REACTION OF 1,2-BORYLPHOSPHINOETHENE WITH PHENYL ISOTHIOCYANATE AND CARBODIIMIDES

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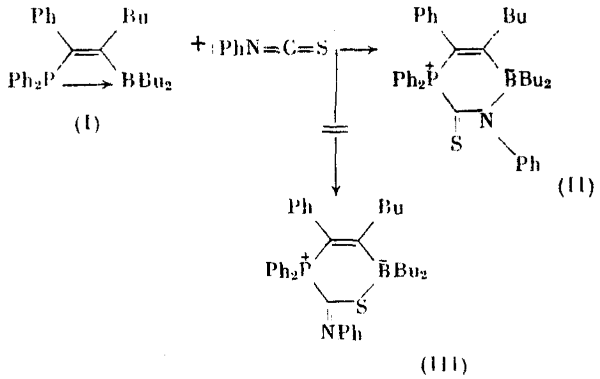
UDC 542.91:547.1'127'118

The reaction of 1-butyl-1-dibutylboryl-2-phenyl-2-diphenylphosphinoethene with phenyl isothiocyanate is a [4 + 2]-cycloadditon that involves the C=N segment of the heterocumulene; it gives 2,2,3-tributyl-6-thioxo-1,4,5,5-tetraphenyl-1-aza-5-phosphine-2-boratacyclohex-3-ene. Similarly products of the reaction of 1,2-borylphosphinoethene with diphenyl- and dicyclohexylcarbodiimides rearrange via the 1,2-B → anionotropic C shift of the butyl fragment; the products are the respective 1,6,6-tributyl-3-imino-4,4,5-triphenyl-2-aza-4-phosphine-1-boratabicyclo[3.1.0]hexanes.

The 1,2-borylphosphinoethenes (I) are distinctly dipolarophilic reagents, because they contain both B^{III} electron-acceptor and P^{III} electron-donor centers. Therefore, these compounds tend to react with compounds that contain short polarized bonds (C=O, C=S) [1, 2]. Such a reaction is a [4 + 2]-cycloaddition that gives cyclic betaines in its first stage. The structure of the final products depends on the kind of reagent with the short bond. Thus, with aldehydes 1-oxa-5-phosphonium 2-boratacyclohex-3-enes with the betaine structure similar to 1,3,2,5-dioxaborataphosphoniarinane are formed [1], whereas with carbon disulfide the charge separation is not so marked [2]. With ketones, azomethines, alkyl and aryl nitrites, and cyanophosphines there is no reaction at all.

We desired to broaden the use of 1,2-borylphosphinoethenes as synthones for new types of heterocycles containing phosphorus and boron; we therefore have studied the reaction of 1-butyl-1-dibutylboryl-2-phenyl-2-diphenylphosphinoethene (I) with phenyl isothiocyanate and diphenyl- and dicyclohexylcarbodiimides.

The reaction of (I) with phenyl isothiocyanate is completed after 5 days at ~20°C. The IR spectrum of the crystallized reaction product lacks a C=N band, but contains a C=C vibration band at 1550 cm^{-1}. The ^{31}P NMR spectrum shows a chemical shift (CS) of −5 ppm, which is very close to that of the 1-oxa-5-phosphinium-2-boratacyclohex-3-enes [1]. We therefore assigned it the structure of 2,2,3-tributyl-6-thioxo-1,4,5,5-tetraphenyl-1-aza-5-phosphinium-2-boratacyclohex-3-ene (II). X-ray diffraction (XRD) analysis confirmed its bipolar structure.* In the previously studied reaction of (I) with carbon disulfide a cyclic



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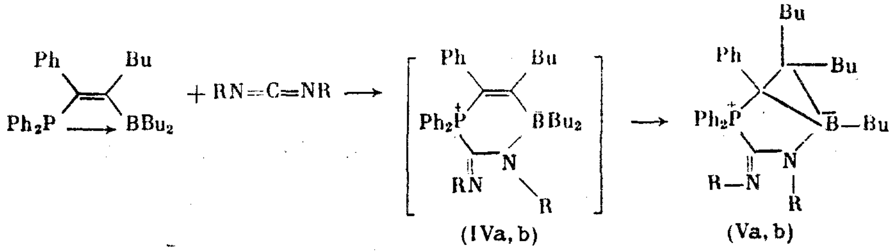
*Complete XRD data for (II) and (Va), obtained by L. F. Chertanova and A. A. Gazikasheva, will be published later.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1209-1211, May, 1991. Original article submitted October 17, 1990.

compound is formed in which boron is bonded to one of the sulfur atoms [2]. Phenyl isothiocyanate reacts with (I) only at the C=N bond. Formation of (III) with an endocyclic sulfur, viz., addition at C=S, was not observed in this reaction.

Like phenyl isothiocyanate, carbodiimides form 1:1 adducts with (I). The reaction with diphenylcarbodiimide is complete after 1 day (monitored by the ^{31}P NMR spectrum) and gives a bright yellow crystalline material with 12 ppm CS. The reaction with dicyclohexylcarbodiimide is somewhat slower; it is finished after 14 days at ~20°C and gives a yellow crystalline product with 8.29 ppm CS. Thus, the CS of the compounds thus obtained is quite different from that of betaine (II) with the six-membered ring. Their IR spectra lack the absorption of the calculated N=C=N segment, and have the characteristic C=N absorption. It should be noted that when the reaction is monitored by ^{31}P NMR there are no signals other than those of the starting (I) and the final product. The structures of the compounds formed could not be established by IR and NMR spectra and elemental analysis. Therefore, the product of the reaction of (I) with diphenylcarbodiimide was analyzed by x-ray diffraction; it has the structure of 1,6,6-tributyl-2,4,4,5-tetraphenyl-3-phenylimino-2-aza-4-phosphinium-1-boratabicyclo[3.1.0]hexane (Va). Apparently (Vb), the product of the addition of dicyclohexylcarbodiimide to (I), has a similar bicyclic structure. We may assume that the first stage of the reaction of (I) with carbodiimides is [4 + 2]-cycloaddition, which gives betaine (IV) with a six-membered ring. But it was not possible to separate or record the intermediates (IV). Apparently it rearranges quite quickly to the bicyclic (V) as a result of a 1,2-anionotropic shift of a butyl group from boron to the α-carbon, followed by an intramolecular nucleophilic attack by the β-carbon on boron.



R = Ph (a), C_6H_{11} (b).

EXPERIMENTAL

^{31}P NMR spectra were recorded with a KGU-4 NMR spectrometer at 10.2 MHz frequency with proton noise suppressor (25.2 MHz), and with a Bruker WM-250 spectrometer (101.27 MHz). The external standard was 85% H_3PO_4. IR spectra were recorded in mineral oil suspension with a UR-20 spectrometer. The synthesis of (I) is given in [1].

2,2,3-Tributyl-6-thioxo-1,4,5,5-tetraphenyl-1-aza-5-phosphinium-2-boratacyclohex-3-ene (II). To 0.5 g (1 mmole) of (I) in 2 ml of benzene was added 0.15 g (1 mmole) of phenyl isothiocyanate. After 5 days the solvent was removed in vacuum, and the crystals that separated were filtered off and washed with acetonitrile. Yield of (II), 0.3 g (47%), mp 168-169°C, δP −5 ppm (C_6H_6). IR spectrum (ν, cm^{-1}): 1550 (C=C). Found, %: C 77.98, H 7.89, N 2.63, P 5.13, S 5.07. $C_{39}H_{47}BNPS$. Calculated, %: C 77.61, H 7.79, N 2.32, P 5.14, S 5.31.

1,6,6-Tributyl-2,4,4,5-tetraphenyl-3-phenylimino-2-aza-4-phosphinium-1-boratabicyclo[3.1.0]hexane (Va). This was obtained similarly to (II), from (I) and diphenylcarbodiimide. The reaction is finished after 1 day at 20°C. Yield of (Va), 65%, mp 127-128°C (acetonitrile); δP +12 ppm (C_6H_6). IR spectrum (ν, cm^{-1}): 1570 (C=N). Found, %: C 81.85, H 8.40, N 4.55, P 5.07. $C_{45}H_{52}BN_2P$. Calculated, %: C 81.57, H 7.85, N 4.23, P 4.68.

1,6,6-Tributyl-4,4,5-triphenyl-2-cyclohexyl-3-cyclohexylimino-2-aza-4-phosphinium-1-boratabicyclo[3.1.0]hexane (Vb). This was obtained similarly to (II), from (I) and dicyclohexylcarbodiimide; the reaction is finished after 14 days. Yield of (Vb), 17%); mp 114-117°C; δP −8.29 ppm (C_6H_6). IR spectrum (ν, cm^{-1}): 1575 (C=N). Found, %: C 80.19, H 9.78, N 4.42, P 4.45. $C_{45}H_{64}BN_2P$. Calculated, %: C 80.11, H 9.49; N 4.15; P 4.60.

The authors thank Academician B. A. Arbuzov for assistance in the completion of this work.

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MELDRUM'S ACID – A REAGENT FOR THE SYNTHESIS OF UNSATURATED γ-LACTONES AND β-ACYLACRYLIC ACIDS

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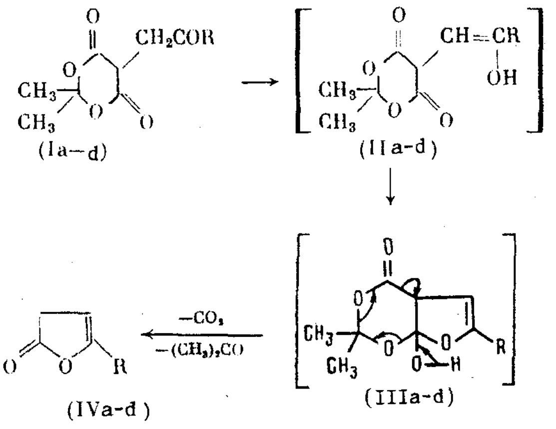
UDC 542.91:547.391.1:
547.384:547.394-314

The thermal cyclization of 2,2-dimethyl-5-(2-aryl-2-oxoethyl)-1,3-dioxan-4,6-diones forms 5-aryl-β,γ-butenolides. Regioselective chlorination of 2,2-dimethyl-5-[2-aryl(alkyl)-2-oxoethyl]-1,3-dioxane-4,6-diones by SO_2Cl_2 gives the 5-chloro derivatives; these are cleaved by aqueous AcOH to the E-β-acylacrylic acids, which are synthones for unsaturated γ-lactones.

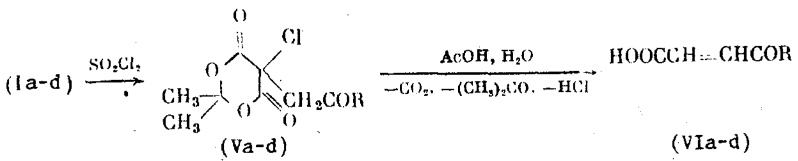
Unsaturated γ-lactone groups (butenolides) are present in many natural and biologically active compounds [1].

In the present work we have studied the synthesis of butenolides and their synthones – the β-acylacrylic acids – from derivatives of Meldrum's acid (Ia-d) by Schemes 1 and 2.

Scheme 1



Scheme 2



R = Ph (a), p-C_6H_4Br (b), C_5H_{11} (c), C_6H_{13} (d).

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1212-1214, May, 1991. Original article submitted September 25, 1990.

0568-5230/91/4005-1090$12.50