that melted at 160–161.5° after crystallization from benzene–ligroin.

Anal. Calcd. for $C_{24}H_{16}O_3$: C, 81.8; H. 4.6. Found: C, 81.7; H, 4.6.

2-Acetoxy-3,5,6-triphenylquinone, prepared from the hydroxyquinone with acetic anhydride and sulfuric acid, formed orange needles that melted at 185.5–187.5° after crystallization from acetic acid.

Anal. Calcd. for $C_{26}H_{18}O_4$: C, 79.2; H, 4 6. Found: C, 79.5; H, 4.5.

The acetate was readily saponified by alcoholic potassium hydroxide.

Summary

2,4,4-Triphenylcyclopentenedione-1,3 is readily alkylated by ethyl bromoacetate, and when the resulting diketoester is treated with sodium ethoxide it undergoes rearrangement to ethyl 3,4,6-triphenylgentisate. A number of transformations of this rearrangement product are described, including its conversion into triphenylhydroquinone and hydroxytriphenylquinone.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Polymerization of Styrene in the Presence of Nitrobenzene, 2,4-Dinitrochlorobenzene and Nitromethane

BY CHARLES C. PRICE AND DOROTHY ANN DURHAM

The few brief observations[1] that certain vinyl-type polymerizations are inhibited or retarded by various aromatic nitro compounds have attracted very little attention. There has been no direct experimental evidence as to the specific nature of the effect and no explanation has been suggested to account for this very interesting phenomenon.

Since the polymerizations which are subject to this effect of aromatic nitro compounds are those which proceed through an intermediate active free radical,[1c,2] there exists the possibility that the active radical may become inactivated by coupling with the aromatic nitro compound. The preparation of polystyrene in the presence of nitrobenzene and 2,4-dinitrochlorobenzene has confirmed this surmise since the samples contained the elements of the nitro compound in a ratio as high as the theoretical ratio of one nitroaryl residue per polymer molecule.

Several samples of polystyrene prepared in the presence of a small amount of 2,4-dinitrochlorobenzene contained chlorine (2.3 to 3.2%) and nitrogen (2.3 to 2.7%) corresponding to one dinitrochlorophenyl group per polymer molecule. A sample of polystyrene prepared in the presence of nitrobenzene contained nitrogen (0.53%) corresponding to one nitrophenyl group for every other polymer molecule.

Several other samples of polystyrene prepared in the presence of smaller amounts of these two nitro compounds also contained the elements of the nitro compound but in an appreciably smaller proportion than the maximum of one per polymer molecule. These results may be accounted for on the basis of competition between the reaction of the growing chain with retarder and the normal cessation process. The chance for normal cessation to occur would, of course, be favored by decreased concentration of the retarder.

The most logical and satisfactory manner to account for the destruction of the activity of the growing free radical polymer chain by reaction with a *molecule* is by a process which will transform the "active" radical into an "inactive" one[3]: the odd electron characteristic of the free radical may only be "neutralized" by pairing with the odd electron of another free radical.

On this basis, the observed coupling of the growing chain with aromatic nitro compounds must involve an intermediate addition compound in which the odd electron has become sufficiently stabilized so that it will no longer add to monomer molecules. Since coupling of free radicals with nitrobenzene takes place principally in the *para*-position, the over-all scheme for the benzoyl peroxide-catalyzed polymerization of styrene in the presence of nitrobenzene may be indicated as follows

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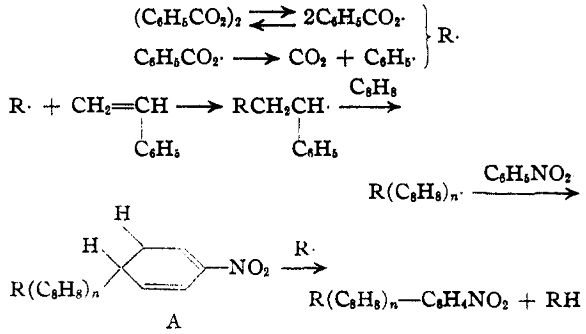
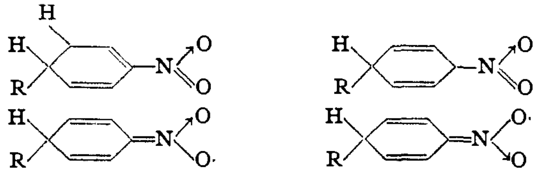
(1) (a) Ostromislensky and Shepard, U. S. Patent 1,550,323, August 18, 1925; (b) Foord, *J. Chem. Soc.*, 48 (1940); (c) Price, Kell and Krebs, THIS JOURNAL, **64**, 1103 (1942).

(2) Staudinger, *Trans. Faraday Soc.*, **32**, 323 (1936); Flory, THIS JOURNAL, **59**, 241, (1937); Schulz and Wittig, *Naturwissenschaften*, **27**, 387, 456 (1939); Schulz, *ibid.*, 659 (1939); Norrish and Brookman, *Proc. Roy. Soc.* (London), **A171**, 147 (1939); Norrish, *Trans. Faraday Soc.*, **35**, 1087 (1939); Kamenskaya and Medvedev, *Acta Physicochem., U. S. S. R.*, **13**, 565 (1940); Melville, *Proc. Roy. Soc.* (London), **A163**, 511 (1937).

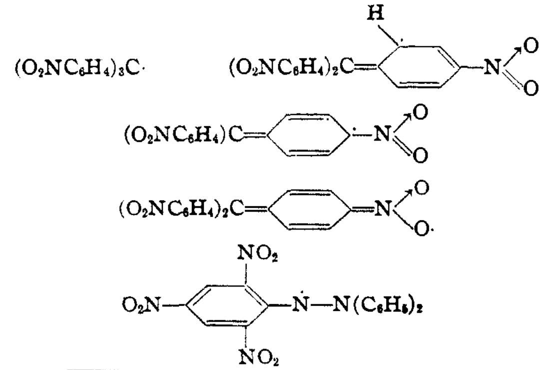
(3) The terms "active" and "inactive" here refer solely to whether or not the radicals are reactive enough to add to a monomer molecule and propagate the polymerization.



A plausible explanation for the effect of the nitro group in promoting such a reaction of the benzene ring with the growing free radical chain,[4] as well as in stabilizing the intermediate addition product (A), is the increased number of possibilities for resonance stabilization in the intermediate A.



This view is substantiated by the fact that an increase in the number of nitro groups increases the retarding influence.[1a] The marked effect of the possibility of resonance with the nitro group in stabilizing a free radical is also indicated by the work of Ziegler and Boye[5] and of Allen and Sugden.[6] The former, working with 4,4′,4″-trinitrotriphenylmethyl, and the latter, with α,α-diphenyl-β-trinitrophenylhydrazyl, have found these substances to be remarkably stable free radicals, existing as such in the solid state.[6]



That the effect of aromatic nitro compounds in retarding free radical polymerization is indeed due to an activation of the aromatic nucleus by the nitro groups and not to a direct reaction of the nitro group itself was substantiated by carrying out the polymerization of styrene in nitromethane. The polymerization proceeded at the normal rate to give a good yield of polymer which contained no detectable amount of nitrogen. The inert character of the nitro group itself toward free radicals was further indicated by the isolation of diphenyl from the decomposition of benzoyl peroxide in nitromethane. Evidently, this solvent is sufficiently inert to allow the highly-reactive phenyl free radicals, formed as intermediates in the reaction, a long enough life for an appreciable number to combine, yielding biphenyl.

Experimental[7]

Polystyrene in the Presence of 2,4-Dinitrochlorobenzene.—A solution of 5 g. of 2,4-dinitrochlorobenzene and 5 g. of benzoyl peroxide in 25 cc. of styrene in a beaker was gradually warmed on a steam-bath. After ten to fifteen minutes the temperature of the reaction mixture reached 95° and then slowly fell to 86°. After three hours, the dark orange, slightly-viscous mixture was cooled, diluted with ether and poured into alcohol. No precipitate formed, indicating that only very low molecular weight polystyrene was present. Addition of a small amount of water precipitated a very viscous, deep orange oil. It was redissolved in 10 cc. of ether and precipitated by pouring into 50 cc. of 90% alcohol. The creamy-white powdery solid (I, 0.7 g.) was reprecipitated once more yielding 0.45 g. for analysis.

Anal. Calcd. for $C_6H_5CO_2(C_8H_8)_{10}C_6H_2(NO_2)_2Cl{\cdot}O_2$: C, 79.97; H, 6.29; N, 2.01; Cl. 2.54; mol. wt., 1390. Found: C. 79.84; H, 6.46; N. 2.26; Cl, 2.33; mol. wt.. 1310 (visc.).[8]

Addition of more water to the mother liquor from the precipitation of I gave another viscous oil. A second reprecipitation gave 1.4 g. of pale orange powder (II). On filtering a solution of 1 g. of this material in 10 cc. of ether into 50 cc. of filtered 90% alcohol, 0.4 g. of ivory-yellow material was obtained.

Anal. Calcd. for $C_6H_5CO_2(C_8H_8)_8C_6H_2(NO_2)_2Cl{\cdot}O$: C, 78.92; H, 6.11; N, 2.39; Cl. 3.03; mol. wt., 1160. Found C, 79.02; H, 6.09; N, 2.44; Cl, 2.84; mol. wt.. 1180 (visc.).[8]

Addition of water to the mother liquor from II gave a third sample (1.3 g.) of polymer. A solution of 1 g. of this material in 10 cc. of ether was filtered into 50 cc. of ice-cold 90% alcohol, yielding 0.25 g. of ivory-yellow powder for analysis. The large loss on reprecipitation of these samples is an indication of the high percentage of very low molecular weight polystyrene present.

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(4) Since this manuscript was submitted this view has been further substantiated by the observation of Fieser, Clapp and Daudt (THIS JOURNAL, **64**, 2052 (1942)) that nitro groups promote the ease of methylation of the benzene ring by means of the methyl radicals from acetyl peroxide, lead tetraacetate and electrolyzed sodium acetate.

(5) Ziegler and Boye, *Ann.*, **458**, 248 (1927).

(6) Allen and Sugden, *J. Chem. Soc.*, 440, (1936).

(7) Analyses by Margaret McCarthy, Dorothy Schneider and Theta Spoor.

(8) Kemp and Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942).

Anal. Calcd. for $C_6H_5CO_2(C_8H_8)_7C_6H_2(NO_2)_2Cl{\cdot}O$: C, 77.62; H, 5.95; N, 2.62; Cl, 3.32; mol. wt., 1070. Found: C. 77.82; H, 6.07; N. 2.66; Cl, 3.20: mol. wt., 1080 (visc.).[8]

A second polymerization, identical with the one above except that only 1.0 g. of 2,4-dinitrochlorobenzene was added, gave 12 g. of pale orange powdery polymer on the first precipitation. A solution of 1 g. of this material in 10 cc. of ether was filtered into 50 cc. of 95% alcohol, yielding 0.8 g. of ivory white powder for analysis. A qualitative test by sodium fusion[9] gave positive results for nitrogen and for halogen.

Anal. Calcd. for $C_6H_5CO_2(C_8H_8)_{13} + C_6H_5(C_8H_8)_{13}O + C_6H_5CO_2(C_8H_8)_{13}C_6H_2(NO_2)_2Cl$: C, 88.28; H, 7.21; N, 0.61; Cl, 0.77; mol. wt. (average), 1530. Found: C, 88.10: H, 7.30; N, 0.47; Cl, 0.89; mol. wt., 1370 (visc.).[8]

Polystyrene in the Presence of Nitrobenzene.—A solution of 3 cc. of nitrobenzene and 10 g. of benzoyl peroxide in 25 cc. of freshly-distilled styrene, was warmed gently at 80–85° for twelve hours. Dioxane was added to the cooled reaction mixture and the polymer was precipitated by pouring into cold alcohol. After several reprecipitations, 6 g. of white powder was obtained. On sodium fusion, this material gave a positive qualitative test for nitrogen.[9]

Anal. Calcd. for $C_6H_5CO_2(C_8H_8)_{12} + C_6H_5(C_8H_8)_{12}$-$C_6H_4NO_2$: C, 89.84; H. 7.36; N, 0.50; mol. wt., 1410. Found: C, 90.01; H. 7.33; N. 0.53; mol. wt., 1300 (visc.).[8]

A second polymerization, using 5 cc. of nitrobenzene, 5 g. of benzoyl peroxide and 25 cc. of styrene was heated on the steam-bath in an evaporating dish. The temperature of the mixture rose to 100°. After an hour at 90° the viscous orange oil was dissolved in ether and precipitated with alcohol yielding 5.5 g. of very pale orange powder. The clear yellow solution of 1 g. of this material in 10 cc. of ether was filtered into 50 cc. of ice-cold 95% alcohol yielding a 0.75-g. sample for analysis.

Anal. Calcd. for $4C_6H_5CO_2(C_8H_8)_{10}O_2 + C_6H_5CO_2$-$(C_8H_8)_9C_6H_4NO_2$: C. 87.28: H, 7.12; N, 0.235; mol. wt., 1190. Found: C. 87.40; H, 7.07: N. 0.22. 0.28; mol. wt., 1130 (visc.).[8]

Polystyrene.—A blank experiment carried out under the same conditions as those above but omitting the retarder indicated its marked effect in moderating the vigor of the reaction and in decreasing the yield and molecular weight of the polymer formed. Actually, both the yield and molecular weight of polymer from this blank undoubtedly would have been still larger if it had been possible to regulate the temperature of the reaction mixture. A solution of 5 g. of benzoyl peroxide in 25 cc. of styrene was warmed to 90° over a period of twenty minutes. The temperature began to rise more rapidly so the mixture was removed from the steam-bath. The temperature continued to rise at an accelerated pace until it reached 140°; the reaction was accompanied by vigorous evolution of gas. The temperature immediately subsided and, after five more minutes at 85°, the viscous mixture was cooled, dissolved in ether and poured into alcohol, yielding 14 g. of snow-white polymer. A solution of 1 g. in 10 cc. of ether was filtered into 50 cc. of 95% alcohol yielding 0.85 g. of polymer for analysis. A qualitative test by sodium fusion[9] gave negative results for nitrogen and for halogen.

Anal. Calcd. for $C_6H_5CO_2(C_8H_8)_{15}$: C, 90.61; H, 7.49: mol. wt., 1680. Found: C, 90.63; H, 7.68: mol. wt.. 1740 (visc.).[8]

Polystyrene in Nitromethane.—A solution of 20 g. of styrene and 3 g. of benzoyl peroxide in 100 g. of nitromethane was heated on a steam-bath (95°) for two hours. The mixture was cooled and poured into cold alcohol. A pale viscous oil separated. The mother liquor was decanted and the polymer was dissolved in 150 cc. of ether. When the solution was poured into 500 cc. of ice-cold alcohol, a white powdery precipitate separated. This was collected by filtration and washed with alcohol. The product weighed 10 to 12 g. A sample for analysis was prepared by dissolving in ether and filtering into three volumes of filtered ice-cold alcohol. Qualitative analyses for nitrogen by sodium fusion, using ferric thiocyanate or Prussian blue as a test.[9] were negative, as were qualitative tests for halogen.

Anal. Calcd. for $C_6H_5CO_2(C_8H_8)_{14}$: C. 90.51; H, 7.46; mol. wt., 1580. Found: C, 90.52; H, 7.46; mol. wt.. 1400 (visc.).[8]

Benzoyl Peroxide and Nitromethane.—A solution of 20 g. (0.08 mole) of benzoyl peroxide in 30 cc. of nitromethane was heated at 100° for forty-eight hours. Extraction of the reaction mixture with sodium bicarbonate yielded 5 g. (0.04 mole) of benzoic acid. Fractional distillation of the organic layer yielded 1 g. (0.007 mole) of biphenyl, m. p. 70°.

Summary

The elements of nitrobenzene and 2,4-dinitrochlorobenzene have been found in polystyrene prepared in the presence of small amounts of these aromatic nitro compounds. This indicates that the retarding effect of such compounds is due to their coupling with the active growing polymer chain.

The effect must be due to the activation of the aromatic nucleus by the nitro groups since nitromethane has been found to be an inert solvent for the polymerization.

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[9] Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 2nd edition, 1941, p. 112.