spectrum had the following simple features: (1) a singlet of relative area nine at τ 9.11 (terminal methyl protons), (2) two close lying singlets at τ 7.52 and 7.48 of relative height 9 to 16 and total relative area 5.4 (methylene and acetyl methyl), and (3) an A_2B_2 pattern in the aromatic proton region,[9] with peaks at τ 2.13, 2.24, and 2.89.

Experimental Section

Nitration of Neopentylbenzene.—The heterogeneous conditions of Brown and Bonner were applied.[3] A mixture of sulfuric acid (29 ml, density 1.86 g/ml) and nitric acid (17 ml, density 1.42 g/ml) was added dropwise over a period of 3 hr to stirred neopentylbenzene (40 g, 0.27 mole) at 25°. The reaction mixture was maintained at 25° for an additional 6 hr, then poured onto ice and extracted with ether. The extract was dried over sodium sulfate and the ether removed by distillation. A small portion of the liquid residue was retained for vpc analysis (Aerograph Hy-Fi, cyanosilicone column). The residue was distilled, yielding 36.3 g (70%) of liquid, bp 83–105° (0.5 mm). A portion, 25 g, was purified by vpc (Aerograph A-700 Autoprep, silicone 710 column) yielding 8.8 g of isomer A, 0.2 g of isomer B, and 9.2 g of *p*-nitroneopentylbenzene, mp 29°.[2]

Isomer A, n^{26}D 1.5150, was later identified as *o*-nitroneopentylbenzene.

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.36; H, 7.82; N, 7.25; mol wt, 193. Found: C, 68.28; H, 7.52; N, 7.42; mol wt (parent peak, mass spectrum), 193.

Isomer B, n^{26}D 1.5193, was later identified as *m*-nitroneopentylbenzene.

Anal. Found: C, 68.38; H, 7.67; N, 7.39; mol wt (parent peak, mass spectrum), 193.

Bromination.—A solution of neopentylbenzene (2.0 g, 0.0135 mole) and bromine (0.0135 mole) in 30 ml of 85% acetic acid was maintained at 25° for 26 hr in the dark. Then the solution was poured into 50 ml of water and extracted with carbon disulfide. The extract was washed with water and then dried over barium oxide. In an analysis of the carbon disulfide solution in the Aerograph Hy-Fi (Carbowax 20 M, furnace temperature 130°) only two symmetrical peaks were obtained: isomer 1 had a retention time of 17 min (relative yield 91.5%), and isomer 2 had a retention time of 14 min (relative yield 8.5%). The carbon disulfide was removed by distillation and the residual oil purified by vpc in a preparative Aerograph A-90P (Carbowax 20 M column). A few drops were isolated of each of isomer 1, n^{26}D 1.5228, and isomer 2, n^{26°D 1.5265, and no other compounds were obtained. Isomer 1 later was shown to be *p*-bromoneopentylbenzene and isomer 2 was shown to be *o*-bromoneopentylbenzene.

Chlorination.—A solution of neopentylbenzene (2.0 g, 0.0135 mole) and chlorine (0.0135 mole) in 10 ml of glacial acetic acid was maintained at 25° for 26 hr in the dark. The acetic acid was removed by fractional distillation. Analysis by vpc (Aerograph Hy-Fi) showed only three compounds present: unchanged neopentylbenzene, chloro isomer 1 (relative yield, 74.5%), and chloro isomer 2 (relative yield 25.5%). The three compounds were separated on the Aerograph A-700 (Silicon 710 column). Chloro isomer 1, n^{26}D 1.5033, later was shown to be *p*-chloroneopentylbenzene. Chloro isomer 2, n^{26}D 1.5062, was shown to be *o*-chloroneopentylbenzene.

Acetylation.—Neopentylbenzene (0.0135 mole) was added over a period of 15 min to a solution of acetyl chloride (0.016 mole) and aluminum chloride (0.014 mole) in 15 ml of carbon disulfide. After 2 hr at room temperature, the reaction mixture was poured onto acidic ice water and extracted with carbon disulfide. The extract was washed and then dried over sodium sulfate. Analysis of the residual oil (2.26 g) on the Aerograph Hy-Fi gave two overlapping peaks (relative area, 5%) and a third separate peak (relative area, 95%) of greater retention time. The compound corresponding to the large peak was isolated by vpc on an Aerograph A-90P (silicone 710 column), 1.30 g, n^{26}D 1.5140. It had a strong band in the carbonyl region of the infrared at 5.95 μ. Its nmr spectrum showed it to be *p*-acetylneopentylbenzene (see Discussion).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 81.42; H, 9.46.

***p*-Neopentylaniline.**—Reduction of *p*-nitroneopentylbenzene (10 g) with hydrazine and palladium on carbon according to the method of Pietra[14] gave *p*-neopentylaniline, which was recrystallized from methanol–water, 8.2 g (95%), mp 56–56.5°.

Anal. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.95; H, 10.41; N, 8.74.

The N-acetyl derivative melted at 165–165.5°.

***o*-Neopentylaniline.**—Reduction of *o*-nitroneopentylbenzene, isomer A, by the method of Pietra,[14] gave 1.25 g (71%) of liquid amine, n^{26}D 1.5290. The parent peak in the mass spectrum, mass 163, corresponds to the molecular weight of *o*-neopentylaniline. The hydrochloride was prepared by bubbling hydrogen chloride into a solution of the amine (1.15 g) in 20 ml of absolute alcohol. The alcohol was evaporated and the residue recrystallized from ethanol–ether, yield 0.76 g, mp 105–106°.

Anal. Calcd for $C_{11}H_{18}ClN$: C, 66.18; H, 9.02; N, 7.01. Found: C, 66.11; H, 9.07; N, 7.17.

***p*-Bromoneopentylbenzene.**—The Sandmeyer procedure described by Fieser,[15] with bromides being used in place of chlorides and acetic acid as the solvent, was applied to 1.5 g of *p*-neopentylaniline and yielded 0.94 g of product. The bromide was further purified by vpc (Aerograph A-90P, Carbowax 20 M column) giving a colorless liquid, n^{26}D 1.5227 (lit.[46] n^{25}D 1.5240). It was identical with isomer 1 obtained in the bromination of neopentylbenzene.

Anal. Calcd for $C_{11}H_{15}Br$: C, 58.15; H, 6.66; Br, 35.18. Found: C, 58.18; H, 6.70; Br, 35.08.

***o*-Bromoneopentylbenzene.**—The procedure used above on *p*-neopentylaniline was applied to *o*-neopentylaniline (1.50 g) to yield 1.03 g of bromo compound. It was further purified by vpc, giving a colorless liquid, n^{26}D 1.5268. The compound was identical with isomer 2 obtained in the bromination of neopentylbenzene.

Anal. Calcd for $C_{11}H_{15}Br$: C, 58.15; H, 6.66; Br, 35.18. Found: C, 58.01; H, 6.78; Br, 35.04.

***o*-Chloroneopentylbenzene.**—The procedure of Fieser,[15] modified by the use of acetic acid as the solvent, was applied to 4 g (0.025 mole) of *o*-neopentylaniline, yielding 1.90 g of *o*-chloroneopentylbenzene. Further purification in an Aerograph Autoprep Model A-700 (silicone 710 column) yielded 1.49 g (40%) of colorless liquid, n^{26}D 1.5064. The compound was identical with isomer 2 obtained in the chlorination of neopentylbenzene.

Anal. Calcd for $C_{11}H_{15}Cl$: C, 72.31; H, 8.28; Cl, 19.41. Found: C, 72.30; H, 8.36; Cl, 19.20.

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[14] S. Pietra, *Ann. Chim.* (Rome), **45**, 850 (1955).

[15] L. F. Fieser, "Organic Experiments," D. C. Heath and Co., Boston, Mass., 1964, p 237.

The Preparation of α-Disulfones by Cobalt(III) Oxidation

George C. Denzer, Jr., Paul Allen, Jr., Patrick Conway, and James M. van der Veen[1]

Department of Chemistry and Chemical Engineering,
Stevens Institute of Technology, Hoboken, New Jersey

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A new method for preparing disulfones in relatively high yield (35 to 56%) has been found (eq 1). A solution of $Co_2(SO_4)_3$ in 10 N H_2SO_4 will oxidize a sulfinic acid to a disulfone rapidly at 5°. Until now, the chief route to disulfones has been permanganate, H_2O_2, or peracetic acid oxidation of the sulfinic acid salts or of disulfides, etc. Yields were often low (4 to 16%) and product purification was sometimes difficult.[2] In

$$2RSO_2H + 2Co^{+3} \longrightarrow RSO_2SO_2R + 2Co^{+2} + 2H^+ \qquad (1)$$

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[1] Author to whom enquiries should be sent.

[2] (a) P. Allen, Jr., L. S. Karger, J. D. Haygood, Jr., and J. Shrensel, *J. Org. Chem.*, **16**, 767 (1951); (b) P. Allen, Jr., and J. W. Brook, *ibid.*, **27**, 1019 (1962).

TABLE I

THE SYNTHESIS OF α-DISULFONES BY COBALT(III) OXIDATION OF SULFINIC ACIDS

α-Disulfone	Mp, °C	Lit. mp, °C	Yield, %	% S Found	% S Calcd	Infrared,[a] μ [b]	Infrared,[a] μ [c]	Infrared,[a] μ [b]	Infrared,[a] μ [d]	Ultraviolet, mμ λ_{max}	Ultraviolet, mμ Log ϵ
$[n\text{-}C_8H_{17}SO_2]_2$	89.0–89.5	89.2–89.8[e]	43[f,g]			7.48			9.04		
$[n\text{-}C_8H_{17}SO_2]_2$	88.0–89.0	89.2–89.8[e]	23[f,h]			7.49			9.04		
$[n\text{-}C_{12}H_{25}SO_2]_2$	100.0–101.0	101.7–102.5[e]	40[f,g]			7.49			9.04		
$[n\text{-}C_{14}H_{29}SO_2]_2$	106.0–106.5	105.3–106.2[e]	35[f,g]			7.48			9.04		
$[C_6H_5SO_2]_2$	196.0–196.5	193–194[i]	65[f,j]			7.49	7.70	8.80	9.42	237	4.30
$[p\text{-}CH_3C_6H_4SO_2]_2$	222	218–220[k]	54[f,j]			7.42	7.70	8.78	9.38	250	4.36
$[m\text{-}NO_2C_6H_4SO_2]_2$	198		43[j]	17.45	17.22	7.50	7.80	8.75	9.42		
$[p\text{-}NO_2C_6H_4SO_2]_2$	246		48[j]	17.11	17.22	7.52	7.78	8.72	9.43		
$[m\text{-}HOOCC_6H_4SO_2]_2$	190		65[j]	17.42	17.25	7.42	7.78	8.71	9.40		
$[p\text{-}HOOCC_6H_4SO_2]_2$	265		65[j]	17.33	17.25	7.42	7.82	8.87	9.42	270	3.73
$[p\text{-}CH_3OC_6H_4SO_2]_2$	232		65[j]			7.52	7.92	8.90	9.42	277	4.45
$[m\text{-}BrC_6H_4SO_2]_2$	190		43[j]	14.46	14.54	7.50	7.78	8.80	9.42	235	4.18
$[p\text{-}BrC_6H_4SO_2]_2$	205		52[j]	14.24	14.54	7.52	7.80	8.88	9.42	262	4.29

[a] KBr pellet. [b] Strong. [c] Weak. [d] Medium. [e] Reference 5. [f] Mixture melting points with authentic sample of the α-disulfone and comparison infrared spectra were satisfactory. [g] The free sulfinic acid was used after liberation from the magnesium salt with 10 N H_2SO_4 plus ether, extraction of the aqueous layer with CH_2Cl_2, drying with $MgSO_4$, and solvent removal in the cold to prevent decomposition of the free acid. [h] RSO_2Mg was used directly. [i] Reference 7. [j] RSO_2Na was used directly. [k] Reference 6.

contrast, the Co^{III} method yields an easily purified product in relatively high yield. The principal by-product is RSO_3H. A possible reaction mechanism is one-electron abstraction to yield a free radical ($RSO_2\cdot$) followed by radical pairing to yield the disulfone (RSO_2SO_2R). Another mechanism involving preliminary coordination of two molecules of RSO_2^- with one Co^{+3} ion can not be excluded *a priori*. Reduction to Co^{I}

$$2RSO_2^- + Co^{+3} \longrightarrow (RSO_2)_2Co^+$$

$$(RSO_2)_2Co^+ \longrightarrow RSO_2SO_2R + Co^+$$

$$Co^+ + Co^{+3} \longrightarrow 2Co^{+2} \qquad \text{(fast)}$$

followed by rapid oxidation to Co^{II} has some parallel to known chromic acid and permanganate pathways where apparent one-electron changes are in fact two-electron changes followed by rapid oxidation.[3]

Experimental Section

Preparation of Cobaltic Sulfate.[4]—$Co_2(SO_4)_3$ was prepared by electrolysis of a saturated $CoSO_4$ solution in 10 N H_2SO_4 at 0° using a platinum anode and copper cathode. The platinum anode had an area of 42 cm^2 and satisfactorily granular product was obtained with a current of 4.5 amp. The light blue solid $Co_2(SO_4)_3$ collected in the porous cup (Coors No. 700) surrounding the anode and could be isolated by decanting the solvent and stored at 0° as a moist solid. A saturated solution of $Co_2(SO_4)_3$ was used in the oxidation studies.

Oxidations.—A chilled solution of the oxidizing reagent was run into a solution (or slurry) of the sulfinic acid in 10 N H_2SO_4 (or 50:50 t-butyl alcohol–10 N H_2SO_4) until the blue-green color of Co^{III} persisted for 1 min. The mixture was immediately run into water and the insoluble disulfone was isolated and purified. The yields, melting points, spectral data, and sulfur analyses for several α-disulfones prepared by Co^{III} oxidation are reported in Table I. In each case the yield is that after one recrystallization from a suitable solvent, benzene for diaryldisulfones and either hexane or CH_2Cl_2 for dialkyldisulfones. Several of the substituted aromatic disulfones have not been reported before, but the analysis data, spectra, and method of preparation support the disulfone structure.[5-7]

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[3] W. A. Waters, *Quart. Rev.* (London), **12**, 277 (1958); R. Stewart, *J. Am. Chem. Soc.*, **79**, 3057 (1957).

[4] S. Swann, Jr., and T. Xanthakos, *ibid.*, **53**, 400 (1931).

[5] See ref 2a.

[6] P. Allen, Jr., and J. W. Brook, *J. Org. Chem.*, **27**, 1019 (1962).

[7] T. P. Hilditch, *J. Chem. Soc.*, **93**, 1526 (1908).

Stereospecific Formation of *cis*-Hydrindan *via* an Organoaluminum Cyclization Reaction[1a]

JOHN J. EISCH[1b] AND G. RONALD HUSK

Department of Chemistry, The Catholic University of America, Washington, D. C. 20017

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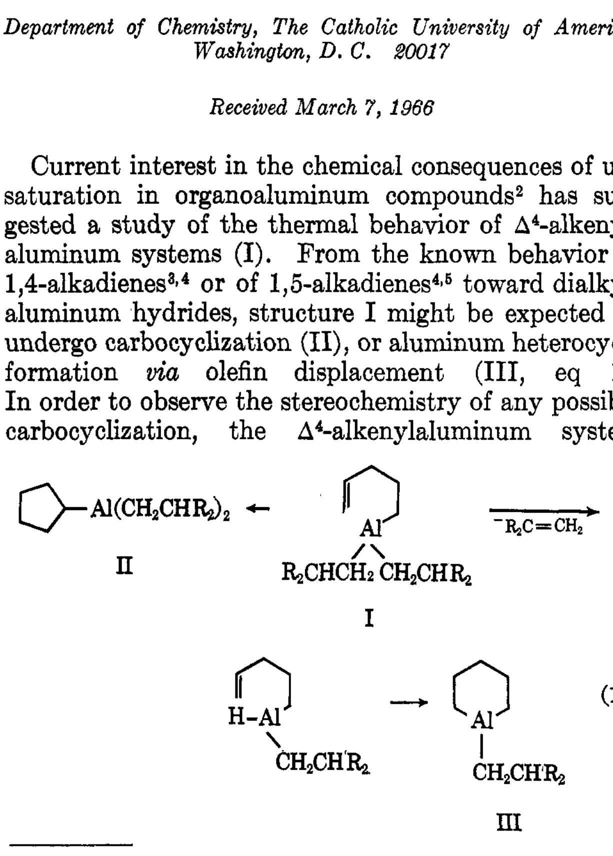
Current interest in the chemical consequences of unsaturation in organoaluminum compounds[2] has suggested a study of the thermal behavior of Δ^4-alkenylaluminum systems (I). From the known behavior of 1,4-alkadienes[3,4] or of 1,5-alkadienes[4,5] toward dialkylaluminum hydrides, structure I might be expected to undergo carbocyclization (II), or aluminum heterocycle formation *via* olefin displacement (III, eq 1). In order to observe the stereochemistry of any possible carbocyclization, the Δ^4-alkenylaluminum system



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[1] (a) Part VII of the series, "Organometallic Compounds of Group III." Previous paper: J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **88**, in press. (b) To whom inquiries should be addressed.

[2] J. J. Eisch, *Trans. N. Y. Acad. Sci.*, **27**, 450 (1965).

[3] R. Polster, *Ann. Chem.*, **654**, 20 (1962).

[4] G. Hata and A. Miyake, *J. Org. Chem.*, **28**, 3237 (1963).

[5] K. Ziegler in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p 234.