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Reaction of dimethyl acetylenedicarboxylate with azides

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Cycloadditions of azides with dimethyl acetylenedicarboxylate are known to give 1,2,3-triazoles (1–4). Recent reports on the preparation of *o*-azidoaniline (5), *o*-diazidobenzene (6), and *o,o'*-diazidobiphenyl (7) have prompted us to examine the reaction of these azides with dimethyl acetylenedicarboxylate. The reaction of *o*-diazidobenzene with dimethyl acetylenedicarboxylate in diethyl ether at room temperature gave a 65% yield of 1,2-bis(4,5-dicarbomethoxy-1,2,3-triazol-1-yl)benzene (I). Its nuclear magnetic resonance spectrum showed two singlets at 6.18 and 6.05 τ, corresponding to a total of 12 protons and assigned to the carbomethoxy protons, and a multiplet centered at 2.23 τ, corresponding to 4 phenyl protons. Similarly, the reaction of *o,o'*-diazidobiphenyl with dimethyl acetylenedicarboxylate gave 2,2'-bis(4,5-dicarbomethoxy-1,2,3-triazol-1-yl)biphenyl (II) in a 70% yield. The identity of this product was established on the basis of its analytical results and spectra. The nuclear magnetic resonance spectrum of II was in full agreement with the assigned structure, and showed two groups of carbomethoxy protons (6.14 and 6.0 τ), each consisting of six protons. In addition, there was a multiplet centered at 2.62 τ, which accounted for eight aromatic protons. The reaction of aniline with dimethyl acetylenedicarboxylate is known to give dimethyl anilinofumarate (III) (8–10). The treatment of *o*-azidoaniline with dimethyl acetylenedicarboxylate gave a product which was identified as dimethyl 2-(4,5-dicarbomethoxy-1,2,3-triazol-1-yl)anilinofumarate (IV). The ease of formation of compounds I, II, and IV suggests that the steric requirements are not too great for these cycloadditions.

The infrared spectra of the 1,2,3-triazoles are reported to show several absorption bands over the range 1 550 – 700 cm^{-1}; these bands include the CH-in-plane, skeleton, and ring-breathing vibrations (11). Recently, Birkofer and Wegner (4) have examined the infrared spectra of several silyl-substituted triazoles, which show characteristic bands over the ranges 1 504 – 1 514, 1 226 – 1 231, 1 020 – 1 047, and 958–992 cm^{-1}. In the triazoles that we have prepared (I, II, and IV), absorption bands were observed over the ranges 1 520 – 1 530, 1 435 – 1 453, 1 200 – 1 235, 1 105 – 1 130, and 1 000 – 1 010 cm^{-1}, as shown in Table I.

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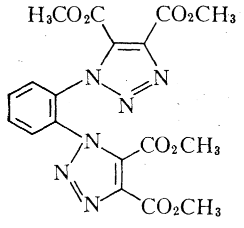

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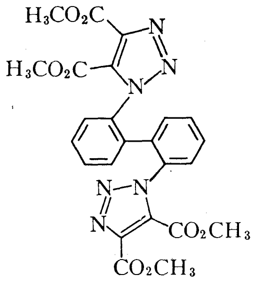

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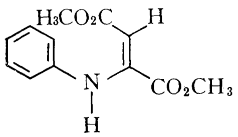

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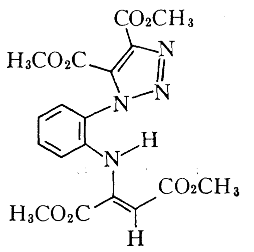

IV

TABLE I

Characteristic vibrations in 4,5-dicarbomethoxy-1,2,3-triazoles

Triazoles derived from:	Band positions (cm^{-1})	
	Ring skeletal	CH-in-plane and ring breathing
Phenyl azide*	1 530, 1 451	1 235, 1 105, 1 010
o-Azidoaniline	1 526, 1 435	1 200, 1 130, 1 000
o-Diazidobenzene	1 520, 1 450	1 220, 1 106, 1 010
o,o′-Diazidobiphenyl	1 524, 1 453	1 220, 1 114, 1 000

*Prepared as in ref. 3.

EXPERIMENTAL

Melting points are uncorrected and were recorded in a Thomas–Hoover melting point apparatus. Infrared spectra were recorded on a Perkin–Elmer model 137 Infracord spectrometer. Nuclear magnetic resonance traces were taken on a Varian A-60 spectrometer, with tetramethylsilane as an internal standard.

o-Azidoaniline

o-Azidoaniline was prepared from *N*-(*o*-nitrophenyl)phthalimide by a reported procedure (5). The infrared spectrum (Nujol) of this compound showed a strong azide band at 2 120 cm^{-1}. The compound was sensitive to light, but could be stored in the dark for a few weeks without appreciable decomposition.

o-Diazidobenzene

A solution of 2.7 g (0.02 mole) of *o*-azidoaniline in 100 ml of 10% HCl kept around 0–5° was diazotized by the addition of 1.4 g (0.02 mole) of sodium nitrite in 10 ml of water. To this mixture was added dropwise a solution of 1.3 g (0.02 mole) of sodium azide in 10 ml of water. The mixture was allowed to warm to room temperature and was extracted with ether. Removal of the solvent under vacuum gave 3.2 g (98%) of *o*-diazidobenzene. Its infrared spectrum (thin film) was in perfect agreement with that reported in the literature (6). No attempt was made to purify this product, and it was used as such for the subsequent experiment.

1,2-Bis(4,5-dicarbomethoxy-1,2,3-triazol-1-yl)benzene (I)

A mixture of *o*-diazidobenzene (1.6 g, 0.01 mole) and dimethyl acetylenedicarboxylate (2.84 g, 0.02 mole) in 10 ml of dry ethyl ether was kept at room temperature for 24 h. Removal of the solvent gave 2.9 g (65%) of 1,2-bis(4,5-dicarbomethoxy-1,2,3-triazol-1-yl)benzene, which melted at 172–173°, after recrystallization from methanol. Its infrared spectrum (KBr pellet) was characterized by the following absorption bands: 1 750 (ester $\rangle C{=}O$), 1 610 (phenyl), and 1 520, 1 450, 1 220, 1 100, and 1 010 cm^{-1} (1,2,3-triazole). Its nuclear magnetic resonance spectrum ($CDCl_3$) showed two singlets at 6.18 and 6.05 τ ($-\overset{O}{\overset{\|}{C}}-OCH_3$, 12 protons) and a multiplet centered around 2.23 τ (phenyl, 4 protons).

Anal. Calcd. for $C_{18}H_{16}O_8N_6$: C, 48.65; H, 3.60; N, 18.92. Found: C, 48.82; H, 3.70; N, 19.17.

o,o′-Diaminobiphenyl (13, 14)

o,o′-Dinitrobiphenyl, m.p. 124° (50%), was prepared from *o*-nitrochlorobenzene by a reported procedure (12).

A mixture of *o,o′*-dinitrobiphenyl (3.7 g, 0.03 mole) and freshly prepared Raney nickel (3 g) in 100 ml of absolute ethanol was hydrogenated at room temperature (hydrogen at 65 p.s.i.) for 2 h. Removal of the catalyst and the solvent yielded a product which, on recrystallization from ethanol, gave *o,o′*-diaminobiphenyl (2.6 g, 96%), m.p. 78°.

o,o′-Diazidobiphenyl

A mixture of *o,o′*-diaminobiphenyl (1.8 g, 0.01 mole), water (10 ml), and 50% sulfuric acid (10 ml) was chilled to −10°. To this mixture was added a solution of sodium nitrite (2 g, 0.02 mole) in 20 ml of water, followed by a solution of sodium azide (1.5 g, 0.02 mole) in 20 ml of water. The precipitated *o,o′*-diazidobiphenyl was filtered off and, on recrystallization from ethanol, melted at 73° (lit. m.p. 73.5° (7)). Its infrared spectrum (KBr pellet) showed a strong absorption band at 2 098 cm^{-1}, characteristic of the azide group.

1,2-Bis(4,5-dicarbomethoxy-1,2,3-triazol-1-yl)biphenyl (II)

A mixture of *o,o′*-diazidobiphenyl (1 g, 0.004 mole) and dimethyl acetylenedicarboxylate (2.41 g, 0.008 mole) in dry ether (25 ml) was kept at room temperature for 24 h. Removal of the solvent and treatment of the residue with methanol gave 1.5 g (70%) of 1,2-bis(4,5-dicarbomethoxy-1,2,3-triazol-1-yl)biphenyl. Recrystallization from a mixture of methanol and chloroform (1:1) gave a colorless crystalline product, m.p. 168–168.5°. Its infrared spectrum (KBr) showed absorption bands at 1 724 (ester $>C{=}O$) and 1 524, 1 453, 1 220, 1 114, and 1 000 cm^{-1} (1,2,3-triazole). Its nuclear magnetic resonance spectrum ($CDCl_3$) showed singlets at 6.1 and 6.14 τ ($—\overset{\overset{O}{\|}}{C}—OCH_3$, six protons each) and a multiplet at 2.62 τ (aromatic, eight protons).

Anal. Calcd. for $C_{24}H_{20}N_6O_8$: C, 55.3; H, 3.4; N, 16.15. Found: C, 55.43; H, 3.9; N, 16.43.

Dimethyl 2-(4,5-Dicarbomethoxy-1,2,3-triazol-1-yl)-anilinofumarate (IV)

A mixture of *o*-azidoaniline (0.5 g, 0.007 mole) and dimethyl acetylenedicarboxylate (0.5 g, 0.008 mole) in dry benzene (5 ml) was kept at room temperature for 24 h. The flask was wrapped with black paper to avoid the decomposition of *o*-azidoaniline. Removal of the solvent and recrystallization from methanol gave a colorless crystalline product (0.43 g, 43%), m.p. 124–125°. Its infrared spectrum (KBr pellet) showed absorption bands at 3 230 (NH), 1 735 (ester $>C{=}O$), 1 675 ($>C{=}C—\overset{\overset{O}{\|}}{C}—$), 1 620 (phenyl), and 1 525, 1 435, 1 200, 1 130, and 1 000 cm^{-1} (1,2,3-triazole).

Anal. Calcd. for $C_{18}H_{18}N_4O_8$: C, 51.67; H, 4.31; N, 13.39. Found: C, 52.16; H, 4.32; N, 13.22.

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Gas chromatography of derivatives of the methyl ethers of D-xylose

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DISCUSSION

The methyl ethers of D-xylose are most commonly encountered in the hydrolysates of methylated, xylose-containing polysaccharides. Although several of the more frequently obtained ethers have previously been separated by gas–liquid chromatography (g.l.c.) as their trimethylsilyl derivatives (1), no complete set of retention data has appeared in the literature.

In this work, carefully standardized conditions were used for the g.l.c. study of three classes of derivatives. All of the possible (cyclic) methyl ethers, except the 5-*O*-methyl compound, were studied and their retention times tabulated. It is expected that the relative retention times are sufficiently reproducible for the qualitative identification of these methyl ethers, provided at least one is available as a standard.

The more common derivatives of reducing sugars used for g.l.c. are the trimethylsilyl, acetyl, and acetylated methyl glycosides and the acetylated alditols. All but the last of these may give rise to more than one product because of the possible formation of α and β anomers and of pyranose and furanose rings. In the xylose

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