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INTRAMOLECULAR CYCLIZATION OF

ALKOXYCARBONYLCARBENES DURING

THERMAL DECOMPOSITION OF ALKYL DIAZOACETATES

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Intramolecular reactions for the cyclization of carbenes generated from aliphatic diazo compounds, which are accompanied by insertion of the carbene center in the C-H bond, are known for diazo ketones and were used to synthesize polycyclic compounds [1]. Up to the present paper, a similar cyclization in the series of alkyl esters of aliphatic diazo acids, together with intermolecular reaction, was observed only during the photolysis of tert-butyl diazoacetate and 2-methyl-2-butyl diazoacetate in cyclohexane as the medium [2].

We were the first to observe the intramolecular cyclization of butoxycarbonylcarbene (Ia) under the conditions for the thermal decomposition of n-butyl diazoacetate (IIa), in isobutylene as the medium, on quartz packing heated to 270-300°C. In the reaction products, besides the butyl esters of 1,1-dimethylcyclopropanecarboxylic acid (IIIa) (yield 15-20%) and a mixture of the isomeric fumaric and maleic acids (IVa) (total yield ~5%), was detected 4-ethyldihydro-2-furanone (yield 2-3%), the product of the intramolecular insertion of the carbene C atom of (Ia) in the β -C-H bond of an alkyl group. Here we were unable to record the formation of alkoxycyclobutanones (VI), which, as was shown by us previously on the example of the pyrolysis of (IIc) [3], can be formed under these conditions as the result of the cycloaddition of alkoxyketenes (VII), the Wolff rearrangement products of carbenes (I), to isobutylene. The absence of butoxycyclobutanones (VIa) in the reaction products can evidently be explained by the difficulty of carbene (Ia) undergoing the Wolff rearrangement, which involves migration of the bulky butoxyl group. The intramolecular cyclization of (Ia) becomes a more favorable process under these conditions (see Scheme 1).

The obtained results made it possible to expect that running the pyrolysis of alkyl diazoacetates (ADA) in the absence of isobutylene, in an inert gas as the medium, will lead to an increase in the selectivity of the process as regards the dihydrofuranones (V). Actually, running the pyrolysis of a mixture of (Ia) vapors and argon in vacuo at $180-200^{\circ}$ C, in an empty quartz tube, made it possible to raise the yield of (Va) to 10-12%. Here in the reaction products, besides (Va), were detected only small amounts of the isomeric (IV) compounds. The pyrolysis of isobutyl diazoacetate (IIb) under analogous conditions led to 4,4-dimethyldihydro-2-furanone (Vb) in higher yield (20%), which is apparently due to the greater ease of inserting the carbene C atom in the tertiary C-H bonds in (Ib) when compared with the secondary bonds in (Ia), and is in agreement with the data given in [4] on the relative reactivity of the various C-H bonds of alkanes in the intermolecular insertion reactions of alkoxycarbonylcarbenes.

The dihydrofuranones (V) synthesized by us find practical use as aromatizing agents [5]. However, even by the best method described in the literature [5, 6], the (V) compounds can be obtained only in 4-5 steps and

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an overall yield of 5-7%. The proposed method for the preparation of dihydrofuranones by the pyrolysis of ADA in an inert gas as the medium differs from the known method as follows: a nearly three times greater yield of the desired product, a substantial simplification of the process by being one-step, and the use of readily available starting compounds, which permits recommending it as a preparative method.

EXPERIMENTAL

The GLC analysis was run on an LKhM-8-MD instrument equipped with a katharometer, and using a $3 \text{ m} \times 2 \text{ mm}$ column packed with 15% Reoplex 400 deposited on Chromaton N-AW-DMCS, a temperature of 150°C, helium as the carrier gas, and a flow rate of 30 ml/min. The PMR spectra were obtained in CCl₄ solution on a Varian DA-60-IL instrument (60 MHz, internal standard = TMS). The IR spectra were taken on a UR-10 instrument, and the mass spectra were taken on a Varian MAT CH-6 instrument.

n-Butyl Diazoacetate (IIa) and Isobutyl Diazoacetate (IIb). The starting (II) compounds were prepared as described in [7], and the corresponding esters of monochloroacetic acid, which are present as impurities, were removed by column chromatography on neutral Al_2O_3 , using a 4:2 hexane-ether mixture as the eluant. Compound (IIa), bp 53-54°C (8 mm); d_4^{20} 1.0244; n_D^{20} 1.4600. Infrared spectrum (ν , cm⁻¹): 2120 (C = N = N), 1695 (C = O). PMR spectrum (δ , ppm): 0.95 m (CH₃), 1.0-2.0 m (CH₂CH₂), 4.08 m (OCH₂), 4.70 s (CH₂). Compound (IIb), bp 58-60°C (8 mm); d_4^{20} 1.1041; n_D^{20} 1.4569. Infrared spectrum (ν , cm⁻¹): 2120 (C = N = N), 1695 (C = O). PMR spectrum (δ , ppm): 0.92 d (2CH₃), 1.91 m (CH), 3.87 d (OCH₂), 4.73 s (CHN₂).

Butyl Ester of 1,1-Dimethylcyclopropanecarboxylic Acid (IIIa). The pyrolysis of (IIa) in isobutylene medium was run as described in [8], using an ADA: hydrocarbon mole ratio = 1:100 and a reactor loaded with quartz packing (inside diameter 1.8 cm, volume of packing 45 cm³, and free space 55 cm³). In this way, from 7.27 g (0.051 mole) of (IIa) we obtained 3.0 g of catalyzate, which, based on the GLC data, contained 22% of (IIIa), 5% of mixed isomeric (IVa), and 2.6% of (Va). Distillation of the catalyzate gave 1.78 g (20%) of 96% pure (IIIa), bp 68-69.5°C (8 mm). Infrared spectrum (ν , cm⁻¹): 1725 (C = O). PMR spectrum (δ , ppm): 0.8-1.8 m (10H), 1.12 s and 1.15 s (2CH₃), and 3.97 t (OCH₂).

<u>4-Ethyldihydro-2-furanone (Va) and 4,4-Dimethyldihydro-2-furanone (Vb)</u>. Through an empty quartz reactor (inside diameter 2 cm, heated volume 150 cm³), connected to a vacuum system (residual pressure 5 torr), at 180°C, in an argon stream, was passed 8.4 g (0.06 mole) of (IIa) in 7 h. In the receiver, cooled to -78° C, was collected 4.3 g of catalyzate, which, based on the GLC data, contained 18% of (Va), 3% of mixed isomeric (IVa), and trace amounts of unidentified impurities. Distillation gave 0.7 g (10.5%) of 95% pure (Va), bp 62-65°C (4 mm); mol. wt. 114 (mass spectrometry). Infrared spectrum (ν , cm⁻¹): 1790 (C = O). PMR spectrum (δ , ppm): 0.91 m (CH₂), 1.48 m (CH₂CH₂), 2.3 m (CH₂CO and CH), 4.02 d (CH₂O).

In a similar manner, but in a yield of 19%, from (IIb) was obtained 97% pure (Vb), bp 89-90°C (2 mm); mol. wt. 114 (mass spectrometry). Infrared spectrum (ν , cm⁻¹): 1790 (C=O). PMR spectrum (δ , ppm): 1.11 s (2CH₃), 2.14 s (CH₂O), 3.8 s (CH₂CO).

CONCLUSIONS

We were the first to observe the intramolecular cyclization of alkoxycarbonylcarbenes under the conditions for the thermal decomposition of alkyl diazoacetates, which proceeds via the insertion of the carbene C atom in the β -C-H bond of the ester group.

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FORMATION OF DIHALOCARBENES BY PYROLYSIS

OF TRIHALOACETIC ACIDS*

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Carboxylic acids when heated are usually either decarboxylated or dehydrated [2]. In contrast, in the pyrolysis of fluoroacetic acids the primary and main step of their decomposition is dehydrofluorination [3, 4], in which connection the main pyrolysis product of CF_3COOH is diffuoroacetate, which, according to [4], is formed via diffuoroacetate.

 $\mathbf{CF_3COOH} \xrightarrow{\mathbf{1)} - \mathbf{HF}} : \mathbf{CF_2} \xrightarrow{\mathbf{CF_3COOH}} \mathbf{CF_3COOCF_2H}$

The participation of : CF_2 in the process is also confirmed by the formation of CHF_2Cl when the pyrolysis is run in excess HCl [4]. However, these data are inadequate for answering the question of whether the kinetically independent difluorocarbene is formed, especially if it is taken into account that the noncarbene transfer of the fluoromethylene fragments to a solid surface is possible [5]. In addition, it seemed of interest to ascertain whether the γ -elimination of HX and formation of the dihalocarbene is characteristic only for the fluoroacetic acids, or whether these processes are also typical for other haloacetic acids.

In order to answer the indicated questions we studied the copyrolysis of trihaloacetic acids CX_3COOH (where X = F, Cl, Br) with excess cyclopentadiene (CPD), which is a good "trap" for dihalocarbenes and forms the monohalobenzenes here [6]. The copyrolysis was run in a quartz reactor loaded with quartz packing in the temperature range 300-500°C, with a contact time of 0.8-1.0 sec, a 10-fold mole excess of CPD, and dilution of the pyrolyzed acids with a 16-fold mole excess of water. Here the formation of the corresponding monohalobenzenes in yields of 20-30% was observed in all cases (Table 1).

As was shown previously [7], the presence of ammonia in the reaction mixture facilitates the cleavage of HX and reduces tar formation during the copyrolysis of haloforms with CPD and its derivatives. As can be seen from Table 1, the addition of ammonia in the given case also increases the selectivity of the process

*See [1] for preliminary communication.

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