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Reaction of Allyl Phenylcarbamate with Benzaldehyde Phenylhydrazones in the Presence of *N*-Chlorobenzenesulfonamide Sodium Salt

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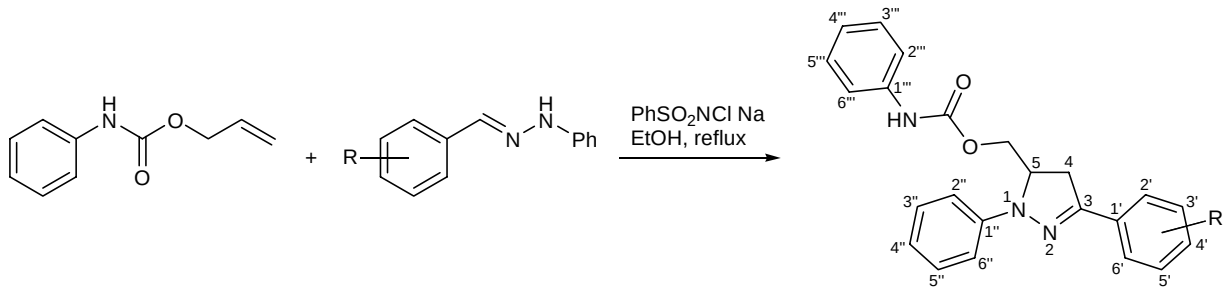
Abstract—Phenylhydrazones derived from 4-bromo-, 4-methoxy-, and 3-nitrobenzaldehydes react with allyl phenylcarbamate in the presence of *N*-chlorobenzenesulfonamide sodium salt to give the corresponding 3-aryl-1-phenyl-5-(phenylcarbamoyloxymethyl)-4,5-dihydro-1*H*-pyrazoles whose structure was confirmed by the IR and ^{1}H and ^{13}C NMR spectra.

We previously studied reactions of allyl and 2-propynyl phenylcarbamates with benzaldehyde oximes in the presence of *N*-chlorobenzenesulfonamide sodium salt; these reactions occurred with high regioselectivity and resulted in formation of 3,5-disubstituted 4,5-dihydroisoxazoles and isoxazoles [1–3]. In continuation of these studies, the present communication reports on reactions of phenylhydrazones derived from substituted benzaldehydes with allyl phenylcarbamate in the presence of *N*-chlorobenzenesulfonamide sodium salt. It should be noted that generation of nitrilimines from aromatic and aliphatic aldehyde phenylhydrazones by the action of *N*-chloro-*p*-toluenesulfonamide sodium salt and addition of these species to acrylonitrile, styrene, and ethyl acrylate with formation of the corresponding dihydropyrazoles were reported for the first time in [4]. *N*-Chlorobenzenesulfonamide sodium salt is more advantageous than lead tetraacetate as a reagent for generation of nitrilimines, for it prevents possible formation of diacylhydrazines [5]. The synthetic potential and specific features of 1,3-dipolar cycloaddition of alkenyl carbamates to nitrilimines generated *in situ* by the action of *N*-chlorobenzenesulfonamide sodium salt on benzaldehyde phenylhydrazones remain almost unstudied.

Reactions of allyl phenylcarbamate (**I**) with benzaldehyde, *p*-bromobenzaldehyde, *m*-nitrobenzaldehyde, and *p*-methoxybenzaldehyde phenylhydrazones **IIa**–**IId** in the presence of *N*-chlorobenzenesulfonamide sodium salt were carried out by heating a mixture of the reactants in boiling ethanol over a period of 3 h. After treatment of the mixture with diethyl ether [1], the precipitate was filtered off, and the product was isolated by column chromatography and was additionally purified by recrystallization from diethyl ether–petroleum ether (1:2).

Scheme 1.



I **IIa–IId** **IIIb–IIId**

II, **III**, R = H (**a**), 4-Br (**b**), 3-O_2N (**c**), 4-MeO (**d**).

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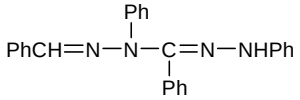
Analysis of the products by IR and ^1H and ^{13}C NMR spectroscopy showed that the cycloaddition of nitrilimines, as well as of unsubstituted and substituted benzonitrile oxides, occurs with high regioselectivity, leading to formation of the corresponding 3-aryl-1-phenyl-5-(phenylcarbamoyloxymethyl)-4,5-dihydropyrazoles **IIIb**–**IIId** in 32–54% yield. The spectral parameters of compounds **IIIb**–**IIId** are consistent with those reported for structurally related compounds [4].

High-melting crystalline products, which were insoluble in diethyl ether, were purified by reprecipitation from DMF with diethyl ether. In the reaction with benzaldehyde phenylhydrazone **IIa**, apart from unreacted carbamate **I**, the only isolated product was a high-melting substance (yield 62%). On the basis of the IR spectrum and elemental composition, this product was assigned the structure of 1,3,4,6-tetraphenyl-1,2,4,5-tetraaza-2,5-hexadiene (**IV**). Presumably, this compound is formed by dimerization of intermediate *C*,*N*-diphenylnitrilimine.



IV

In the reactions with the other hydrazones, the yields of the high-melting products were considerably lower. Relatively low yields of dihydropyrazoles **IIIb**–**IIId**, as well as formation of nitrilimine dimerization products, may be rationalized in terms of higher reactivity of nitrilimines as compared to benzonitrile oxides and low reactivity of allyl phenylcarbamate as dipolarophile. Nevertheless, despite the above drawbacks, the reaction of benzaldehyde phenylhydrazones with allyl phenylcarbamate in the presence of *N*-chlorobenzenesulfonamide sodium salt provides a convenient method for the synthesis of 1,3,5-trisubstituted dihydropyrazoles.

EXPERIMENTAL

The IR spectra were recorded in the range from 4000 to 400 cm^{-1} on an IKS-29 spectrometer from samples dispersed in mineral oil. The ^1H NMR spectra were recorded on a Bruker AC-200 instrument at 200.13 MHz) from solutions in acetone-d_6 using tetramethylsilane as internal reference. The ^{13}C NMR spectra were measured in acetone-d_6 on a Bruker WM-400 spectrometer (100 MHz) with complete decoupling from protons. The purity of the products was checked by TLC on Silufol UV-254 plates.

3-(4-Bromphenyl)-1-phenyl-5-(phenylcarbamoyloxymethyl)-4,5-dihydropyrazole (IIIb). A mixture of 0.70 g (3.96 mmol) of allyl phenylcarbamate (**I**), 1.10 g (4.0 mmol) of phenylhydrazone **IIb**, and 1.12 g (4.18 mmol) of *N*-chlorobenzenesulfonamide sodium salt trihydrate in 16 ml of anhydrous ethanol was heated for 3 h under reflux. The precipitate was filtered off, the solvent was distilled off from the filtrate, and the residue was treated with methylene chloride (2×25 ml). The extract was washed with water (2×25 ml) and 1 N aqueous sodium hydroxide (2×50 ml) and dried over sodium sulfate, the solvent was removed, the residue was dissolved in 15 ml of diethyl ether, the solution was cooled, and the crystals were filtered off. The ether solution was applied to a column charged with silica gel L 100/160 μm, and the column was eluted with diethyl ether to isolate 0.89 g (50%) of compound **IIIb**. Light yellow crystals, mp 125–126°C (from diethyl ether–petroleum ether, 1:2). IR spectrum, ν, cm^{-1}: 3340 (NH); 1725 (C=O); 1610, 1585, 1530 (C=C_{arom}). ^1H NMR spectrum, δ, ppm (*J*, Hz): 8.54 br.s (1H, NH), 8.02 d (2H, H_{arom}, *J* = 8.3), 7.94 d (2H, H_{arom}, *J* = 8.3), 7.40 d (2H, H_{arom}, *J* = 8.8), 7.21 m (2H, H_{arom}), 6.97 m (6H, H_{arom}), 4.28 m (2H, OCH_2), 3.93 m (1H, 5-H), 3.41 d.d (1H, 4-H, *J* = 8.4, 12.2), 3.20 d.d (1H, 4-H, *J* = 8.0, 12.2). ^{13}C NMR spectrum, δ_C, ppm: 38.52 (C^4), 56.80 (OCH_2), 58.43 (C^5), 112.04 ($C^{2''}$, $C^{6''}$), 119.10 ($C^{4''}$), 119.19 ($C^{2'''}$, $C^{6'''}$), 122.51 ($C^{3'''}$, $C^{5'''}$), 123.42 ($C^{4'}$), 123.55 ($C^{4'''}$), 127.52 ($C^{2'}$, C^6), 127.76 ($C^{3''}$, $C^{5''}$), 129.71 ($C^{1'}$), 130.32 ($C^{3'}$, $C^{5'}$), 134.04 ($C^{1'''}$), 145.72 ($C^{1''}$), 148.38 (C=N), 154.31 (C=O). Found, %: C 61.09; H 4.14; N 9.27. $C_{23}H_{20}BrN_3O_2$. Calculated, %: C 61.33; H 4.44; N 9.33.

3-(*m*-Nitrophenyl)-1-phenyl-5-(phenylcarbamoyloxymethyl)-4,5-dihydropyrazole (IIIc) was synthesized in a similar way from 0.35 g (1.98 mmol) of allyl phenylcarbamate (**I**), 0.48 g (1.99 mmol) of *m*-nitrobenzaldehyde phenylhydrazone (**IIc**), and 0.56 g (2.09 mmol) of *N*-chlorobenzenesulfonamide sodium salt trihydrate. Yield 0.40 g (54%). Light yellow crystals, mp 105–107°C (from diethyl ether–petroleum ether, 1:2). IR spectrum, ν, cm^{-1}: 3340 (NH); 1720 (C=O); 1610, 1585, 1535 (C=C_{arom}); 1530, 1355 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 8.66 br.s (1H, NH), 8.20 d (1H, H_{arom}, *J* = 7.7), 8.02 s (1H, H_{arom}), 7.94 t (1H, H_{arom}, *J* = 7.7), 7.36 d (2H, H_{arom}, *J* = 7), 7.21 t (3H, H_{arom}, *J* = 7.8), 6.94 m (6H,

H_{arom}), 4.26 m (2H, OCH_2), 3.94 m (1H, 5-H), 3.50 d.d (1H, 4-H, J = 7.8, 10.2), 3.44 d.d (1H, 4-H, J = 8.3, 10.2). ^{13}C NMR spectrum, δ_C, ppm: 38.52 (C^4), 55.62 (OCH_2), 58.39 (C^5), 112.03 ($C^{2''}$, $C^{6''}$), 119.12 ($C^{4''}$), 119.18 ($C^{2'''}$, $C^{6'''}$), 122.02 ($C^{2'}$), 122.54 ($C^{3'''}$, $C^{5'''}$), 123.51 ($C^{4'''}$), 125.08 ($C^{4'}$), 127.67 ($C^{3''}$, $C^{5''}$), 129.21 ($C^{5'}$), 132.76 ($C^{1'}$), 133.92 ($C^{6'}$), 134.57 ($C^{1'''}$), 145.95 ($C^{1''}$), 146.88 ($C^{3'}$), 148.42 (C=N), 153.87 (C=O). Found, %: C 66.10; H 4.78; N 13.19. $C_{23}H_{20}N_4O_4$. Calculated, %: C 66.35; H 4.81; N 13.46.

3-(4-Methoxyphenyl)-1-phenyl-5-(phenylcarbamoyloxymethyl)-4,5-dihydropyrazole (IIId) was synthesized in a similar way from 0.35 g (1.98 mmol) of allyl phenylcarbamate (**I**), 0.45 g (1.99 mmol) of *p*-methoxybenzaldehyde phenylhydrazone (**IId**), and 0.56 g (2.09 mmol) of *N*-chlorobenzenesulfonamide sodium salt trihydrate. Yield 0.25 g (32%). Light yellow crystals, mp 95–97°C (from diethyl ether–petroleum ether, 1:2). IR spectrum, ν, cm^{-1}: 3340 (NH); 1725 (C=O); 1620, 1575, 1535 (C=C_{arom}). ^1H NMR spectrum, δ, ppm (*J*, Hz): 8.50 br.s (1H, NH), 7.87 d (2H, H_{arom}, J = 8.4), 7.36 d (2H, H_{arom}, J = 8.8), 7.20 m (3H, H_{arom}), 7.07 m (5H, H_{arom}), 6.67 d (2H, H_{arom}, J = 8.4), 4.28 m (2H, OCH_2), 3.90 m (1H, 5-H), 3.62 s (3H, OMe), 3.53 d.d (1H, 4-H, J = 8.5, 10.2), 3.47 d.d (1H, 4-H, J = 7.8, 10.2). ^{13}C NMR spectrum, δ_C, ppm: 38.48 (C^4), 55.10 (OMe), 56.85 (OCH_2), 58.37 (C^5), 112.04 ($C^{2''}$, $C^{6''}$), 112.90 ($C^{3'}$, $C^{5'}$), 119.10 ($C^{4''}$), 119.17 ($C^{2'''}$, $C^{6'''}$), 122.54 ($C^{3'''}$, $C^{5'''}$), 123.54 ($C^{4'''}$), 124.60 ($C^{1'}$), 127.87 ($C^{2'}$, $C^{6'}$), 127.92 ($C^{3''}$, $C^{5''}$), 134.01 ($C^{1'''}$), 145.34 ($C^{1''}$), 148.36 (C=N), 154.43 (C=O), 159.21 ($C^{4'}$). Found, %: C 71.59; H 6.02; N 10.30. $C_{24}H_{23}N_3O_3$. Calculated, %: C 71.82; H 5.74; N 10.47.

1,3,4,6-Tetraphenyl-1,2,4,5-tetraaza-2,5-hexadiene (IV) was isolated as a crystalline substance. Yield 62%, mp 202°C; published data [5]: mp 200–202°C. IR spectrum, ν, cm^{-1}: 3330 (NH), 1620–1535 (C=C_{arom}). Found, %: C 79.78; H 5.48; N 14.44. $C_{26}H_{22}N_4$. Calculated, %: C 80.00; H 5.54; N 14.36.

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