anol whereby 305 mg. of crystals was obtained, m. p. 97–104°. Repeated recrystallization from methanol–ether served to raise the melting point to 104–107°. Chromatography on alumina provided fractions eluted with petroleum ether, petroleum ether–benzene and benzene, which after recrystallization from methanol melted between 97° and 110° over a range of several degrees.

Anal. Calcd. for $C_{27}H_{44}O_2S_2$: C, 69.78; H, 9.54; S, 13.80. Calcd. for $C_{26}H_{38}O_2S$: C, 74.58; H, 9.51; S, 7.96. Found: C, 73.14; H, 9.37; S, 9.62.

5-Pregnen-3β-ol Acetate.—Two hundred milligrams of the above crystalline mixture (m. p. 104–107°) was dissolved in 20 ml. of absolute ethanol and after adding about 2 g. of Raney nickel prepared according to Mozingo, *et al.*,[8] was refluxed for five hours. The catalyst was filtered and washed several times with hot ethanol and then with acetone. The combined filtrate and washings were evaporated *in vacuo* and the residual oil was recrystallized from methanol or acetone affording 135 mg. (82%) of elongated prisms, m. p. 151–152°. This melting point was not depressed on mixing with an authentic sample of 5-pregnen-3β-ol acetate,[9] m. p. 147–149.5°; $[α]^{20}D$ −60° (*c*, 0.8 in chloroform).

Anal. Calcd. for $C_{23}H_{36}O_2$: C, 80.18; H, 10.53. Found: C, 80.60; 80.55; H, 10.16, 10.03.

The above acetate was saponified with methanolic potassium hydroxide to form 5-pregnen-3β-ol, m. p. 136–137°. The mixture with an authentic sample[9] (m. p. 133–134°) melted at 133–135°; $[α]^{20}D$ −57° (*c*, 0.95 in chloroform).

Anal. Calcd. for $C_{21}H_{34}O$: C, 83.39; H, 11.33. Found: C, 83.64; H, 11.31.

4-Pregnen-3-one.—Sixty-five milligrams of the above pregnenol was dried by evaporating a solution of this material in dry benzene and redissolved in 1.5 ml. of dry benzene. Dry acetone (0.75 ml.) and 75 mg. aluminum *t*-butylate were added and the mixture was heated in a sealed tube for twelve hours on the water-bath. After cooling, the mixture was dissolved in a large amount of ether and the solution was washed twice with 2 *N* hydrochloric acid, twice with 2 *N* sodium carbonate, three times with water, and dried over anhydrous sodium sulfate. After evaporation, the crystalline residue was purified by chromatography on alumina. Elution with mixtures of benzene–petroleum ether afforded 52 mg. of needles (80%), which after recrystallization from methanol melted at 96–98°. The 2,4-dinitrophenylhydrazone melted after recrystallization from ethanol 196–198°. Marker and Lawson[5] reported, respectively, 90° and 198°.

(9) This compound was obtained through the courtesy of Professor Fieser's laboratory.

WORCESTER FOUNDATION FOR
EXPERIMENTAL BIOLOGY
SHREWSBURY, MASS. RECEIVED DECEMBER 8, 1949

A New Preparation of 1,3-Dichloro-2,4,6-trinitrobenzene[1]

BY H. B. HASS,[2] H. FEUER AND A. A. HARBAN[3]

Boyer, Spencer and Wright[4] described the synthesis of 2,4,6-trinitrochlorobenzene by the reaction of phosgene on dry pyridinium picrate. The application of this technique for the synthesis of 1,3-dichloro-2,4,6-trinitrobenzene (chlo-

(1) Abstracted from a thesis by Arthur A. Harban, submitted to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1948.

(2) Present address: General Aniline and Film Corp., New York, N. Y.

(3) Present address: Standard Oil Company, Whiting, Ind.

(4) Boyer, Spencer and Wright *Can. J. Research,* **24B**, 200 (1946).

ropicryl chloride) was unsuccessful and resulted once in a violent detonation when the dry pyridinium salt of 2,4,6-trinitroresorcinol (styphnic acid) was treated with phosgene under elevated pressure. However, it was found that if phosgene was introduced into an acetone suspension of pyridinium styphnate, chloropicryl chloride was obtained in 70% yield. The effect of different experimental conditions on the conversion of pyridinium styphnate to chloropicryl chloride was observed. The highest yield was obtained when at least three moles of phosgene were used per mole of pyridinium styphnate. The solvent used exerted a profound influence on the reaction. When acetone or methyl ethyl ketone was used, good conversions could be obtained; however, no chloropicryl chloride was formed when dioxane or benzene was employed. The reaction was carried out in the temperature range 30–60° with good results; at higher temperatures the side reactions with phosgene and ketone solvents became excessive and it was difficult to isolate the chloropicryl chloride. The purification step involved the separation of chloropicryl chloride from a mixture containing acetone, pyridinium styphnate, pyridinium chloride, pyridinium chloropicrate (formed in the reaction) and the reaction product of acetone with phosgene.

In the course of the investigation it was found that pyridinium styphnate could be prepared containing either one or two moles of pyridine per mole of styphnic acid depending on the method of preparation. The salt containing two moles of pyridine is relatively unstable and loses pyridine on heating to form the more stable mono-pyridinium salt.[5]

Experimental

Preparation of 1,3-Dichloro-2,4,6-trinitrobenzene.—A suspension of 279.5 g. (0.86 mole) of pyridinium styphnate in two liters of acetone was prepared in a three-necked flask equipped with thermometer, stirrer and gas inlet tube. The mixture was heated to 35° and held at this temperature by cooling while 295 g. (2.97 moles) of phosgene was introduced over a period of 8.8 hours. The solution was allowed to come to 23° and stand for twenty-two hours. It was then placed in a separatory funnel attached to a flask of boiling water through which steam was passed. The solution was run into this flask at a rate such that the acetone solvent distilled over as fast as it was introduced. When all of the solvent had been stripped off in this manner, the residue in the flask was cooled and the crystalline material which had formed was filtered off and dried. This material was then leached with several portions of warm benzene. The residue from the benzene leaching process amounted to 26 g. containing a mixture of pyridinium styphnate and pyridinium chloropicrate. The benzene extract was evaporated to dryness to give chloropicryl chloride. This was further purified by recrystallization from a mixture containing equal parts of ethanol and chloroform. A total of 166.5 g. (68.5%) was obtained, m. p. 126.5–127°; lit. value[6] 128°.

The α-naphthylamine addition compound melted at 125–127°; lit. value[6] 125–127°. Treatment of chloropicryl chloride with gaseous ammonia in alcohol gave 2,4,6-

(5) Hoo, Mah and Sah, *Science Repts. Natl. Tsinghua Univ.,* **2**, 151 (1933).

(6) Sudborough and Picton, *J. Chem. Soc.,* **89**, 591 (1906).

trinitro-1,3-benzenediamine, m. p. 275–277°; lit. value 275°.[7]

Purification and Identification of the Pyridinium Salt of Chloropicric Acid.—The benzene-insoluble residue obtained in the preparation and purification of chloropicryl chloride was recrystallized from acetone and dissolved in a 1.5% sodium hydroxide solution. The deep red solution which resulted was distilled to dryness at reduced pressure. The distillate contained pyridine which was identified by the preparation of its styphnic acid salt. The residue in the flask was dissolved in 20 ml. of water and acidified with dilute sulfuric acid to give crystals which upon recrystallization from carbon tetrachloride melted at 113–113.5°; lit. value[6] 114°.

Anal. Calcd. for $C_6H_2O_7N_3Cl$: Cl, 13.45. Found: Cl, 13.30.

The identity with chloropicric acid was further ascertained by converting it with gaseous ammonia to 3-amino-2,4,6-trinitrophenol, m. p. 222–223° (cor.), lit. value[9] 219° (uncor.). The acidic portion of the original salt was therefore chloropicric acid, and the basic portion was pyridine. As a final check, the pyridinium salt of the material identified as chloropicric acid was prepared and it was found to melt at 159–161° and to give no melting point depression when mixed with the original material.

Preparation of Dipyridinium Styphnate.—To 50 g. (0.20 mole) of dry styphnic acid was added 200 g. (2.53 moles) of pyridine. The thick slurry which formed was stirred until the reaction was complete. The excess pyridine was filtered off and the yellow product was washed with ether. After drying, 77 g. (93.8%) of salt was obtained, m. p. 173–176°; neut. equiv. calcd. for $C_{16}H_{13}O_8N_5$ 201.6; found, 198.2. When the salt was heated at 60° for eight days, it was converted quantitatively into the monopyridinium styphnate.[10]

(7) Korner and Contardi, *Atti. acad. Lincei*, **17**, I, 473 (1908).

(8) Hodgson and Moore, *J. Chem. Soc.*, **127**, 1603 (1925).

(9) Blanksma, *Rec. trav. chim.*, **21**, 259 (1902).

(10) Financial support of this research was supplied by the United States Office of Naval Research.

DEPARTMENT OF CHEMISTRY
PURDUE RESEARCH FOUNDATION
PURDUE UNIVERSITY   RECEIVED NOVEMBER 16, 1949

Electric Moments of Isomeric Trifluoromethyl Styrenes

BY GERARD KRAUS AND ANTHONY B. CONCIATORI

The recent trend in plastics research toward the preparation of polymers with high softening points and great resistance to chemical changes at high temperatures has created considerable interest in monomers with large dipole moments.[1] In the course of a study of certain fluorine derivatives of styrene we have determined the electric moments of ortho-, meta- and para-trifluoromethylstyrene in benzene and *n*-heptane solution with the results listed in Table I.

TABLE I

Trifluoromethyl-styrene isomer	Moment (Debye units)		Calculated
	Solvent benzene	Solvent heptane	
Ortho	2.40	2.45	2.38
Meta	2.48	2.52	2.50
Para	2.44	..	2.42

In computing the moments the small atomic polarization was neglected. The values ob-

(1) Mark, *Chem. Eng. News*, **27**, 138 (1949).

tained from measurement in heptane solution are seen to be somewhat larger than those obtained with benzene as the solvent, the difference being of the same order of magnitude as found by Freiser and co-workers with other aromatic fluorine compounds.[2] Unfortunately the quantity of *p*-trifluoromethylstyrene available to us was too small to permit a reliable determination of its moment in *n*-heptane solution to be made.

The calculated values were obtained by vector addition using the data

Group moment of —CF_3 2.56[2]
Group moment of —$HC=CH_2$ 0.37[3]

The direction of the vinyl group moment was obtained from the dipole moments of para substituted styrenes by means of the well known expression

$$\cos \theta = \frac{\mu^2 - m_1^2 - m_2^2}{2m_1m_2} \tag{1}$$

From the data of Otto and Wenzke[3] on *p*-chlorostyrene, *p*-bromostyrene, *p*-methylstyrene and *p*-ethylstyrene θ was computed as 123°, 132°, 110° and 105°, respectively. In view of the small magnitude of the styrene moment the calculation is rather sensitive to small errors and the agreement must be regarded as satisfactory. In calculating the moments in Table I we have set θ equal to 117.5°, the average of the above values. The dipole moment of the para isomer is readily obtained from equation (1). Since free rotation about the bond between the vinyl group and the ring appears improbable on account of resonance, it seems most likely that the vinyl group is coplanar with the ring occupying either of two positions, which might be termed *cis*- and *trans*-. Assuming an even distribution of the molecules between the *cis*- and *trans*-forms leads to a calculated moment of 2.50D for the meta isomer. In *o*-trifluoromethylstyrene the proximity of the two negative groups would tend to favor the *trans*-form. In calculating its moment we have assumed this isomer to be entirely *trans*.

Otto and Wenzke[3] admit the possibility of their value of 0.37D for the dipole moment of styrene being too high, the true value being perhaps in the neighborhood of 0.2D. If this were the case the angle θ in equation (1) would have to equal very nearly 180° and the calculated moments for the trifluoromethyl styrenes would be: ortho, 2.62D; meta, 2.52D; para, 2.36D. Our results appear to favor the higher value for the electric moment of styrene.

Experimental

Apparatus.—The dielectric constant determinations were carried out by a resonance method with a probable error in ϵ of 0.08%. The electrical apparatus consisted of a voltage regulated power supply, an electron coupled oscillator, detector, and a direct current amplifier. The plate circuit of the oscillator was tuned to the second harmonic of the grid circuit so that the frequency of os-

(2) Freiser, Hobbs and Gross, THIS JOURNAL, **71**, 111 (1949).

(3) Otto and Wenzke, *ibid.*, **57**, 294 (1935).