acetone or alcohol resulted in recovery of 80–90% of the chloromethyl benzoate.

p-Tolylsulfonylcarbinyl p-Toluenesulfonate.—A solution of 19.7 g. of the carbinol I in 35 ml. of dry dioxane was slowly poured with cooling into 30 ml. of dioxane containing 9.5 g. of pyridine and 22.8 g. of p-toluenesulfonyl chloride. The mixture, after standing for ten days, was poured into water and an ether extract washed with aqueous sodium bicarbonate and water. The ether contained 17.24 g. (48%) of solid, m.p. 45–58°, which upon recrystallization from petroleum ether–benzene gave 1.01 g. (3%) of the presumed tosylate, m.p. 84–86°. Further recrystallization gave an unstable crystalline solid with a constant m.p. of 86–88°.

Anal. Calcd. for $C_{15}H_{16}O_5S_2$: S, 18.84. Found: S, 18.79.

The mother liquor yielded 11.9 g. (33%) of material which seemed to be the crude tosylate, m.p. 43–51°, undepressed by the analytically pure sample. Reduction with lithium aluminum hydride gave di-p-tolyl disulfide and p-thiocresol rather than methyl p-tolyl sulfone which reported reductions of tosylates to hydrocarbons[9] might lead one to expect.

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[9] J. Strating and H. J. Backer, *Rec. trav. chim.*, **69**, 638 (1950); H. Schmid and P. Karrer, *Helv. Chim. Acta*, **32**, 1371 (1949).

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Tetramethylthiophene and Tetramethylfuran

BY RUSSELL GAERTNER AND RICHARD G. TONKYN

In connection with an unsuccessful attempt to use a simple thiophene[1] as a diene in the Diels–Alder reaction,[2] useful syntheses for tetramethylthiophene (I) and tetramethylfuran (II) were developed.

2,5-Dimethylthiophene was chloromethylated to give 3,4-bis-(chloromethyl)-2,5-dimethylthiophene, which was reduced to I by lithium aluminum hydride. Maleic anhydride did not react with I, even in boiling nitrobenzene, but added to II at room temperature. The furan (II) was obtained by dehydration of 3,4-dimethyl-2,5-hexanedione with acetic anhydride and zinc chloride. Acetonylacetone was also converted to 2,5-dimethylfuran by these reagents[3] (71% yield).

Experimental[4]

3,4-Bis-(chloromethyl)-2,5-dimethylthiophene.—To a solution of 72.4 g. of s-trioxane in 75 ml. of concd. hydrochloric acid which had been saturated below 50° with hydrogen chloride was added dropwise and with stirring 30 g. of 2,5-dimethylthiophene. The blue mixture was stirred for two hours, diluted with three volumes of water, and extracted with ether and petroleum ether. The extracts were washed successively with dilute hydrochloric acid, water, 5% sodium bisulfite, water, and dilute sodium hydroxide. The solid obtained by evaporation of the solvents was recrystallized from hexane by cooling the solution in the refrigerator. Colorless needles (28 g., 50% yield) were obtained; m.p. 73°.

The twice recrystallized material was sublimed *in vacuo* before analysis; m.p. 73.0–73.4°.

Anal. Calcd. for $C_8H_{10}Cl_2S$: C, 45.94; H, 4.82. Found: C, 46.04; H, 4.86.

The product reacted immediately with alcoholic silver nitrate. It did not form a Grignard reagent in the "cyclic reactor"[5] as evidenced by the negative Gilman color test.[6]

Tetramethylthiophene (I).—Reduction[7] of 13 g. of the chloromethyl compound with 6.3 g. of lithium aluminum hydride yielded 5.8 g. (67%) of colorless I[8]; b.p. 74–79° (15 mm.); n^{20}_{D} 1.5199. An attempted low-pressure hydrogenation of the halide over platinum oxide and then 10% palladium-on-charcoal was unsuccessful; the recovered material in dioxane was reduced with stannous chloride[9] to give I in 54% yield. The action of phosphorus pentasulfide on 3,4-dimethyl-2,5-hexanedione[10] gave I in only 8% yield in a single small run. No product could be detected in mixtures of I with a tenfold excess of maleic anhydride in boiling benzene after four days or in boiling nitrobenzene after four hours.

Tetramethylfuran (II).—A mixture of 15 g. of 3,4-dimethyl-2,5-hexanedione,[10] 12 g. of acetic anhydride and 0.5 g. of anhydrous zinc chloride was heated under reflux for three hours after the initial exothermic reaction subsided. The mixture was made alkaline with 6 N sodium hydroxide and distilled with steam. The II[11] weighed 6.5 g. (49%); b.p. 145–148° (748 mm.); n^{20}_{D} 1.4550.

By a similar procedure, 114 g. of acetonylacetone, 112 g. of the anhydride and 1 g. of zinc chloride gave 69 g. (71%) of 2,5-dimethylfuran[12]; b.p. 92.5–94°; n^{20}_{D} 1.4470.

A yellow solution of 3 g. of II and 3.2 g. of maleic anhydride in 30 ml. of absolute ether was allowed to stand at room temperature overnight and then cooled at −15° for 24 hours. After being recrystallized from petroleum ether–ether, the yellow crystals gave white needles (3.2 g., 64%); m.p. 95–96°. They sublimed readily at 2 mm.; m.p. 95.8–96.6°.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 64.85; H, 6.35. Found: C, 65.00; H, 6.52.

The adduct, presumably tetramethyl-3,6-endoxotetrahydrophthalic anhydride, absorbed about a mole of hydrogen over platinum oxide.

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[1] Only highly arylated, fused thiophenes have been found to add maleic anhydride as do dienes; for a summary, see Kloetzel in Adams, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 36–37.

[2] Alkylated naphthalenes were reported by Kloetzel, *et al.*, THIS JOURNAL, **72**, 273, 1991 (1950), to add maleic anhydride across the 1- and 4-positions in the substituted ring; it seemed likely that a similar effect might operate in the thiophene series.

[3] The use of acetic anhydride in this dehydration is apparently novel and was suggested by the observation of Hurd, Roach and Edwards, *ibid.*, **66**, 2013 (1944), that ketene effects this conversion.

[4] Melting points are corrected; boiling points are not. Microanalyses were by Micro-Tech Laboratories, Skokie, Illinois. Properties of known compounds agreed satisfactorily with those in the listed references.

[5] Under similar conditions 2-thenyl chloride forms high yields of Grignard reagent: *cf.* Gaertner, THIS JOURNAL, **73**, 3934 (1951).

[6] Gilman and Schulze, *ibid.*, **47**, 2002 (1925); Gilman and Heck, *ibid.*, **52**, 4949 (1930).

[7] Johnson, Blizzard and Carhart, *ibid.*, **70**, 3664 (1948).

[8] Zelinsky, *Ber.*, **21**, 1835 (1888).

[9] Wood and Fieser, THIS JOURNAL, **62**, 2674 (1940).

[10] Moore, *J. Chem. Soc.*, 236 (1951).

[11] Willstätter and Clarke, *Ber.*, **47**, 308 (1914).

[12] v. Auwers, *Ann.*, **408**, 271 (1915).

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Streaming Birefringence in Aqueous Solutions of Poly-4-vinyl-n-butylpyridinium Bromide

BY RAYMOND M. FUOSS WITH RUDOLF SIGNER

Previous work[1] on polyelectrolytes suggests that the configuration of charged macromolecules is a function of the concentration: at moderate concentration, many counter ions are held in the vicinity of the polyion by electrostatic attraction, with the result that the net charge per macroion is small, and the latter can assume approximately the statistical coil configuration of a neutral polymer. On dilution, counter ions escape into the bulk of the solvent between polyions, thereby increasing the net charge, with the result that intramolecular repulsion causes the coil to expand, and in the limit of infinite dilution, to assume a rod-like configuration. Measurement of streaming bire-

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[1] R. M. Fuoss and G. I. Cathers, *J. Polymer Sci.*, **2**, 12 (1947); R. M. Fuoss and W. N. Maclay, *ibid.*, **6**, 305 (1951).