SELECTIVE OXIDATION OF AROMATIC SUBSTITUENTS IN ALICYCLIC COMPOUNDS BY OZONOLYSIS IN AN ESTER SOLVENT

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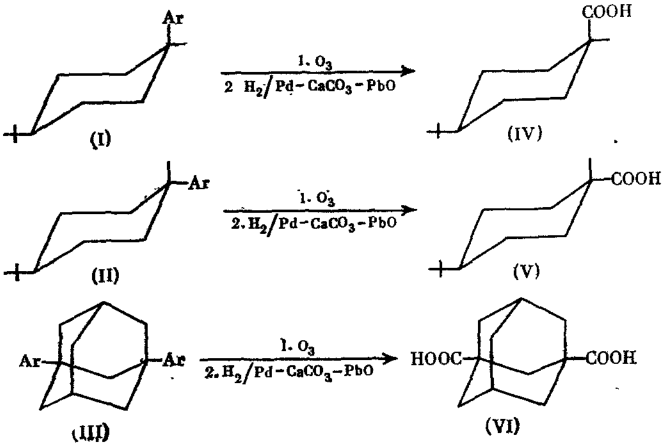
The ozonolytic cleavage of an aryl group in alicyclic compounds serves as a convenient path for the synthesis of cycloaliphatic carboxylic acids [1]. A new and efficient method for the ozonolysis of olefins to carboxylic acids was reported by us previously [2]. This method has now been used successfully for the selective oxidation of aromatic substituents in alicyclic compounds.

The ozonolysis of the cis- (I) and trans- (II) 1-methyl-1-(p-anisyl)-4-tert-butylcyclohexanes and 1,3-bis(p-anisyl)adamantane (III) in ethyl acetate, followed by conversion of the ozonolysis peroxide product on Lindlar catalyst in a hydrogen atmosphere, respectively, gave the cis- (IV) and trans- (V) 1-methyl-4-tert-butylcyclohexanecarboxylic acids and 1,3-adamantanedicarboxylic acid (VI) in ~60% yield.



Ar = p-anisole

EXPERIMENTAL

The IR spectra were obtained on a UR-20 spectrometer (Nujol mull). The mass spectrum was recorded on an MKh-1306 instrument at an ionization chamber temperature of 160°C and an ionizing voltage of 70 eV.

cis-1-Methyl-4-tert-butylcyclohexanecarboxylic Acid (IV). An ozone–ozygen mixture (5.5% O_3) was passed at a rate of 30 liters/h through a solution of 0.21 g of (I) in 40 ml of abs. ethyl acetate at −50° until the CO_2 evolution ceased [checked by using $Ba(OH)_2$ solution, ~3 h]. To the reaction mixture after blowing with N_2 was added 0.1 g of Lindlar catalyst [3] and the mixture was stirred in an H_2 atmosphere until the test for peroxide compounds was negative (test using acidified aqueous KI solution). The catalyst was filtered, the solvent was vacuum-distilled, the residue (0.2 g) was treated with 10% $NaHCO_3$ solution, and the alkaline solution was washed with cyclohexane, acidified with conc. HCl, and extracted with cyclohexane. We obtained 0.1 g (62.5%) of (IV), mp 131-132.5° (80% ethanol), cf. [1]. Infrared spectrum (ν, cm^{-1}): 945 m, 1110 w, 1145 w, 1180 w, 1200 w-m, 1245 m, 1280 w, 1302 w-m, 1705 s, 2400-3500 br. s.

trans-1-Methyl-4-tert-butylcyclohexanecarboxylic Acid (V). This was obtained from (II), the same as described above. Yield 60%, mp 143-144° (80% ethanol), cf. [1].

Infrared spectrum (ν, cm^{-1}): 960 m, 1150 w, 1180 w, 1200 w, 1220 w, 1260 w, 1300 m, 1705 s, 2400-3500 br. s.

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1,3-Adamantanedicarboxylic Acid (VI). The same as described above, the ozonolysis of 2 g of (III) in 200 ml of abs. ethyl acetate (~15 h) and subsequent workup gave 0.8 g (62%) of (VI), mp 274-275° (methanol), cf. [4].

Dimethyl Ester of 1,3-Adamantanedicarboxylic Acid. Obtained by treating (VI) with an ether solution of diazomethane, mp 61-62°, cf. [5]. Mass spectrum [m/e (I, %)]: 252 (M^+, 7.0), 221 ($M^+ - OCH_3$; 0.16), 193 ($M^+ - CO_2CH_3$; 100), 161 (23.6), 133 (70.1), 105 (15.3), 93 (15.0), 91 (30.7), 79 (17.1), 77 (16.4), 59 (20.5).

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CONCLUSIONS

A method was proposed for the selective conversion of aryl-substituted alicyclic compounds to cycloaliphatic carboxylic acids by ozonolysis in ethyl acetate, followed by conversion of the ozonolysis peroxide product on Lindlar catalyst in a hydrogen atmosphere.

LITERATURE CITED

1. P. J. Beeby and S. Sternhell, Austral. J. Chem., 24, 809 (1971).
2. V. N. Odinokov, L. P. Zhemaiduk, and G. A. Tolstikov, Izv. Akad. Nauk SSSR, Ser. Khim., 1900 (1976); V. N. Odinokov, L. P. Zhemaiduk, and G. A. Tolstikov, Zh. Org. Khim., 14, 54 (1978).
3. L. Fieser and M. Fieser, Reagents for Organic Synthesis [Russian translation], Vol. 2, Mir (1970), p. 136.
4. L. N. Butenko, V. E. Derbisher, A. P. Khardin, and A. I. Shreibert, Zh. Org. Khim., 9, 728 (1973).
5. H. Stetter and C. Wulff, Chem. Ber., 93, 1366 (1960).

EFFECT OF TEMPERATURE VARIATION ON COURSE OF TELOMERIZATION OF PROPYLENE WITH METHYL CHLOROACETATE

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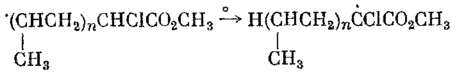
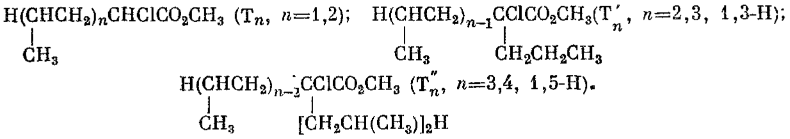
The telomerization of propylene with methyl chloroacetate goes with rearrangement of the growing radicals with a 1,3- (n = 1) and 1,5- (n = 2) migration of the H atom [1, 2].



$$^{\cdot}(\underset{\substack{|\\CH_3}}{CH}CH_2)_nCHClCO_2CH_3 \xrightarrow{\circ} H(\underset{\substack{|\\CH_3}}{CH}CH_2)_n\dot{C}ClCO_2CH_3$$

Three series of telomer homologs are formed as a result:



$$H(\underset{\substack{|\\CH_3}}{CH}CH_2)_nCHClCO_2CH_3\ (T_n,\ n=1,2);\quad H(\underset{\substack{|\\CH_3}}{CH}CH_2)_{n-1}\underset{\substack{|\\CH_2CH_2CH_3}}{C}ClCO_2CH_3(T'_n,\ n=2,3,\ 1,3\text{-}H);$$
$$H(\underset{\substack{|\\CH_3}}{CH}CH_2)_{n-2}\underset{\substack{|\\[CH_2CH(CH_3)]_2H}}{C}ClCO_2CH_3\ (T''_n,\ n=3,4,\ 1,5\text{-}H).$$

The enumerated telomers were previously isolated in the pure form (T'_4 and T''_4 as a mixture), and their structure was confirmed by the PMR and ^{13}NMR spectral data [1, 2].

The telomers of the T_n ($n \geq 3$) series are absent in the higher telomerization products. The coupling of the two types of hydrogen migration in one process makes it possible to compare the effect of variation in the reaction temperature on their course under strictly comparable conditions.

We started with the premise that the less favorable the process (in the given case the 1,3-H shift when compared with the 1,5-H shift) the more it is affected by variation in the reaction conditions. By finding the

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