Esters of Benzenepentol (Pentahydroxybenzene)

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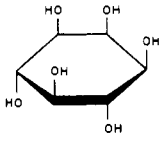
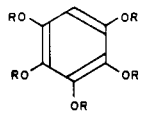
Several esters of benzenepentol (pentahydroxybenzene) have been prepared by one-step aromatization of *myo*-inositol and characterized.

ONE-STEP aromatization of *myo*-inositol (I) (a cyclohexanehexol) following treatment with methyl sulfoxide–acetic anhydride in the presence of pyridine has been reported previously (*4*); the product, namely, pentaacetoxybenzene (IIb) was isolated in about 50% yield.



I



II

a. R = H
b. R = CH_3CO
c. R = CH_3CH_2CO
d. R = $CH_3CH_2CH_2CO$
e. R = $(CH_3)_2CHCO$

To test the general applicability of this procedure (*4*), compound I was separately treated with propionic, butyric, and isobutyric anhydrides. As expected, compound I was converted into the corresponding fatty acid esters (IIc-IIe) of benzenepentol (IIa); these are now described.

To obtain the maximum yield of product, the reaction for the preparation of esters IIc, IId, and IIe has been conducted at a temperature slightly higher than that used in the preparation of IIb. However, the ratio of starting material to reagents was kept essentially the same; use of a larger quantity of I, or any change in the proportions of the reagents used, usually lowered the yield of the product to 10–15%.

Comparison of yields of the various esters shows that, whereas the pentaacetate IIb can be obtained in the range of 40–50% yield, the yields of esters IIc, IId, and IIe lie in the range of 20–30%. This lower yield may be occasioned by steric difficulty in aromatization of the inositol ester intermediate when the carbon chain of the acid anhydride is lengthened.

Benzenepentol (pentahydroxybenzene, IIa) and its acetate (IIb) were prepared in low yield by hydrolysis of triaminopyrogallol (*3*); IIa was supposedly prepared by hydrolysis of 2,6-diaminophloroglucinol trimethyl ether (*7*). Recently (*5*), IIb was obtained on acetylation and aromatization of an enolic form of a diketoinositol. Other derivatives of IIa have been prepared by the six-step synthesis of Baker (*1*), starting from pyrogallol, or by the diazomethane ring-enlargement of croconic acid (*8*). The methylated derivatives of benzenepentol (IIa) (*1, 6*), especially pentamethoxybenzoic acid (*2*), are widely distributed in nature.

EXPERIMENTAL

Melting points were determined in a silicone oil bath, and are corrected. The infrared spectra were recorded, for Nujol mulls, with a Perkin-Elmer grating Model 257 spectrophotometer, and the ultraviolet spectra with a Beckman DK-2 spectrophotometer. The samples for analysis were dried at 78°/0.1 torr (compounds IIc, IId, IIe) or 110°/0.1 torr (compounds IIa, IIb) for 2 hours.

Pentaacetate (IIb). This compound was prepared, according to a published procedure (*4*) in 46–52% yield; m.p. 166–168° C. [from 2-to-1 (v./v.) ethanol-glacial acetic acid]; λ_{max}^{MeOH} 268 nm. ($\epsilon \sim 600$); ν_{max}^{Nujol} C=O (ester) at 1788 (s) and 1725 (w) cm.$^{-1}$; phenyl ring at 1620 (m) and 1490 (w) cm.$^{-1}$; acetyl bands at 1245 (m), 1190 (w), and 1170 (s) cm.$^{-1}$

Pentapropionate (IIc). A mixture of *myo*-inositol (2 grams), propionic anhydride (10 ml.), dry pyridine (5 ml.), and dry methyl sulfoxide (30 ml.) was placed in an Erlenmeyer flask (100 ml.), and stirred (magnetic bar) at 70° to 80° for 50 minutes in the hood. The solid gradually dissolved to a dark-brown solution; this was poured onto crushed ice (250 grams) and stirred for 30 minutes at room temperature. The product, which separated as a viscous mass, was separated by decantation of the supernatant liquor, and was stirred with cold 60% ethanol (50 ml.) for 20 minutes, to give off-white crystals (1.1–1.2 grams). Further dilution of the filtrate with water, and cooling (overnight) gave an additional crop of 0.1–0.2 gram. Total yield, 1.20–1.48 grams (25–30%). The crude pentapropionoxybenzene (IIc) was recrystallized from 80% ethanol (carbon), and finally from 95% ethanol; colorless prisms, m.p. 126–127° C. Anal. Calcd. for $C_{21}H_{26}O_{10}$: C, 57.54; H, 5.95. Found: C, 57.45; H, 5.85. λ_{max}^{MeOH} 266 nm., ($\epsilon \sim 720$); ν_{max}^{Nujol} C=O (ester) at 1770 (s) cm.$^{-1}$; phenyl ring at 1618 (m) and 1490 (m) cm.$^{-1}$; acyl bands at 1238 (m), 1190 (w), and 1170 (w) cm.$^{-1}$

Pentabutyrate (IId). The pentabutyrate was prepared by a method similar to that used to prepare the pentapropionate; yield 1.3–1.48 grams (23–26%); pentabutyroxybenzene m.p. 114–115° C. (from 95% ethanol containing 5% of acetic acid). Anal. Calcd. for $C_{26}H_{36}O_{10}$: C, 61.40; H, 7.13. Found: C, 61.55; H, 7.21. λ_{max}^{MeOH} 265.5 nm. ($\epsilon \sim 690$); ν_{max}^{Nujol} C=O (ester) at 1770 (s) cm.$^{-1}$; phenyl ring at 1610 (m) and 1488 (m) cm.$^{-1}$; acyl bands at 1242 (m), 1228 (m), and 1190 (m) cm.$^{-1}$

Pentaisobutyrate (IIe). The pentaisobutyrate was prepared by an analogous procedure; yield 1.2–1.3 grams (21–23%); pentaisobutyroxybenzene, m.p. 132–134° C. (from 60% aq. ethanol containing 10% of acetic acid, and then from 95% ethanol). Anal. Calcd. for $C_{26}H_{36}O_{10}$: C, 61.40; H, 7.13. Found: C, 61.20; H, 7.22. λ_{max}^{MeOH} 264 nm. ($\epsilon \sim 700$); ν_{max}^{Nujol} C=O (ester) at 1780 (s) cm.$^{-1}$; phenyl ring at 1610 (w) and 1490 (sh) cm.$^{-1}$; acyl bands at 1210 (s) and 1180 (m) cm.$^{-1}$ The product, dried at room temperature, melted at 74–76° C., and contained 0.25 mole of water of crystallization. Anal. Calcd. for $C_{26}H_{36}O_{10} \cdot 0.25\ H_2O$; C, 60.92; H, 7.07. Found: C, 61.00; H, 7.16. λ_{max}^{MeOH} 264 nm. ($\epsilon \sim 660$). The mixture also contained a small proportion of a compound which melted at 168° C., shrinking at 156° C. (from ethanol, dried at 110°/0.01 torr for 3 hours), and which is believed to be benzenehexol (hexahydroxybenzene) hexaisobutyrate (infrared spectrum); the formation of this compound may involve a triketoinositol intermediate (*4, 5*).

Benzenepentol (Pentahydroxybenzene; IIa). A mixture of 3 grams (8.1 mmoles) of pentaacetoxybenzene (IIb) (m.p.

166° C.), 150 ml. of methanol, and 15 ml. of concentrated hydrochloric acid was refluxed for 20 minutes under a stream of nitrogen. Evaporation of the light-yellow solution under diminished pressure gave a light-colored solid. Trituration of this solid with cold ether (10 ml.) gave crude benzenepentol; pale-yellow crystals, weight 1.00–1.05 grams (77–81%).

For recrystallization, 0.5 gram was dissolved in warm *p*-dioxane (18 ml.) and quickly filtered (molecular sieves), and the filtrate was kept at 15° for 30 minutes. The crystals were filtered off, washed with cold 1-to-1 (v./v.) *p*-dioxane–pentane (5 ml.), and while still containing solvent (to avoid oxidation by air), were dried in a vacuum desiccator, giving white to pinkish crystals of benzenepentol, 0.3 gram. Saturation of the filtrate with pentane and cooling, gave an additional crop (0.15 gram); total 0.45 gram (90%). The compound does not melt, but decomposes at 264–269° C.; it was identical to an authentic sample (*3*, *5*).

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New Alkylsulfenyl *N,N*-Dialkyldithiocarbamates

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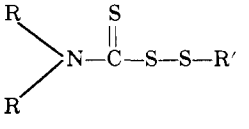
Twelve alkylsulfenyl *N,N*-dialkyldithiocarbamates have been prepared by the reaction of sodium *N,N*-dialkyldithiocarbamates with alkylsulfenyl chlorides. The alkylsulfenyl chlorides were prepared by the reaction of chlorine with alkyl disulfides.

THREE METHODS have been reported for the preparation of alkylsulfenyl *N,N*-dialkyldithiocarbamates. Watson (*8*) used *N,N*-dialkyldithiocarbamate ions as nucleophiles for the displacement of the sulfite ion in alkylthiosulfuric acids. Hunt (*5*) used a similar method which consists of an *in situ* reaction of an alkyl mercaptan with thiocyanogen to form a reactive sulfur-sulfur bond which is cleaved by the *N,N*-dialkyldithiocarbamate ion. A recent review by Kice (*6*) discusses mechanisms of sulfur-sulfur bond cleavage.

The compounds reported in this paper (Table I) were prepared by the reaction of sodium *N,N*-dialkyldithiocar-

Table I. Alkylsulfenyl *N,N*-Dialkyldithiocarbamates



Compound	R′	R	B.P., °C./Mm.	n_D^T	λ_{max}^{EtOH} Mμ	10^3	Analysis, %[a] C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found	S Calcd.	S Found
I	*t*-C_4H_9	C_2H_5	114–15/0.12–0.15	1.5768^{25}	284	7.55	45.52	45.75	8.07	8.20	5.90	6.09	40.51	40.45
					243	7.6								
II	*t*-C_4H_9	CH_3	110–18/0.28–0.47[b] (m.p. 70–72.5°)		281	6.7	40.15	40.38	7.22	7.21	6.69	6.53	45.94	46.07
					240	7.6								
III	*t*-C_4H_9	*n*-C_4H_9	140–4/0.08–0.12[c]	$1.5487^{26.5}$	284	7.4	53.19	53.22	9.27	9.15	4.77	5.00	32.77	33.00
					246	7.12								
IV	*n*-C_4H_9	*n*-C_3H_7	132–7/0.07	$1.5578^{26.5}$	282	7.43	49.76	49.91	8.73	8.82	5.28	5.26	36.23	36.02
V	*n*-C_4H_9	CH_3	113–16/0.05[d]	1.5933^{25}	278	8.35	40.15	40.28	7.22	7.26	6.69	6.49	45.94	45.98
VI	C_2H_5	C_2H_5	101–7/0.015–0.07	1.5945^{24}	281	8.71	40.15	40.05	7.22	7.39	6.69	6.53	45.94	45.72
VII	C_2H_5	CH_3	99–101/0.05[e]	1.6272^{25}	281	7.25	33.12	33.30	6.11	6.01	7.72	7.90	53.04	52.94
VIII	C_2H_5	*n*-C_3H_7	99–101.5/0.05–0.06	1.5740^{25}	282	8.15	45.52	45.64	8.07	8.15	5.90	6.03	40.51	40.29
IX	*n*-C_4H_9	*n*-C_4H_9	160–2/0.37	1.5477^{27}	282	7.16	53.19	53.05	9.27	9.29	4.77	4.63	32.77	32.64
X	*n*-C_4H_9	C_2H_5	113.5–17/0.19	1.5708^{27}	281	8.17	45.52	45.36	8.07	8.11	5.90	5.74	40.51	40.36
XI	C_2H_5	*n*-C_4H_9	133–6/0.11–0.17	1.5596^{27}	282	8.15	49.76	49.85	8.73	8.91	5.28	5.34	36.23	36.36
XII	*t*-C_4H_9	*n*-C_3H_7	128.5–35/0.04–0.06[f]	1.5613^{26}	284	7.43	49.76	49.62	8.73	8.62	5.28	5.41	36.23	36.01
					243	7.19								

[a] Performed by Galbraith Laboratories, Knoxville, Tenn. [b] Reported b.p. 125° C./0.7 mm. (*7*) and m.p. 69–70° C. (*4*). [c] Reported 173–77°/1.0 mm. Hg (*7*). [d] Reported b.p. 170–75°/2.0 mm. (*5*). [e] Reported b.p. 100–02°/0.005 mm., n_D^{20} 1.6119 (*8*). [f] Reported m.p. 61° C. (*4*).

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