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A FUSED PYRROLIDOTRIAZOLE DERIVATIVE FROM BIS(ETHYLSULPHONYL)-(2,3-*O*-ISOPROPYLIDENE-4-*O*-METHANESULPHONYL-α-D-LYXOPYRANOSYL)METHANE

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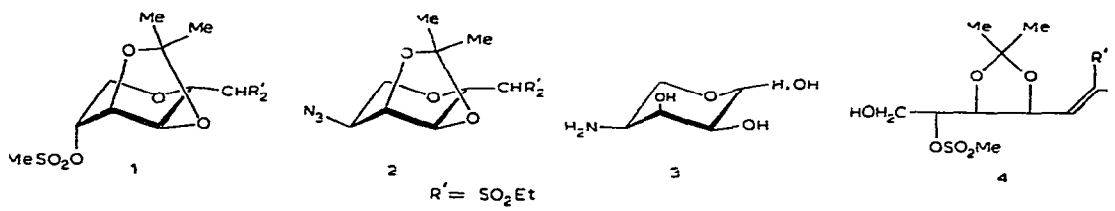
ABSTRACT

Reaction of bis(ethylsulphonyl)-(2,3-*O*-isopropylidene-4-*O*-methanesulphonyl-α-D-lyxopyranosyl)methane (**1**) with sodium azide in *N*,*N*-dimethylformamide gave 1(*S*)-hydroxymethyl-2(*R*),3(*S*)-isopropylidenedioxypyrrolido-[1,2-*c*]-4-ethylsulphonyl-1,2,3-triazole (**5**). The latter was identified by p.m.r. and mass spectrometry, and by degradation to, and unambiguous synthesis of, 4-ethylsulphonyl-1,2,3-triazole (**17**).

INTRODUCTION

A synthesis of 4-amino-4-deoxy-L-ribose (**3**) was contemplated from bis-(ethylsulphonyl)-α-D-lyxopyranosylmethane, using D-galactose as starting material, by conversion into the 2,3-*O*-isopropylidene-4-*O*-methanesulphonyl derivative[1] (**1**), then reaction with azide anion to give the 4-azido derivative (**2**), and subsequent hydrolysis, reduction, and degradation with base. However, the initial reaction with azide gave a novel and unexpected crystalline compound *X* ($C_{11}H_{17}N_3O_5S$). A preliminary communication on the structure of this compound has been published[2].



DISCUSSION

Compound *X* showed i.r. absorption at 1546 cm^{-1}, suggesting –N=N–, =C=N–, or =C=C=, and no absorptions for azido and sulphonate groups. A crys-

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talline benzoate, $C_{18}H_{21}N_3O_6S$, was obtained, thereby indicating the presence of one hydroxyl group. The p.m.r. spectrum of the benzoate revealed that the *O*-isopropylidene group had been retained together with one ethylsulphonyl group, and confirmed that the methanesulphonate group of **1** had been eliminated. Signals for five other hydrogen substituents were detected, whose coupling constants suggested the presence of the grouping $-{}^{1'}CH_2-{}^{1}\underset{|}{CH}-{}^{2}\underset{|}{CH}-{}^{3}CH-$. Acid hydrolysis of *X* removed the isopropylidene group to give a triol ($C_8H_{13}N_3O_5S$) with λ_{max} 223 nm; the p.m.r. spectrum of the tribenzoate derivative confirmed the above arrangement and showed that the isopropylidene group was originally at C-3 and C-2, since the signals due to H-3 and H-2 had moved downfield as a result of the deshielding effect of the benzoate groups. Compound *X* was shown to be a primary alcohol from its n.m.r. spectrum in methyl sulphoxide. Furthermore, it gave a methanesulphonate in pyridine at $-10°$, whereas at room temperature a monochloro derivative was isolated due to nucleophilic displacement of the methanesulphonyloxy substituent by chloride anion. A mono-iodo derivative was prepared from both the methanesulphonate and the chloride, and gave the expected *C*-methyl derivative on hydrogenation in ethanolic sodium hydrogen carbonate. However, hydrogenation of the iodide in 5% methanolic sodium hydroxide gave another *C*-methyl derivative, in which the ethylsulphonyl group was absent, as shown by the n.m.r. spectrum which also revealed a new 1-proton signal at very low field in the aromatic region. Hence, it may be deduced that the starting material, bis(ethylsulphonyl)-(2,3-*O*-isopropylidene-4-*O*-methanesulphonyl-α-D-lyxopyranosyl)methane (**1**), undergoes ring opening to give the alkene **4** which reacts with azide to give the triazole **5** as the only plausible structure, since there is no epimine[3] present. The triazole structure **5** accounts for its stability towards hydrogenation [4–6] and for the low-field signal in the n.m.r. spectrum of **13**. All of the derivatives prepared from **5** absorbed at ~220 nm, as expected for triazoles[7,8].

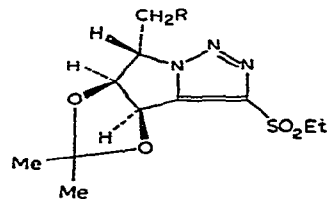
The structure of **5** was confirmed by oxidation of the derived triol **11**. The optically active **11** reduced 1.65–1.75 mol. of periodate, no formic acid being released;

TABLE I

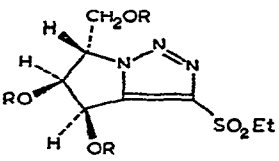
CHEMICAL SHIFTS (τ) AND FIRST-ORDER COUPLING CONSTANTS (Hz) AT 100 MHz

Compound[a]	*H-1*	*H-2*	*H-3*	*H-1'*	*OH*	*Aromatic H*	$J_{1,2}$	$J_{2,3}$
5[b]	5.0 cm[c]	4.65 q	4.4 d	cm	4.7 t	—	0.75	5.5
6	4.8 cm	4.55 q	4.2 d	5.15 d	—	—	0.5	5.5
11	—	—	4.45 d	—	—	—	—	5.0
12	4.6 cm	3.55 q	3.1 d	4.9 d	—	—	3.5	6.0
8	4.8 cm	4.65 q	4.3 d	5.85 d	—	—	0.5	5.5
9	5.05 cm	4.8 q	4.2 d	6.2 d	—	—	1.0	5.5
10	5.15 cm	4.85 q	4.25 d	8.35 d	—	—	1.25	5.5
13	5.4 cm	4.65 q	4.45 d	8.3 d	—	2.43	5.0	5.0

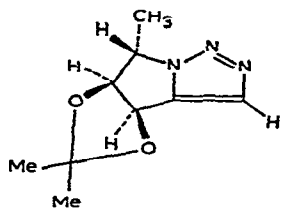
[a]In $CDCl_3$. [b]In Me_2SO. [c]d = doublet, t = triplet, q = quartet, cm = complex multiplet.



5 R = OH
6 R = OBz
7 R = OMs
8 R = Cl
9 R = I
10 R = H



11 R = H
12 R = Bz



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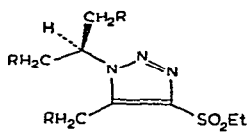
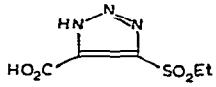
immediate reduction of the product with sodium borohydride gave the optically inactive triol (**14**). Further oxidation of **14** with alkaline potassium permanganate at 100° gave the carboxylic acid **16**, which showed a broad absorption at 220 nm and required 1.7 mol. of alkali for neutralisation, as recorded for a similar compound[9]. Decarboxylation of **16** at 190° afforded the triazole **17**, whose n.m.r. spectrum confirmed the presence of NH, ethyl, and aromatic protons.

An unambiguous synthesis of the triazole **17** was undertaken, starting with



14 R = OH
15 R = OBz



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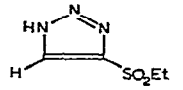

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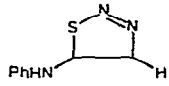

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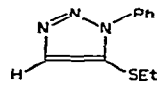

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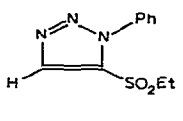

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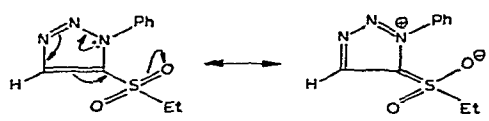
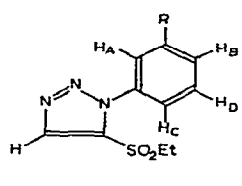


20a



21 R = NO_2
22 R = NH_2

5-phenylamino-1,2,3-thiadiazole (**18**) which was converted[10,11] in alkaline solution containing ethyl iodide into 1-phenyl-5-ethylthio-1,2,3-triazole (**19**) and then oxidised to the sulphone **20**. Unactivated alkyl[12] and aryl[13,14] groups attached to a triazole nitrogen atom are not readily oxidised, but, since *p*-aminophenyl substituents can be oxidised, the phenyltriazole **20** was nitrated to give 1-(*m*-nitrophenyl)-5-ethylsulphonyl-1,2,3-triazole (**21**), in contrast to the results of Dimroth[13], Baltzer and Pechmann[14], and others[15,16] who obtained *p*-substituted products from phenyltriazole systems. The p.m.r. spectrum of **21** showed an ABCD system for the phenyl protons with H_A as a triplet (τ 3.4) overlapping the sextet of H_B (τ 3.7), H_C as a sextet (τ 5.9), and H_D as a triplet (τ 7.1), giving ring coupling-constants of J_{ortho} 7, J_{meta} 2, and J_{para} 0 Hz. Substitution occurred at the *meta* position because of quaternisation

of the nitrogen atom attached to the phenyl group, through the strong electron-withdrawing effect of the ethylsulphonyl group (**20**a).

Reduction of the *m*-nitrophenyl derivative **21** with hydrazine–Raney nickel gave the *m*-aminophenyl derivative **22** which was oxidised to afford 4-ethylsulphonyl-1, 2,3-triazole (**17**), identical with the product obtained previously by degradation of **5**. The original product **5** possibly arose from the hex-1-ene **4** by 1,3-dipolar addition of azide followed by elimination of the methanesulphonyloxy group and one of the ethylsulphonyl groups. The addition of phenyl azide to 1-bromo-1-chlorosulphonyl-ethylene was observed by Rondestvedt and Chang[17] to give 1-phenyl-4-bromo-1,2,3-triazole, by 1,3-dipolar addition and elimination of the chlorosulphonyl group. The formation of 4-phenyl-3-bromopyrazole from 4-phenyl-3-nitro-3-bromopyrazole[18] is also a related reaction.

The p.m.r. spectrum of the monobenzoate **6** was consistent with the stereochemistry assigned to the parent triazole derivative **5**, namely 1(*S*)-hydroxymethyl-2(*R*),3(*S*)-isopropylidenedioxypyrrolido-[1,2-*c*]-4-ethylsulphonyl-1,2,3-triazole, and the coupling constant $J_{2,3}$ 1.0 revealed that inversion of configuration had occurred at C-4 in the elimination of methanesulphonate group of **1**.

The mass spectrum of the triazole **5** showed an (M+1) peak (*m/e* 304), as revealed by an increase in the intensity of the peak as the square of the monitor current, whereas the parent ion (*m/e* 303) increased linearly. At the same monitor current, but with increasing ion repeater voltages, the (M + 1) ion decreased in intensity compared with the parent ion. De Jongh and Biemann[19] found that isopropylidene derivatives usually show (M+1) peaks, due to the presence of the 1,3-dioxolane rings, which also lose a methyl group giving an intense peak at (M−15). Likewise, the triazole **5** showed an (M−15) fragment at *m/e* 288. However, we attribute the (M+1) peak of **5** to the ethylsulphonyl group since the mass spectrum of diethylsulphonylmethane showed an intense (M+1) peak.

EXPERIMENTAL

Melting points were determined on a Kofler micro-heating stage. T.l.c. was carried out with Merck Kieselgel G, and column chromatography with "Davison" silica gel (grade 950; 60–200 mesh). All solutions were concentrated under diminished pressure. Optical rotations were determined at 25° ±2°, unless otherwise stated.

1,1-Bis(ethylsulphonyl)-(2,3-O-isopropylidene-4-O-methanesulphonyl-α-D-lyxopyranosyl)methane (**1**). — A solution of bis(ethylsulphonyl)-(2,3-*O*-isopropylidene-α-D-lyxopyranosyl)methane[20] (5.36 g) in dry pyridine (7 ml) was cooled to 0°, and methanesulphonyl chloride (3 ml) was added slowly. After 1.5 h at room temperature, excess methanesulphonyl chloride was decomposed by the slow addition of water. The resultant mixture was extracted with chloroform, the extract was washed with aqueous sodium hydrogen carbonate and water, and concentrated. The syrupy residue was crystallized and recrystallized from ethanol to give **1** (4.64 g, 71%), m.p.

139–140°, $[\alpha]_D$ +16° (*c* 2, chloroform) (Found: C, 37.6; H, 5.8. $C_{14}H_{26}O_{10}S_3$ calc.: C, 37.4; H, 5.8%).

1(S)-*Hydroxymethyl-2*(R),*3*(S)-*isopropylidenedioxypyrrolido*-[*1,2*-c]-*4-ethylsulphonyl-1,2,3-triazole* (**5**). — A solution of **1** (2.2 g) and sodium azide (410 mg) in ethanol was boiled for 24 h. Concentration of the reaction mixture yielded a crystalline residue, which was collected and washed with water. Recrystallization from methanol afforded **5** (1.34 g, 89%), m.p. 193–195°, $[\alpha]_D$ +95° (*c* 1.14, pyridine) (Found: C, 43.45; H, 5.75; N, 14.0; S, 10.5. $C_{11}H_{17}N_3O_5S$ calc.: C, 43.55; H, 5.6; N, 13.85; S, 10.55%).

1(S)-*Benzoyloxymethyl-2*(R),*3*(S)-*isopropylidenedioxypyrrolido*-[*1,2*-c]-*4-ethylsulphonyl-1,2,3-triazole* (**6**). — To a solution of **5** (405 mg) in dry pyridine (4 ml) was added benzoyl chloride (2 ml). After 24 h at room temperature, excess benzoyl chloride was decomposed with water, and the mixture was extracted with dichloromethane. The extract was washed with aqueous sodium hydrogen carbonate and then water, and concentrated to a syrup which crystallized from methanol. Recrystallization from methanol afforded **6** (346 mg, 63%), m.p. 122–124°, $[\alpha]_D$ +89° (*c* 2.12, chloroform) (Found: C, 53.1; H, 5.3; N, 10.25; S, 7.8. $C_{18}H_{21}N_3O_6S$ calc.: C, 53.1; H, 5.15; N, 10.3; S, 7.85%).

1(S)-*Hydroxymethyl-2*(R),*3*(S)-*dihydroxypyrrolido*-[*1,2*-c]-*4-ethylsulphonyl-1,2,3-triazole* (**11**). — A solution of the triazole **5** in methanol (36 ml) containing M hydrochloric acid (42 ml) was refluxed for 4 h, and then concentrated. The syrupy residue was crystallized and recrystallized from 2-propanol to afford **11** (1.56 g, 94%), m.p. 134–135°, $[\alpha]_D$ +31° (*c* 1, water), λ_{max} 223 nm (Found: C, 36.5; H, 5.0; N, 16.1; S, 12.4. $C_8H_{13}N_3O_5S$ calc.: C, 36.5; H, 4.95; N, 16.0; S, 12.15%).

Reaction of **11** with sodium metaperiodate was complete after 15 min, and, in duplicate experiments, the uptake of periodate was 1.69 and 1.75 mol. No formic acid was liberated. With lead tetra-acetate, reaction was also complete after 15 min, and in three experiments the uptake of oxidant was 1.14, 1.06, and 1.18 mol.

To a solution of **11** (213 mg) in dry pyridine (8 ml) was added benzoyl chloride (4 ml), and the mixture was shaken for 24 h at room temperature. Excess benzoyl chloride was then decomposed by the slow addition of water, and the mixture was extracted with dichloromethane as described above. The syrupy residue was crystallized and recrystallized from ethanol to give the tribenzoate **12** (374 mg, 80%), m.p. 152–154°, $[\alpha]_D$ +47° (*c* 2.4, chloroform) (Found: C, 60.45; H, 4.35; N, 7.3; S, 5.65. $C_{29}H_{25}N_3O_8S$ calc.: C, 60.5; H, 4.35; N, 7.3; S, 5.56%).

1(S)-*Methanesulphonyloxymethyl-2*(R),*3*(S)-O-*isopropylidenedioxypyrrolido*-[*1,2*-c]-*4-ethylsulphonyl-1,2,3-triazole* (**7**). — To a solution of the triazole **5** (1.94 g) in dry pyridine (6 ml) at −10° was added methanesulphonyl chloride (3 ml). After 1 h at −10°, excess methanesulphonyl chloride was decomposed by the slow addition of water, keeping the temperature of the reaction mixture below 0°. The mixture was then extracted with chloroform as described above. Recrystallization of the residue from methanol gave **7** (1.43 g, 58%), m.p. 126–128°, $[\alpha]_D$ +61° (*c* 2.08, acetone) (Found: C, 37.75; H, 5.1; N, 10.95; S, 16.55. $C_{12}H_{19}N_3O_7S_2$ calc.: C, 37.8; H, 5.0; N, 11.0; S, 16.8%).

1(S)-*Chloromethyl-2*(R),*3*(S)-*isopropylidenedioxypyrrolido*-[*1,2*-c]-*4-ethylsulphonyl-1,2,3-triazole* (**8**). — To a solution of the triazole **5** (712 mg) in dry pyridine (6 ml) was added methanesulphonyl chloride (3 ml). The solution was stored at room temperature for 2.5 h. T.l.c. (chloroform) then indicated that ~95% of the product was the methanesulphonate and only ~5% was the chloro derivative. Excess methanesulphonyl chloride was decomposed by the addition of water. The mixture was extracted with chloroform as described above and the syrupy residue was crystallized and recrystallized from methanol to give **8** (549 mg, 74%), m.p. 175–176°, $[\alpha]_D^{29}$ +113° (*c* 1.8, chloroform) (Found: C, 41.0; H, 5.0; Cl, 11.35; N, 13.2; S, 9.75. $C_{11}H_{16}ClN_3O_4S$ calc.: C, 41.05; H, 5.0; Cl, 11.05; N, 13.05; S, 9.95%).

1(S)-*Chloromethyl-2*(R),*3*(S)-*dibenzoyloxypyrrolido*-[*1,2*-c]-*4-ethylsulphonyl-1,2,3-triazole*. — The chloro derivative **8** (219 mg) was hydrolysed by refluxing in a mixture of acetone (5 ml) and M hydrochloric acid (6 ml) for 6 h. Concentration of the hydrolysate yielded a syrup which was dissolved in dry pyridine (4 ml), and benzoyl chloride (2 ml) was then added. After standing overnight at room temperature, the excess benzoyl chloride was decomposed by the slow addition of water and the product was extracted with dichloromethane as described above. Crystallization and recrystallization of the syrupy product from methanol gave the title compound (208 mg, 63%), m.p. 137–139° (Found: C, 53.7; H, 4.25; Cl, 7.5; N, 8.85; S,6.7. $C_{22}H_{20}ClN_3O_6S$ calc.: C, 53.95; H, 4.1; Cl, 7.25; N, 8.6; S, 6.55%).

1(S)-*Iodomethyl-2*(R),*3*(S)-*isopropylidenedioxypyrrolido*-[*1,2*-c]-*4-ethylsulphonyl-1,2,3-triazole* (**9**). — A solution of the triazole **7** (873 mg) and sodium iodide (550 mg) in butanone (50 ml) was refluxed for 16 h. The cooled mixture was filtered and concentrated, and the residue extracted with chloroform. The extract was washed with aqueous sodium thiosulphate and then water, and concentrated. Crystallization and recrystallization of the syrupy residue from methanol gave **9** (691 mg, 72%), m.p. 168–170°, $[\alpha]_D^{29}$ +75° (*c* 1.86, chloroform) (Found: C, 32.15; H, 3.9; I, 30.7; N, 10.0; S, 7.75. $C_{11}H_{16}IN_3O_4S$ calc.: C, 31.95; H, 3.85; I, 30.75; N, 10.15; S, 7.75%).

1(S)-*Methyl-2*(R),*3*(S)-*isopropylidenedioxypyrrolido*-[*1,2*-c]-*4-ethylsulphonyl*-[*1,2,3*]-*triazole* (**10**). — A suspension of **9** (642 mg) and sodium hydrogen carbonate (3 g) in hot ethanol (75 ml) was hydrogenated at 65° and 48 p.s.i. for 6 h in the presence of T-4 Raney nickel[21]. The cooled suspension was then filtered and concentrated. The syrupy residue was fractionated on a column of silica gel, using a mixture of ether–light petroleum (b.p. 40–60°) (3:1). The required fraction was concentrated, to give **10** (218 mg, 49%) which, after recrystallization from ethyl acetate–light petroleum (b.p. 60–80°), had m.p. 127–129°, $[\alpha]_D$ +122° (*c* 1.14, chloroform), λ_{max} 220 nm (Found: C, 45.9; H, 6.05; N, 14.75. $C_{11}H_{17}N_3O_4S$ calc.: C, 46.0; H, 5.9; N, 14.65%).

1(S)-*Methyl-2*(R),*3*(S)-*isopropylidenedioxypyrrolido*-[*1,2*-c]-*1,2,3-triazole* (**13**). — To a solution of **9** (514 mg) in hot ethanol (75 ml) was added a 5% solution of sodium hydroxide in methanol (20 ml). The resulting solution was hydrogenated at 65° and 4 atmos. for 6 h in the presence of T-4 Raney nickel. The cooled suspension was then filtered, concentrated to small volume (~10 ml), diluted with water to ~50 ml, and

extracted with chloroform, and the extract was concentrated. The syrupy residue was fractionated on a column of silica gel, using ether–light petroleum (b.p. 40–60°) (3:1) as eluant. The required fraction was concentrated to give **13** (76 mg, 31%) as a solid, $[\alpha]_D$ +72° (*c* 0.64, chloroform), λ_{max} 223 nm (Found: C, 55.1; N, 6.85; N, 21.2. $C_9H_{13}N_3O_2$ calc.: C, 55.4; H, 6.65; N, 21.55%).

1-[2-(1,3-Dihydroxypropyl)]-4-ethylsulphonyl-5-hydroxymethyl-1,2,3-triazole (**14**). — A solution of the triol **11** (4 g) and sodium metaperiodate (6.5 g) in water (50 ml) was stored at room temperature for 1 h and then deionised with an equimolar mixture of Amberlite IR-120(H^+) and IR-45(OH^-) resins. The solution was immediately added to a solution of sodium borohydride (3 g) in water (5 ml). After 1.5 h at room temperature, excess borohydride was decomposed by glacial acetic acid, and the resultant solution was deionised with Amberlite IR-120(H^+) resin and concentrated. Methanol was distilled several times from the residue to remove the boric acid. The final, syrupy residue was extracted with hot ethyl acetate, and the extract was filtered and concentrated to a syrup, which crystallized from ethyl acetate. Recrystallization afforded **14** (2.7 g, 68%), m.p. 105–107°, $[\alpha]_D^{28}$ +1° (*c* 2.5, water), λ_{max} 220 nm (Found: C, 36.3; H, 5.85; N, 16.0; S, 11.95. $C_8H_{15}N_3O_5S$ calc.: C, 36.25; H, 5.65; N, 15.85; S, 12.05%).

Benzoylation of **14**, in the usual way, gave the tribenzoate **15** (261 mg, 60%), m.p. 103–106°, $[\alpha]_D^{28}$ 0° (*c* 1.64, chloroform) (Found: C, 60.15; H, 4.75; N, 7.15; S, 5.4. $C_{29}H_{27}N_3O_8S$ calc.: C, 60.3; H, 4.7; N, 7.3; S, 5.55%).

4-Ethylsulphonyl-1,2,3-triazole-5-carboxylic acid monohydrate (**16**). — A solution of potasium hydroxide (240 mg), **14** (720 mg), and potassium permanganate (2.7 g) in water (20 ml) was refluxed for 3 h. Excess potassium permanganate was then decomposed with methanol, and the solution was filtered, deionised with Amberlite IR-120(H^+) resin, and concentrated. The syrupy residue was crystallized and recrystallized from ethyl acetate–light petroleum (b.p. 40–60°) to give **16** as a monohydrate (491 mg, 81%), m.p. 177–179°, λ_{max} 221 nm (Found: C, 27.2; H, 4.15; N, 18.8; S, 14.2. $C_5H_9N_3O_5S$ calc.: C, 26.9; H, 4.05; N, 18.85; S, 14.35%).

4-Ethylsulphonyl-1,2,3-triazole (**17**). — The carboxylic acid **16** (1.05 g) was heated at 185° for 3 h and then sublimed at 140°/10^{-4} mmHg. The compound was further purified by fractionation on a column of silica gel, using chloroform as eluent. Concentration of the required fraction yielded a syrup, which crystallized on storage to give **17** (662 mg, 85%), m.p. 73–75° (Found: C, 29.9; H, 4.6; N, 26.25; S, 19.6. $C_4H_7N_3O_2S$ calc.: C, 29.8; H, 4.35; N, 26.1; S, 19.85%).

1-Phenyl-5-ethylsulphonyl-1,2,3-triazole (**20**). — A suspension of 5-phenylamino-1,2,3-thiadiazole[22,23] (6.56 g) in a solution of water (60 ml) and sodium hydroxide (2 g) was heated on a boiling water-bath until dissolution occurred and was then filtered through a pad of activated charcoal. The cooled filtrate was stirred with ethyl iodide (15 ml) for 20 h, and then extracted with ether. Concentration of the extract gave 1-phenyl-5-ethylthio-1,2,3-triazole (**19**) as a liquid (6.84 g, 90%), which was purified by fractionation on a column of silica gel, using ether–light petroleum (b.p.

40–60°) (1:2) (Found: C, 58.65; H, 5.3; N, 20.3. $C_{10}H_{11}N_3S$ calc.: C, 58.55; H, 5.35; N, 20.45%).

A solution of **19** (6.84 g) in methanol (100 ml) was cooled to between −10 and −20°, and aqueous peroxypropionic acid[24] (30 ml) added. After standing for 16 h at room temperature, the solution was diluted with water and then extracted with chloroform as described above. The syrupy residue was crystallized from methanol–water to give **20** (7.1 g, 90%), m.p. 94–95° (Found: C, 50.75; H, 4.89; N, 17.7; S, 13.45. $C_{10}H_{11}N_3O_2S$ calc.: C, 50.65; H, 4.65; N, 17.7; S, 13.5%).

1-(m-*Nitrophenyl)-5-ethylsulphonyl-1,2,3-triazole* (**21**). — A suspension of **20** (12.4 g) in conc. sulphuric acid (70 ml) was cooled to 10–20° and mixed with a solution containing conc. sulphuric acid (25 ml) and conc. nitric acid (4 ml, 1 mol.). The mixture was heated on a boiling water bath for 30 min, then cooled, and poured into cold water (700 ml). The crystalline product was collected and recrystallised from ethanol to give **21** (13.2 g, 89%), m.p. 128–130° (Found: C, 42.4; H, 3.75; N, 19.75; S, 11.35. $C_{10}H_{10}N_4O_4S$ calc.: C, 42.55; H, 3.55; N, 19.85; S, 11.35%).

1-(m-*Aminophenyl)-5-ethylsulphonyl-1,2,3-triazole* (**22**). — To a mixture of **21** (13.2 g) and T-4 Raney nickel (~10 ml) in ethanol (100 ml) was added slowly a 64% solution of hydrazine (30 ml). The mixture was left at room temperature for 3 h, and then filtered and concentrated to a syrup which crystallized from methanol–water to give **22** (9.59 g, 81%), m.p. 131–132° (Found: C, 47.55; H, 4.8; N, 22.2; S, 12.6. $C_{10}H_{15}N_4O_2S$ calc.: C, 47.6; H, 4.75; N, 22.2; S, 12.7%).

4-Ethylsulphonyl-1,2,3-triazole (**17**). — A mixture of **22** (5.1 g) with a solution of potassium hydroxide (2 g) and potassium permanganate (10 g) in water (150 ml) was refluxed. Potassium permanganate (20 g) was added portionwise to the mixture. After 21 h, excess potassium permanganate was decomposed with methanol, and the mixture was filtered, deionised by Amberlite IR-120(H^+) resin, and concentrated. The syrupy residue was fractionated on a column of silica gel using chloroform. Concentration of the appropriate fraction gave **17** (1.69 g, 52%), m.p. 76–78° (Found: C, 29.7; H, 4.5; N, 26.05; S, 19.75. $C_4H_7N_3O_2S$ calc.: C, 29.8; H, 4.35; N, 26.1; S, 19.85%).

The i.r. spectrum and the n.m.r. spectrum of **17** were identical with those obtained from the compound prepared by the degradation of **5**.

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