Anal. Calcd for $C_{45}H_{36}O_8 \cdot C_6H_6$: C, 78.24; H, 5.73; benzene, 9.96. Found: C, 78.75; H, 5.73; benzene 7.08.

5-*O*-Trityl-2-deoxy-D-ribose Ethylene Mercaptal (V).—A solution of 8.8 g (0.042 mole) of 2-deoxy-D-ribose ethylene mercaptal[4] and 12.3 g (0.043 mole) of trityl chloride in 70 ml of anhydrous pyridine was allowed to stand at room temperature for 3 days. The reaction mixture was poured into a mixture of 350 g of ice and 270 ml of $CHCl_3$ with stirring. After the ice had melted, the $CHCl_3$ layer was removed. The aqueous layer was extracted with 80 ml of $CHCl_3$. The combined $CHCl_3$ solutions were washed as in the previously described acylation but using 120-ml portions. The $CHCl_3$ solution was dried ($MgSO_4$), filtered, and evaporated to dryness under reduced pressure. The residue (23.6 g) was chromatographed on 600 g of alumina as previously described but packing and eluting with C_6H_6–$CHCl_3$–CH_3OH (78:20:2) and collecting one hundred 10-ml fractions. Fractions 14–40 were combined and evaporated to dryness under reduced pressure. The residue (19.8 g) was crystallized from 150 ml of C_6H_6–C_6H_{12} (1:2) to give 6.9 g (36%) of crystalline solid, mp 125–128°.

A portion of the product was recrystallized twice from the same solvent system; mp 130–132°, $[\alpha]^{25}D$ −8.8° (*c* 4, $CHCl_3$). The ultraviolet spectrum (C_2H_5OH) had maxima at 230 mμ (ε 8150), 253 (896), and 258 (874) with shoulders at 264 and 269 mμ. The infrared spectrum had bands at 3500, 3470, 1590, 1580, 1485, 1065, 775, 760, 740, 705, 700, 690, and 630 cm^{-1}. The nmr spectrum (in $CDCl_3$) had a doublet of doublets centered at δ 1.86 (2 H), a triplet centered at 2.66 (2 H), a singlet at 3.13 (4 H), multiple peaks centered at 3.37 (2 H), multiple peaks centered at 3.89 (2 H), a triplet centered at 4.66 (1 H), and multiple peaks at 7.22–7.58 (15 H).

Anal. Calcd for $C_{29}H_{28}S_2O_3$: C, 68.99; H, 6.23; S, 14.17; O, 10.61. Found: C, 69.17; H, 6.25; S, 14.22; O, 11.08.

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Carboranes. II. An Analog of 1,4-(Dimethanesulfonoxy)butane[1,2]

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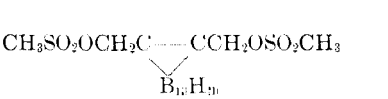
The preparation of a boron-containing bismethanesulfonate was undertaken for possible application in neutron-capture therapy.[3] An *o*-carborane analog of the alkylating agent, bis(methanesulfonoxy)butane (Myleran),[1] was synthesized from 1,4-bismethanesulfonoxybutyne for evaluation in tumor-bearing animals.



Experimental Section[5]

1,4-Bismethanesulfonoxybutyne.—An experimental preparative procedure and the physical characteristics of this compound have not been described, though pharmacological studies are reported.[6] A similar procedure to that described for the sulfonation of dihydroxyalkynes[7] was used.

A solution of 8.6 g (0.1 mole) of 1,4-butynediol in 15.8 g (0.2 mole) of pyridine was added to 100 ml of a 1:1 mixture of THF and ethyl ether. To this stirred anhydrous solution, 22.9 g (0.2 mole) of ethanesulfonyl chloride was added dropwise, maintaining the temperature of the reaction mixture below 5°. Upon completion of the addition, the mixture was stirred for 4 hr at the same temperature. The solution was then concentrated under reduced pressure to one-third of its volume. The pyridine hydrochloride was discarded and the filtrate was treated with an equal volume of water. The mixture became warm and two layers separated. The upper, organic phase was removed and concentrated to an oil which solidified on treatment with ethanol. This product, 5.1 g (21%), was recrystallized from 2 vol of ethanol and yielded white crystals, mp 85.5–86.5°.

Anal. Calcd for $C_8H_{16}O_6S_2$: C, 29.74; H, 4.16; S, 26.47. Found: C, 29.88; H, 4.15; S, 26.23.

1,2-Bis(methanesulfonoxymethyl)carborane.—A solution of 4.84 g (0.02 mole) of 1,4-bis(methanesulfonoxybutyne) and 2.44 g (0.02 mole) of sublimed decaborane ($B_{10}H_{14}$) in 50 ml of dry acetonitrile was refluxed for 28 hr. The solvent was then removed under reduced pressure and the residue was refluxed in 40 ml of methanol for 4 hr. Removal of the alcohol on a rotatory evaporator left an oil from which 3.4 g (47%) of a crude solid was obtained by use of an ethanol–water mixture. Recrystallization from ethanol yielded 1.5 g of the pure carborane, mp 93–94°.

Anal. Calcd for $C_6H_{20}B_{10}O_6S_2$: C, 19.98; H, 5.59; B, 30.01; S, 17.79. Found: C, 20.23; H, 5.56; B, 29.81; S, 17.54.

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Some Hydrazine Derivatives of (4-Biphenylyl)glyoxal

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4-Biphenylglyoxal and its derivatives have been shown by Cavallini and his co-workers[1] to have both *in vitro* and *in vivo* activity against several viruses. The data presented by these workers indicated that a high degree of antiviral activity was associated with the condensation products of biphenylylglyoxals and *p*-aminobenzoic acid, and that these derivatives were better absorbed than the parent glyoxal. In the antibacterial nitrofurans, condensation with a substituted hydrazine confers activity on the weakly active aldehyde.[2] It was of interest therefore to prepare similar derivatives of (4-biphenylyl)glyoxal to compare their activity with that of the parent compound. This communication describes the synthesis of the derivatives listed in Table I.

These compounds, unlike the parent biphenylylglyoxal, did not possess *in vivo* activity against herpes simplex or the influenza PR8 virus.[3]

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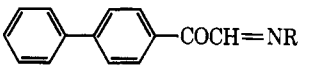
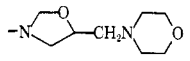
TABLE I

HYDRAZINE DERIVATIVES OF (4-BIPHENYLYL)GLYOXAL



Compd	R	Mp, °C	Formula	C, % Calcd	C, % Found	H, % Calcd	H, % Found	N, % Calcd	N, % Found	Equiv wt Calcd	Equiv wt Found
I	$-N(CONH_2)CH_2CO_2H$	205–206[a]	$C_{17}H_{15}N_3O_4$	62.8	62.7	4.65	4.77	...	...	325	322
II		178–180[a]	$C_{22}H_{23}N_3O_4$	67.2	67.0	5.89	6.03	...	...	393	396
III		277[a]	$C_{17}H_{13}N_3O_3$	66.4	66.6	4.26	4.15	...	...	301	304
IV	$-NHCH_2CH_2OH$	120–122	$C_{16}H_{16}N_2O_2$	71.6	71.6	6.03	6.14	10.4	10.4	...	...
V	$-NHCH_2CO_2C_2H_5$	96–98[b]	$C_{18}H_{18}N_2O_3$	70.3	70.0	6.22	5.95	8.6	8.9	...	...
VI	$-NHCH_3$	107–108[c]	$C_{15}H_{14}N_2O$	75.6	75.7	5.92	5.81	11.8	11.9	...	...
VII	$-N(CH_3)_2$	114–115	$C_{16}H_{16}N_2O$	76.2	76.2	6.34	6.20	11.1	11.2	...	...

[a] Recrystallized from EtOH. [b] From benzene. [c] From petroleum ether (60–80°).

Experimental Section[4]

Intermediate Hydrazines.—Semicarbazidoacetic acid,[5] 3-amino-5-morpholinomethyl-2-oxozalidine (prepared *in situ* from the benzylidene derivative[6]), 1-aminohydantoin,[7] and ethyl hydrazinoacetate[8] were made by procedures based on literature preparations. The remaining hydrazines were obtained from commercial sources.

Preparation of Hydrazones.—The hydrazones listed in Table I were prepared from 4-biphenylylglyoxal hydrate and the hydrazine in a solvent such as ethanol or aqueous ethanol, and the method is typified by the following example.

Ethyl (4-Biphenylylglyoxylidene)hydrazinoacetate (V).—To a stirred solution of 4-biphenylylglyoxal hydrate (18.3 g, 0.08 mole) in hot ethyl alcohol (100 ml) was added a solution of ethyl hydrazinoacetate hydrochloride (12.4 g, 0.08 mole) in hot water. The solution was adjusted to pH 6 by the addition of sodium acetate and stirring was continued until it had attained room temperature. The solid which separated on standing overnight was collected and recrystallized from benzene affording the pure hydrazone as slender needles, mp 96–98°, yield 12.1 g (49%).

Infrared Spectra.—The infrared spectra of the hydrazone derivatives I, II, III, and VII showed the expected aromatic carbonyl absorptions at 1650–1654 cm^{-1} but those of IV, V, and VI were anomalous and lacked the expected carbonyl or amino absorptions. The latter phenomenon is attributed to intramolecular hydrogen bonding involving the proton on the secondary nitrogen atom. Infrared spectra of V and VI in CCl_4 solution (1, 0.5, and 0.25%) lacked absorptions in the carbonyl region but peaks due to bonded hydroxyl or amino groups appeared at 3458, 3420, and 3210 cm^{-1}.

(4) Melting points were recorded using an Electrothermal melting point apparatus comprising a gas-heated block and a thermometer calibrated for exposed stem. Microanalyses are by Mr. M. Graham and spectra by Miss E. V. Eggington. The infrared spectra of all of the products were recorded with a Hilger H. 800 instrument.

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Synthesis of 1-Benzyltryptamine

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1-Benzyltryptamine is related to a series of potent serotonin antagonists, *e.g.*, 1-benzyl-2-methyl-5-methoxytryptamine (BAS),[2] and has been prepared in 40–50% yield by the Fischer cyclization of 4-aminobutyraldehyde benzylphenylhydrazone.[3,4]

We have prepared 1-benzyltryptamine and the α-methyl homolog in comparable yields in a three-step synthesis as described in the Experimental Section.

Experimental Section[5]

The properties of I–VII are listed in Table I.

1-Benzyl-3-indolealdehyde (I).—A mixture of 145 g (1.0 mole) of 3-indolealdehyde,[6] 125 ml of benzyl chloride, 140 g of anhydrous K_2CO_3, and 300 ml of pure dimethylforamide (DMF) was vigorously stirred and heated for 2 hr, the cooled solution was poured into 2 l. of water, and the precipitated solid was collected, dried, and recrystallized.

1-Benzyl-3-(2-nitrovinyl)indole (II).—The aldehyde I (23.5 g, 0.1 mole) was heated for 30 min with 100 ml of nitromethane and 6 g of NH_4OAc. After cooling, the yellow precipitate was filtered off and washed with methanol.

1-Benzyltryptamine (III).—A solution of 27.8 g (0.1 mole) of II in 150 ml of tetrahydrofuran (THF) was added to 21.0 g of $LiAlH_4$ in 200 ml of THF. The mixture was stirred and refluxed for 1.5 hr, cooled, treated with THF–water (3:1) until evolution of hydrogen ceased, and filtered, the solvents were removed, and the residue was distilled under reduced pressure.

1-Benzyl-3-(2-methyl-2-nitrovinyl)indole (IV). A.—Compound I (94.0 g, 0.4 mole) heated with 100 ml of nitroethane and 20 g of NH_4OAc at 100° for 30 min gave a yellow product.

B.—3-(2-Methyl-2-nitrovinyl)indole[7] (20.2 g, 0.1 mole), 14 ml of benzyl chloride, 14.0 g of anhydrous K_2CO_3, and 150 ml of DMF were stirred and heated together at 110–120° for 3 hr. The mixture was poured into cold water and the solid precipitate was collected and recrystallized.

An attempt to obtain this compound from 3-(2-methyl-2-nitrovinyl)indole and benzoyl chloride in pyridine at room temperature was unsuccessful.

1-Benzyl-*dl*-α-methyltryptamine (V).—Compound IV (14.6 g 0.05 mole) was dissolved in 400 ml of ether–THF (1:1) and added to 8.5 g of $LiAlH_4$ in 200 ml of ether. The mixture was stirred for 2 hr, decomposed by adding 20 ml of ethyl acetate followed by 35 ml of 15% NaOH, and filtered off. The filtrate was concentrated, and the basic residue was distilled under reduced pressure.

1-Benzoyl-3-(2-methyl-2-nitrovinyl)indole (VI).—Benzoyl chloride (7 ml) was slowly added to 10.1 g (0.05 mole) of 3-(2-

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