1962).

[2] *Org. Synthesis Coll. Vol.* IV p. 755.

[3] G. Eglinton and M. Whiting. *J. Chem. Soc.* 3600 (1950).

[4] G. Eglinton and M. Whiting, *J. Chem. Soc.* 3052 (1953).

[5] P. Veeravagu, R. T. Arnold and E. W. Eigenmann *J. Amer. Chem. Soc.* **86**, 3072 (1964).

2-(*Pent-4'-ynyl*)-2-*ethoxycarbonylcyclopentanone* (II)

Method A. Freshly distilled 2-ethoxycarbonylcyclopentanone (23·4 g) in dry toluene (150 ml) was added dropwise to a well stirred suspension of powdered Na (3·4 g) in dry toluene (150 ml) previously cooled to −5°. The temp was held between −5° and 0° during the addition. 1-bromopent-4-yne (26·1 g) was added to the cold suspension in one portion and the mixture refluxed until the $FeCl_3$ ($CHCl_3$) test was negative (ca. 15 hr). The solution was washed with dil NaOHaq, water and dried. Distillation of the residual oil after removal of the solvent gave II as a clear oil (20·7 g) b.p. 94–96/0·3 mm. (Found: C, 70·39; H, 8·31. $C_{13}H_{18}O_3$ requires: C, 70·27; H, 8·11%.) IR spectrum (ν max cm^{-1}) in CCl_4 showed bands at 1748 (cyclopentanone C = 0), an anomalous doublet at 1730 and 1722 (ester C = 0), 3300 ($\equiv$C—H) and 2120 (C$\equiv$C—H). NMR spectrum (τ) in CCl_4 showed bands at 7·5 (triplet; 1 acetylenic proton); 5·85 (quartet; methylene of ethyl ester); 8·78 (triplet; methyl of ethyl ester).

Method B. Pent-1-yne-5-O-tosylate (21·41/g) was added as in previous method to a toluene suspension of the Na salt of 2-ethoxycarbonylcyclopentanone (11·7 g) and the mixture refluxed for 15 hr. The product (7·5 g) was extracted as in previous method and was found to be identical to II.

2-(4'-*Oxo-pentyl*)-2-*ethoxycarbonylcyclopentanone* (III)

A solution of the acetylenic keto ester (7·8 g) in MeOH (15 ml) was added slowly with stirring to a catalyst mixture prepared by warming together red HgO (0·5 g), BF_3-etherate complex (0·2 ml), trichloracetic acid (10 mg) and MeOH (1 ml). The reaction mixture was stirred for 2 hr and then poured into 5 ml 4N H_2SO_4. The acid solution was extracted with ether and the ether extract washed with $NaHCO_3$aq, water and dried. Removal of the solvent followed by distillation gave a clear liquid (5·8 g) b.p. 110–111/0·07 mm. (Found: C, 64·92; H, 9·19. $C_{13}H_{20}O_4$ requires: C, 65·0; H, 8·33%). The IR spectrum (ν max cm^{-1}) in CCl_4 showed bands at 1753 (cyclopentanone C=O), 1722 (chain C=O) and an inflection ca. 1731 (ester C=O). The NMR spectrum (τ) in CCl_4 showed bands at 5·85 (quartet; methylene of methyl ester); 8·78 (triplet; methyl of methyl ester); 7·95 (singlet; methyl of methyl ketone).

Ethyl 2-*acetylbicyclo* (3.3.0)*oct*-1(2)-*ene*-5-*carboxylate* (I)

The methyl ketone (5 g) was added slowly with stirring to ice-cold conc H_2SO_4 (15 ml). The mixture was stirred for 4 hr and then poured into ice-water and extracted with ether. The ether extract was washed successively with water, $NaHCO_3$aq, water and then dried. Removal of the solvent and distillation gave a clear oil bp 107–108/0·2 mm. The semicarbazone crystallized from MeOH in needles m.p. 187–189° λ_{max}^{EtOH} 274 mμ (ε 19,200). The 2,4-dinitrophenylhydrazone crystallized from MeOH in plates mp 138–140 $\lambda_{max}^{CHCl_3}$ 389 mμ (ε 27,950) i.e. not as reported but consistent with an α,β ene-one dinitrophenylhydrazone.

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