Compound (VIIb), bp 95-96°C; PMR spectrum (δ, ppm): 4.70-6.28 m (3H), 1.57-3.12 m (6H), 0.95 d (J = 7 Hg, 3H).

Compound (VII), bp 108-109°; n_D²⁵ 1.4285; mass spectrum, m/e (%): 96(4), 81(13), 69(53), 68(100), 67(40), 55(5), 54(3), 53(19), 41(13); IR spectrum (ν, cm⁻¹): 710 (w), 965, 1375, 1445, 2975, 3020.

The IR and PMR spectra of methylhexadiene (IX) agreed with the data given in [10].

The hydrogenation of 0.315 g of the codimers fraction in 3.0 ml of n-hexane at 25° in the presence of 0.20 g of Pt/C (Pt content = 10%) until the H₂ absorption ceased (98 ml/756 mm) gave a mixture of 47% of (XIa), 10.5% of (XIb), 20.5% of (XII), 0.9% of (XIII), 19% of (XIV), and 2.0% of (XV), which were identified employing chromato-mass spectroscopy.

The PD conversion was 55%, and the total yield of codimers when based on converted PD was 72%.

CONCLUSIONS

The codimerization of either 1,3-butadiene or 1,3-pentadiene with ethylene in the presence of the catalyst system $C_{5}H_{5}Ti[OSi(CH_{3})_{3}]_{3}$ -CH₃MgI assures the selective synthesis of vinyl-cyclobutanes.

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REACTION OF ACYL ISOCYANATES WITH AROMATIC ALDAZINES

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Continuing our study of the reactions of acyl isocyanates with compounds that contain a C=N bond, we studied the reactions with aromatic aldazines.

It is known that azines react with heterocumulenes on the type of a combined bis-1,3cross cycloaddition with the formation of substituted triazolo[1,2-a]triazoles [1-4]. As a result, the formation of substituted triazolo[1,2-a]triazoles, the [4+2]-mono- and biscycloadducts, could be expected from the reaction of acyl isocyanates with aromatic aldazines.

We studied the reaction of benzoyl (I), trichloroacetyl (II), and trifluoroacetyl (III) isocyanate with benzalazine, p-methoxybenzalazine, and p-dimethylaminobenzalazine. Since (I) reacts with the benzal- and p-methoxybenzalazines to give substituted triazolotriazoles [1], we studied its reaction with p-dimethylbenzalazine, which led to perhydro-2,6-dibenzoyl-1,5-bis(dimethylaminophenyl)triazolo[1,2-a]triazole-3,7-dione (IV). The IR spectrum of (IV) has absorption bands at 1760 and 1680 cm⁻¹ (stretching vibrations of C=O group). In addi-

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tion, the structure of (IV) is confirmed by the data of the PMR spectrum, which has the following signals (δ , ppm): 8.50 s (2H, CH), 6.68 d and 7.63 d (J_{ortho} = 6.6 Hz, 8H, protons of p-disubstituted benzene ring), and 3.06 s [12H, (CH₃)₂N].



Compound (II) reacts in a similar manner with p-dimethylaminobenzalazine. The structure of (V) was established on the basis of the elemental analysis and the IR and PMR spectral data. The IR spectrum has the following characteristic absorption bands (ν , cm⁻¹): 1750 (cyclic C=O), 1720 (acyl C=O). PMR spectrum of (V) (δ , ppm): 3.06 s [12 H, (CH₃)₂N], 6.57 d and 7.54 d (J_{ortho} = 6.6 Hz, 8H, protons of p-disubstituted benzene ring), 8.15 s (2H, CH).

Compound (II) reacted with benzalazine only under drastic conditions to give the N-unsubstituted triazolo-triazole (VI), which is evidently formed from perhydro-2,6-di(trichloroacetyl)-1,5-diphenyltriazolo[1,2-a]triazole-3,7-dione due to hydrolysis of the C(0)=N bond by atmospheric moisture; the melting point of our obtained (VI) agrees with the data given in [1, 4].

The reaction of (III) with all the studied azines, and also the reaction of (II) with p-methoxybenzalazine, gave compounds whose structure, when based on the elemental analysis and the IR and PMR spectral data, corresponded to the mono-[4+2]-cycloadducts, namely 5-aryl-ideneamino-6-aryl-2-trihalomethyl-2,3-dehydro-4-oxo-1,3,5-oxadiazines.



Infrared spectra of (VII)-(X) (ν , cm⁻¹): 1670-1690 (C=0), 1615-1630 (C=N). PMR spectrum of (VII) (δ , ppm): 6.90 s (1H, cyclic CH), 7.50 s (5H, C₆H₅CHO), 8.15 m (5H, C₆H₅CH=N), 9.31 s (1H, CH=N).

EXPERIMENTAL

The IR spectra were recorded as Nujol mulls on a UR-10 spectrometer, equipped with NaCl and LiF prisms. The PMR spectra of (V) and (VI) were taken in $(CD_3)_2CO$ solution, and that of (VII) was taken as CHCl₃ solution, on a T-60 spectrometer, while the spectrum of (IV) was taken as CH₂Cl₂ solution on a NA-100D spectrometer.

Perhydro-2,6-dibenzoyl-1,5-bis(p-dimethylaminophenyl)triazolo[1,2-a]triazole-3,7-dione (IV). To a solution of 0.5 g of (I) in 10 ml of abs. CHCl₃ was added in drops a solution of $\overline{0.51}$ g of p-dimethylaminobenzalazine in 10 ml of abs. CHCl₃, after which the mixture was kept for 4 days at $\sim 20^{\circ}$ C and then evaporated in vacuo. The residue was rubbed with hexane, and the crystals were filtered and washed in succession with ether and hexane to give 0.76 g (75% yield) of (IV) with mp 155-160° (decomp.). Found: C 69.68; H 5.35%. C₃₄H₃₂O₄N₆. Calculated: C 69-38; H 5.44%.

Perhydro-2,6-di(trichloroacety1)-1,5-bis(p-dimethylaminophenyl)triazolo[1,2-a]triazole-3,7-dione (V). To a solution of 1.67 g of p-dimethylaminobenzalazine in 30 ml of CHCl₃ was added in drops a solution of 2.1 g of (II) in 15 ml of CHCl₃, after which the mixture was kept for a week at \sim 20°C and then evaporated in vacuo. The residue was rubbed with hexane, and the crystals were washed in succession with ether and hexane to give 3.0 g (85% yield) of (V) with mp 70-73° (decomp.). Found: C 42.72; H 3.48; Cl 31.62%. C₂₄H₂₂O₄N₆Cl₆. Calculated: C 42.92; H 3.27; Cl 31.74%. <u>Perhydro-1,5-diphenyltriazolo[1,2-a]triazole-3,7-dione (VI)</u>. To a solution of 1.8 g of (II) in 10 ml of C₆H₆ was added in drops a solution of 1.2 g of benzalazine in 5 ml of C₆H₆, and then the mixture was heated at reflux for 14 days. Crystals were obtained by cooling, which were washed with ether to give 2.3 g (82%) of (VI) with mp 235°. In addition, we isolated 0.5 g of trichloroacetamide with mp 139-141°.

<u>5-p-Methoxybenzylideneamino-6-p-methoxyphenyl-2-trichloromethyl-2,3-dehydro-1,3,5-oxadia-zin-4-one (VIII)</u>. To a solution of 1.48 g of (II) in 12 ml of CHCl₃ was added a solution of 2.1 g of p-methoxybenzalazine in 30 ml of CHCl₃, and the mixture was heated at 50-60° for 14 days, cooled, and evaporated in vacuo. The crystalline residue was washed with abs. ether to give 3.0 g (88%) of (VIII) with mp 137-138°. Found: C 49-69; H 3.73; Cl 23.00%. $C_{19}H_{16}O_4N_3Cl_3$. Calculated: C 49.95; H 3.50; Cl 23.33%.

5-p-Dimethylaminobenzylideneamino-6-p-dimethylaminophenyl-2-trifluoromethyl-2, 3-dehydro-1,3,5-oxadiazin-4-one (X). To a solution of 1.2 g of (III) in 20 ml of abs. C₆H₆ was addeda solution of 1.16 g of p-dimethylaminobenzalazine in 10 ml of abs. C₆H₆, and the crystalswere filtered and washed in succession with ether and benzene to give 1.89 g (90%) of (X) withmp 102-103°. Found: C 50.42; H 4.01%. C₂₁H₂₂O₂N₃F₃. Calculated: C 50.35; H 3.85%.

 $\frac{5-p-Methoxybenzylideneamino-6-p-methoxyphenyl-2-trifluoromethyl-2,3-dehydro-1,3,5-oxadia$ zin-4-one (IX). To a solution of 1.75 g of (III) in 20 ml of 1,2-dichloroethane was added3.30 g of p-methoxybenzalazine in 10 ml of 1,2-dichloroethane, after which the mixture waskept at 18-20° for 24 h, the solvent was removed in vacuo, and the residue was recrystallizedfrom C₆H₆ to give 2.52 g (50%) of (IX) with mp 149-150°. Found: C 56.13; H 4.07%. C₁₉H₁₆O₄N₃F₃.Calculated: C 56.02; H 3.96%.

 $\frac{5-\text{Benzylideneamino-6-phenyl-2-trifluoromethyl-2,3-dehydro-1,3,5-oxadiazin-4-one (VII).}{\text{To a solution of 1.65 g of (III) in 10 ml of abs. ether was added a solution of 2.46 g of benzalazine in 10 ml of abs. ether. After 15 min the obtained pale yellow crystals were filtered and washed with ether to give 2.4 g (64%) of (VII) with mp 176-178°. Found: C 58.72; H 3.48%. C₁₇H₁₂O₂N₃F₃. Calculated: C 58.78; H 3.45%.$

CONCLUSIONS

1. Benzoyl and trichloroacetyl isocyanates react with p-dimethylaminobenzalazine and benzalazine on the type of bis-1,3-dipolar cycloaddition to give substituted triazolo[1,2-a]triazoles.

2. Trifluoroacetyl isocyanate reacts with aromatic aldazines on the type of mono-[4+2]cycloaddition. Trichloroacetyl isocyanate reacts in a similar manner with p-methoxybenzalazine.

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