purification. An analytical sample was purified by flash chromatography on silica gel (15 cm × 2.5 cm i.d.) eluted with hexane/EtOAc (9:2): IR (film) 3340, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 6 H), 0.90 (s, 9 H), 1.18 (d, 3 H, J = 5.5 Hz), 1.23–1.65 (m, 14 H), 1.95 (br s, 1 H), 2.10–2.20 (m, 4 H), 3.62 (t, 2 H, J = 6.5 Hz), 3.75–3.85 (m, 1 H); mass spectrum, m/e (relative intensity) 283 (17), 189 (10), 95 (78), 75 (100), 45 (52); high-resolution mass spectrum calcd for $C_{20}H_{40}O_2Si$ m/e 340.2797, obsd 340.2785; $[\alpha]^{31}_D$ + 3.6° (c 1.82, $CHCl_3$).

Preparation of (13*S*)-13-[(2-Methoxyethoxy)methoxy]-(*Z*)-5-tetradecen-1-ol ((13*S*)-17). The hydroxyl function of (13*S*)-**14** was protected as the MEM ether, via standard procedures.[18] The crude product was flash chromatographed in three batches on silica gel (20 cm × 5 cm i.d.) eluted with hexane/EtOAc (9:1), giving (13*S*)-**15**: 14.8 g (78%); IR (film) 1100, 1039 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 6 H), 0.90 (s, 9 H), 1.16 (d, 3 H, J = 5.5 Hz), 1.23–1.65 (m, 14 H), 2.10–2.20 (m, 4 H), 3.40 (s, 3 H), 3.53–3.60 (m, 2 H), 3.63 (t, 2 H, J = 6.5 Hz), 3.68–3.75 (m, 3 H), 4.73 (d, 1 H, J = 7.5 Hz), 4.79 (d, 1 H, J = 7.5 Hz); $[\alpha]^{31}_D$ +4.8° (c 4.94, $CHCl_3$). Anal. Calcd for $C_{24}H_{48}O_4Si$: C, 67.24; H, 11.29. Found: C, 67.29; H, 11.48.

P-2 nickel (1 mmol) was used to reduce alkyne (13*S*)-**15** (9.85 g, 23 mmol) via the published method.[9] The product (13*S*)-**16** (9.9 g, 100%, >98% pure by GLC) was used without further purification: IR (film) 1100, 1039 cm^{-1}; ^1H NMR (C_6D_6) δ 0.13 (s, 6 H), 1.05 (s, 9 H), 1.19 (d, 2 H, J = 5.5 Hz), 1.26–1.70 (m, 14 H), 2.09–2.19 (m, 4 H), 3.2 (s, 3 H), 3.34 (t, 2 H, J = 5.5 Hz), 3.61 (t, 2 H, J = 6.5 Hz), 3.70–3.80 (m, 3 H), 4.74 (d, 1 H, J = 7.5 Hz), 4.79 (d, 1 H, J = 7.5 Hz), 5.5–5.55 (m, 2 H); mass spectrum (CI, isobutane), m/e 431 (P + 1); high-resolution mass spectrum calcd for $C_{24}H_{50}O_4Si$ m/e 430.3478, obsd 430.3460; $[\alpha]^{33}_D$ +4.7° (c 4.17, $CHCl_3$).

Crude (13*S*)-**16** (9.4 g, 22 mmol) was stirred at room temperature for 24 h in 100 mL of AcOH/THF/H_2O (3:1:1). The solution was concentrated under reduced pressure, and the silanol removed by pumping under high vacuum (0.1 mmHg) for 12 h at 40 °C. The resulting (13*S*)-**17** (6.9 g, 100%, >95% pure by GLC) was used without further purification: IR (film) 3420, 1100, 1038 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (d, 3 H, J = 5.5 Hz), 1.25–1.48 (m, 10 H), 1.49–1.64 (m, 4 H), 1.98–2.10 (m, 5 H), 3.40 (s, 3 H), 3.57 (t, 2 H, J = 5.5 Hz), 3.65 (t, 2 H, J = 6.5 Hz), 3.68–3.75 (m, 3 H), 4.72 (d, 1 H, J = 7.5 Hz), 4.78 (d, 1 H, J = 7.5 Hz), 5.30–5.40 (m, 2 H); $[\alpha]^{34}_D$ +6.5° (c 2.31, $CHCl_3$). Anal. Calcd for $C_{18}H_{36}O_4$: C, 68.31; H, 11.47. Found: C, 68.19; H, 11.29.

Preparation of (13*S*)-13-[(2-Methoxyethoxy)methoxy]-(*Z*)-5-tetradecenoic Acid ((13*S*)-18). Alcohol (13*S*)-**17** was oxidized to (13*S*)-**18** (95%, >90% pure by GLC of the methyl ester (CH_2N_2)) with pyridinium dichromate in DMF, following the normal procedure.[18] An analytical sample was further purified by flash chromatography on silica gel (15 cm × 2.5 cm i.d.), eluting with hexane/EtOAc/AcOH (100:20:1): IR (film) 3550–2200, 1729 cm^{-1}; ^1H NMR (C_6H_6) δ 1.18 (d, 3 H, J = 5.5 Hz), 1.32–1.52 (m, 10 H), 1.58–1.72 (m, 4 H), 2.00–2.15 (m, 4 H), 2.19 (t, 2 H, J = 7.0 Hz), 3.20 (s, 3 H), 3.43 (t, 2 H, J = 4.5 Hz), 3.65–3.82 (m, 3 H), 4.77 (d, 1 H, J = 7.5 Hz), 4.81 (d, 1 H, J = 7.5 Hz), (br s, 1 H); high-resolution mass spectrum, calcd for $C_{18}H_{33}O_5$ (P − 1) 329.2328, obsd 329.2335; $[\alpha]^{33}_D$ +7.2° (c 3.33, $CHCl_3$).

Preparation of (13*S*)-13-Hydroxy-(*Z*)-5-tetradecenoic Acid ((13*S*)-19). Deprotection of (13*S*)-**18** (6.37 g, 19 mmol) was carried out as described for **9**. Purification by flash chromatography on silica gel (20 cm × 5 cm i.d.) with hexane/EtOAc/AcOH (75:25:1) yielded (13*S*)-**19** (3.34 g, 72%) as a colorless oil: IR (film) 3600–2300, 1711 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (d, 2 H, J = 5.5 Hz), 1.25–1.57 (m, 10 H), 1.73 (quintet, 2 H, J = 6 Hz), 1.98–2.10 (m, 2 H), 2.10–2.18 (m, 2 H), 2.38 (t, 2 H, J = 7.0 Hz), 3.82–3.90 (m, 1 H), 5.30–5.38 (m, 1 H), 5.42–5.50 (m, 1 H), 7.0–7.5 (br s, 2 H); mass spectrum of the methyl ester (CH_2N_2), m/e (relative intensity) 238 (3.5), 81 (100), 67 (94), 55 (83), 45 (72); high-resolution mass spectrum, calcd for $C_{14}H_{26}O_3$ m/e 242.1882, obsd 242.1880; $[\alpha]^{32}_D$ +4.9° (c 4.06, $CHCl_3$).

Preparation of (13*S*)-13-Methyl-(*Z*)-5-tridecenolide ((13*S*)-2). A solution of 2-chloro-*N*-methylpyridinium iodide (4.2 g, 17 mmol) in dry acetonitrile (250 mL) was heated to reflux under argon. A solution of (13*S*)-**19** (1.0 g, 4.1 mmol) and triethylamine (3.4 g, 34 mmol) in dry acetonitrile (250 mL) was added dropwise over 6 h. The resulting solution was refluxed a further 2 h, cooled, and concentrated. The concentrate was poured into water (100 mL) and extracted with pentane (3 × 50 mL). The combined pentane extracts were washed with water, dried over anhydrous $MgSO_4$, and concentrated. The resulting product was flash chromatographed on silica gel (18 cm × 2.5 cm i.d.), eluting with hexane/EtOAc (40:1) to give (13*S*)-**2** (494 mg, 49%). This (13*S*)-**2** was spectrally and chromatographically identical with **2** isolated from *C. pusillus*: IR (film) 1725, 1248, 1216 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (d, 2 H, 5.5 Hz), 1.25–1.68 (m, 13 H), 1.70–1.78 (m, 1 H), 1.78–1.98 (m, 2 H, 2.17–2.37 (m, 2 H), 2.23 (ddd, 1 H), J = 2.5, 9, 15 Hz), 2.44 (ddd, 1 H, J = 2.5, 9, 15 Hz), 4.94–5.03 (m, 1 H), 5.33 (td, 1 H, J = 4.5, 10.5 Hz), 5.40 (td, 1 H, J = 4.5, 10.5 Hz); mass spectrum, m/e (relative intensity) 224 (9.1), 81 (94.5), 67 (91.5), 55 (77.1), 41 (100); high-resolution mass spectrum, calcd for $C_{14}H_{24}O_2$ m/e 224.1776, obsd 224.1776; (13*S*)-(+)-**2**, $[\alpha]^{32}_D$ +49.6° (c 4.62, $CHCl_3$); (13*R*)-(−)-**2**, $[\alpha]^{35}_D$ −46.4° (c 2.19, $CHCl_3$).

Acknowledgment. We thank the NSERC of Canada for continued support of this work through Operating Grant A0851, a Strategic Grant (open), and a Postgraduate Fellowship (J.G.M.). We also thank Dr. Harold Pierce, Jr., Dr. Aldona Pierce, and Dr. John Borden for assistance in isolation and identification of natural **1** and **2**.

Registry No. **1**, 87371-99-1; (*S*)-(+)-**2**, 87420-69-7; (*R*)-(−)-**2**, 87420-70-0; (±)-**2**, 77761-59-2; **3**, 629-41-4; **4**, 50816-19-8; **5**, 87372-00-7; **6**, 87372-01-8; **7**, 87372-02-9; **8**, 87372-03-0; **9**, 87372-04-1; **10**, 87372-05-2; **10** pyridylthio ester, 87372-06-3; **11b**, 16088-62-3; **12**, 73448-13-2; **13**, 87372-07-4; (*S*)-**14**, 87372-08-5; (*S*)-**15**, 87372-09-6; (*S*)-**16**, 87372-10-9; (*S*)-**17**, 87372-11-0; (*S*)-**18**, 87372-12-1; (*S*)-**19**, 87420-71-1; lithium acetylide, 1111-64-4; ethylene oxide, 75-21-8; 5-hexyn-1-ol, 928-90-5; 1-chloro-5-iodopentane, 60274-60-4.

Lithium Bromide Catalyzed Homologation of Aldehydes with Aryldiazomethanes

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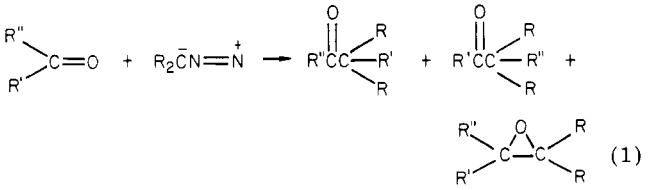
Received March 16, 1983

In the course of an investigation of the reaction of organolithium compounds with *N*-nitrosoformamides,[1] the beneficial effect of lithium bromide on stereoselective dimerization of aryldiazomethanes to *cis*-stilbenes and on the homologation of aromatic aldehydes with phenyldiazomethane was observed.[2,3] The present paper describes a more detailed study of the latter reaction.[4]

Although the homologation of carbonyl compounds with diazoalkanes can be useful for the elaboration of carbon–carbon bonds, epoxide formation as well as the possible generation of the isomeric homologated product may detract from its usefulness (eq 1).[4] Lewis acids and aliphatic



(1)

alcohols have been shown to be valuable in promoting homologation though the various factors that may affect

† Taken in part from the B.S. Thesis of Carol A. Loeschorn, University of Massachusetts at Boston, June 1982.

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0022-3263/83/1948-4407$01.50/0

Table I. Homologation of Aldehydes with Aryldiazomethanes[a]

RCHO	% yield		
	$C_6H_5CHN_2$	p-$CH_3C_6H_4CHN_2$	p-$ClC_6H_4CHN_2$
C_6H_5CHO	92	99	86
p-ClC_6H_4CHO	100		84
o-$NO_2C_6H_4CHO$	100		
m-$NO_2C_6H_4CHO$	90		
p-$NO_2C_6H_4CHO$	100	92	*b*
o-$CH_3C_6H_4CHO$	87		
p-$CH_3C_6H_4CHO$	84		
p-$CH_3OC_6H_4CHO$	90		52[c]
3,4-$OCH_2OC_6H_3CHO$	91		
3,4,5-$(MeO)_3C_6H_2CHO$	95		
2-C_4H_3SCHO	87		
2-C_4H_3OCHO	100		
4-C_5H_4NCHO	72[c]		
CH_3CH_2CHO	81		
$(CH_3)_2CHCH_2CHO$	91		

[a] The yields given in the table were estimated by NMR integration; the product was isolated in each case, except where noted. [b] No yield could be determined because of the use of an excess amount of starting aldehyde. Even though this reaction was not repeated, the ketone was isolated. [c] Based on the isolated product.

the course of this reaction are far from being well-understood.[4]

Several aspects of the lithium bromide promoted homologation of aldehydes with aryldiazomethanes were investigated. The results reported in Table I were obtained with equivalent amounts of the aldehydes and aryldiazomethanes in the presence of a tenfold excess of lithium bromide in diethyl ether. In most cases the reaction proceeds in excellent yields and homologation with substituted aryldiazomethanes works equally well. Desoxybenzoins with electron-donating groups at the para position of the ring bearing the carbonyl group may be readily obtained via the Friedel–Crafts reaction. This is not the case for compounds with these same substituents at the ortho or meta positions; *o*-tolualdehyde underwent clean homologation in excellent yield. The preparation of desoxybenzoins bearing electron-withdrawing groups at *any* position of the carbonyl-bearing benzene ring is difficult if not impossible by a Friedel–Crafts reaction. In contrast even *o*-nitrobenzaldehyde gave a nearly quantitative yield of the corresponging desoxybenzoin by the present procedure. Those aldehydes bearing electron-withdrawing groups reacted very rapidly, actually resembling a titration with the disappearance of the wine-red color of phenyldiazomethane serving as visual evidence of the progress of the reaction. It is to be emphasized that even with the nitro-substituted benzaldehydes, the homologation did *not* proceed in the absence of lithium bromide. An example of the efficacy and the utility of the homologation may be illustrated by a comparison of this one-step, quantitative formation of α-phenyl-*p*-nitroacetophenone with the five-step synthesis used by Zimmer and Bercz[5] to prepare the same compound. The complete failure of *p*-(dimethylamino)benzaldehyde to be homologated under these conditions might be understood in terms of preferential complexation of the lithium ions with the amine nitrogen, resulting in precipitation of the substrate;[6] this view was supported by the formation of a precipitate when the homologation was attempted by the "lithium bromide saturated ether" technique (vide infra). Precipitate formation was also observed with 2-pyrrylaldehyde and this may also explain the difficulties encountered with 4-nicotinaldehyde. With no encumbrance at the position α to the carbonyl group, the homologation proceeded very smoothly; propionaldehyde and isovaleraldehyde afforded good yields of the expected ketones (see Table I). Little or none of the anticipated product was obtained with diphenylacetaldehyde, isobutyraldehyde, and pivalaldehyde.[7]

In view of the fact that the phenyldiazomethane used in these early experiments was prepared by the mercury (or manganese) oxide oxidation of benzalhydrazone[8] in the presence of *methanolic* potassium hydroxide, it was necessary to establish the reality of the effect of lithium bromide on the homologation. The necessity of lithium bromide for smooth homologation under these conditions was established in several different runs;[9] neither mercury ions nor manganese ions catalyzed the homologation to any great extent.[10] Homologation of benzaldehyde with phenyldiazomethane generated from benzaldehyde trisylhydrazone[11] occurred as readily as in the previous cases but only in the presence of lithium bromide. A limited effort was made to extend the scope of the lithium bromide homologation. Very complex mixtures (by NMR) were obtained with phenylglyoxal and cinnamaldehyde, while chloral afforded, besides a large amount of benzalazine, a roughly 1:1 mixture of the ketone (42%) and the epoxide (58%) along with trace amounts of benzaldehyde.[10]

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(6) Decreased reactivity of the carbonyl group by the dimethylamino group seems an unlikely explanation in view of the result obtained with 3,4,5-trimethoxybenzaldehyde (see Table I).
(7) The very odd results obtained in these cases clearly suggest that further investigation is warranted.
(8) J.-P. Anselme, *Org. Prep. Proced.*, 1, 73 (1969).
(9) Whenever a control reaction was performed in the present study, a given preparation of phenyldiazomethane was *always* divided in two or more portions in order to minimize spurious results.
(10) (a) Apparently lithium iodide promotes the homologation since benzoin was the product isolated. This reaction will be discussed in a separate publication. (b) These experiments were performed because desoxybenzoin was often a product in the homologation of *substituted* benzaldehydes with the phenyldiazomethane prepared by oxidation of benzaldehye hydrazone. The ion-promoted oxidation of diazoalkanes with oxygen will be the subject of a separate publication.
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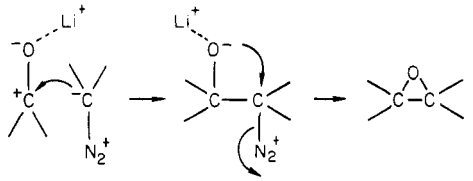
The homologation of benzaldehyde with 1 equiv of phenyldiazomethane proceeds equally well when a lithium bromide saturated diethyl ether solution was used.[12] Although homologation of the other aldehydes listed in Table I was not carried out under these conditions, there is no obvious reason to believe that it should not occur as well. Sodium, potassium and tetraethylammonium bromide did not promote the homologation of benzaldehyde with phenyldiazomethane; little if any homologation was observed with lithium fluoride and chloride; lithium iodide gave anomalous results.[10a] It is interesting to note that magnesium bromide resulted in nearly quantitative conversion of phenyldiazomethane to benzyl bromide. In lithium bromide saturated acetonitrile or THF, the homologation of benzaldehyde proceeded, albeit in only 33% and 42% yields, respectively; the major product was the oxidized product, benzaldehyde (66% and 58%).[10b]

There is so far no general mechanism capable of accounting for all the experimental data on the homologation of carbonyl compounds with diazoalkanes.[4] The very reasonable view of the effect of alcohols and Lewis acids in promoting the formation of the carbonyl compounds at the expense of the epoxides may be utilized for the present results. Indeed one may envisage that complexation of the small, protonlike lithium ion with the carbonyl oxygen[13] should not only enhance nucleophilic attack by the carbon of the diazoalkane group but also discourage nucleophilic displacement by the oxygen to give the epoxide; stilbene



oxide was *not* converted to desoxybenzoin under the conditions of the reaction. However, the present results make it more obvious than ever that a considerable amount of careful studies will be required in order to unravel all the possible factors affecting the homologation of carbonyl compounds.

Experimental Section

All melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were run on a Perkin-Elmer Infracord 137 neat or as KBr pellets. NMR spectra were obtained on a Hitachi Perkin-Elmer R-24 with Me_4Si as an internal standard at 60 MHz. Elemental analyses were performed by the Microanalysis Laboratory at the University of Massachusetts, Amherst. UV determinations were run on a Beckman Spectrophotometer Acta C111. The mass spectra were taken on a Varian MAT-44 mass spectrophotometer. The yields were calculated from the NMR spectra in the following manner. After workup of the product mixture, the amount of unconsumed aldehyde was calculated by the integration of the aldehyde hydrogen. This amount was then subtracted from the total amount of starting aldehyde and the difference then used as a basis for the calculation of the yields.

Benzaldehyde,[8] *p*-tolualdehyde,[14] and *p*-chlorobenzaldehyde[14] hydrazones were prepared according to the literature procedures in 69%, 43%, and 75% yields, respectively. The aryldiazomethanes were prepared by the reported procedure. The concentration of the phenyldiazomethane was determined by UV analysis (ϵ 3.11 × 10^4, 277 nm).[15] A measured portion was carefully evaporated to afford a red oil, which was treated with excess acetic acid; the yield of benzyl acetate was then determined.

Homologation of Aldehydes with Aryldiazomethanes. General Procedure. To a stirred mixture of the aldehyde (0.015 mol) and a ten fold equivalent of lithium bromide in 100 mL of anhydrous ether cooled in an ice–salt bath (−5 to 0 °C) was added through an addition funnel a dilute solution of approximately 0.015 mol of phenyldiazomethane in 125 mL of anhydrous ether. The reaction flask was protected from light with aluminum foil. The length of time for completion of the reaction varied from immediate reaction to a couple of days depending upon the aldehyde employed. The completion of the reaction was heralded by the disappearance of the deep wine-red color of the phenyldiazomethane. Water was added and the ethereal layer was separated and dried over magnesium sulfate for 1–2 h. The ether was removed in vacuo, leaving the crude product. Purification varied depending upon the product to be isolated. The yields given were estimated from the NMR, and the weights are those of the crude products.

Desoxybenzoin (2.0 g, 92%), white crystals (EtOH); mp 55–56 °C (lit.[16] mp 60 °C); IR (KBr) 1680 cm^{-1}; NMR ($CDCl_3$) δ 7.95 (m, 4 H), 7.28 (m, 5 H), 4.20 (s, 2 H).

α-Phenyl-*p*-chloroacetophenone (4.02 g, 100%), pale yellow crystals (EtOH); mp 103–105 °C (lit.[17] mp 106–106.5 °C); IR (KBr) 1687 cm^{-1}; NMR ($CDCl_3$) δ 7.48 (m, 9 H), 4.19 (s, 2 H).

α-Phenyl-*o*-nitroacetophenone (2.59 g, 90%), pale yellow crystals (EtOH); mp 74–74.5 °C (lit.[18] mp 73–74 °C); IR (KBr) 1700 cm^{-1}; NMR ($CDCl_3$) δ 7.58 (m, 9 H), 4.09 (s, 2 H).

α-Phenyl-*m*-nitroacetophenone (2.09 g, 90%), pale yellow crystals (EtOH); mp 112–113 °C; IR (KBr) 1682 cm^{-1}; NMR ($CDCl_3$) δ 7.58 (m, 9 H), 4.30 (s, 2 H). Anal. Calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.59; N, 5.80. Found: C, 69.47; H, 4.51; N, 5.83.

α-Phenyl-*p*-nitroacetophenone (3.07 g, 100%), off-white crystals (EtOH); mp 159–160 °C (lit.[19,5] mp 159–160, 160–160.5 °C); IR (KBr) 1687 cm^{-1}; NMR (acetone-d_6, Me_2SO) δ 8.39 (s, 4 H), 7.36 (s, 5 H), 4.54 (s, 2 H).

α-Phenyl-*o*-methylacetophenone (2.50 g, 87%), yellow liquid (unpurified); IR (neat) 1698 cm^{-1}; its structure was confirmed by the addition of an authentic sample[31] to the NMR sample; NMR ($CDCl_3$) δ 7.12 (s, 9 H), 4.02 (s, 3 H), 2.38 (s, 3 H).

α-Phenyl-*p*-methylacetophenone (1.9 g, 84%), white crystals (EtOH); mp 108–110 °C (lit.[20] mp 108–109 °C); IR (KBr) 1684 cm^{-1}; NMR ($CDCl_3$) δ 7.86 (s, 1 H), 7.71 (s, 1 H), 7.18 (s, 5 H), 7.06 (s, 2 H), 4.19 (s, 2 H), 2.35 (s, 3 H).

α-Phenyl-*p*-methoxyacetophenone (2.7 g, 90%), white crystals (EtOH); mp 71–73 °C (lit.[21] mp 76–78 °C); IR (KBr) 1675 cm^{-1}; NMR ($CDCl_3$) δ 8.08 (s, 1 H), 7.91 (s, 1 H), 7.27 (s, 5 H), 6.96 (s, 1 H), 6.80 (s, 1 H), 4.20 (s, 2 H), 3.80 (s, 3 H).

α-Phenyl-3,4,5-trimethoxyacetophenone (3.67 g, 95%), white crystals (EtOH); mp 98–99 °C (lit.[22] mp 99 °C); IR (KBr) 1693 cm^{-1}; NMR ($CDCl_3$) δ 7.28 (s, 7 H), 4.21 (s, 2 H), 3.88, 3.87 (s, 9 H).

Benzyl piperonyl ketone (1.60 g, 91%), taupe crystals (EtOH); mp 89–90.5 °C; IR (KBr) 1677 cm^{-1}; NMR ($CDCl_3$) δ 7.11 (m, 8 H), 5.87 (s, 2 H), 4.09 (s, 2 H). Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 75.10; H, 4.93.

α-(*p*-Chlorophenyl)acetophenone (2.92 g, 86%), white crystals (EtOH); mp 135–136 °C (lit.[23] mp 136–137 °C); IR (KBr) 1700 cm^{-1}; NMR ($CDCl_3$) δ 7.95 (m, 2 H), 7.34 (m, 7 H), 4.19 (s, 2 H).

(12) Lithium bromide is dissolved to an extent of 48 mg/mL in diethyl ether. The amount of lithium bromide dissolved by ether was determined by allowing a volume of anhydrous ether to stir with an excess of lithium bromide (3 h) at 10 °C and evaporation of the resulting ethereal solution of lithium bromide; however, even under these conditions, *p*-(dimethylamino)benzaldehydes failed to react.

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α-(p-Chlorophenyl)-p-nitroacetophenone (1.18 g),[24] pale yellow crystals (EtOH); mp 115–116 °C; IR (KBr) 1687 cm^{-1}; NMR ($CDCl_3$) δ 8.18 (m, 4 H), 7.17 (m, 4 H), 4.26 (s, 2 H); MS, *m/e* 275 (3, M^+), 150 (100), 75 (48), 104 (46), 50 (45), 125 (41). Anal. Calcd for $C_{14}H_{10}ClNO_3$: C, 60.99; H, 3.63; Cl, 12.86; N, 5.08. Found: C, 61.42; H, 3.60; Cl, 12.65; N, 5.37.

α-(p-Chlorophenyl)-p-methoxyacetophenone (3.01 g, 52%), white crystals (EtOH); mp 130–131 °C; IR (KBr) 1667 cm^{-1}; NMR ($CDCl_3$) δ 7.40 (m, 8 H), 4.14 (s, 2 H), 3.80 (s, 3 H). MS, *m/e* 260 (1, M^+), 135 (100), 77 (39), 92 (31). Anal. Calcd for $C_{15}H_{13}ClO_2$: C, 69.09; H, 5.01. Found: C, 68.81; H, 4.86.

α-(p-Chlorophenyl)-p-chloroacetophenone (3.58 g, 84%), pale yellow crystals (EtOH); mp 110.5–113 °C (lit.[25] mp 113–114 °C); IR (KBr) 1687 cm^{-1}; NMR ($CDCl_3$) δ 7.45 (m, 8 H), 4.17 (s, 5 H).

α-(p-Tolyl)acetophenone (3.2 g, 99%), pale yellow crystals (EtOH); mp 91–94 °C (lit.[24] mp 95.5 °C); IR (KBr) 1680 cm^{-1}; NMR ($CDCl_3$) δ 7.81 (m, 2 H), 7.32 (m, 3 H), 7.02 (s, 4 H), 4.10 (s, 2 H), 2.19 (s, 3 H).

α-(p-Tolyl)-p-nitroacetophenone (2.73 g, 92%), white crystals (EtOH); mp 130–132 °C; NMR ($CDCl_3$) δ 8.12 (d, 4 H), 7.08 (s, 4 H), 4.22 (s, 2 H), 2.28 (s, 3 H); MS, *m/e* 255 (2.5, M^+), 105 (100), 77 (19). Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.68; H, 5.09; N, 5.47.

1-(2-Furyl)-2-phenylethanone (2.1 g, 100%), red-brown, viscous liquid (unpurified liquid); semicarbazone mp 165–167 °C (lit.[26] mp 166–168 °C); IR (neat) 1667 cm^{-1}; NMR ($CDCl_3$) δ 7.13 (m, 6 H), 6.26 (q, 2 H), 3.97 (s, 2 H).

1-(2-Thienyl)-2-phenylethanone (2.1 g, 87%), taupe crystals (column chromatography); mp 47–48 °C (lit.[27] mp 48–49 °C); IR (KBr) 1654 cm^{-1}; NMR ($CDCl_3$) δ 7.20 (m, 8 H), 4.00 (s, 2 H).

1-(4-Pyridyl)-2-phenylethanone, lit.[28] mp 96 °C, was isolated in 72%; recrystallization of a sample from petroleum ether–carbon tetrachloride gave an analytical sample as a colorless solid: mp 95–96 °C; NMR ($CDCl_3$) δ 8.8 (m, 2 H), 7.7 (m, 2 H), 7.3 (s, 5 H), 4.25 (s, 2 H). Anal. Calcd for $C_{13}H_{11}NO$: C, 79.16; H, 5.62; N, 7.10. Found: C, 78.96; H, 5.49; N, 7.06.

1-(2-Pyrryl)-2-phenylethanone, lit.[29] mp 95 °C, could not be induced to crystallize from the dark purple reaction mixture. Its NMR spectrum displayed a CH_2 at δ 3.97, consistent with that expected for the homologated product; the NMR spectrum also indicated the presence of *cis*- and *trans*-stilbene in addition to benzaldehyde and benzyl bromide.

1-Phenyl-2-butanone (5.2 g, 81%), clear liquid (distillation); IR (neat) 1701 cm^{-1}; the structure was confirmed by the addition of an authentic sample[30] to the NMR sample; NMR ($CDCl_3$) δ 7.19 (s, 5 H), 3.60 (s, 2 H), 2.40 (q, 2 H), 1.00 (t, 3 H).

4-Methyl-1-phenyl-2-pentanone (1.0 g, 91%), yellow liquid (unpurified); IR (neat) 1717 cm^{-1}; NMR ($CDCl_3$) δ 7.2 (s, 5 H), 4.1 (s, 2 H), 2.26 (d, 2 H), 1.55 (m, 1 H), 0.88 (d, 6 H).

1,1,1-Trichloro-3-phenyl-2-propanone could not be isolated from the yellow solution whose NMR spectrum displayed a sharp singlet at δ 4.18 and doublets at δ 3.80 and 4.30 (epoxide). The yields of the ketone and the epoxide were estimated from integration of the peaks; traces of benzaldehyde were detected.

Registry No. C_6H_5CHO, 100-52-7; *p*-ClC_6H_4CHO, 104-88-1; *o*-$NO_2C_6H_4CHO$, 552-89-6; *m*-$NO_2C_6H_4CHO$, 99-61-6; *p*-$NO_2C_6H_4CHO$, 555-16-8; *o*-$CH_3C_6H_4CHO$, 529-20-4; *p*-$CH_3C_6H_4CHO$, 104-87-0; *p*-$CH_3OC_6H_4CHO$, 123-11-5; 3,4-$OCH_2OC_6H_3CHO$, 120-57-0; 3,4,5-$(MeO)_3C_6H_2CHO$, 86-81-7; 2-C_4H_3SCHO, 98-03-3; 2-C_4H_3OCHO, 98-01-1; 4-C_5H_4NCHO, 872-85-5; CH_3CH_2CHO, 123-38-6; $(CH_3)_2CHCH_2CHO$, 590-86-3; $C_6H_5CHN_2$, 766-91-6; *p*-$CH_3C_6H_4CHN_2$, 23304-24-7; *p*-$ClC_6H_4CHN_2$, 19277-54-4; deoxybenzoin, 451-40-1; α-phenyl-*p*-chloroacetophenone, 1889-71-0; α-phenyl-*o*-nitroacetophenone, 29236-59-7; α-phenyl-*m*-nitroacetophenone, 55251-37-1; α-phenyl-*p*-nitroacetophenone, 3769-84-4; α-phenyl-*o*-methylacetophenone, 16216-13-0; α-phenyl-*p*-methylacetophenone, 2001-28-7; α-phenyl-*p*-methoxyacetophenone, 1023-17-2; α-phenyl-3,4,5-trimethoxyacetophenone, 87282-25-5; benzyl piperonyl ketone, 87282-26-6; α-(*p*-chlorophenyl)acetophenone, 6332-83-8; α-(*p*-chlorophenyl)-*p*-nitroacetophenone, 87282-27-7; α-(*p*-chlorophenyl)-*p*-methoxyacetophenone, 52578-11-7; α-(*p*-chlorophenyl)-*p*-chloroacetophenone, 51490-05-2; α-(*p*-tolyl)acetophenone, 2430-99-1; α-(*p*-tolyl)-*p*-nitroacetophenone, 87282-28-8; 1-(2-furyl)-2-phenylethanone, 86607-65-0; 1-(2-thienyl)-2-phenylethanone, 13196-28-6; 1-(4-pyridyl)-2-phenylethanone, 1017-24-9; 1-(2-pyrryl)-2-phenylethanone, 13169-74-9; 1-phenyl-2-butanone, 1007-32-5; 4-methyl-1-phenyl-2-pentanone, 5349-62-2; 1,1,1-trichloro-3-phenyl-2-propanone, 709-78-4.

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An Aristolane Sesquiterpenoid from the Sea Pen *Scytalium splendens*

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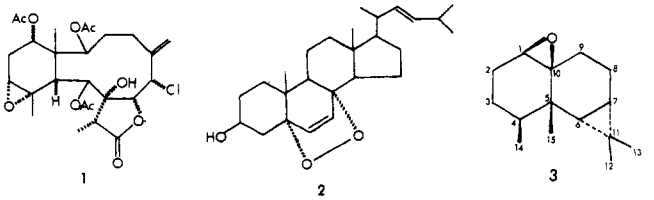
Received April 25, 1983

The coelenterates have been extensively investigated for terpenoids, especially the orders Alcyonacea (soft corals) and Gorgonacea (sea fans and sea whips).[1] The order Pennatulacea (sea pens), on the other hand, has received relatively little attention.[1,2] Chlorinated diterpenoids of the briarein type, such as stylatulide (**1**), have been reported from two different genera of sea pens, *Ptilosarcus gurneyi* and *Stylatula* sp.,[1,2] while dechlorinated analogues were recently found in *Scytalium tentaculatum*.[3] A fourth genus, *Virgularia*, elaborates rare C_{26} steroid peroxides exemplified by **2**.[4] We now report the isolation of a rearranged sesquiterpenoid (**3**) from *Scytalium splendens* collected off Penhu Island southwest of Taiwan.



Methanol extracts of the organisms were partitioned between ethyl acetate and water, and the ethyl acetate fractions were chromatographed on silica gel to give the sesquiterpenoid in 0.06% yield (dry weight). High-resolution mass spectroscopy established its formula as $C_{15}H_{24}O$. The absence of vinyl hydrogens in the ^1H NMR spectrum and vinyl, carbonyl, or acetylenic carbons in the ^{13}C NMR spectrum requires a tetracyclic skeletal system for the molecule. IR spectroscopy confirmed the absence

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0022-3263/83/1948-4410$01.50/0