

A red coloration was developed with aqueous and alcoholic ferric chloride solution.

5-Hydroxy-4-pyrone-2-methylisothiuronium Chloride.

—To a solution of 9.6 g. (0.06 mole) of chlorokojic acid in 100 ml. of absolute ethanol was added 4.6 g. (0.06 mole) of thiourea, and the mixture was refluxed with stirring for one and one-half hours, a crystalline precipitate forming after approximately fifteen minutes. The mixture was cooled to 15°, filtered, washed with anhydrous ether and recrystallized twice from ethanol to give 6 g. (49.3% yield) of a product melting at 155°.

Anal. Calcd. for $C_7H_7ClN_2O_5S$: N, 11.84. Found: N, 11.52.

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Syntheses from Acetoheterocycles

During a preliminary study on syntheses from 2-acetofuran, 2-acetothiophene and 2-acetopyridine, it was found desirable to prepare the pyruvic esters and glycidic esters derived therefrom. A search of the literature has revealed that only thenoylpyruvic ester¹ had been synthesized and investigated. It has been found possible to prepare the desired glycidates by the interaction of the appropriate ketone with ethyl bromoacetate in the presence of sodium ethoxide,² and the acyl pyruvates were made from the ketone and diethyl oxalate using the same condensing agent.

Experimental

Ethyl Furoylpyruvate.—The method of Darzens² was followed, with modifications as indicated below.

Anhydrous sodium ethoxide under toluene was prepared in the usual manner in a 500-ml. three-neck flask fitted with a sealed Hershberg stirrer, dropping funnel, thermometer and reflux condenser with drying tube, from 3.6 g. (0.16 mole) of sodium, 7.5 g. (0.16 mole) of anhydrous ethanol and 100 ml. of anhydrous toluene. The alkoxide suspension was chilled to 0° and a solution of 16.5 g. (0.15 mole) of 2-acetyl furan and 23.4 g. (0.16 mole) of diethyl oxalate in 50 ml. of anhydrous toluene was added at that temperature with vigorous stirring during thirty minutes. The heavy suspension was stirred at 0 + 5° for an additional hour and at room temperature for two hours. After filtration by suction, the precipitate was washed thoroughly with anhydrous ether, dissolved in cold water and acidified with glacial acetic acid. Extraction with ether, drying and removal of the solvent by distillation left a solid which, on several crystallizations from hexane, gave 10 g. (31.7% yield) of yellow crystals melting at 70°.³

*Anal.*⁴ Calcd. for $C_{10}H_{10}O_5$: C, 57.15; H, 4.80. Found: C, 56.69; H, 4.54.

Ethyl Nicotinoylpyruvate.—From 3-acetopyridine and diethyl oxalate as above, except that the aqueous solution, after acidification with glacial acetic acid, was brought to pH 7.1 with sodium carbonate solution before extraction with ether; m. p. 66°; 51% yield (recrystallized from hexane).

Anal. Calcd. for $C_{11}H_{11}NO_4$: C, 59.72; H, 5.08. Found: C, 59.81; H, 4.53.

Both new compounds gave red colorations with aqueous and alcoholic ferric chloride solutions.

Ethyl β -Methyl- β -(2'-thienyl)-glycidate.—Alcohol-free sodium ethoxide was prepared in the usual manner from 0.75 mole of sodium and 0.75 mole of anhydrous ethanol in 250 ml. of dry toluene.

To a 1000-ml. interjoint flask containing a sealed Hershberg stirrer, dropping funnel (drying tube) and reflux condenser (drying tube), was added 63 g. (0.5 mole) of 2-acetothiophene, 83.5 g. (0.53 mole) of ethyl bromoacetate and 250 ml. of anhydrous toluene. Stirring was initiated and the mixture was chilled to 0–5°. The sodium ethoxide suspended in toluene was added during five hours at that temperature and, after addition was complete, that temperature was maintained for an additional two hours. After standing overnight at room temperature, the mixture was poured into 500 ml. of ice and water with stirring, cautiously acidified with glacial acetic acid and separated. The aqueous layer was extracted with 100 ml. of toluene, which was then added to the initial toluene fraction. The combined organic layer was washed with dilute sodium bicarbonate solution, dried over sodium sulfate and fractionated to give 54 g. (51% yield) of a product boiling at 122–125° (2 mm.). A considerable amount of 2-acetothiophene was recovered in the forecut.

Anal. Calcd. for $C_{10}H_{12}O_3S$: C, 56.58; H, 5.75. Found: C, 56.30; H, 5.56.

Ethyl β -Methyl- β -(3'-pyridyl)-glycidate.—From 3-acetopyridine and ethyl bromoacetate as above. The acidified reaction mixture was brought to pH 7.1 with 10% sodium carbonate solution. The remainder of the procedure followed the directions above; yield, 30%; b. p. 110–112° (2 mm.).

Anal. Calcd. for $C_{11}H_{12}NO_3$: C, 63.75; H, 6.32. Found: C, 64.03; H, 6.02.

Ethyl β -Methyl- β -(2'-furyl)-glycidate.—From 2-acetofuran and ethyl bromoacetate; yield, 42.1%; b. p. 122–9° (2 mm.).

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.16. Found: C, 60.90; H, 6.21.

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6-Chloro-2-naphthylmethylcarbinol, 6-Chloro-2-vinylnaphthalene and Related Compounds

6-Chloro-2-naphthylmethylcarbinol.—6-Chloro-2-acetonaphthone (4.6 g., m. p. 81–82°) and 8 g. of aluminum isopropylate were boiled in 50 ml. of acetone for one and one-half hours. After hydrolysis, the product was taken up in ether, washed, dried and the solvent evaporated to leave 3.8 g. (82.5%) of white solid carbinol, m. p. 99–100.5°. Recrystallization from Skellysolve "F" raised the melting point to 101.8–102.2°.

Anal. Calcd. for $C_{12}H_{11}ClO$: C, 69.75; H, 5.35; Cl, 17.16. Found: C, 69.78; H, 5.31; Cl, 17.30.

The same product, obtained in 75–80% yield by reduction with lithium aluminum hydride, was purified by distillation, b. p. 135° (0.3 mm.).

The β -naphthylurethan, prepared in benzene solution, melted at 153–154°.

Anal. Calcd. for $C_{22}H_{17}ClNO_2$: C, 73.69; H, 4.57; N, 3.74; Cl, 9.46. Found: C, 73.66; H, 4.72; N, 3.86; Cl, 9.45.

6-Chloro-2-naphthylmethylcarbinyl Chloride.—The carbinol (20 g.), dissolved in 200 ml. of ether, was treated with 250 ml. of concentrated hydrochloric acid. A precipitate formed immediately, which was collected and recrystallized from Skellysolve "F" to give crops of crystals, totalling 22.7 g. (84%), melting from 79–81°. Two recrystallizations from the same solvent raised the melting point to 80.5–81.5°.

Anal. Calcd. for $C_{12}H_{10}Cl_2$: C, 64.02; H, 4.48. Found: C, 64.15; H, 4.44.

(1) Jacobs, Winstein, Ralls and Robson, *J. Org. Chem.*, **11**, 30 (1946).

(1) Angeli, *Gazz. chim. ital.*, **21**, 444 (1891).

(2) Darzens, *Compt. rend.*, **139**, 1215 (1904).

(3) Melting points were taken on a Fisher-Johns apparatus.

(4) Analyses by Oakwold Laboratories, Alexandria, Virginia.

6-Chloro-2-naphthylmethylcarbinyl Methyl Ether.—A solution of 10 g. of the carbinyl chloride and 40 g. of potassium hydroxide in 300 ml. of methanol was refluxed for two hours, poured into water, and most of the alcohol removed by distillation. On cooling, the oil (6.5 g., 77.5%) solidified and was then purified by distillation, b. p. 104° (0.5 mm.), 89.5–90.5° (0.11 mm.) and 87.0° (0.08 mm.); yield, 6.1 g. (72.7%), m. p. 37.5–40°. No suitable solvent for recrystallization was found, so a center cut from the distillation was analyzed.

Anal. Calcd. for $C_{18}H_{18}ClO$: C, 70.75; H, 5.94; Cl, 16.07. Found: C, 70.72; H, 5.98; Cl, 15.74.

6-Chloro-2-vinylnaphthalene.—A mixture of 3.3 g. of carbinol and 8 g. of potassium acid sulfate was heated under a pressure of 0.2 mm. A white solid sublimed at about 125°; yield, 2.8 g. (90%), m. p. 102–107°. Recrystalliza-

tion from Skellysolve "F" and then 95% ethanol raised the melting point to 111.5–112.6°.

Anal. Calcd. for $C_{12}H_9Cl$: C, 76.20; H, 5.11; Cl, 18.79. Found: C, 76.39; H, 4.81; Cl, 18.80.

The **dibromide**, prepared in cold chloroform solution and recrystallized from 95% ethanol, melted at 98–99°.

Anal. Calcd. for $C_{12}H_7Br_2Cl$: C, 41.36; H, 2.58; halogen, 58.35. Found: C, 41.77; H, 3.11; halogen, 58.52.

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COMMUNICATIONS TO THE EDITOR

FRIEDEL-CRAFTS COPOLYMERIZATION

Sir:

Copolymerization studies have been used extensively to elucidate the nature of the propagation step in free radical reactions. We have now obtained some data on copolymerizations induced by Friedel-Crafts catalysts. The systems investigated contained stannic chloride, carbon tetrachloride, and derivatives of styrene. In the systems styrene/*p*-chlorostyrene and α -methylstyrene/*p*-chlorostyrene, the over-all reaction rate was lower when more *p*-chlorostyrene was present. The proportion of *p*-chlorostyrene in the copolymer was lower than in the monomer mixture from which it was derived throughout the entire composition range.¹ The results obtained with styrene/*p*-chlorostyrene are summarized in Table I. These composition results were plotted, correction being made for the finite conversions, and were then fitted by the theoretical copolymer composition equation. The following monomer reactivity ratios were found: $r_1 = 2.7 \pm 0.3$, $r_2 = 0.35 \pm 0.05$. The corresponding figures for the free radical polymerization are $r_1 = 0.74$, $r_2 = 1.02$.² Thus, while *p*-chlorostyrene adds slightly faster than styrene to both styrene and *p*-chlorostyrene *free radicals*, the reverse is true with respect to *carbonium ion* addition. Experiments involving different catalyst concentrations yielded the same values of r_1 and r_2 , within experimental error.

Mayo and Lewis³ report that polymerization of styrene-methyl methacrylate mixtures with stannic chloride yields almost exclusively polystyrene. Experiments with α -methylstyrene/*p*-

TABLE I
COPOLYMERIZATION OF STYRENE (M_1) AND *p*-CHLORO-
STYRENE (M_2) IN CARBON TETRACHLORIDE AT 32°^a

Monomer concn. moles/l.	Time, hr.	Con- ver- sion, % ^b	Ap- prox. rate ^c	M_2^d	Cl in poly- mer, %	m_2^e
1.864	5.1	48.3	8.5	9.08	1.86	5.56
1.798	1.8	19.66	3.71	11.3
1.709	2.4	12.2	5.2	39.27	7.03	22.2
1.501	7.0	50.00	9.70	31.4
1.663	5.1	24.1	4.7	49.89	9.97	32.4
1.605	7.4	60.63	12.39	41.35
1.615	5.1	17.1	3.4	60.70	12.40	41.35
1.543	3.8	16.9	4.5	69.33	14.13	48.1
1.505	7.3	13.6	1.9	84.16	19.43	70.3
1.484	5.6	20.5	1.9	89.21	20.39	74.6
1.555	0.4	7.6	19.0 ^f	100.00	25.41	99.0

^a The experiments were carried out in reaction cells sealed at 1 mm. pressure. All solutions contained 2% by weight $SnCl_4$ on the monomers. ^b By bromine addition to residual monomers. Both styrene and *p*-chlorostyrene add Br_2 quantitatively. ^c % conversion divided by time of experiment. ^d M_2 = mole % *p*-chlorostyrene in monomer mixture. ^e m_2 = mole % *p*-chlorostyrene in copolymer. ^f A mixture of nitrobenzene-carbon tetrachloride was used as solvent in this experiment.

chlorostyrene by the authors and by Mr. L. Arond indicated that α -methylstyrene is even more reactive with carbonium ions than is styrene. The order of reactivity with carbonium ions thus seems to be α -methylstyrene > styrene > *p*-chlorostyrene > 2,5-dichlorostyrene and methyl methacrylate.

Our interpretation of these results involves as a dominant factor the polarization of the double bond by substituents. Introduction of (electron-withdrawing) chlorine atoms into the benzene ring of styrene reduces the reactivity of the double bond for carbonium ions. Introduction of the electron-donating methyl group in the α -position *increases* the reactivity with carbonium ions. The low reactivity of methyl methacrylate can be

(1) Mr. J. Stewart of Standard Oil Co. of N. J. obtains similar results with styrene/2,5-dichlorostyrene; apparently 2,5-dichlorostyrene is even *less* reactive than *p*-chlorostyrene (private communication).

(2) C. Walling, E. R. Briggs, K. S. Wolfstirn and F. R. Mayo, *THIS JOURNAL*, **70**, 1537 (1948).

(3) F. R. Mayo and F. M. Lewis, *THIS JOURNAL*, **66**, 1594 (1944).