A.—A polymerization of 10% aqueous ethylenimine was conducted at room temperature with 5 mole % hydrochloric acid. After 3 days, conversion had reached 90%. The solution was evaporated, and the polymer was treated with excess benzoyl chloride and 10% sodium hydroxide. The polymer was refluxed with 10% sodium carbonate solution for 2 hr. to extract residual acids. It was dried and titrated in aqueous ethanol solution with hydrochloric acid. There was required 0.223 equiv./base mole ($C_9H_9NO$) to reduce the pH from 8.42 to 3.0. The ratio of secondary to tertiary amide by infrared measurement was 0.33.

*Anal.* Calcd. for $C_{29}H_{32}N_4O_3$, $C_6H_5CONHCH_2CH_2NCH_2CH_2N[C(O)C_6H_5]CH_2CH_2N[C(O)C_6H_5]CH_2CH_2$–: C, 71.9; H, 6.61; N, 11.57. Found: C, 69.30; H, 6.38; Cl, 1.21; N, 10.75.

B.—PEI benzamide sample B was prepared as C except that chloroform was present during benzoylation. The ratio of secondary to tertiary amide by infrared measurement was 0.51.

*Anal.* Found: C, 66.52; H, 6.41; Cl, 5.22; N, 8.93.

C.—Polyethylenimine was prepared by refluxing undiluted monomer and adding 0.5 mole % of 1.0 *N* hydrochloric acid. Polymerization was essentially complete in 2 hr. The acid was added slowly in dropwise fashion to prevent local overheating and runaway polymerization. A sample of the polyethylenimine was treated with excess benzoyl chloride and 10% sodium hydroxide solution with cooling to keep the temperature from rising above room temperature. The polymer was dissolved in chloroform, precipitated in pentane, and dried. A greater than 100% yield of tan powder was obtained. The polymer was heated as a melt with 10% sodium carbonate solution for several hours to extract residual benzoic and hydrochloric acid. On cooling and drying it could be again powdered.

*Anal.* Found: C, 70.9; H, 6.59; N, 11.89 (corrected for presence of 0.84% chloride).

The ratio of secondary to tertiary amide by infrared measurement was 0.43. An aqueous ethanol solution required 0.25 equiv./base mole ($C_9H_9NO$) of hydrochloric acid to reduce the pH from 7.85 to 3.0. (An additional 0.035 equiv. of base is presumed to have been present combined with HCl.) The polymer was then heated in alcoholic sodium hydroxide to hydrolyze any benzamide and after recovery the ratio of secondary to tertiary amide found to be 0.51.

**Molecular Weight Measurements of Polyethylenimine.**—Diffusion and sedimentation velocity constants were measured in a Spinco ultracentrifuge in ethanol solution at 30°, the former at low speed (Table X).

TABLE X

MOLECULAR WEIGHT AND VISCOSITY OF POLYETHYLENIMINE

$$M = \frac{RT}{1 - \bar{\nu}\rho}\frac{S_0}{D_0} = 9.202 \times 10^{10}\frac{S_0}{D_0}$$

$R = 8.316 \times 10^7$ $T = 303.2$

$\rho = 0.7809$ g./cc. $\bar{\nu} = 0.930$ cc./g.

$\rho$ = density of solvent; $\bar{\nu}$ = specific volume of polymer in solution

| Sample | $D_0 \times 10^7$ cm.$^2$ sec.$^{-1}$ | $S_0 \times 10^{13}$ svedbergs | $\overline{M}$ | Viscosity,[a] c.p.s. |
|---|---|---|---|---|
| *b* | 6.0 | 2.24 | 30,000 | 1.14 |
| *c* | 8.4 | 1.05 | 11,500 | 1.12 |

[a] Measured in 1% solution at pH 11. [b] A commercial polymer. [c] A laboratory sample made by refluxing 10 ml. of monomer, adding 1 ml. of 1 *N* HCl, and warming overnight on steam bath.

**Acknowledgment.**—The ultracentrifuge molecular weight measurements were made by Dr. H. W. McCormick, the analog and digital programming of the ethylenimine case was done by Dr. T. Chiu, kinetic treatment of the N-methylethylenimine case was due to Dr. J. Huff, and analog programming was due to C. E. Fahlgren (all of The Dow Chemical Company).

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# Reactions of *p*-Tolylsulfonylmethylmagnesium Bromide with α,β-Unsaturated Aldehydes and Ketones

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*p*-Tolylsulfonylmethylmagnesium bromide (II) reacted with crotonaldehyde, cinnamaldehyde, *trans*-4-phenyl-3-buten-2-one, benzalacetophenone, and 1,5-diphenyl-2,4-pentadienone, to give the 1,2-addition products in good to excellent yields. In this respect, the sulfonyl Grignard reagent behaved differently from conventional organomagnesium compounds which normally give large amounts of 1,4 products with α,β-unsaturated ketones. The presence of cuprous chloride did not affect the course of the reaction between II and benzalacetophenone. Alcohol products could be dehydrated to afford multiply unsaturated substances. The tertiary alcohols prepared from α,β-unsaturated ketones were extremely nonlabile toward derivative formation.

Grignard reagents of sulfones, typified by *p*-tolylsulfonylmethylmagnesium bromide (II), have been

$p$-$C_7H_7SO_2CH_2MgBr$
II

extensively studied by Field and co-workers.[2–8] Such reagents were found to behave in a manner resembling that of other Grignard reagents in their reactions with carbonyl compounds, nitriles, esters, isocyanates, and in alkylation reactions. Earlier workers had shown that α-halomagnesium derivatives of sulfones undergo acylation,[9–11] carbonation,[9,12] alkylation,[10] halogenolysis,[9,13] and hydrolysis.[9,13]

Our interest in the reactions of Grignard reagents of sulfones with α,β-unsaturated aldehydes and ketones was prompted by two considerations. The reactions were predicted to give rise to unsaturated alcohols and/or saturated ketones which are difficultly obtainable by other conceivable reactions. If indeed the hydroxy sulfones were obtained, they could presumably be converted to butadienes and other conjugate systems. Baliah and Shanmuganathan[14] have shown that methylsulfonylmethylmagnesium bromide and cinnamaldehyde react to give an unsaturated

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(1) This work was supported in part by National Science Foundation Grant GE 4064 (Undergraduate Research Participation).

(2) L. Field, *J. Am. Chem. Soc.*, **74**, 3919 (1952).

(3) L. Field and J. W. McFarland, *ibid.*, **75**, 5582 (1953).

(4) L. Field, *ibid.*, **78**, 92 (1956).

(5) L. Field, J. E. Lawson, and J. W. McFarland, *ibid.*, **78**, 4389 (1956).

(6) L. Field and R. D. Clark, *J. Org. Chem.*, **22**, 1129 (1957).

(7) L. Field, J. R. Holsten, and R. D. Clark, *J. Am. Chem. Soc.*, **81**, 2572 (1959).

(8) L. Field and E. T. Boyd, *J. Org. Chem.*, **26**, 1787 (1961).

(9) E. P. Kohler and H. A. Potter, *J. Am. Chem. Soc.*, **57**, 1316 (1935).

(10) E. P. Kohler and M. Tishler, *ibid.*, **57**, 217 (1935).

(11) E. P. Kohler and H. A. Potter, *ibid.*, **58**, 2166 (1936).

(12) H. Gilman and F. J. Webb, *ibid.*, **71**, 4062 (1949).

(13) W. M. Ziegler and R. Connor, *ibid.*, **62**, 2596 (1940).

(14) V. Baliah and S. Shanmuganathan, *J. Org. Chem.*, **23**, 1233 (1958).

alcohol which may be dehydrated to 1-(methylsulfonyl)-4-phenyl-1,3-butadiene.

It was also of interest to study the mode of addition to unsaturated carbonyl systems. Such a study would allow a comparison of sulfonyl Grignard reagents with typical Grignard reagents by measuring the amounts of 1,2- and 1,4-addition products. Field[7] concluded from alkylation studies that Grignard reagents of sulfones more closely resemble typical organomagnesium compounds than they do carbanion salts, but are less nucleophilic than typical Grignard reagents owing to the strong inductive effect of the sulfonyl group. It seems reasonable to assume that II would have greater ionic character than a Grignard reagent such as phenylmagnesium bromide.

The factors which determine the ratio of 1,2- to 1,4-addition of Grignard reagents to $\alpha,\beta$-unsaturated carbonyl compounds are undoubtedly many and complex.[15-17] Although the amount of previous investigation in this area has been impressively great, few studies have been carried out to compare different organometallics in their reactions with a given substrate. Further complicating the problem is the fact that in many of the earlier studies only one product was reported and that not always in high yield.

Crotonaldehyde in its reactions with Grignard reagents gives predominantly 1,2-addition, phenylmagnesium bromide having been reported to give 70–90% of 1,2-addition and only traces of 1,4-addition along with condensation.[18] In like manner, cinnamaldehyde gives primarily reaction at the carbonyl and very little conjugate addition.[14,19]

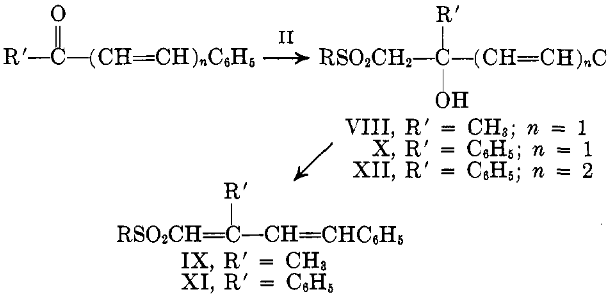
*p*-Tolylsulfonylmethylmagnesium bromide (II) added to crotonaldehyde to give an excellent yield (90%) of carbonyl addition product, 1-(*p*-tolylsulfonyl)-2-hydroxy-3-pentene (III), characterized by its benzoate IV.

$$\underset{\text{I}}{RSO_2CH_3} \xrightarrow{C_2H_5MgBr} \underset{\text{II}}{RSO_2CH_2MgBr} \xrightarrow[R' = CH_3,\ C_6H_5]{R'CH{=}CHCHO}$$

$$\underset{\substack{\text{III, } R' = CH_3\\ \text{V, } R' = C_6H_5}}{RSO_2CH_2CHOHCH{=}CHR'} \longrightarrow \underset{\text{VII, } R' = C_6H_5}{RSO_2(CH{=}CH)_2R'}$$

II and cinnamaldehyde gave an almost quantitative yield (99.3%) of 1-(*p*-tolylsulfonyl)-2-hydroxy-4-phenyl-3-butene (V). The 1,2-addition product was converted to its acetate VI and also dehydrated by phosphoric acid to 1-(*p*-tolylsulfonyl)-4-phenyl-1,3-butadiene (VII). In both of the preceding reactions with unsaturated aldehydes, II behaved in all respects like typical organomagnesium compounds.

The close similarity of II to conventional organomagnesium compounds began to disappear in the reactions with $\alpha,\beta$-unsaturated ketones. 4-Phenyl-3-buten-2-one was shown by Kohler to give approximately a 3:2 ratio of 1,4- to 1,2-addition products with ethylmagnesium bromide[20] and 64.4% of 1,4-addition product with cyclohexylmagnesium bromide.[21] Phenylmagnesium bromide apparently gave both types of addition but in low yields.[20] Recently, House and co-workers obtained a preponderance of 1,2-addition with methyl- and phenylmagnesium reagents but largely conjugate addition with the ethyl reagent. The addition of *trans*-4-phenyl-3-buten-2-one to a slurry of II afforded 66.8% of the 1,2-product, 1-(*p*-tolylsulfonyl)-2-hydroxy-2-methyl-4-phenyl-3-butene (VIII). Although VIII could be isolated in pure form, it slowly underwent decomposition on standing in the laboratory. This most likely involved dehydration and subsequent polymerization of the diene. In support of this hypothesis was the fact that, if during isolation of the products the solvent was removed at atmospheric pressure rather than under reduced pressure, VIII was not obtained but a low yield (10.1%) of dehydrated product, 1-(*p*-tolylsulfonyl)-2-methyl-4-phenyl-1,3-butadiene (IX), along with oils and tars. VIII was characterized by dehydrating it directly to IX. All attempts to prepare customary derivatives of the hydroxy group failed; some dehydration was observed.



$$R'{-}\overset{\overset{O}{\|}}{C}{-}(CH{=}CH)_nC_6H_5 \xrightarrow{\text{II}} RSO_2CH_2{-}\overset{R'}{\underset{OH}{C}}{-}(CH{=}CH)_nC_6H_5$$

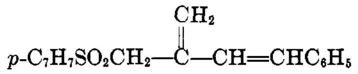
VIII, R' = $CH_3$; $n = 1$
X, R' = $C_6H_5$; $n = 1$
XII, R' = $C_6H_5$; $n = 2$

$$\swarrow$$

$$RSO_2CH{=}\overset{R'}{C}{-}CH{=}CHC_6H_5$$

IX, R' = $CH_3$
XI, R' = $C_6H_5$

The dehydrated product IX presented not only the possibility of various geometrical isomers but also the possibility of two structural isomers, IX and IXa.



$$p\text{-}C_7H_7SO_2CH_2{-}\overset{\overset{CH_2}{\|}}{C}{-}CH{=}CHC_6H_5$$

IXa

The activating influence of the sulfonyl group on the adjacent methylene hydrogens would have been expected to cause dehydration primarily to IX. That the product isolated in all instances was IX and not IXa was clearly demonstrated by the use of n.m.r. spectroscopy. The n.m.r. spectrum of IX showed a 3H singlet at $\tau$ 7.66 and another 3H singlet at 7.80, which could be assigned to the 2-methyl group and the ring methyl group, respectively.

The addition of organomagnesium derivatives to benzalacetophenone gives predominantly 1,4-addition products, phenylmagnesium bromide giving as high as 94% conjugate addition,[20,22] and methyl and ethyl reagents also affording largely 1,4-addition.[15] When phenyl derivatives of electropositive metals such as Ca, K, Na, and Li were used, however, the products were mainly from 1,2-addition.[23] In the reaction of II with benzalacetophenone no 1,4-addition product

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[15] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall Co., Inc., New York, N. Y., 1954, pp. 196–238.

[16] H. O. House, D. D. Traficante, and R. A. Evans, *J. Org. Chem.*, **28**, 348 (1963).

[17] J. Klein, *Tetrahedron*, **20**, 465 (1964).

[18] (a) H. Burton, *J. Chem. Soc.*, 455 (1929); (b) E. C. Coyner and G. A. Ropp, *J. Am. Chem. Soc.*, **69**, 2231 (1947); (c) P. G. Stevens, *ibid.*, **57**, 1112 (1935); (d) ref. 15, pp. 200, 201.

[19] (a) E. P. Kohler, *Am. Chem. J.*, **31**, 642 (1904); (b) K. N. Campbell and B. K. Campbell, *Proc. Indiana Acad. Sci.*, **50**, 87 (1940); (c) ref. 15, pp. 202, 203.

[20] E. P. Kohler, *Am. Chem. J.*, **38**, 511 (1907).

[21] E. P. Kohler and M. C. Burnley, *ibid.*, **43**, 412 (1910).

[22] (a) W. I. O'Sullivan, F. W. Swamer, W. J. Humphlett, and C. R. Hauser, *J. Org. Chem.*, **26**, 2306 (1961); (b) ref. 15, pp. 206, 207.

[23] H. Gilman and R. H. Kirby, *J. Am. Chem. Soc.*, **63**, 2046 (1941).

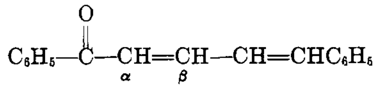
was isolated but an 81% yield of the 1,2-product, 1-(*p*-tolylsulfonyl)-2-hydroxy-2,4-diphenyl-3-butene (X).

Kharasch and Tawney[24] demonstrated that the presence of small amounts of cuprous chloride could cause methylmagnesium bromide to shift from 90.8% 1,2-addition to 82.5% 1,4-addition to isophorone. Similar inductions of 1,4-addition have been reported by Birch and Robinson,[25] Ruzicka and co-workers,[26] Stoll and Commarmont,[27] and by House.[16] In those cases where 1,4-addition has been induced, it might be postulated that the metal salts in some fashion polarized the carbon-to-carbon double bond, thereby making it more susceptible to attack. The additon of 1 mole % of cuprous chloride caused little, if any, change in the reaction of II and benzalacetophenone, a 75% yield of X being obtained.[28]

The unsaturated hydroxy sulfone X appeared to be considerably more stable than the alcohol VIII. X, like the other hydroxy sulfones prepared, may possibly exist in different stereoisomeric forms. Only one product was isolated, however, that melting at 144–145°.

X was dehydrated by both thionyl chloride and acetyl chloride to 1-(*p*-tolylsulfonyl)-2,4-diphenyl-1,3-butadiene (XI). The tertiary alcohol was inert toward derivatizing reagents including acetic anhydride, benzoyl chloride, and 3,5-dinitrobenzoyl chloride.

From a steric viewpoint alone, it would be difficult to predict the ratio of 1,2- to 1,4-addition in reactions involving benzalacetophenone since there is a phenyl group joining the β-carbon as well as a similar group joining the carbonyl carbon. It is realized, however, that stereochemistry and many other factors contribute to the activation energies for normal and conjugate addition and that the activation energies may be different for any particular Grignard reaction.[17] In the case of 1,5-diphenyl-2,4-pentadienone steric hindrance at the β-carbon should not be great and it might be expected that 1,4-addition would be favored over 1,2-



$$C_6H_5\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}\underset{\alpha}{CH}\text{=}\underset{\beta}{CH}\text{—}CH\text{=}CHC_6H_5$$

or 1,6-addition. The limited study of this unsaturated ketone with ethyl, phenyl, and benzyl Grignard reagents does indicate that 1,4-addition predominates.[29] It was, therefore, surprising to find that II added to the ketone to afford 80.4% of the 1,2-product, 1-(*p*-tolylsulfonyl)-2-hydroxy-2,6-diphenyl-3,5-hexadiene (XII).

XII, like the other tertiary alcohols prepared, reacted with neither acetic anhydride nor benzoyl chloride. The tertiary sulfonyl alcohols appear to be even less reactive toward derivatizing agents than are the simpler tertiary alcohols.

All of the results obtained indicate that II shows great preference for 1,2- over 1,4-addition. Exactly what this means mechanistically is difficult to assess since the mechanism for neither normal nor conjugate addition of organometallic compounds to unsaturated aldehydes and ketones is known. Cyclic transition states have been proposed for both reactions,[16,30–32] but the precise natures of such states are no better known than the nature of the organometallic substance itself.[33] At any rate, such cyclic transition states are highly improbable in reactions involving organometallics of the more electropositive metals because of the slight coordination capability of those metals. Active metal compounds give predominantly 1,2-addition,[23] suggesting that cyclic transition states are unnecessary for at least some normal additions and also suggesting that the ratio of 1,2- to 1,4-addition increases with decreasing ability of the metal to coordinate. That the magnesium of the sulfonyl Grignard reagent has less coordination capability than that of conventional Grignard reagents was shown by the nonsolvation of the reagent by ether.[4] This behavior was explained by the intermolecular association of Mg and $-SO_2-$ groups in the Grignard molecules. It is quite possible that sulfonyl Grignard reagents and organometallic compounds of the "active" metals undergo reactions involving a carbanion-type addition to the carbonyl carbon, but this remains to be established.

Identification of the sulfonyl alcohols consisted of elementary analyses, infrared absorption, n.m.r., and the preparation of derivatives and/or dehydration. Each of the alcohols showed infrared absorption in the region of 3550–3600 cm.$^{-1}$ and exhibited hydroxyl hydrogen peaks in the $\tau$ 5.0–5.5 region of the n.m.r. spectrum.

## Experimental

**Reactions of *p*-Tolylsulfonylmethylmagnesium Bromide (II).**—Methyl *p*-tolyl sulfone (I) was prepared from methyl iodide and sodium *p*-toluenesulfinate in 94.5% yield, m.p. 85.5–86.5°, by a procedure based on that of Otto.[34] *p*-Tolylsulfonylmethylmagnesium bromide (II) was prepared by adding a benzene solution of I to 5% excess of ethylmagnesium bromide in ether.[2,13] The sulfonyl Grignard reagent formed an insoluble, white slurry in the ether–benzene solvent system.

**A. With Crotonaldehyde.**—To a suspension of II, prepared from 12.75 g. (0.075 mole) of I, in ether–benzene, was added with stirring under nitrogen a solution of 5.39 g. (0.077 mole) of freshly distilled crotonaldehyde in 30 ml. of benzene during 10 min. There resulted from the slightly exothermic reaction a clear solution which was stirred at room temperature for an additional 4 hr. Hydrolysis was effected with 100 ml. of cold 1 *N* HCl solution and the organic extract was washed to neutrality with water and dried over anhydrous magnesium sulfate. Removal of solvent under reduced pressure gave an oil (17.53 g., 97.4%). Washing with petroleum ether (b.p. 30–60°) gave 16.2 g. (90%) of slightly oily 1-(*p*-tolylsulfonyl)-2-hydroxy-3-pentene (III), m.p. 40–44°. Recrystallization from 1:1 ether–petroleum ether afforded white needles with a constant melting point of 45.5–46.5°.

*Anal.* Calcd. for $C_{12}H_{16}O_3S$: C, 60.00; H, 6.67. Found: C, 59.84; H, 6.35.

The infrared spectrum of III showed characteristic O–H absorption at 3550 cm.$^{-1}$ and no carbonyl absorption.

The benzoate IV was prepared by heating 1.25 g. of III and 1.0 ml. of benzoyl chloride in 4.0 ml. of pyridine in a 100° oil

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[24] M. S. Kharasch and P. O. Tawney, *J. Am. Chem. Soc.*, **63**, 2308 (1941).

[25] A. J. Birch and R. Robinson, *J. Chem. Soc.*, 501 (1943).

[26] G. Buchi, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, **31**, 241 (1948).

[27] M. Stoll and A. Commarmont, *ibid.*, **31**, 554, (1948).

[28] See M. S. Kharasch and D. C. Sayles [*J. Am. Chem. Soc.*, **64**, 2972 (1942)] for another instance in which 1,4-addition was not induced.

[29] E. P. Kohler, *Ber.*, **38**, 1203 (1905).

[30] C. G. Swain and H. B. Boyles, *J. Am. Chem. Soc.*, **73**, 870 (1951).

[31] (a) R. E. Lutz and C. J. Kibler, *ibid.*, **62**, 360 (1940); (b) see also E. R. Alexander and G. R. Coraor, *ibid.*, **73**, 2721 (1951).

[32] C. G. Swain and L. Kent, *ibid.*, **72**, 518 (1950).

[33] For leading references, see D. O. Cowan, J. Hsu, and J. D. Roberts, *J. Org. Chem.*, **29**, 3688 (1964).

[34] R. Otto, *Ber.*, **18**, 161 (1885).

bath for 15 min.[35] Following the usual work-up procedure, 0.80 g. (44.7%) of solid was obtained, m.p. 70–72°. IV was recrystallized from ether–petroleum ether to a constant melting point of 72–73°.

*Anal.* Calcd. for $C_{19}H_{20}O_4S$: C, 66.27; H, 5.81; S, 9.30. Found: C, 66.05; H, 6.00; S, 9.32.

**B. With Cinnamaldehyde.**—Freshly distilled cinnamaldehyde (10.20 g., 0.077 mole) in 50 ml. of benzene was added during 20 min. to a slurry of II prepared from 12.75 g. (0.075 mole) of I. The resulting solution was stirred for 3.5 hr. at room temperature. Hydrolysis and isolation of the product as with III gave 17.37 g. (99.3%) of yellow solid, m.p. 60–63°. Recrystallization from 1:1 ether–petroleum ether gave 1-(*p*-tolylsulfonyl)-2-hydroxy-4-phenyl-3-butene (V) with a constant melting point of 77.5–79°.

*Anal.* Calcd. for $C_{17}H_{18}O_3S$: C, 67.55; H, 5.96; S, 10.66. Found: C, 67.77; H, 6.28; S, 10.66.

V showed O–H absorption at 3550 cm.$^{-1}$, but no carbonyl absorption.

The acetate of V was prepared by heating 1.0 g. of V, 2.0 ml. of dry pyridine, and 7.0 ml. of acetic anhydride at 90° for 15 min.[36] Pouring the mixture into ice–water produced 1.05 g. (92%) of white solid, m.p. 95–97°. Recrystallization from benzene–petroleum ether gave the acetate (VI) with a constant melting point of 97–99°.

*Anal.* Calcd. for $C_{19}H_{20}O_4S$: C, 66.27; H, 5.81; S, 9.30. Found: C, 65.96; H, 5.71; S, 9.22.

V was dehydrated using the procedure of Baliah and Shanmuganathan.[14] From 2.0 g. of V and 4.0 ml. of 85% phosphoric acid was obtained 1.76 g. (93.5%) of white solid, m.p. 103–133°. Recrystallization from ethanol gave 1-(*p*-tolylsulfonyl)-4-phenyl-1,3-butadiene (VII) with a constant melting point of 134–135.5°.

*Anal.* Calcd. for $C_{17}H_{16}O_2S$: C, 71.83; H, 5.63; S, 11.27. Found: C, 71.93; H, 5.90; S, 11.53.

**C. With *trans*-4-Phenyl-3-buten-2-one.**—A solution of 11.23 g. (0.077 mole) of *trans*-4-phenyl-3-buten-2-one in 30 ml. of benzene was added during 15 min. to II which was prepared from 12.75 g. (0.075 mole) of I. After the solution was stirred for 4 hr., hydrolysis and isolation produced 22.0 g. of semisolid. Crystallization from ether–petroleum ether afforded 13.48 g. (56.9%) of white solid, m.p. 89–91°. A second crop of crystals weighed 2.35 g. (9.9 %), m.p. 89–90°. Recrystallization from ethanol–water gave 1-(*p*-tolylsulfonyl)-2-hydroxy-2-methyl-4-phenyl-3-butene (VIII) with a constant melting point of 90–92°.

*Anal.* Calcd. for $C_{18}H_{20}O_3S$: C, 68.35; H, 6.33; S, 10.13. Found: C, 68.41; H, 6.45; S, 10.21.

The infrared spectrum of VIII contained O–H absorption at 3600 cm.$^{-1}$ and carbonyl absorption was absent.

In another attempt to prepare VIII, identical with the above except that the solvent was removed at atmospheric pressure rather than at approximately 25 mm., an oil which could not be crystallized was obtained along with 2.4 g. (10.1%) of a white solid melting at 153–160°. The solid (IX) was recrystallized from ethanol and from benzene to a constant melting point of 174–176°. The infrared spectrum showed the absence of O–H absorption and was consistent with the dehydrated product, 1-(*p*-tolylsulfonyl)-2-methyl-4-phenyl-1,3-butadiene. The n.m.r. spectrum showed a 3H singlet at $\tau$ 7.66 and another 3H singlet at $\tau$ 7.80 which could be assigned to the 2-methyl group and the ring methyl group, respectively.

*Anal.* Calcd. for $C_{18}H_{18}O_2S$: C, 72.48; H, 6.04; S, 10.74. Found: C, 72.34; H, 6.24; S, 11.08.

IX was prepared directly in 43.3% yield by mixing 1.0 g. of VIII, 2.5 ml. of dry pyridine, 6.0 ml. of benzene, and 1.0 ml. of thionyl chloride, and allowing the mixture to react at room temperature for 15 min., m.p. 156–172°. Recrystallization from ethanol produced material with a melting point of 173–175°, m.m.p. (with IX above) 173–175°.

An attempt to prepare the acetate by heating 1.0 g. of VIII with 4.0 ml. of acetic anhydride and 2.0 ml. of dry pyridine for 10 min. at 100°[36] gave starting material (0.99 g., 99%), m.p. 88–90°, m.m.p. (with VIII) 89–91°.

**D. With Benzalacetophenone.**—Benzalacetophenone (10.67 g., 0.0513 mole) in 20 ml. of benzene was added to a slurry of II prepared from 8.50 g. (0.050 mole) of I during 15 min. The mixture was stirred at ambient temperature for 4 hr. and hydrolyzed. A white precipitate formed during hydrolysis and was collected, weight 14.2 g. (75.1%), m.p. 138–140°. Recrystallization from ethanol gave 1-(*p*-tolylsulfonyl)-2-hydroxy-2,4-diphenyl-3-butene (X) with a constant melting point of 144–145°, showing infrared absorption at 3600 cm.$^{-1}$ but none in the carbonyl region.

An additional 1.11 g. (5.9%) of X was obtained by work-up of the reaction mixture, m.p. 132–136°. Recrystallization from ethanol gave needles with a constant melting point of 144–145°, which were identical by mixture melting point and infrared with X above.

*Anal.* Calcd. for $C_{23}H_{22}O_3S$: C, 73.02; H, 5.82; S, 8.47. Found: C, 73.23; H, 6.00; S, 8.35.

In a second experiment identical with the one above, except that 1 mole % of cuprous chloride was added to the sulfonyl Grignard reagent before the ketone was added, a 75% yield of X was obtained.

A third experiment using 16.02 g. (0.077 mole) of benzalacetophenone and the Grignard reagent from 12.75 g. (0.075 mole) of I gave 14.63 g. (51.6%) of precipitate of X during hydrolysis, m.p. 136–140°. When the organic portion of the filtrate was concentrated at atmospheric pressure, an oil resulted. Slurrying with ethanol produced 5.61 g. (20.7%) of white solid, m.p. 170–175°. Recrystallization from ethanol gave 1-(*p*-tolylsulfonyl)-2,4-diphenyl-1,3-butadiene (XI) with a constant melting point of 179.5–180.5°.

*Anal.* Calcd. for $C_{23}H_{20}O_2S$: C, 76.67; H, 5.56; S, 8.89. Found: C, 76.45; H, 5.88; S, 8.75.

X was converted to XI by a procedure based on that of Fuson and Bannister.[37] From 2.0 g. of X, 12.0 ml. of dry benzene, and 5.0 ml. of dry pyridine there was obtained 0.87 g. (45.5%) of white solid, m.p. 174–176°. Recrystallization from ethanol gave material with a constant melting point of 177–178°, m.m.p. (with XI prepared above) 177–179°.

XI was also prepared by heating 0.5 g. of X and 0.1 g. of acetyl chloride under reflux for 10 min. Upon addition of the mixture to ice–water, white crystals appeared, m.p. 157–160°. Recrystallization from ethanol gave solid with m.p. 178–180°, m.m.p. (with pure XI) 177–179°.

Starting alcohol was recovered from attempts to derivatize X with acetic anhydride, benzoyl chloride, or 3,5-dinitrobenzoyl chloride.[36]

**E. With 1,5-Diphenyl-2,4-pentadienone.**—A benzene solution of 18.04 g. (0.077 mole) of 1,5-diphenyl-2,4-pentadienone was added to II, prepared from 12.75 g. (0.075 mole) of I, during 20 min. After stirring at room temperature for 3.5 hr., subsequent hydrolysis gave 20.03 g. (66.1%) of precipitated 1-(*p*-tolylsulfonyl)-2-hydroxy-2,6-diphenyl-3,5-hexadiene (XII), m.p. 126–128°. Recrystallization from ethanol gave a product with a constant melting point of 127–128°. Work-up of the organic layer of the hydrolysis mixture gave another 4.32 g. (14.3%) of XII, m.p. 124–126°. After a sample had been in the laboratory for 1 year its melting point had dropped to 111–113°. Recrystallization from ethanol, however, raised the melting point to 127–128°. The infrared spectrum of XII showed O–H absorption at approximately 3600 cm.$^{-1}$ and no carbonyl band.

*Anal.* Calcd. for $C_{25}H_{24}O_3S$: C, 74.26; H, 5.94; S, 7.92. Found: C, 74.50; H, 6.23; S, 7.73.

The use of acetic anhydride and benzoyl chloride in efforts to prepare derivatives of XII[36] resulted in the recovery of starting material. Phosphoric acid (85%) and thionyl chloride caused considerable decomposition of XII. In each of the latter two cases a very small amount of solid was obtained which after many recrystallizations melted in the range of 170–175°. Infrared analyses showed the absence of O–H absorption, suggesting dehydrated product, but attempts at further purification have been unsuccessful. Each reaction produced considerable amounts of tar along with what appeared to be polymeric material.

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# The Reaction of Ammonia with Acylated Disaccharides. IV. The Structure of the 1,1-Bis(acetamido)-1-deoxyaldobiitols

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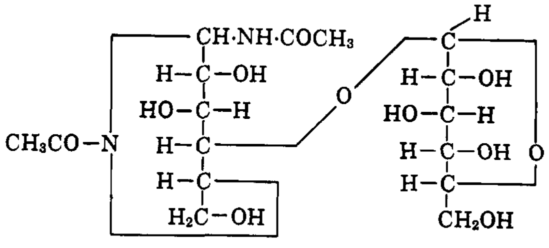
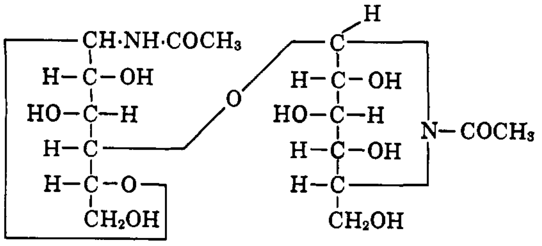
By means of methylation and hydrolysis techniques it was demonstrated that the 1,1-bis(acetamido)-1-deoxycellobiitol, the 1,1-bis(acetamido)-1-deoxylactitol, and the 1,1-bis(acetamido)-1-deoxymaltitol obtained by the reaction of ammonia upon the corresponding acetylated aldobioses have an acyclic structure in the nitrogenated moiety. The separation of a mixture of 2,3,5,6-tetra-*O*-methyl-D-glucose and 2,3,4,6-tetra-*O*-methyl-D-glucose by gas–liquid and by anion-exchange resin chromatographies is described.

The reaction of ammonia with acetylated disaccharides[1,2] afforded substances which possessed the structure of a disaccharide with two acetamide groups on C-1 and which can be designated as 1,1-bis(acetamide)-1-deoxyaldobiitols.[3]

Zechmeister and Tóth[4] described the reaction of liquid ammonia with octa-*O*-acetylcellobiose and isolated a 1,1-bis(acetamido)-1-deoxycellobiitol, for which they proposed the two possible structures I or II.

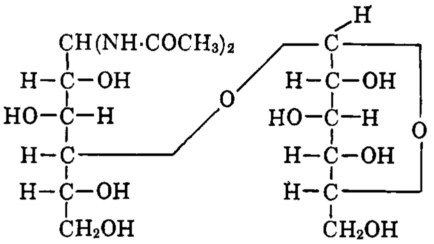


I



II

According to studies performed on the mechanism of this reaction,[5] which is intramolecular, the structure II would not be probable; the analytical data for structure I do not permit a clear distinction between such a structure and the acyclic one (III) which we proposed[1] for 1,1-bis(acetamido)-1-deoxycellobiitol.



III

This structure agrees with that already postulated for analogous monosaccharide derivatives.[6]

Similar open-chain structures were proposed for 1,1-bis(acetamido)-1-deoxymaltitol[2] and for 1,1-bis(acetamido)-1-deoxylactitol.[2] These substances can crystallize with solvent, and the analytical data depend on the drying conditions.

However, the possibility of a ring as shown in I cannot be excluded and recently a group of sugars has been described which bear a nitrogen atom on the hemiacetal ring, such as 5-acetamido-5-deoxy-D-ribopyranose,[7] 5-acetamido-5-deoxy-D-xylopyranose,[7,9] 5-acetamido-5-deoxy-L-arabinopyranose,[7,8] and 5-acetamido-5-deoxy-L-xylopyranose.[10] Although these substances have been obtained by a different path, a similar heterocyclic ring could be possible in I.

We clarified the structure of 1,1-bis(acetamido)-1-deoxycellobiitol, 1,1-bis(acetamido)-1-deoxylactitol, and 1,1-bis(acetamido)-1-deoxymaltitol through a methylation technique which confirmed the acyclic structure in the nitrogenated moiety of these disaccharides, represented by III for the former compound. The usual technique of methylation with dimethyl sulfate in alkaline solution[11] was inadequate for these substances because of their sensitivity to strong alkali. The technique of Kuhn and Baer[12] with methyl iodide and barium oxide in dimethylformamide does not present any difficulty, provided that certain soluble barium

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[3] These substances have been already designated as "aldobiosediamides" or as N,N′-diacylaldobiosylidenediamines, but the name given throughout the text as derivatives of the parent disaccharide alditol seems preferable, considering the acyclic structure of these substances.

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