the temperature of the reaction mixture had returned to 150° C, 100 ml of diglyme was added, together with 2.5 grams of cuprous chloride and 0.5 gram of copper powder.

The temperature was gradually increased to 160° C. and 20.6 grams (0.067 mole) of 4′-bromo-*m*-terphenyl, dissolved in 40 ml of diglyme, was added dropwise. The reaction was allowed to continue for 10 hours at 185° C. It was then diluted with ethyl ether and filtered. The ether layer was washed with 2 × 100 ml of 25% aqueous potassium hydroxide, followed by water washing until neutral. The aqueous washes were extracted with 2 × 100 ml of ethyl ether. The ether layers were combined, washed with distilled water until neutral, dried over magnesium sulfate, and filtered. A brown viscous liquid was obtained upon removal of the ether. This material was distilled to obtain 10 grams of forecut, bp 80–337° C./0.07 mm, and 23.5 grams of 4′-[*m*-(*m*-phenoxyphenoxy)phenoxy]-*m*-terphenyl, bp 337° C./0.07 mm., as a yellow viscous liquid.

Final purification was effected as described above for the other ethers prepared.

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3,3′-Biscoumarins

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Five 3,3′-biscoumarins, none of which have been reported previously, were synthesized by a modification of the Perkin reaction.

A MIXTURE consisting of 0.1 mole of anhydrous powdered potassium succinate and 0.2 mole of the aldehyde was thoroughly mixed with 40 ml. of acetic anhydride in a flask and then heated in a Hi-Temp oil bath, already at equilibrium between 155° and 160° C. for 30 to 45 minutes. The mixtures were diluted with 300 ml. of water, cooled, and filtered and the precipitates dried in air. The compounds were powdered and dried 3 days in a vacuum desiccator over Drierite.

A sample of each compound was purified by extraction with heptane, then ethyl acetate, and finally with boiling ethanol. The samples thus purified gave the analyses and infrared data shown in Table I.

One gram of compound 1 after having been treated as

Table I. Biscoumarins

	Aldehyde Used	M.P., °C.	Yields, %	Formula	Calculated			Found		
					C	H	Other	C	H	Other
1.	Salicylaldehyde	328	97	$C_{18}H_{10}O_4$	74.47	3.47		74.55	3.69	
2.	5-Chloro-salicylaldehyde	>360	98	$C_{18}H_8Cl_2O_4$	60.19	2.24	19.74(Cl)	59.89	2.36	19.75(Cl)
3.	3-Methoxy salicylaldehyde	346–348	99	$C_{20}H_{14}O_6$	68.56	4.02		68.36	4.06	
4.	2-Hydroxy-1-naphthaldehyde	>360	97	$C_{26}H_{14}O_4$	79.99	3.61		80.28	3.82	
5.	5-Bromo-salicylaldehyde	>360	100	$C_{18}H_8Br_2O_4$	48.25	1.79	35.66(Br)	48.53	2.01	35.77(Br)

1. 3,3′-Biscoumarin- 1703[a]
2. 6,6′-Dichloro-3,3′-biscoumarin- 1707
3. 8,8′-Dimethoxy-3,3′-biscoumarin- 1707
4. 2,2′-Bis(3*H*-naphtho[2,1-*b*]pyran-3,3′-dione- 1710
5. 6,6′-Dibromo-3,3′-biscoumarin- 1715

[a] Carbonyl absorption of infrared spectrum in cm.$^{-1}$ KBr pellet taken on Beckman IR-8.

described, was partially dissolved in 20 ml. of dimethyl sulfoxide, filtered, and precipitated with 100 ml. of heptane. This produced about 100 mg. of a light yellow compound having the same melting point as the tan substance obtained before.

Hindered carbonyl compounds such as 2-hydroxyacetophenone and 4,6-dimethoxy-2-hydroxybenzaldehyde were treated exactly like the compounds of the 1 to 5 series, except that the reaction time was extended to 3 hours, but did not give biscoumarins. NMR analysis indicated that the products were 4-methyl-3-hydroxycoumarin acetate and 5,7-dimethoxy-3-hydroxycoumarin acetate. Analyses from three repeated preparations gave acceptable carbon, but hydrogen determinations were consistently 1% too high.

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Derivatives of Thionyl Imide

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The reaction of thionyl chloride with H_2NNR_2 (R = alkyl) yields derivatives of thionyl imide with the formula $OSNNR_2$. Infrared and proton NMR spectral data are given. *N*-(Dimethylamino)thionyl imide did not react with methyl iodide. This is attributed to electron delocalization, hence a lack of basic sites, in the molecule of the thionyl imide derivative.

THIONYL IMIDE, O=S=N—H, can be synthesized in the gas-phase reaction of thionyl chloride and ammonia (*8*). The monomeric form is unstable and polymerizes readily. However, derivatives with the formula O=S=N—R (R = organic group) do not show the instability of the parent compound (*2*). These have been referred to as thionyl imines as well as sulfinyl amines. Work by Michaelis had established the existence of compounds with the general formula $O{=}S{=}N{-}N(R)C_6H_5$ (R = H, CH_3, $CH_2C_6H_5$) (*4, 5, 6*). The compounds had been named as sulfinyl hydrazines; however, they should be considered derivatives of thionyl imide. More recently, Klamann *et al.* prepared the same compounds with a modification of the procedure of Michaelis (*3*). The general method was the reaction of thionyl chloride with the substituted hydrazine (phenylhydrazine, 1-phenyl-1-methylhydrazine, and 1-phenyl-1-benzylhydrazine) in chloroform in the presence of pyridine. Middleton used a transthionylation reaction to prepare thionyl imide derivatives (*7*). This was also a procedure used by Michaelis.

This investigation was undertaken to extend the series of known compounds containing the O=S=N—N group. Compounds containing only alkyl substituents were prepared, but only with further modifications of previously used procedures.

EXPERIMENTAL

Materials. 1,1-Dimethylhydrazine (J. T. Baker Chemical Co.) was distilled and stored over potassium hydroxide (b.p. 63° C.). Triethylamine (Matheson, Coleman and Bell) was distilled and stored over calcium hydride (b.p. 90° C.). Pyridine was used as obtained from Allied Chemical. Thionyl chloride (Matheson, Coleman and Bell) was fractionated using a 30-mm. column filled with Raschig rings. The middle fraction (b.p. 76–78° C.) was reserved in a tightly closed flask in a refrigerator until use. *N*-Aminopiperidine and *N*-aminohomopiperidine (Aldrich Chemical Co.) were distilled prior to use (b.p. 70° C. at 50 mm., 100° C. at 50 mm., respectively). *N*-Aminomorpholine, also obtained from Aldrich Chemical Co., was used as received. Diethyl ether and benzene were dried with calcium hydride, chloroform with calcium chloride.

Analyses. Elemental analyses were performed by A. Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, West Germany. Melting points were determined in capillary tubes using a Thomas-Hoover melting point apparatus. A Beckman IR 8 was used to record the infrared spectra. The NMR spectra were obtained on a Varian A-60 spectrometer. Tetramethylsilane was the internal standard for all samples.

Preparation of N-(Dimethylamino)thionyl Imide, $OSNN(CH_3)_2$. A 500-ml. three-necked flask was equipped with a vapor seal stirring apparatus, a KOH-filled drying tube, and a 125-ml. pressure-equalizing dropping funnel. A solution of 22.8 ml. of 1,1-dimethylhydrazine (18.0 grams, 0.30 mole), 84 ml. of triethylamine (60.6 grams, 0.60 mole), and 300 ml. of anhydrous ether was prepared in the flask. To this was added over a period of 3 hours with stirring and ice bath cooling, a solution of 21.6 ml. of thionyl chloride (35.7 grams, 0.30 mole) in 50 ml. of anhydrous ether. A pale yellow solution with a white solid resulted. After the reaction mixture had come to room temperature, the solid, triethylamine hydrochloride, was quickly filtered from the solution and dried in vacuo. A nearly quantitative yield was obtained [m.p. 245–54° C., lit. 254° C. (*1*)]. The ether was removed from the filtrate with a flash evaporator. Distillation of the resulting yellow liquid (88° C., 50 mm.) gave 18.4 grams (58% of theory) of *N*-(dimethylamino)-thionyl imide. The compound is soluble in water as well as in the common organic solvents. Analytical and spectral data are given in Tables I, II, and III.

Dry benzene can also be used as a solvent for the reaction. Chloroform is also suitable. However, since triethylamine