(1450), and 282 (1415); nmr ($CDCl_3$ plus some DMSO-d_6) δ 6.15 (s, aromatic), 3.27 (s, SCH_2CH_2S), 2.60 and 2.14 (two m, H-1 and H-2), 1.95 (q, H-4), and 1.04 (t, H-5); low-resolution mass spectrum, molecular ion m/e 270 (55%), major fragments m/e (rel intensity) 241 (45), 177 (25), 137 (30), 133 (100), 123 (40), and 44 (30); high-resolution mass spectrum, molecular ion m/e 270.0765 ($C_{13}H_{18}O_2S_2$).

(6a*R*:10a*R*)-6a,7,10,10a-Tetrahydro-6,6,9-trimethyl-3-pentyl-6*H*-dibenzo[*b*,*d*]pyran-1-ol-3′-one Dithioethylene Acetal (13).—A mixture of 5.162 g (19.1 mmol) of **12**, 2.83 g (20.8 mmol) of **5**, and 575 mg of *p*-toluenesulfonic acid monohydrate in 200 ml of benzene was heated under reflux for 35 min, cooled, and washed onto a column of silica gel. Elution with benzene and dichloromethane gave 3.647 g (47%) of **13** as a colorless oil, suitable for use in subsequent steps: ir ($CHCl_3$) 3600, 1625, and 1580 cm^{-1}; uv max (EtOH) 235 nm (infl) (ϵ 12,200), 275 (1500), and 282 (1400); nmr ($CDCl_3$) δ 6.28 and 6.10 (two d, H-2 and H-4), 5.42 (m, H-8), 4.87 (s, OH), 3.24 (s, SCH_2CH_2S), 1.68 (s, 9-CH_3), 1.36 and 1.09 (two s, 6,6-diCH_3), and 1.07 (t, H-5′); low-resolution mass spectrum, molecular ion m/e 404 (35%), major fragments m/e (rel intensity) 311 (60), 271 (100), and 133 (80).

(6a*R*:10a*R*:3′*RS*)-6a,7,10,10a-Tetrahydro-6,6,9-trimethyl-3-(3-hydroxypentyl)-6*H*-dibenzo[*b*,*d*]pyran-1-ol (2).—A heterogeneous mixture of 3.02 g (7.5 mmol) of **13**, 3.00 g of mercuric chloride, and 3.00 g of cadmium carbonate in 300 ml of acetone and 15 ml of water was stirred at room temperature for 16 hr. Another 3.00 g of each inorganic salt was added, and 7 hr later a further 3.00 g of each salt was again added. The reaction was stirred for an additional 20 hr, the inorganic salts were removed by filtration through a filter aid, and the acetone was evaporated under vacuum. The residue was shaken with ether; the ether layer was washed with water, 10% potassium iodide solution, and water, dried, and concentrated. The green residue was dissolved in benzene and adsorbed onto a column of silica gel. Elution with 15–20% ether in dichloromethane gave 1.40 g of the ketone **14** as a light tan oil, almost homogeneous by tlc in 15% ethyl acetate in benzene. This oil was dissolved in 12 ml of ethanol, and 200 mg of sodium borohydride was added. The reaction was stirred for 2.5 hr, during which time an additional 125 mg of sodium borohydride was added. The reaction was diluted with water, acidified with hydrochloric acid, and extracted with dichloromethane. The extracts were washed with sodium bicarbonate solution, dried, and concentrated to 1.2 g of a yellow foam. This was chromatographed over silica gel. Twenty per cent ether in dichloromethane eluted 445 mg (17%) of **2** as a colorless foam: homogeneous by tlc in 15% ethyl acetate in benzene; ir ($CHCl_3$) 3605, 1625, and 1590 cm^{-1}; uv max (EtOH) 230 nm (infl) (ϵ 10,600), 276 (1330), and 283 (1380); nmr ($CDCl_3$) δ 6.35 (OH), 6.25 and 6.14 (two sharp m, H-2 and H-4), 5.42 (m, H-8), 3.55 (m, H-3′), 3.21 (br d, H-10a), 2.09 (OH), 1.65 (s, 9-CH_3), 1.35 and 1.07 (two s, 6,6-diCH_3), 0.90 (t, H-5′); low-resolution mass spectrum, molecular ion m/e 330 (25%), major fragment m/e (rel intensity) 258 (100); high-resolution mass spectrum, molecular ion m/e 330.2196 ($C_{21}H_{30}O_3$).

(6a*R*:10a*R*:3′*RS*)-6a,7,10,10a-Tetrahydro-6,6,9-trimethyl-3-(3-acetoxypentyl)-6*H*-dibenzo[*b*,*d*]pyran-1-ol Acetate (15).—A sample of **2** was acetylated with acetic anhydride in pyridine overnight at room temperature. The solution was then poured into water and extracted with dichloromethane. The solution was dried and concentrated. The residue was dissolved in benzene and adsorbed onto a column of silica gel. Elution with 5% ether in dichloromethane gave **15** as a colorless oil, homogeneous by tlc in benzene: nmr ($CDCl_3$) δ 6.54 and 6.39 (two sharp m, H-2 and H-4), 5.43 (m, H-8), 4.84 (t, H-3′), 2.25 and 2.01 (two s, OAc's), 1.68 (s, 9-CH_3), 1.37 and 1.08 (two s, 6,6-diCH_3), and 0.88 (t, H-5′); compatible[9] with the time-averaged 100 scan spectrum obtained from the metabolically derived **15**; low-resolution mass spectrum, molecular ion m/e 414 (100%), major fragments m/e (rel intensity) 372 (90), 312 (35), 298 (45), 289 (40), and 258 (70); high-resolution mass spectrum, molecular ion m/e 414.2385 ($C_{25}H_{34}O_5$).

Registry No.—**1** (1′-*R* isomer), 34589-81-6; **1** (1′-*S* isomer), 34589-82-7; **2** (3′-*R* isomer), 34589-83-8; **2** (3′-*S* isomer), 34589-84-9; **6**, 34589-85-0; **7**, 34589-86-1; **8** (1′-*R* isomer), 34589-87-2; **8** (1′-*S* isomer), 34589-88-3; **10**, 34589-89-4; **11**, 34589-90-7; **12**, 34589-91-8; **13**, 34635-37-5; **15** (3′-*R* isomer), 34589-92-9; **15** (3′-*S* isomer), 34589-93-0.

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1- and 3-Methoxy-3-phenyloxindoles. A Rearrangement of a Methoxy Group from Nitrogen to Carbon

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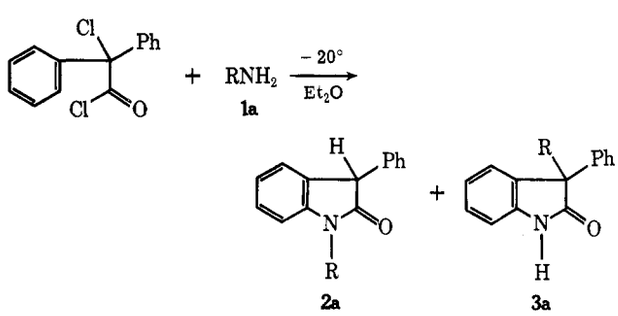
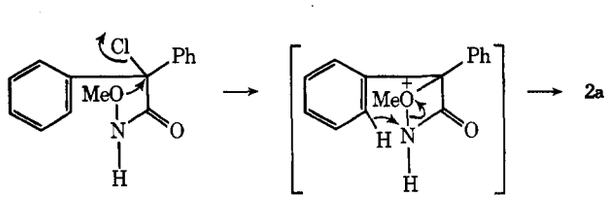
In connection with other work we desired 1-methoxy-3-phenyloxindole (**2a**). The preparation of **2a** should be analogous to that of 1-dimethylamino-3-phenyloxindole (**2b**). Compound **2b** is prepared[1] by the reaction at −20° between α,α-diphenylchloroacetyl chloride and *N*,*N*-dimethylhydrazine (**1b**). When this reaction was performed using methoxyamine (**1a**) the product isolated (by crystallization from aqueous methanol) had melting point, ir (N–H present), and nmr (Ar-CHC:O absent) properties strongly suggesting that it was 3-methoxy-3-phenyloxindole (**3a**). Comparison



a series, R = OCH_3
b series, R = $N(CH_3)_2$

with an authentic sample[2] confirmed this assignment.

When the crude oily reaction product, essentially solvent-free, was allowed to stand, the desired **2a** very slowly crystallized first and could be picked out. The residual oil afforded **3a**. The isolated ratio of **2a** to **3a** was approximately 1:4. Neither **2a** nor **3a** could be isomerized to the other by boiling in ether, by recrystallization, or by seeding the melt. This suggests that the isomerization occurs during the initial reaction steps, in



(1) R. F. Meyer, *J. Org. Chem.*, **30**, 3451 (1965).
(2) J. M. Bruce and F. K. Sutcliffe, *J. Chem. Soc.*, 4789 (1957). We thank Professor Bruce for kindly supplying a sample of **3a**.

spite of the low temperature. A four-membered ring intermediate is conceivable.

The reaction using **1b** was reexamined. There was no spectral evidence for the formation of **3b**; the exclusive product was the expected **2b**.

Experimental Section

Melting points are uncorrected. Ir (KBr) spectra were recorded on a Perkin-Elmer Infracord spectrometer; nmr spectra on a Perkin-Elmer Hitachi R-20 instrument ($CDCl_3$ solvent, TMS standard). Microanalyses are by Galbraith Laboratories, Knoxville, Tenn.

1-Methoxy- and 3-Methoxy-3-phenyloxindoles.—In a flask equipped with a magnetic stirrer, a dropping funnel, and drying tubes were placed 7.25 g (0.0265 mol) of α,α-diphenylchloroacetyl chloride (Aldrich) and 75 ml of dry ether. The funnel was charged with a solution of 4.7 g (0.1 mol) of methoxyamine[3] in 25 ml of ether. The mixture was kept near −20° with a Dry Ice–acetone bath while the amine was added slowly with stirring. The slurry was allowed to warm to room temperature and was stirred for an additional 4 hr. Water (100 ml) was added and the layers were separated. The ether layer was washed with 2 × 50 ml of water, dried (K_2CO_3), and evaporated to leave a pale yellow oil. When left at room temperature, this deposited transparent cubes during a period of 5 weeks. These were removed manually and triturated with a 1:1 benzene–hexane mixture at room temperature. There was obtained 0.95 g (15%) of **2a**, mp 93–95°. Its ir spectrum showed no N–H stretching, while its nmr spectrum exhibited a three-proton singlet at 4.01 ppm ($NOCH_3$) and a one-proton singlet at 4.54 ppm ($Ar_2CHC{:}O$).

Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.30; H, 5.51; N, 5.70.

The oil left after the removal of **2a** was crystallized from aqueous methanol to give 4.0 g (63%) of **3a**, mp 168–169°. Its spectra showed N–H stretching at 3200 cm^{-1} and no proton resonance near 4.5 ppm. It was identical, by ir and nmr spectral comparisons and by mixture melting point, with an authentic sample of **3a**.[2] When the total crude reaction product was crystallized directly from aqueous methanol the less soluble **3a** was isolated first.

Except for the N–H region, the ir spectra of **2a** and **3a** differ significantly only below 1200 cm^{-1}. **2a** exhibited bands at 1065, 759, and 748 cm^{-1} not shown by **3a**, whereas **3a** showed bands at 1118, 1095, 773, 753, and 706 cm^{-1}.

When **1b** was used, the crude reaction product showed no evidence in its ir or nmr spectra that any **3b** was present, and only **2b**[1] was isolated.

Attempted Isomerizations of 2a and 3a.—A mixture of 0.24 g of **2a**, 0.08 g of methoxyamine hydrochloride, and 20 ml of ether was refluxed with stirring for 6 hr and filtered. Evaporation of the filtrate gave a quantitative recovery of **2a**, identified by its melting point and ir spectrum. Similarly, **3a** was recovered unchanged. Further, **2a** and **3a** were recovered unchanged, even when seeded with the other, when each was recrystallized from aqueous methanol or from a melt.

In similar experiments, **2b** did not isomerize to **3b**.

Registry No.—**2a**, 34638-56-7; **3a**, 34638-57-8.

(3) T. C. Bissot, R. W. Parry, and D. H. Campbell, *J. Amer. Chem. Soc.*, **79**, 796 (1957).

Reductive Cleavage of Sulfonamides with Sodium Bis(2-methoxyethoxy)aluminum Hydride

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We wish to report that the new versatile reducing agent sodium bis(2-methoxyethoxy)aluminum hydride (SMAH),[1] in contrast to lithium aluminum hydride ($LiAlH_4$),[2] is a useful reagent for the regeneration of primary and secondary aliphatic and aromatic amines from the corresponding sulfonamides. This reaction provides an additional approach that complements those methods reported[2,4] for carrying out this transformation. The usual procedure consists of refluxing a mixture of the sulfonamide and excess SMAH (mole ratio 1:4) in an aromatic hydrocarbon or, if desired, in an ethereal solvent such as glyme, until sulfonamide is consumed. Addition of water or alkali quenches the reaction, and the amine may be isolated by standard procedures. Typical results are recorded in Table I.[5,6]

TABLE I

CLEAVAGE OF SULFONAMIDES WITH $NaAlH_2(OCH_2CH_2OCH_3)_2$

Series	Sulfonamides (1)	Product (2)	Solvent	Yield,[a] %
a	*N*-Tosylpiperidine	Piperidine	Benzene	75[b]
b	*N*-Tosyldeoxyephedrine	Deoxyephedrine	Benzene	64[b]
			Glyme	77[b]
c	*N*-Mesyldeoxyephedrine	Deoxyephedrine	Benzene	67[b]
d	(*S*)-*N*-Tosylamphetamine	(*S*)-Amphetamine	Toluene	27[b]
e	*cis*- and *trans*-1,5-Bis(tosyl)-3,7-dihydroxyoctahydro-1,5-diazocine[c]	*cis*-3,7-Dihydroxyoctahydro-1,5-diazocine[c]	Benzene	33[d]
f	*N*-Tosyl-2-(*N*-methylaminomethyl)-2-phenyl-1,3-dioxolane	2-(*N*-Methylaminomethyl)-2-phenyl-1,3-dioxolane	Toluene	56[e]
g	1-Tosylaziridine	*N*-Tosylethylamine	Benzene	100
h	2g	Ethylamine	Toluene	57[b]
i	3-Methoxymethoxy-3-phenyl-1-tosylazetidine[f]	3-Methoxymethoxy-3-phenylazetidine[f]	Benzene	69[g]
j	*N*-Mesylaniline	Aniline	Toluene	63[h]

[a] No special effort was made to optimize yields. [b] Isolated as picrate and compared by ir, melting point (and $[\alpha]_D$ where applicable) with an authentic sample. [c] No attempt was made to purify the trans product.[5] [d] Isolated as the ditosylate. [e] Yield as distilled free amine. [f] Reference 6. [g] Isolated as the hemioxalate. [h] Isolated as hydrochloride and compared as in *b*.

With the exception of (*S*)-*N*-tosylamphetamine (**1e**), it can be seen from Table I that both toluenesulfonamides and methanesulfonamides are cleaved by this reagent in acceptable yield. Although reduction of tertiary sulfonamides is generally readily carried

(1) (a) V. Bazant, M. Capka, M. Cerny, V. Chvalovsky, K. Kochloefl, M. Kraus, and J. Malek, *Tetrahedron Lett.*, 3303 (1968); (b) M. Cerny and J. Malek, *ibid.*, 1739 (1969); (c) M. Cerny, J. Malek, M. Capka, and V. Chvalovsky, *Collect. Czech. Chem. Commun.*, **34**, 1025 (1969); (d) M. Capka, V. Chvalovsky, K. Kochloefl, and M. Kraus, *ibid.*, **34**, 118 (1969).

(2) S. Searles and S. Nukina, *Chem. Rev.*, **59**, 1077 (1959); *cf.* p 1094. Primary sulfonamides have not been cleaved with $LiAlH_4$. Secondary sulfonamides (generally aniline derivatives) have been cleaved by using unusually vigorous conditions for this reagent, *e.g.*, reduction of *N*-ethyl-*p*-toluenesulfonanilide at 120° in dibutyl ether.[3]

(3) D. Klamann, *Monatsh. Chem.*, **84**, 651 (1953).

(4) (a) L. Horner and H. Neumann, *Chem. Ber.*, **98**, 3462 (1965); (b) W. D. Closson, P. Wriede, and S. Bank, *J. Amer. Chem. Soc.*, **88**, 1581 (1966); (c) S. Ji, L. B. Gortler, A. Waring, A. Battisti, S. Bank, W. D. Closson, and P. Wriede, *ibid.*, **89**, 5311 (1967); (d) K. Okamura, T. Iwasaki, M. Matsuoka, and K. Matsumoto, *Chem. Ind. (London)*, 929 (1971).

(5) W. W. Paudler, A. G. Zeiler, and G. R. Gapski, *J. Org. Chem.*, **34**, 1001 (1969).

(6) E. H. Gold, *J. Amer. Chem. Soc.*, **93**, 2793 (1971).