PREPARATION OF 3,3-DISUBSTITUTED CYCLOPROPANES BY THE DEHYDRO-HALOGENATION OF MONOHALOCYCLOPROPANES UNDER PHASE TRANSFER CATALYSIS CONDITIONS

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The most efficient method reported for the preparation of cyclopropenes entails the dehydrohalogenation of monohalocyclopropanes by the action of potassium tert-butylate in DMSO [1]. In particular, the use of this method with 1-halo-2,2-dimethylcyclopropanes (I) gives 3,3-dimethylcyclopropene (II) in 74% yield in the case of chloride (Ia) and 84% in the case of bromide (Ib) [2], while its use with 1-bromospiro[2.3]hexane (III) gives spiro[2.3]hex-1ene (IV) in 43% yield [3]. In our recent work [4], we reported the facile dehydrohalogenation of 1-alkyl-2-halocyclopropanes by the action of solid KOH or NaOH in DMSO in the presence of a phase transfer catalyst (PTC), namely, either dibenzo-18-crown-6 (DB-18-C-6) or triethylbenzylammonium chloride (TEBA) at 80-150°C with the formation of 2-alkyl-1-(2-alkyldenecyclopropyl)cyclopropanes as the major products. Using these results [4], we have developed a convenient synthesis for 3,3-disubstituted cyclopropenes from the corresponding halocyclopropanes by the action of solid KOH in DMSO in the presence of PTC at 95-125°C and halocyclopropane:KOH:DMSO:PTC mole ratio equal to 1:3:10:0.0003.

Thus, the action of solid KOH on 1-halo-2,2-dimethylcyclopropanes (I) in DMSO in the presence of TEBA or DB-18-C-6 at 100-125°C gave 3,3-dimethylcyclopropene (II). The yield of (II) was 82% from chloride (Ia) and 92% from bromide (Ib).

$$\underbrace{\overset{\text{Me}}{\underset{\text{Me}}{(I)}}}_{\text{Me}} \underbrace{\overset{\text{KoH}/,\text{DMSO}}{\underset{\text{DB-18-C-6 or TEBA.}}{\overset{\text{Me}}{\underset{\text{Me}}{(II)}}}} \underbrace{\overset{\text{Me}}{\underset{\text{Me}}{\underset{\text{Me}}{(II)}}}$$

where X = C1 (a) and Br (b).

Similarly, 1-bromospiro[2.3]hexane (III) in the presence of DB-18-C-6 with constant removal in vacuum gave spiro[2.3]hex-1-ene (IV) in 70% yield.



Under the same conditions, 1-bromo-2-methyl-2-phenylcyclopropane (V) gave 1-methyl-1-phenylcyclopropene (VI) in 51% yield.



The purity of the cyclopropenes prepared was 99-100% as indicated by gas-liquid chromatographic analysis and their structures were confirmed by spectral analysis.

EXPERIMENTAL

The gas-liquid chromatographic analysis was carried out on an LKhM-8MD chromatograph with katharometer detector on a 300 \times 0.3-cm column packed with 5% SE-30 on Chromatone N-AW-DMCS or *Deceased.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2820-2822, December, 1984. Original article submitted May 7, 1984.

UDC 542.944.6:547.512

15% Carbowax 20M on Chromatone N-AW-DMCS and helium gas carrier flow rate of 30 ml/min. The PMR spectra were taken on a Tesla BS-467 spectrometer at 60 MHz in CC14 with TMS as the internal standard. The mass spectra were taken on a Varian MAT-111 chromato-mass spectrometer. The IR spectra were taken on a UR-20 spectrometer.

The starting halocyclopropanes were obtained by the incomplete reduction of the corresponding gem-dihalocyclopropanes prepared in 70-80% yield by the addition of dihalomethylene to olefins according to our previous work [5].

The conversion of 1,1-dichloro-2,2-dimethylcyclopropane to 1-chloro-2,2-dimethylcyclopropane (Ia) [6] was accomplished by the action of zinc powder in DMSO at 120°C according to our previous procedure [7] in 85% yield.

The analogous reduction of the corresponding gem-dibromides by zinc powder in methanol at 20°C with 80-90% yields according to our earlier procedure [8] gave 1-bromo-2,2-dimethyl-cyclopropane (IIb) [6], 1-bromospiro[2.3]hexane (III) [3], and 1-bromo-2-methyl-2-phenyl-cyclopropane (V) [6]. The physical constants and spectral data for (I), (III), and (V) were identical to those reported by Bolesov et al. [3, 6].

<u>3,3-Dimethylcyclopropene (II)</u>. A sample of 0.25 mole (Ia) at 125°C or (Ib) at 110°C was added over 10 min to a vigorously stirred mixture of 42 g (0.75 mole) KOH powder, 0.1 g DB-18-C-6 or TEBA, and 50 ml abs. DMSO. Product (II) [8, 9] was collected in a trap cooled to -78°C in 82% yield from (Ia) and in 92% yield from (Ib), bp 14°C, 99% purity as indicated by gasliquid chromatography. IR spectrum (CCl₄, ν , cm⁻¹): 1625 (C=C). PMR spectrum (δ , ppm): 1.15 s (6H), 7.30 s (2H). Mass spectrum, m/z: 68 M⁺.

<u>Spiro[2.3]hex-1-ene (IV)</u>. A sample of 16.2 g (0.10 mole) (III) was added with vigorous stirring to a mixture of 20 g (0.35 mole) KOH powder, 0.1 g DB-18-C-6, and 25 ml abs. DMSO at 95-100°C over 1 h with constant vacuum transfer (at 500 mm Hg) to a trap at -78°C. Then, the mixture was maintained under these conditions for an additional 1.5 h. Distillation of the product collected in the trap gave 5.6 g (70%) (IV) [3], bp 60°C, 100% purity as indicated by gas—liquid chromatography. PMR spectrum (CC1₄, δ , ppm): 1.60-2.55 m (6H), 7.40 m (2H).

<u>3-Methyl-3-phenylcyclopropene (VI)</u>. Under analogous conditions, a sample of 21.1 g (0.1 mole) (V) at 110°C and 50 mm Hg residual pressure gave 6.7 g (51%) (VI) [6], bp 72°C (20 mm), 100% purity as indicated by gas—liquid chromatography. PMR spectrum (CCl₄, δ , ppm): 1.57 s (3H), 7.07 s (5H), and 7.13 (2H).

CONCLUSIONS

A convenient preparative method was developed for the synthesis of 3,3-disubstituted cyclopropenes in yields up to 90% for 3,3-dimethylcyclopropene, spiro[2.3]hex-l-ene, and 3-methyl-3-phenylcyclopropene from the corresponding monohalocyclopropanes by the action of solid KOH in DMSO in the presence of phase transfer catalysts.

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