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 $C_{15}H_{12}O_4N_2$: 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

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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).