Anal. Calcd. for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74; O, 15.37. Found: C, 77.30; H, 7.88; O, 15.50.

Infrared absorption (KBr): 1833, 1760 cm.$^{-1}$ (anhydride).

1-Cyclooctylcyclooctene. This product was obtained according to the method described by Reppe *et al.*[5] in 66% yield. It had b.p. 135–140°/2 mm. The cyclooctene which was required as starting material was prepared in 70–80% yield by dehydration of cyclooctanol b.p. 120°/37 mm. with 85% phosphoric acid.[8] It had b.p. 142–146°.

1- or 2-Cyclooctylcycloocta-1,3-diene. A mixture of 1-cyclooctylcyclooctene (4.5 g.), *N*-bromosuccinimide (3.65 g.; 1 equiv.), and carbon tetrachloride (50 ml.) was refluxed for 15 min. The reaction was over in 10 min. The succinimide was filtered, the solvent was removed by distillation and collidine (25 ml.) was added. An immediate precipitation of collidine hydrobromide occurred. The mixture was refluxed for 2 hr. to ensure completion of the dehydrobromination. Filtration of the solution after cooling afforded crystalline collidine hydrobromide (3.8 g.; theory 4 g.). The residual collidine was removed in the usual way and the *diene* was distilled, b.p. 105–110°/0.2 mm. (3.5 g.). No adduct could be obtained from the diene with maleic anhydride.

Dimethyl 3,4,5,6-dicyclooctano-3,6-dihydrophthalate. A mixture of 1,1′-dicyclooctenyl (10.9 g.) and dimethyl acetylenedicarboxylate (7.1 g.) was heated on the steam bath for 8 hr. Trituration of an aliquot (1.5 g.) of the cooled reaction mixture with methanol gave the *ester* (1.2 g.; 80%), m.p. 115° (from methanol).

Anal. Calcd. for $C_{22}H_{32}O_4$: C, 73.30; H, 8.95; O, 17.75. Found: C, 72.66; H, 9.04; O, 17.90.

Infrared absorption ($CHCl_3$): broad band, 1710–1735 cm.$^{-1}$ (C=O of ester).

Saponification of the rest of the crude ester afforded the crude acid (15.3 g.), which after recrystallization from glacial acetic acid afforded the *dienic acid*, m.p. 205° (sintering at 200°).

Anal. Calcd. for $C_{20}H_{28}O_4$: C, 72.26; H, 8.49; O, 19.25. Found: C, 71.80; H, 8.07; O, 19.26.

Aromatization with 1 mole of NBS afforded the aromatic anhydride, m.p. 199–200°.

Reaction between 1,1′-dicyclooctenyl and p-benzoquinone. A mixture of the diene (40 g.; 2 equiv.) and *p*-benzoquinone (10 g.) was heated on the steam bath. After 30 min. of heating the liquid mass solidified. After an additional 1 hr. the mixture was again liquid and after one more hour it afforded a yellow crystalline mass. Methylcyclohexane was added and the pink solid (26 g.) was filtered. It formed needles, m.p. 186° (from wet benzene) and was phenolic. (Infrared band at 3330 cm.$^{-1}$). This is therefore *5,6,7,8-dicyclooctano-5,8-dihydronaphthalene-1,4-diol* in the form of its monohydrate.

Anal. Calcd. for $C_{22}H_{30}O_2 \cdot H_2O$: C, 76.70; H, 9.36; O, 13.93. Found: C, 77.11; H, 9.63; O, 13.99.

The solvent was removed from the mother liquor, a small amount of 2-propanol was added, and the solution was refrigerated. The yellow solid was filtered (2 g.) and had m.p. 252° (from dioxane). Infrared absorption ($CHCl_3$): 1710 cm.$^{-1}$ (satd. C=O). This is *1,2,3,4,5,6,7,8-tetracyclooctano-1,4,4a,5,8,8a,9a,10a-octahydro-9,10-anthraquinone.*

Anal. Calcd. for $C_{38}H_{56}O_2$: C, 83.77; H, 10.36. Found: C, 83.09; H, 10.16.

1,2,3,4-Dicyclooctano-1,4,4a,9a-tetrahydro-9,10-anthraquinone. A mixture of the diene (24 g.) and 1,4-naphthoquinone (17.5 g.) was heated on the steam bath for 1 hr. and afforded a brown glassy mass. Trituration with methylcyclohexane afforded a tan solid which was filtered (32 g.; 72%). The dark brown mother liquor deposited a further crop of large transparent rhombs (8 g.). The *diketone* had m.p. 155° (from methylcyclohexane or isopropanol). Infrared absorption (KBr): 1695 cm.$^{-1}$ (C=O adjacent to aromatic ring).

Anal. Calcd. for $C_{26}H_{32}O_2$: C, 82.93; H, 8.57; O, 8.50. Found: C, 82.37; H, 8.57; O, 8.85.

1,1′-Dicyclohexenyl (Ib). (Experiment carried out by M. Berdichev). The pinacol from cyclohexanone was prepared in the usual way.[2] Dehydration with phosphorus oxychloride in pyridine as described for the various pinacol homologs afforded the *diene*, b.p. 70–76°/0.05 mm. (95% yield).

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(8) *Cf. Org. Syntheses*, **Coll. Vol. II**, 152 (1943).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Reactions of Aromatic Sulfonyl Chlorides with Organocadmium Reagents*,[1]

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Aromatic sulfonyl chlorides react with diarylcadmium reagents to form simple or mixed aryl sulfones in fair yields; sulfinic acids and aryl halides are by-products. Aromatic sulfonyl chlorides react with dialkylcadmium reagents to yield alkyl chlorides and solid products; the latter react with hydrochloric acid to form arylsulfinic acids, and with nitric acid to give *N,N*-bis(arenesulfonyl)hydroxylamines.

The interaction of organocadmium reagents with acyl chlorides is an accepted method for preparation of ketones.[3] By analogy, the interaction of the cadmium reagents with sulfonyl chlorides might well be expected to yield sulfones. This reaction, if successful, might become the method of choice for production of mixed sulfones, RSO_2R'.

There appears to be but one published reference to the interaction of a sulfonyl chloride with an organocadmium compound, namely, that of Gilman and Nelson.[4] They reported that from 0.3 mole of benzenesulfonyl chloride and diphenylcadmium (prepared from 0.34 mole of phenylmagnesium bromide and 0.17 mole of anhydrous cadmium chloride), and subsequent acidification of the reac-

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(3) (*a*) J. Cason, *Chem. Revs.*, **40,** 15 (1947). (*b*) D. A. Shirley, *Org. Reactions*, VIII, 28 (1954).

(4) H. Gilman and J. F. Nelson, *Rec. trav. chim.*, **55,** 518 (1936).

TABLE I

PRODUCTS OF INTERACTION OF ARYLSULFONYL CHLORIDES AND ARYLCADMIUM REAGENTS

Reactants		Sulfone		Arylsulfinic Acid	
R—SO_2Cl	$R_2'Cd$	R—SO_2—R′		R—SO_2H	
R—	R′—	Yield, %	M.p., °C.	Yield, %	M.p., °C.
—C_6H_5	C_6H_5—	46	122–123[a]	25[b]	—
—$C_6H_4CH_3$-*p*	C_6H_5—	41	124.5–125.0[c]	8.5	88–90[d]
—$C_6H_3(CH_3)_2$-2,5	C_6H_5—	42[e]	108.0–110.5	12.7	82–84[f]
—$C_6H_3Cl_2$-2,5	C_6H_5—	31	144–146[g]	43	120–123[h]
—$C_6H_3Cl_2$-3,4	C_6H_5—	36	121.5–122.5[i]	45	95–97[j]
$C_{10}H_7$-2	C_6H_5—	30	114.5–115.5[k]	3.1	101–104[l]
C_6H_5	C_6H_4Cl-4	60.5	90.5–91.5[m]		
C_6H_5—	$CH_3OC_6H_4$-4	[n]	(m.p. of *p,p′*-dianisyl)[n]		

[a] H. Berckurtz and R. Otto [*Ber.*, **11**, 2066 (1878)] reported m.p. 124°. [b] Identified as the ferric benzenesulfinate. [c] A. Michael and A. Adair [*Ber.*, **11**, 116 (1878)] reported m.p. 124.5°. [d] E. Knoevenagel and J. Kenner [*Ber.*, **41**, 3318 (1908)]. [e] *Anal.* Calcd. for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.72. Found: C, 67.86; H, 5.61. [f] Ref. (*d*) reported m.p. 84–85°. [g] J. Huismann (Ger. Pat. **701,954**) [*Chem. Abstr.*, **36**, 98 (1942)] reported m.p. 146°. [h] S. Smiles and D. T. Gibson [*J. Chem. Soc.*, **125**, 176 (1924)] reported m.p. 122°. [i] Ref. (*g*) reported m.p. 125°. [j] The *S*-benzylthiuronium derivative of 3,4-dichlorobenzenesulfinic acid was prepared, m.p. 180–182°. *Anal.* Calcd. for $C_{14}H_{14}Cl_2N_2O_2S$: N, 7.42. Found: N, 7.61; this derivative has been reported as melting at 170–171° by F. Kurzer and J. R. Powell, *J. Chem. Soc.*, 3730 (1952). [k] A. Michael and A. Adair [*Ber.*, **10**, 585 (1877)] reported m.p. 115.6°. [l] E. Gessner [*Ber.*, **9**, 1502 (1876)] reported m.p. 105°. [m] H. Meyer [*Ann.*, **433**, 327 (1923)] reported m.p. 93°. [n] A. Gillmeister [*Ber.*, **30**, 2849] reported m.p. 172° for *p,p′*-dianisyl; in this experiment was obtained a 73% yield of *p,p′*-dianisyl of m.p. 172°.

tion mixture, was obtained a 15% yield of diphenylsulfone and some benzenesulfinic acid.[4a]

In the present study, the results of Gilman and Nelson have been confirmed; a slightly better yield of sulfone resulted from "inverse addition" of the diphenylcadmium solution to benzenesulfonyl chloride. The latter procedure, however, is more time consuming, since filtration from the cadmium and magnesium halides is necessary in order to facilitate dropwise addition of the organocadmium reagent. Utilization of a twofold excess of diphenylcadmium results in a slightly higher yield of sulfone, but employment of boiling benzene, in place of ether, as a solvent was detrimental. This study was extended to include interaction of diphenylcadmium with other arylsulfonyl chlorides and to reaction between bis (4-chlorophenyl) cadmium and benzenesulfonyl chloride; in each case, the anticipated sulfone was the chief product formed (see Table I).

In an attempt to prepare 4-methoxyphenyl phenyl sulfone, it was found that, as Grignard[5] had stated, *p*-methoxyphenylmagnesium bromide is only slightly soluble in ether. The corresponding bis-(4-methoxyphenyl)cadmium appeared to be even less soluble than the Grignard reagent; because of the difficulty of filtering and assaying the organocadmium content of the nonhomogeneous mixture, therefore, the benzenesulfonyl chloride was added directly to the latter. After the reaction mixture was processed in the usual manner, the only product which could be isolated was *p*-*p*-bianisyl, obtained in 73% yield.

In sharp contrast to the successful preparations of diaryl sulfones was the failure to obtain any ethyl phenyl sulfone from interaction of diethylcadmium and benzenesulfonyl chloride under the conditions satisfactory for production of aryl sulfones. Although precipitation of solid material occurred, separation and subsequent hydrolysis of the latter under various conditions yielded no sulfone.

Decomposition of the solid reaction product, from interaction of a dialkylcadmium and an arylsulfonyl chloride, by treatment with hydrochloric acid or sulfuric acid permitted recovery of some of that sulfonic acid, together with some of the corresponding sulfinic acid. In one case, that most thoroughly investigated, much of the alkyl group was recovered as the alkyl chloride (not the bromide initially used). When decomposition of the addition product was accomplished with nitric acid, however, a wholly different product resulted. Thus, for example, the same product was obtained regardless of whether diethylcadmium or dipropylcadmium reacted with the sulfonyl chloride. The reaction product was shown to be *N,N*-bis(benzenesulfonyl) hydroxylamine, $(C_6H_5SO_2)_2NOH$.

The presence of sulfinic acid, in the mixture resulting from acidification of the solid reaction product derived from an arylsulfonyl chloride and a dialkylcadmium, suggests that it reacts with nitrous acid (derived from partial reduction of nitric acid by the organic matter present) to form the

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(4a) A Referee has called attention to the fact that the reaction of Grignard reagents with aromatic sulfonyl halides is a well known process for the preparation of certain sulfones in indifferent yields (see M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, 1954, Prentice-Hall, Inc., New York, pp. 1290–1294). It appears that use of diarylcadmiums is productive of better yields than is utilization of aryl Grignard reagents; seemingly, in two cases alkylmagnesium halides have produced sulfones, in contrast to the failure of dialkylcadmiums, but in these two cases no statement of yield is given.

(5) V. Grignard, E. Bellet and Ch. Courtot, *Ann. chim.*, (9) **4**, 28 (1915).

disulfonylhydroxylamine derivative in the usual manner. Such a series of events explains why the hydroxylamine derivatives are formed only under certain conditions falling in a narrow range of concentrations and temperatures.

It was instructive to study the interaction of benzenesulfonyl chloride and dihexylcadmium; again, treatment of the addition compound with nitric acid yielded *N*,*N*-bis(benzenesulfonyl)hydroxylamine, and the major portion of the hexyl group was recovered in the form of hexyl chloride. Decomposition with nitric acid of the reaction product between benzenesulfonyl chloride and diphenylcadmium likewise yielded *N*,*N*-bis(benzenesulfonyl)hydroxylamine. Finally, interaction of either diethylcadmium or dipropylcadmium with *p*-toluenesulfonyl chloride gave a product which reacted with nitric acid to produce *N*,*N*-bis(*p*-tolylsulfonyl)hydroxylamine.

EXPERIMENTAL

Preparation of organocadmium reagents. These were prepared in the usual manner[3a] by interaction of an ether solution of a Grignard reagent with anhydrous cadmium chloride. After a Gilman test for the Grignard reagent was found to be negative, the mixture was filtered, as rapidly as possible, through paper on a Buchner funnel and placed, in a well-stoppered container, in a refrigerator. After several hours, the clear amber solution could be decanted, from the grey sludge which had deposited, and was assayed before further use.

Preparation of aryl sulfones. Apparatus typical of use for Grignard reactions was employed. One hundred milliliters of 2*N* diphenylcadmium solution, diluted with anhydrous ether, was slowly dropped into a well-stirred solution of 0.2 mole of arylsulfonyl chloride; a somewhat gummy, white precipitate appeared. The addition of 100 ml. of 5*N* hydrochloric acid caused partial solution of the solid material. The two liquid phases were separated and the ether layer was washed with 10% sodium hydroxide solution; from the alkaline solution, after acidification, sulfinic acid was recoverable. The ether layer was concentrated and subjected to steam distillation; the residue contained most of the sulfone. Additional sulfone was recovered by working up the material which had not been dissolved by the acid. Certain data concerning the products of these reactions are listed in Table I.

Additional experiments were carried out in attempts to improve the yields of sulfones. For example, use of "inverse addition" of the filtered solution of diphenylcadmium reagent to the solution in ether of benzenesulfonyl chloride produced a slightly better (46% *vs.* 36%) yield of sulfone. However, the advantage of the slightly higher yield is offset by the time-consuming sequence of filtration from inorganic salts, subsequent period of standing in a refrigerator, and final decantation or filtration before assay of the cadmium reagent solution. Using a twofold excess of diphenylcadmium resulted in a small enhancement (4%) in yield. No improvement in yield resulted from replacement of the ether by means of benzene or anisole.

Interaction of benzenesulfonyl chloride and dialkylcadmiums. To one molar equivalent of benzenesulfonyl chloride was added 0.5 molar equivalent of filtered diethylcadmium in ether; the mixture formed a thick, white precipitate. The latter stood overnight before it was decomposed by treatment with 10% hydrochloric acid. The resulting slurry was filtered, the layers of the filtrate were separated, and the aqueous layer was extracted with chloroform. Evaporation of the ether and chloroform extracts yielded a very small amount of liquid, presumably benzenesulfonyl chloride. The solid, previously removed by filtration, was dried and triturated successively with dioxane, acetone, and hot benzene. Virtually no extractive material was thus recovered. The residual dry material, which contained carbon, hydrogen, chlorine, sulfur, and cadmium (and presumably oxygen), was set aside as Compound I.

Similar results were noted when other dialkylcadmium reagents reacted with benzenesulfonyl chloride. The solid products, similar to Compound I, represented between 87% and 118% of the sum of the weights of the reactants.

Compound I was insoluble in water, dilute alkali, and common organic solvents, but dissolved slowly in hot, dilute acids. The analytical data for chlorine (14.3%) and sulfur (21.2%) checked well with those calculated for $[(C_6H_5SO_2Cl)_2 \cdot (C_2H_5)_2Cd]$. The hydrolysis of this solid material by means of either warm hydrochloric acid or sulfuric acid (2–10%) resulted only in formation of solutions from which no organic matter could be obtained by organic solvent extraction. Concentration of the acidic solutions yielded crystalline material which decolorized potassium permanganate solution, and could be identified as benzenesulfinic acid.

To a solution of 100 ml. of water and 7.5 ml. of concentrated nitric acid, heated to 70–75°, was added 10 g. of Compound I (these concentrations and temperature are critical), followed immediately by 10 ml. of ethyl alcohol. The mixture was stirred vigorously for 5 min., while the temperature was maintained at 70–75°, then was chilled rapidly and placed in a refrigerator for 6–8 hr., when precipitation of crystals was virtually complete; yield, 2.5 g.; m.p. 85–107°. Purification was conveniently accomplished by solution in hot, 5% sodium hydroxide solution, with filtration and subsequent acidification and chilling. Final recrystallization from chloroform yielded material melting at 115–118° (dec.). The same product (Compound II) resulted from interaction of benzenesulfonyl chloride with dipropylcadmium with subsequent decomposition of the reaction product with nitric acid.

Anal. Calcd. for $C_{12}H_{11}NO_5S_2$: C, 46.00; H, 3.55; N, 4.47; S, 19.64. Found: C, 45.69; H, 3.44; N, 5.32; S, 20.46; analyses by Geller Microchemical Laboratory.

Similarly, a product [Compound III, of m.p. 124–126° (dec.)] was obtained by nitric acid treatment of the solid produced by interaction of *p*-toluenesulfonyl chloride with either diethylcadmium or dipropylcadmium.

Interaction of benzenesulfonyl chloride and dihexylcadmium. To 53 g. (0.3 mole) of benzenesulfonyl chloride, dissolved in 150 ml. of anhydrous ether, was added 250 ml. of 1.2*N* dihexylcadmium solution (0.15 mole of dihexylcadmium). The mixture was stirred for 1 hr., centrifuged, the white, solid material washed with ether and dried in a vacuum oven and dessicator. The ethereal solution was fractionated to give a heart-fraction of b.p. 133–135°; n_D^{20} 1.4215; d_4^{20} 0.884. The material contained chlorine, but not sulfur or bromine. This material was identified as hexyl chloride, despite the fact that hexyl bromide had been used initially. The highest boiling fraction was identified as benzenesulfonic acid by conversion into its amide.

The solid material, obtained by centrifugation, represented 84% of the combined weights of reactants, and, treated with warm nitric acid and alcohol, yielded a white crystalline solid of m.p. 119–121° (dec.); the melting point behavior was unchanged in mixture with Compound II.

Non-aqueous titration of Compound II in benzene with sodium methoxide, using thymol blue as indicator, showed an equivalent weight of 142. The compound was dissolved in excess standard sodium hydroxide solution and back-titrated with hydrochloric acid, using a Beckmann *p*H meter; at *p*H 7.3, the neutral equivalent was found to be 140, very strong buffering action was apparent in the *p*H region 3–4. The molecular weight was determined, ebulliometrically in anhydrous ether, to be 279–302. This compound readily reduced potassium permanganate to manganous ion in sodium hydroxide solution. From the solution resulting from oxidation in acetone solution could be recovered benzenesulfonate as the *S*-benzylthiuronium derivative. Compound II gave no positive test for the presence of a sulfhydryl group.

The physical properties and analytical composition found for Compound II were suggestive of those listed for *N*,*N*-bis(benzenesulfonyl)hydroxylamine.[6] The latter, therefore, was synthesized, according to the directions of Koenigs,[6] through interaction of sodium benzenesulfinate and sodium nitrate in hydrochloric acid solution; white crystals were obtained, which melted, alone or in mixture with Compound II, at 115–118° (dec.). The infrared absorption spectra of both samples were identical.

Formation of N,N-bis(benzenesulfonyl)hydroxylamine by treatment with nitric acid of the reaction product of diphenylcadmium and benzenesulfonyl chloride. It was of interest to demonstrate that this hydroxylamine derivative can result from use of an arylcadmium reagent as well as from dialkylcadmiums. To a solution of 3.8 g. (0.02 mole) of benzenesulfonyl chloride in anhydrous ether was added 10 ml. of 2.0*N* diphenylcadmium solution (0.01 mole diphenylcadmium). The precipitated solid was removed, washed with ether, and dried before being mixed at 70° with 100 ml. of water, 7.5 ml. of concd. nitric acid, and 10 ml. of ethyl alcohol. The mixture was stirred for 5 min. before being chilled; seemingly, much of the original product had not dissolved. Next day, the mixture was filtered, the solid was triturated with hot 5% sodium hydroxide solution and filtered; the filtrate was acidified and the precipitated material was removed, dried, and recrystallized from chloroform. The melting point of this sample, alone or in admixture with the authentic hydroxylamine derivative, was 115–117°.

Identity of Compound III [N,N-bis(p-tolylsulfonyl)-hydroxylamine]. This substance closely resembled Compound II in physical and chemical properties, and in composition.

Anal. Calcd. for $C_{14}H_{15}NO_2S$: C, 49.35; H, 4.41; N, 4.08; O, 23.41; S, 18.76. Found: C, 49.53; H, 4.60; N, 3.61; O, 23.73; S, 18.56, analyses by Huffman Microchemical Laboratory.

The infrared absorption spectrum of this tolyl derivative was quite similar to that of the lower homolog of established structure; the former, therefore, is formulated as *N*,*N*-bis-(*p*-tolylsulfonyl)hydroxylamine.

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[CONTRIBUTION FROM THE SCHERING CORP. AND THE UNIVERSITY OF GLASGOW]

11-Oxygenated Steroids. XVIII. Wagner-Meerwein Rearrangement of Some 17α-Hydroxysteroids*

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The rearrangements of pregnane-3α,11β,17α,20β-tetrol 3,20-diacetate and 5-pregnene-3β,17α,20β-triol 3,20-diacetate by the action of *p*-toluenesulfonic acid in acetic acid–acetic anhydride solution, to 18-nor-17β-methyl-17-iso-12-pregnene-3α,11β,20β-triol 3,11,20-triacetate and 18-nor-17β-methyl-17-iso-5,12-pregnadiene-3β,20β-diol 3,20-diacetate, respectively are described. Under the same conditions, pregnane-3α,17α,20β-triol-11-one 3,20-diacetate affords the unrearranged 3,17,-20-triacetate. The mechanism is discussed.

Subsequent to the discoveries that the tertiary 17α-hydroxyl group[2] and the 11β-hydroxyl group[3] can be acetylated with acetic anhydride in the presence of an acid catalyst, we had occasion to investigate the possibility of acetylating pregnane-3α,-11β, 17α, 20β-tetrol 3,20-diacetate[4] (I) in an acetic anhydride–acetic acid-*p*-toluenesulfonic acid system at room temperature. We found that two products were produced, II and III, yields of the former averaging about 60% and those of the latter about 10%.

The structure of III was readily apparent. Infrared examination revealed the absence of hydroxyl groups and the presence of intense acetate absorptions. The empirical formula derived from carbon-hydrogen analyses was consistent with the presence of four acetate groups. Treatment of III with excess lithium aluminum hydride afforded the parent tetrol IV,[4] identical with an authentic sample, and acetylation of IV with acetic anhydride in pyridine regenerated I.

The structure of II was considerably more complex. From the infrared absorption spectrum it was possible to decide that there was no hydroxyl present, that there were probably three acetate groups, and possibly a trisubstituted unsaturation. Carbon-hydrogen analyses were in reasonable accord with the formula $C_{27}H_{40}O_6$, which corresponded to three

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* This paper is a contribution in honor of Lyndon F. Small, former Editor of the Journal.

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