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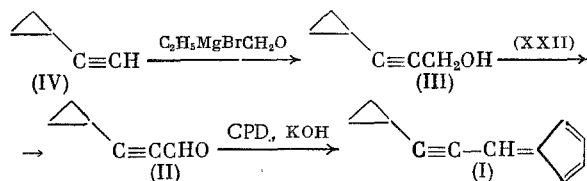
SYNTHESIS OF CYCLOPROPYLETHYNYLFULVENE — THE FIRST ACETYLENIC FULVENE

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Fulvenes are of interest as organic intermediates with high reactivity and highly unsaturated models for theoretical studies [1, 2]. 6-Alkenylfulvenes are often starting materials for the synthesis of physiologically active natural compounds [3]. The unsaturation of fulvenes is responsible for their ready oxidizability and low thermal stability. Until recently, the question of the existence of fulvenes with acetylenic substituents, in particular, 6-ethynylfulvenes, remained open.

We have synthesized the first acetylenic fulvene, namely 6-(cyclopropylethynyl)fulvene (I) by the reaction of cyclopropylpropionaldehyde (II) with cyclopentadiene (CPD). Previously unreported aldehyde (II) was prepared by the oxidation of 3-cyclopropyl-2-propyn-1-ol (III) by pyridinium chlorochromate (PCC) according to Corey and Suggs [4]. Alcohol (III), in turn, was synthesized by the Iotsich reaction from cyclopropylacetylene (IV). Aldehyde (II) is unstable in pure form and upon distillation even in vacuum in an argon atmosphere rapidly turns red and polymerizes. The yield of (II) (without separation from the reaction mass according to gas-liquid chromatographic data) is 85-90%, which drops to 55% upon distillation. Thus a solution of (II) in CH_2Cl_2 obtained immediately after oxidation of (III) was used in the synthesis of (I).



The reaction of (II) with CPD was carried out in the presence of solid KOH in CH_2Cl_2 . The mole ratio (II):CPD:KOH = 1:5:4 was found to be optimal and gave a 57% yield of (I). Alteration of either this ratio or the temperature leads to a marked drop in the yield of (I) (see Table 1). Fulvene (I) may be stored briefly as a solution in CCl_4 at from -5°C to -10°C . Thus, (I) is significantly less stable than 6-vinylfulvenes [1, 2].

EXPERIMENTAL

The gas-liquid chromatographic analysis was carried out on an LKhM-8MD chromatograph with a katharometer detector on $300 \times 0.3\text{-cm}$ columns packed with 5% SE-30 on Chromatone N-AW-DMCS or 15% Carbowax 20M on Chromatone N-AW-DMCS with 30 ml/min helium carrier gas flow rate. The PMR spectra were taken on a Tesla BS-467 spectrometer at 60 MHz relative to TMS as the internal standard. The IR spectra were taken on a UR-20 spectrometer.

Starting cyclopropylacetylene (IV) was obtained from methyl cyclopropyl ketone according to our previous procedure [5] and PCC was obtained according to Corey and Suggs [4].

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TABLE 1

Number of moles per mole (II)			T., °C	Yield of (I) in % relative to (II)	Number of moles per mole (II)			T., °C	Yield of (I) in % relative to (II)
CPD	KOH	CH ₂ Cl ₂			CPD	KOH	CH ₂ Cl ₂		
1	1	1	23	10,5	5	4	5	23	44,0
1	1	1,5	-20	4,5	5	4	5	-10	57,0
2	1	2	-10	9,0	10	9	5	-10	23,0
5	1	2	-10	3,5	10	9	5	-40	27,0

3-Cyclopropyl-2-propyn-1-ol (III). A solution of 39.6 g (0.6 mole) cyclopropylacetylene in 50 ml abs. ether was added over 40 min to the Grignard reagent prepared from 110 g (1 mole) C₂H₅Br and 28.8 g (1.2 mole) magnesium filings in 1 liter abs. ether at 0°C. The rate of addition was monitored relative to the rate of gas liberation. After warming to 20°C, the mixture was heated at reflux for 1 h and then CH₂O gas obtained by heating 75 g (2.5 moles) anhydrous paraformaldehyde was introduced at 0°C. The mixture was heated at reflux for an additional 30 min and was acidified by the addition of 30% H₂SO₄ with stirring. The organic layer was separated, washed with 2% HCl and sat. aq. Na₂CO₃, dried over MgSO₄, and evaporated. A solid product was filtered off the residue. Distillation of the filtrate gave 40.4 g (70%) (III), bp 78-79°C (10 mm), n_D^{20} 1.4915. Found: C 74.63; H 8.41%. C₆H₈O. Calculated: C 74.96; H 8.40%. PMR spectrum (CHCl₃, δ , ppm): 0.65 m (4 H, 2CH₂ in cyclo-C₃H₅), 1.1 m (1H, CH in cyclo-C₃H₅), 3.26 br. s (1H, OH), 4.05 d (2H, CH₂O, J = 2.1 Hz). IR spectrum (CCl₄, ν , cm⁻¹): 2235 s (C≡C), 3340 s (OH).

Cyclopropylpropionaldehyde (II). A solution of 6 g (0.06 mole) (III) in 20 ml abs. CH₂Cl₂ was added dropwise over 10 min in an argon stream to a mixture of 19.2 g (0.12 mole) PCC in 103 ml abs. CH₂Cl₂ cooled to 10°C in an argon atmosphere. The reaction was monitored by gas-liquid chromatography. After 3 h, when all (III) had reacted, the mixture was passed through neutral alumina with abs. CH₂Cl₂ as the eluent. Distillation of the eluate gave (II) in 55% yield, bp 68°C (25 mm), n_D^{20} 1.3701. PMR spectrum (CCl₄, δ , ppm): 0.75-1.12 m (4H, 2CH₂ in cyclo-C₃H₅), 1.15-1.65 m (1H, CH in cyclo-C₃H₅), 9.0 d (1H, CHO, J = 2 Hz). IR spectrum (CCl₄, ν , cm⁻¹): 1658 (C=O), 2190 and 2210 (C≡C). The yield of (II) without isolation from the eluate was 85% as indicated by gas-liquid chromatography.

6-Cyclopropylethynylfulvene (I). A solution of 1 g (0.01 mole) (II) in 20 ml CH₂Cl₂ was added with stirring over 40 min to a mixture of 3.5 g (0.05 mole) freshly distilled DPD, 1.7 g (0.4 mole) solid KOH and 50 ml CH₂Cl₂ cooled to -10°C. After 2 h, the reaction mass was washed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic solutions were combined and dried over Na₂SO₄. The solvents were distilled off. The residue was dissolved in pentane and the solution was passed through a layer of silica gel L100/60 and neutral alumina LSL 5/40. The pentane solution was evaporated and the residue was subjected to chromatography on silica gel L100/60. A 1:10 ether-pentane mixture was used as the eluent. The eluate was evaporated in vacuum. The residue contained (I) with 95% purity (57% yield). PMR spectrum (CCl₄, δ , ppm): 0.67-0.95 m (4H, 2CH₂ in cyclo-C₃H₅), 1.1-1.5 m (1H, CH in cyclo-C₃H₅), 5.9-6.4 m (5H, 4CH in cyclo-C₅H₄ and 1H in C=CCH). IR spectrum (CCl₄, ν , cm⁻¹): 2204 and 2211 (C≡C), 1640-1612 (C=C).

CONCLUSIONS

Previously unreported 3-cyclopropyl-2-propyn-1-ol and cyclopropylpropionaldehyde were synthesized. This aldehyde yielded the first reported acetylenic fulvene, namely 6-(cyclopropylethynyl)fulvene, which is rather stable in solution in the cold.

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