REACTIONS OF PHENYL-SUBSTITUTED HETEROCYCLIC COMPOUNDS

I. NITRATION OF 2-PHENYL-1,2,3,2H-TRIAZOLE[1]

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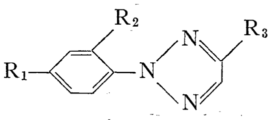
Received September 27, 1962

ABSTRACT

Structures have been assigned to the mono-, di-, and tri-nitration products of 2-phenyl-1,2,3,2H-triazole, on the basis, partly, of ultraviolet absorption spectra. The pattern of nitration closely resembles that of 1-phenylpyrazole. A compound previously described as 2-(*o*-nitrophenyl)-1,2,3,2H-triazole is actually 4-nitro-2-*p*-nitrophenyl-1,2,3,2H-triazole.

Riebsomer (1) investigated the nitration of 2-phenyl-1,2,3,2H-triazole (I) by mixed acids at 20°, and obtained two products, having m.p. 183° and 125°. He suggested that the higher-melting compound was 2-*p*-nitrophenyl-1,2,3,2H-triazole, and that the lower-melting compound was the ortho isomer. We required these substances as intermediates in the syntheses of 2-*p*-biphenylyl-1,2,3,2H-triazole (II) and 2-*o*-biphenylyl-1,2,3,2H-triazole (III), so Riebsomer's experiments were repeated.



I: $R_1 = R_2 = R_3 = H$
II: $R_1 = Ph; R_2 = R_3 = H$
III: $R_1 = R_3 = H; R_2 = Ph$
IV: $R_1 = R_3 = Ph; R_2 = H$

The higher-melting compound had the characteristics reported by Riebsomer, and its ultraviolet absorption was closely similar to that of 1-*p*-nitrophenylpyrazole (see Table I).

TABLE I
Ultraviolet absorption maxima of corresponding phenyltriazoles and phenylpyrazoles

1,2,3,2H-Triazole	λ_{max} (mμ)	log ϵ	Pyrazole	λ_{max} (mμ)	log ϵ
2-Phenyl	263	4.13	1-Phenyl	252	4.13
2-*p*-Nitrophenyl	306	4.09	1-*p*-Nitrophenyl*	312–314	4.24
4-Nitro-2-*p*-nitrophenyl	304	4.36	4-Nitro-1-*p*-nitrophenyl*	306	4.37
2-*p*-Biphenylyl	286	4.50	1-(2,4-Dinitrophenyl)	306	3.85
			1-*p*-Biphenylyl	280	4.50

*From DalMonte *et al.* (4).

Since the replacement of —CH: by —N: in heteroaromatic systems generally has little influence on ultraviolet absorption (2), correspondingly substituted 1-phenylpyrazoles and 2-phenyl-1,2,3,2H-triazoles should have similar electronic spectra, and assignments

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of structure can be based on such similarities. Further, the infrared spectra of the higher-melting compound showed strong bands at 1345 and 1530 cm^{-1}, corresponding to the symmetric and asymmetric N—O stretching vibrations, closely similar in frequency to those noted for 1-*p*-nitrophenylpyrazole (1341 and 1527 cm^{-1}). Present work (3) indicates that these band positions are characteristic of a *p*-nitro substituent in N-phenylated pyrazoles and imidazoles, and it seems likely that the correlation extends to phenyltriazoles.

Additional evidence in support of Riebsomer's assignment for the compound of m.p. 183° was obtained after reduction to the corresponding amine, followed by diazotization of the amine and Gomberg arylation of benzene. This yielded a biphenylyltriazole with ultraviolet absorption closely resembling that of 1-*p*-biphenylylpyrazole (3; see Table I), and showing strong infrared absorption in the C—H out-of-plane deformation region at 700, 765–770 (phenyl group), 850 (para substitution), and 950–965 cm^{-1} (triazole ring), to which structure II is assigned.

The lower-melting compound mentioned by Riebsomer was also obtained in our nitrations, although the melting point was raised to 140° by adsorption chromatography and crystallization. The ultraviolet absorption of this product differed markedly from that of 1-*o*-nitrophenylpyrazole, thus excluding the structure suggested by Riebsomer. Furthermore, the analytical results reported previously (nitrogen analyses) (1) do not distinguish between a mono- and a di-nitrophenyltriazole. Our analytical figures show that the compound, m.p. 140°, is a dinitro-2-phenyl-1,2,3,2H-triazole. Ultraviolet absorption data do not distinguish unequivocally between the two most likely structures, i.e., 4-nitro-2-*p*-nitrophenyl-1,2,3,2H-triazole and 2-(2,4-dinitrophenyl)-1,2,3,2H-triazole, since the spectra of the correspondingly substituted pyrazoles are fairly similar to one another and to the spectra of the compound of m.p. 140° (see Table I).

However, 2-(2,4-dinitrophenyl)-1,2,3,2H-triazole should readily undergo nucleophilic fission of the inter-ring C—N bond (compare 1-(2,4-dinitrophenyl)pyrazole (5, 6)), and the dinitrophenyltriazole, m.p. 140°, was unaffected by boiling with methanolic sodium methoxide, thus leading to the conclusion that the compound of m.p. 140° is 4-nitro-2-*p*-nitrophenyl-1,2,3,2H-triazole. Reduction of 4-nitro-2-*p*-nitrophenyl-1,2,3,2H-triazole as for 2-*p*-nitrophenyl-1,2,3,2H-triazole, followed by tetrazotization and Gomberg arylation of benzene, yielded 2-*p*-biphenylyl-4-phenyl-1,2,3,2H-triazole (IV).

Further nitration of 2-*p*-nitrophenyl-1,2,3,2H-triazole at 25° was found to yield 4-nitro-2-*p*-nitrophenyl-1,2,3,2H-triazole (compare the behavior of 1-*p*-nitrophenylpyrazole (5)), while nitration of the mono- or di-nitro compounds at 80°, or of the dinitro compound at 25°, yielded 2-(2,4-dinitrophenyl)-4-nitro-1,2,3,2H-triazole. Proof of structure of the trinitro compound was obtained by fission with methanolic sodium methoxide to yield 2,4-dinitroanisole.

Exclusive mononitration of 2-phenyl-1,2,3,2H-triazole to the *p*-nitrophenyltriazole can be effected in good yield by nitric acid in acetic anhydride, a more selective attacking reagent than nitric acid – sulphuric acid.

The general conditions necessary for the stepwise nitration of 2-phenyl-1,2,3,2H-triazole thus show close correspondence with those for 1-phenylpyrazole (5), notwithstanding the presence of an additional electron-attracting nitrogen atom in the triazole.

EXPERIMENTAL

General

Analyses were by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., U.S.A. Infrared spectra were recorded using a Unicam SP100 spectrophotometer (samples were examined using the potassium chloride disk technique) and ultraviolet spectra were measured in 95% ethanol using a Beckman DK-2A Ratio-Recording spectrophotometer; melting points were determined on a Fisher–Johns melting point apparatus and are uncorrected.

2-Phenyl-1,2,3,2H-triazole (I)

This compound, b.p. 228°, was prepared by oxidation of glyoxal bisphenylhydrazone with copper (II) sulphate (Riebsomer (1)).

Nitrations

(a) Of the Phenyltriazole (I) by Mixed Acids at 20°

The conditions employed were essentially those reported previously (1). 2-Phenyl-1,2,3,2H-triazole (7 g) in sulphuric acid (*d* 1.84, 20 ml) was nitrated by addition of nitric acid (*d* 1.42, 10 ml) over 1 hour at 20°. The reaction mixture was poured onto crushed ice and the precipitate was collected and washed repeatedly with cold ethanol. Crystallization from ethanol gave light yellow needles (5.5 g) of 2-*p*-nitrophenyl-1,2,3,2H-triazole, m.p. 183°. Anal. Calc. for $C_8H_6N_4O_2$: C, 50.53; H, 3.18%. Found: C, 50.33; H, 2.90%. Ultraviolet absorption: see Table I.

The ethanol washings and the mother liquor from the crystallizations were combined and the solvent was removed under reduced pressure. The residue was dissolved in benzene and chromatographed on alumina. Removal of solvent from the eluate, followed by crystallization from ethanol, yielded light yellow needles, m.p. 140° (0.98 g), presumed to be 4-nitro-2-*p*-nitrophenyl-1,2,3,2H-triazole. Anal. Calc. for $C_8H_5N_5O_4$: C, 40.86; H, 2.14; N, 29.78%. Found: C, 41.01; H, 2.34; N, 29.85%. Ultraviolet absorption: see Table I.

(b) Of the Phenyltriazole (I) by Nitric Acid – Acetic Anhydride

To 2-phenyl-1,2,3,2H-triazole (5 g) in acetic anhydride (50 ml) was added nitric acid (*d* 1.52, 25 ml) in acetic anhydride (25 ml) at ca. 15°. Precipitation commenced almost immediately; after 1 hour, the mixture was poured onto ice, and the product was collected and crystallized from ethanol, giving 2-*p*-nitrophenyl-1,2,3,2H-triazole (5.3 g), m.p. 183°. No lower-melting nitration products were isolated.

(c) Of 2-Nitrophenyl-1,2,3,2H-triazole by Mixed Acids at 25°

2-*p*-Nitrophenyl-1,2,3,2H-triazole (1.4 g) was nitrated at 25° using the general conditions of part (*a*) above. Repeated crystallization of the reaction product from ethanol yielded 4-nitro-2-*p*-nitrophenyl-1,2,3,2H-triazole (1.3 g), m.p. 140°, identical in all respects with the lower-melting product from the nitration of I. Anal. Found: C, 41.14; H, 2.01; N, 29.60%.

(d) Of 2-p-Nitrophenyl-1,2,3,2H-triazole or 4-Nitro-2-p-nitrophenyl-1,2,3,2H-triazole at 80°, or of 4-Nitro-2-p-nitrophenyl-1,2,3,2H-triazole at 25°

These reactions were carried out using the conditions noted in part (*a*) above. Both the mono- and the di-nitro compounds (in sulphuric acid) gave a blue color on addition of nitric acid: completion of reaction was indicated by a color change to yellow. The products of all three reactions were needles, m.p. 104°, of 2-(2,4-dinitrophenyl)-4-nitro-1,2,3,2H-triazole. Anal. calc. for $C_8H_4N_6O_6$: C, 34.30; H, 1.44%. Found: C, 34.02; H, 1.52%. Ultraviolet absorption: λ_{max} 285 mμ, log ϵ 4.24. Yields were as follows: 2.4 g from 2.5 g mononitro compound at 80°, 0.65 g from 0.80 g dinitro compound at 80°, and 0.30 g from 1.0 g dinitro compound at 25°.

Proof of Structure of 2-(2,4-Dinitrophenyl)-1,2,3,2H-triazole

The trinitro compound (1.0 g) in methanol (25 ml) was heated under reflux with 0.6 *N* methanolic sodium methoxide (20 ml) for 10 minutes. The reaction mixture was poured onto ice, and the resulting precipitate was collected, dried, dissolved in benzene, and chromatographed on alumina. Evaporation of the eluate yielded 2,4-dinitroanisole (0.45 g), m.p. 87°, identical (m.p., mixed m.p., infrared and ultraviolet absorption) with an authentic sample.

2-p-Biphenylyl-1,2,3,2H-triazole (II)

2-*p*-Nitrophenyl-1,2,3,2H-triazole (2.0 g) was quantitatively reduced to the corresponding amine by tin and hydrochloric acid, and converted into the diazonium chloride by standard procedures. The diazo solution thus obtained was stirred vigorously with benzene at 5°, after buffering to pH 5 with sodium acetate. The mixture was allowed to reach room temperature with continuous stirring, and the benzene layer was chromatographed on alumina. Evaporation of the eluate, followed by crystallization from ethanol, yielded 2-*p*-biphenylyl-1,2,3,2H-triazole (0.5 g), m.p. 90°. Anal. Calc. for $C_{14}H_{11}N_3$: C, 76.00; H, 5.01%. Found: C, 75.80; H, 5.30%. Ultraviolet absorption: see Table I.

2-p-Biphenylyl-4-phenyl-1,2,3,2H-triazole (IV)

Similar reduction of 4-nitro-2-*p*-nitrophenyl-1,2,3,2H-triazole by tin and hydrochloric acid, followed by tetrazotization and reaction of the buffered tetrazonium salt solution with benzene, gave 2-*p*-biphenylyl-4-phenyl-1,2,3,2H-triazole, m.p. 124°, in poor yield. Anal. Calc. for $C_{20}H_{15}N_3$: C, 80.80; H, 5.08%. Found: C, 80.58; H, 5.69%. Ultraviolet absorption: λ_{max} 308 mμ, log ϵ 4.52.

ACKNOWLEDGMENTS

We thank the National Research Council for generous support through Operating and Equipment Grants, Mr. M. A. Khan for furnishing reference samples, and Miss J. Murphy for skilled assistance with spectrophotometry.

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