From 55 g. of the aldehyde and 65 g. of malonic acid in 75 cc. of pyridine and 1 cc. of piperidine there was obtained after sixteen hours of heating on the steam-bath and acidification with 20% hydrochloric acid, 71.3 g. (99% yield) of *p*-methoxycinnamic acid, m. p. 171.6-173.2°, clearing at 188-189.5°. This substance is known to form liquid crystals on melting; reported m. p. 170[8] and 186°.[9] Hydrogenation of this acid (35.6 g.) in glacial acetic acid (200 cc.) over Adams catalyst (0.1 g.) gave a quantitative yield (36.0 g.) of crude β-*p*-methoxyphenylpropionic acid, m. p. 100-104°. For the cyclizations it was found desirable to recrystallize this product three times from alcohol, giving material melting at 103.5-104° (reported m. p. 104°[10]).

Cyclization with Hydrogen Fluoride.—A solution of 3.04 g. of β-*p*-methoxyphenylpropionic acid in about 100 cc. of anhydrous hydrogen fluoride was allowed to stand in a platinum vessel overnight. The material which remained was dissolved in ether, washed with water and then with 5% sodium bicarbonate solution. Acidification of the bicarbonate washings afforded 2.86 g. (94% recovery) of unchanged acid I, m. p. 103-104°. The neutral material amounted to 81 mg. (3% yield) of colorless 6-methoxyhydrindone-1, m. p. 105-108°. The ketone crystallized from alcohol in the form of long needles, m. p. 108-109° (reported, 109°[2,11]).

When 4.01 g. of the acid I was treated as described above except that the reaction mixture was allowed to remain in a closed copper bomb for five days, the yield of ketone II was 1.31 g. (36%), m. p. 106-107.5°. The uncyclized acid amounted to 2.30 g. (57% recovery), m. p. 102-103°

Cyclization by the Friedel-Crafts Method.—Three grams of β-*p*-methoxyphenylpropionic acid and 3.64 g. of phosphorus pentachloride were mixed with shaking in a 50-cc. Claisen flask. The mixture melted and hydrogen chloride was evolved. After the initial reaction, the volatile phosphorus compounds were removed at the water pump by heating the flask in an oil-bath at 80-90°. The almost colorless acid chloride was then transferred with the aid of 70 cc. of dry, thiophene free benzene into a flame-dried, three-necked 500-cc. flask fitted with a calcium chloride tube, a Hershberg stirrer and a rubber-tubed addition flask[12] containing 2.33 g. of fresh aluminum chloride. The solution was chilled (ice-bath) just to the solidification point and the aluminum chloride was added in portions over a period of ten to fifteen minutes. After stirring for three and one-half hours at room temperature the dark-red addition complex was decomposed with a mixture of ice and concentrated hydrochloric acid, and the mixture was worked up by extraction with ether and washing thoroughly with 2% potassium hydroxide solution containing salt to minimize emulsion formation. Evaporation of the dried (over anhydrous sodium sulfate) organic layer afforded 2.29 g. (85% yield) of colorless needles of 6-methoxyhydrindone-1, m. p. 103-105°. After recrystallization from alcohol the m. p. was 108-109°. The best recovery (about 94%) of pure material, m. p. 108-109°, was obtained by reduced pressure evaporative distillation of the crude ketone.

Acidification of the alkaline washings gave 130 mg. (4% recovery) of crude starting acid I.

When the reaction time was extended to twenty hours the yield of ketone, m. p. 104-106°, was 86%. When only one-half hour was allowed for the reaction the yield of neutral material dropped to 60%.

In one experiment the volatile phosphorus compounds were not removed. The neutral fraction obtained from 3.00 g. of I amounted to 1.86 g. (69% yield) of very crude dark semi-solid ketone, m. p. after drying on a porous plate, 105-106°. The recovered acid I amounted to 0.650 g. (22%), m. p. 99-101°.

An attempt to cyclize the acid chloride of I with stannic chloride gave a poor (about 10%) yield of crude ketone II.

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[8] Knoevenagel, *Ber.*, **31**, 2596 (1898).

[9] Bowden, "The Phase Rule and Phase Reactions," Macmillan and Co., London, 1938, p. 277.

[10] Barger and Walpole, *J. Chem. Soc.*, 1720 (1909).

[11] Ingold and Piggott, *ibid.*, 1469 (1923).

[12] Fieser, "Experiments in Organic Chemistry," 2nd. ed., D. C. Heath and Co., Boston, Mass., 1941, p. 311.

Reaction of Furfural Derivatives with Maleic Anhydride

BY WERNER HERZ

During an investigation of the behavior of some substituted furans toward maleic anhydride, products have been obtained in several instances which indicate that a series of reactions previously observed by La Parola[1] can be extended to derivatives of furfural. The latter isolated N-substituted maleamic acids from reaction mixtures containing maleic anhydride and certain Schiff bases. Corresponding substances, N-methylmaleamic acid, previously reported by Piutti and Giustiniani,[2] and N-*o*-chlorophenylmaleamic acid, were obtained by the author when furfurylidenemethylamine and furfurylidene-*o*-chloroaniline were treated with maleic anhydride. Addition of the anhydride to furfural phenylhydrazone, resulting in furfural 1-maleylphenylhydrazone and paralleling the addition to benzaldehyde phenylhydrazone reported by La Parola, was also noted.

Experimental[3]

N-Methylmaleamic Acid.—A solution of 20 g. of furfurylidenemethylamine in 150 ml. of ether was shaken with 25 g. of maleic anhydride, added in small portions. A heavy yellow precipitate was formed almost immediately with evolution of much heat. Two recrystallizations from a mixture of alcohol and ether gave 27 g. of white plates, m. p. 154°, five degrees higher than reported by Piutti and Giustiniani.[2] From hot glacial acetic acid, the product separates in the form of white needles. The crystals are soluble in water, dilute acid, acetic acid and hot ligroin, very soluble in dilute base and alcohol and only slightly soluble in ether, cold ligroin and carbon tetrachloride. Upon boiling with concd. sodium hydroxide, the odor of methylamine becomes noticeable.

Anal. Calcd. for $C_5H_7O_3N$: C, 46.51; H, 5.43; neut. equiv., 129. Found: C, 46.59; H, 5.42; neut. equiv., 128.

N-*o*-Chlorophenylmaleamic Acid.—To a solution of 6 g. of furfurylidene-*o*-chloroaniline in 25 ml. of ether was added 4 g. of maleic anhydride, with boiling until dissolved. Needles began to separate soon; after standing overnight, the crystal mass was separated by filtration and recrystallized twice from ether. Four grams of product, light-green needles, m. p. 132°, was obtained. The long needles are soluble in alcohol, hot water and dilute base, and partially soluble in ether. Upon boiling with strong sodium hydroxide, *o*-chloroaniline separates.

For purposes of comparison, the acid was also prepared by the method of Hurd, Roe and Williams.[4] One and eight-tenths grams of the product, m. p. 132°, was obtained from 1.5 g. of *o*-chloroaniline and 1.2 g. of maleic anhydride. A mixed melting point determination established the identity of the two substances.[5]

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[1] La Parola, *Gazz. chim. ital.*, **64**, 919 (1934); **65**, 624 (1935).

[2] Piutti and Giustiniani, *ibid.*, **26** I, 431 (1896).

[3] All melting points are uncorrected.

[4] Hurd, Roe and Williams, *J. Org. Chem.*, **2**, 314 (1937).

[5] Also prepared by the same method were the following unlisted compounds: N-*m*-chlorophenylmaleamic acid, light-green needles from alcohol, m. p. 187-188°; N-*p*-chlorophenylmaleamic acid, light-green needles from alcohol, m. p. 199°.

Anal. Calcd. for $C_{10}H_8O_3NCl$: C, 53.33; H, 3.56; neut. equiv., 225. Found: C, 53.30; H, 3.50; neut. equiv., 221.

Furfural 1-Maleylphenylhydrazone.—Four grams of maleic anhydride reacted with 6.5 g. of furfural phenylhydrazone in 35 ml. of ether. Yellow crystals appeared in a few hours. After two recrystallizations from a mixture of alcohol and ether the bright yellow needles, obtained in a yield of 7 g., soluble in alcohol, slightly soluble in water and insoluble in ether, have a melting point of 113–114°. The structure was confirmed by boiling with dilute base; furfural phenylhydrazone and fumaric acid were identified as decomposition products.

Anal. Calcd. for $C_{16}H_{12}O_4N_2$: C, 63.38; H, 4.22; neut. equiv., 284. Found: C, 63.41; H, 4.21; neut. equiv., 281.

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The Addition of Triarylmethyls to Monoölefins

BY C. S. MARVEL, JOSEPH DEC AND JAMES O. CORNER

The conjugate addition of triarylmethyls to systems such as butadiene, isoprene, and even maleic anhydride has been described by Conant and Scherp[1] and Conant and Chow.[2] We have found that tribiphenylmethyl and triphenylmethyl add to styrene and triphenylmethyl adds to vinyl acetate to give products composed of one molecule of olefin and two molecules of free radical. Thus, this addition reaction of triarylmethyls is not as restricted as was previously indicated.

It is of some interest to note that it is not easily possible to distinguish whether there is formed a compound made up of two styrene units and two triarylmethyl radicals or of one styrene unit and two triarylmethyl radicals because of the close similarity of the analyses of the two possible addition products and the high molecular weight of the triarylmethyl. To make certain of this point, *p*-chlorostyrene was used as the styrene nucleus and chlorine analysis of the product showed that two radicals combine with one olefin nucleus. To show the general character of the reaction, *m*-nitrostyrene was also used and the addition product was isolated in fair yields.

Vinyl acetate also adds triphenylmethyl but no reaction was observed with tribiphenylmethyl and stilbene, anthracene, 1-pentene, and *β*-methylstyrene. The same radical did react with cyclohexene, vinyl chloride and 1,1-diphenylethylene as evidenced by the disappearance of color in the reaction mixture. However, no identifiable products could be isolated from these reaction mixtures.

The exact structure of these addition products has not been established although it seems probable that they are formed by addition to the single double bond. It is conceivable that conjugate addition may have occurred in the styrenes with resultant substitution in the ring.

Experimental

Addition of Triarylmethyl Free Radicals to Vinyl Monomers.—In a 50-cc. distilling flask with the sidearm removed and the neck constricted were placed 0.01 mole of the triarylchloromethane, 0.02 mole of the freshly distilled vinyl monomer and 40 cc. of thiophene-free benzene. The solution was frozen by immersing the flask in an acetone–Dry Ice-bath. Molecular silver (0.04 mole) was then added and the flask was evacuated to a pressure of about 3 mm. and sealed. The flask was warmed to melt the benzene and was then placed on the mechanical shaker for an hour at the end of which time the color of the free radical had appeared. The flask was kept in the dark at 50° when tribiphenylmethyl was used and at room temperature when triphenylmethyl was used and was shaken occasionally. The color of the free radical disappeared in about a week. The flask was then opened and the solid was removed by filtration. The filtrates from five such flasks were combined, evaporated to a volume of 50 cc., diluted with 80 cc. of low boiling petroleum ether and chilled. The white crystals which separated were removed and recrystallized from benzene and low-boiling petroleum ether. Data on the products of several such reactions are shown in Table I.

TABLE I

ADDITION OF TRIARYLMETHYL FREE RADICALS TO VINYL MONOMERS

				Analyses, %					
				Calcd.[d]			Found		
Free radical	Vinyl monomer	Yield, %	M. p., °C.	C	H	Mol. wt.	C	H	Mol. wt.
Tribiphenylmethyl	Styrene	71	184–185.5	94.06	5.94	1046	93.60	5.97	1149,[b] 1198
Tribiphenylmethyl	*p*-Chlorostryene	97	196–198	91.03	5.69	1080 Cl, 3.28	90.62	5.81	1125[b] Cl, 3.26
Triphenylmethyl	Styrene	16	187–188[a]	93.56	6.44	590	93.37	6.63	590,[c] 611[c]
Triphenylmethyl	*p*-Chlorostyrene	32	185–186	88.39	5.92	Cl, 5.68	88.58	6.17	Cl, 5.50
Triphenylmethyl	*m*-Nitrostyrene	29	227–228[a]	86.93	5.83	N, 2.20	87.32	6.17	N, 2.57
Triphenylmethyl	Vinyl acetate	4	209–210[a]	88.11	6.29		87.59	6.12	

[a] Determined on Maquenne block. [b] Determined by ebullioscopic method in benzene. [c] Determined by ebullioscopic method in chloroform. [d] Calculated for the addition of two free radical units to one vinyl monomer unit.

Attempted Addition of Triarylmethyls to Other Unsaturated Compounds.—Reactions similar to those described above were carried out using tribiphenylmethyl and a variety of unsaturated compounds. The color of the free radical was discharged by vinyl chloride, 1,1-diphenylethylene, and cyclohexene after standing at 50° for two months but no well-defined products could be isolated. Ethyl acrylate reacted in nine days to give a small amount of tribiphenylcarbinol as the only pure product. Stilbene, anthracene, 1-pentene and *β*-methylstyrene did not react with tribiphenylmethyl after standing at 50° for two months and at room temperature for two years.

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[1] Conant and Scherp, THIS JOURNAL, 53, 1941 (1931).

[2] Conant and Chow, *ibid.*, 55, 3475 (1933).