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PHEROMONES OF COLEOPTERA.

COMMUNICATION 3. SYNTHESIS OF R-γ-HEXANOLIDE FROM D-MANNITOL*

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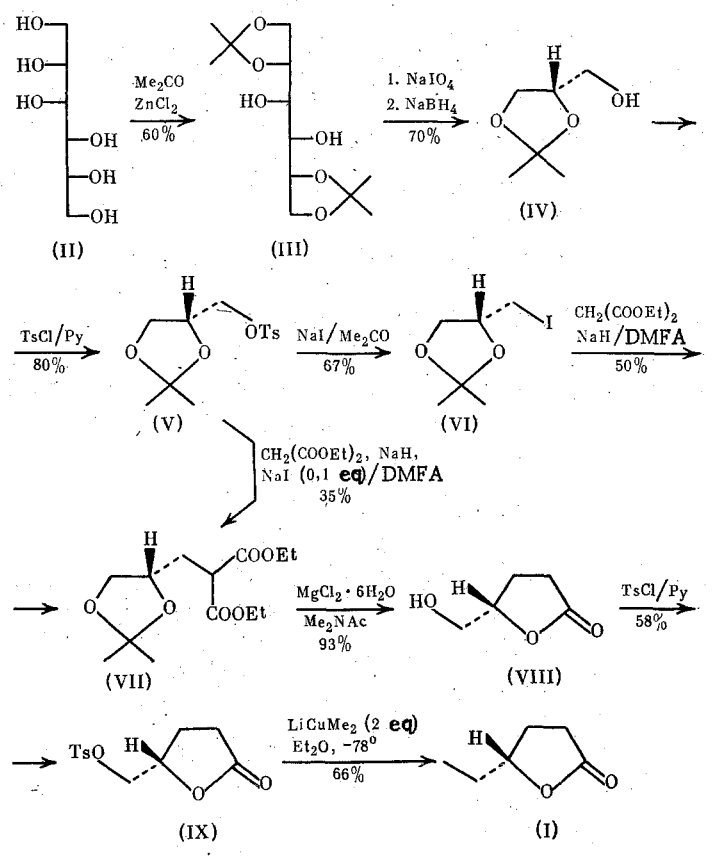
R-γ-Hexanolide (I), contained in the multicomponent sex pheromone of the beetle *Trogoderma glabrum*, was produced earlier in an optically active form from S-glutamic acid [2], D-gluconolactone [3], and by enantioselective and microbiological reactions [4-6]. In this work we present a simple method of synthesis of (I) from D-mannitol (II) according to the following scheme:



1,2:5,6-O-Diisopropylidene-D-mannitol (III) is produced by a well-known method [7] and is converted to S-1,2-O-isopropylideneglycerol (IV) and then to the corresponding tosylate (V) and iodide (VI), as described in [8, 9]. Condensation of the iodide (VI) with diethyl malonate in DMFA in the presence of NaH leads to the ethyl ester of S-4,5-O-isopropylidene-4,5-dihydroxy-2-ethoxycarbonylpentanoic acid (VII), which, when heated with $MgCl_2 \cdot 6H_2O$ in dimethyl-

*For communication 2, see [1].

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acetamide, undergoes hydrolysis, decarboxylation, and recyclization to the known S-5-hydroxy-γ-pentanolide (VIII) [9]. The hydroxylactone (VIII) is converted to the corresponding tosylate (IX) according to the procedure of [2], and then (I) is produced by the reaction with lithium dimethyl cuprate in abs. ether. Thus, the approach to synthesis that we have developed is essentially a combination of two syntheses – the production of (VIII) from (II) [9] and the production of (I) from (VIII) [2]. The total yield of (I) from (II) is 3.0-3.5% (in eight steps), which is comparable with other methods of synthesis of (I).

To simplify the synthetic scheme we can eliminate the step of production of the iodide (VI) (performed in an autoclave) and can perform the alkylation of diethyl malonate directly by the tosylate (V), adding 10 mole % dry NaI to the reaction mixture. In this case the yield of the diester (VII) is 35%, whereas in the two-step method of its production (V) → (VI) → (VII) the total yield is 33.5%. Virtually no formation of (VII) occurs in the presence of NaI.

EXPERIMENTAL

Compounds (I) and (III)-(IX), produced according to the procedures of [2, 7-9], had values of the melting point, $[\alpha]_D$, IR, PMR, and mass spectra coinciding with the literature data. To obtain the optically pure tosylate (V) with $[\alpha]_D$ −8.6° from the optically pure alcohol (IV) ($[\alpha]_D$ +15.2°), thorough drying of the reagents and recrystallization of p-$CH_3C_6H_4SO_2Cl$ from $CHCl_3$–petroleum ether is necessary; traces of moisture and acid induced a significant racemization of (IV) (cf. [10]) and the formation of inactive (V).

S-Diether (VII). In a tared three-necked flask, NaH was washed with pentane and dried under vacuum under Ar to constant weight. A solution of 24 mmoles diethyl malonate in 20 ml DMFA was poured into a suspension of 25 mmoles NaH in 20 ml abs. DMFA at 10-15°C, mixed for 30 min, and 20 mmoles (V) and 2.0 mmoles of dry NaI in 20 ml DMFA were introduced. The mixture was heated under Ar (100°C, 3 h) and then treated as in [9]. Redistillation yielded pure (VII), bp 92-97°C (0.2 mm), n_D^{23} 1.4370, $[\alpha]_D$ −6.8° (C 4.0, MeOH), yield 35%.

CONCLUSIONS

R-γ-Hexanolide, a component of the sex pheromone of the beetle *Trogoderma glabrum*, was produced from D-mannitol in seven steps with a total yield of 3-3.5%.

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