stand for two or three days, although in some instances the reaction was complete after a twenty-four hour period. If the solid products did not separate from the mother liquor, the ethyl acetate was removed by evaporation on a steam-bath under a hood. Trituration of the residue with cold alcohol caused crystallization in such cases.

7-Hydroxy-2-anthryl-9-benzopyrone.—When 2.06 g. (0.01 mole) of 9-anthraldehyde and 1.36 g. (0.01 mole) of resacetophenone were dissolved in ethyl acetate and treated with dry hydrogen chloride, the solution remained quite clear. However, after standing overnight, a solid material separated; this was collected and recrystallized from ethyl alcohol and water (charcoal) to give light cream needles. Since this product was too light in color to be the chalcone, ring closure must have occurred to give the corresponding flavanone (cf. Russell and Clark[6]); yield, 2 g. (59%). *Anal.* Calcd. for $C_{23}H_{16}O_3$: C, 81.17; H, 4.71; mol. wt., 340. Found: C, 80.58; H, 4.75; mol. wt., 336.

2',4'-Dihydroxy-9-anthralacetophenone.—Procedure B. (This was the only case in which alkaline condensing agents were used.) In a nitrogen atmosphere 10.3 g. (0.05 mole) of 9-anthraldehyde and 6.8 g. (0.05 mole) of resacetophenone were dissolved in 350 cc. of methyl alcohol containing 15 g. of potassium hydroxide. The solution was refluxed for seven hours, and during this period the color changed from orange to deep red. One-half of the alcohol was then removed by distillation. The solution was cooled and made acid with 50% acetic acid. The chalcone which separated was removed by filtration. After several re-

crystallizations from methanol and water (charcoal) bright red-orange prisms of pure chalcone were obtained; yield, 7 g. *Anal.* Calcd. for $C_{23}H_{16}O_3$: C, 81.17; H, 4.71; mol. wt., 340. Found: C, 80.56; H, 4.81; mol. wt., 344.

Summary

1. Through the condensation of 9-anthraldehyde with various hydroxylated acetophenones there has been prepared a series of 9-anthralacetophenones. These are colored materials analogous to the simpler benzalacetophenones but are more brilliant and deeper in color.

2. In one case a hydroxy-2-anthryl-9-benzopyrone, analogous to the 2-phenylbenzopyrones (flavanones), was obtained.

3. Condensation of 9-anthraldehyde with methyl beta-naphthyl ketone gives a bright yellow product analogous to benzalacetophenone (chalcone).

4. It is established that the familiar syntheses of the simpler natural coloring matters (chalcones and flavanones) can be extended to the preparation of analogous compounds containing at least one anthracene nucleus.


Addition Polymerization Catalyzed by Substituted Acyl Peroxides

By Charles C. Price, Robert W. Kell and Edwin Krebs

The suggestion of Staudinger[1] that, under certain conditions, addition polymerization proceeds by means of a chain reaction involving successive addition of monomer molecules to an active free radical intermediate is now widely accepted.[2]

$$R\cdot + CH_2::CHX \longrightarrow R:CH_2:CHX\cdot \longrightarrow$$
$$R(CH_2CHX)_nCH_2CHX\cdot$$
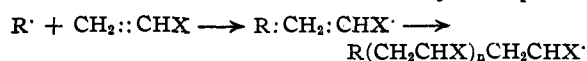
The nature of various processes which might initiate such a chain reaction has been a matter of considerable speculation.[2,3] Schulz and Wittig have shown, however, that the free radicals formed from dissociation of tetraphenylsuccinonitrile[4] or from the decomposition of benzene azotriphenylmethane $(C_6H_5N=NC(C_6H_5)_3)$[5] are capable of catalyzing the polymerization of styrene.

Several investigators[6] have recently suggested that catalysis by acyl peroxides is due to their thermal decomposition to active free radicals,[7] a mechanism which has been found to be in complete accord with the kinetics of the peroxide-catalyzed polymerization of d-s-butyl α-chloroacrylate.[8]

$$(RCO_2)_2 \longrightarrow RCO_2\cdot + R\cdot + CO_2$$

If these free radicals are responsible for the initiation of the polymerization, the polymer molecules so formed should contain fragments from the catalyst. The presence of these fragments in polystyrene and polymethyl methacrylate has now been established by carrying out the polymerizations in the presence of peroxides containing an atom or group, the presence of

(1) Staudinger. *Trans. Faraday Soc.*. **32**, 323 (1936).

(2) See. *e. g.*. Flory. This Journal. **59**, 241 (1937); Mark and Raff. "High Polymeric Reactions." Interscience Publishers. New York. N. Y.. 1941.

(3) Irany. This Journal. **62**, 2690 (1940).

(4) Schulz and Wittig. *Naturwissenschaften*. **27**, 387, 456 (1939).

(5) Schulz, *ibid.*, **27**, 659 (1939).

(6) Norrish and Brookman. *Proc. Roy. Soc.* (London), **171A**. 147 (1939); Norrish, *Trans. Faraday Soc.*, **35**. 1087 (1939); Kamenskaya and Medvedev. *Acta Physicochem.*, *U. S. S. R.*, **13**, 565 (1940).

(7) Hey and Waters. *Chem. Rev.*, **21**, 169 (1937).

(8) Price and Kell, This Journal, **63**, 2798 (1941).

which could be readily confirmed by analysis of the polymer. The table of data summarizing the experiments shows that samples of polystyrene prepared in the presence of *p*-bromobenzoyl peroxide, anisoyl peroxide or chloroacetyl peroxide and samples of polymethyl methacrylate prepared in the presence of chloroacetyl peroxide contain an average of from one-half to two and one-half groups derived from the peroxide per polymer molecule.

Included in the table of data are the results of control experiments in which the peroxide was omitted. In the case of styrene at 95°, the yield of polymer was lower and the molecular weight of the product much higher for the controls than for the experiments with a peroxide. For styrene at 25° and for methyl methacrylate at 25 and 65°, no detectable amount of polymer was formed in the absence of a peroxide. It is generally accepted[2,3,9] that the most logical explanation for these effects exerted by a peroxide on the course of addition polymerization, both as to rate and degree of polymerization, is as a catalyst for the initiation process.

Since Schulz and Husemann[9] have shown that the molecular weight of polystyrene prepared in the presence of benzoyl peroxide is inversely proportional to the square root of the peroxide concentration, relatively large proportions of peroxide were used in the polymerizations for the specific purpose of reducing the size of the polymers. In fact, this inverse proportionality between the molecular weight of polystyrene and the square root of the catalyst concentration is of further significance in the present discussion since it is in accord with the mechanism for polymerization suggested by Price and Kell.[10] If, on the other hand, the fragments from the peroxide had been included in the polymer molecules by reaction of an active chain (generated by some other agent) with a peroxide molecule, the size of the polymer should have been inversely proportional to the first power of the peroxide concentration.

The fact that the polystyrene prepared in the presence of *p*-bromobenzoyl peroxide yielded no *p*-bromobenzoic acid after refluxing with 20% aqueous potassium hydroxide for two days indi-

cates that the fragments from the peroxide which were present in the polymer were principally *p*-bromophenyl fragments rather than *p*-bromobenzoate fragments. This hypothesis is supported further by the analytical data for the polymer sample, since the carbon, hydrogen and bromine analyses account entirely for the composition of the sample.

The authors wish to express their indebtedness to the Graduate School of the University of Illinois for assistance granted one of us (Edwin Krebs) in connection with this investigation.

Experimental[11]

The procedure of Vanino and Uhlfelder[12] for the preparation of *p*-bromobenzoyl and anisoyl peroxides was modified somewhat since a superior yield of product was obtained by addition of a benzene solution of the acid chloride to aqueous sodium peroxide rather than by use of a homogeneous reaction mixture in acetone. *p*-Bromobenzoyl peroxide, for example, was prepared by adding 8.5 g. (0.039 mole) of *p*-bromobenzoyl chloride in 10 cc. of benzene slowly with vigorous stirring to 5 g. (0.064 mole) of sodium peroxide in 50 cc. of ice-cold water. The white precipitate was collected and recrystallized from methyl alcohol; the pure white crystals (5.5 g., 71%) melted at 143.5° with decomposition.[13]

Anal. Calcd. for $C_{14}H_8O_4Br_2$: C, 42.11; H, 2.02. Found: C, 42.00; H, 2.29.

Anisoyl peroxide, prepared from 15 g. (0.088 mole) of anisoyl chloride and 4.8 g. (0.058 mole) of sodium peroxide in a similar manner in 96% yield, melted at 127–128°[12] after recrystallization from dioxane and ligroin, taking care to avoid excessive heating. Crystalline chloroacetyl peroxide separated from a reaction mixture of sodium peroxide (2 g.) chloroacetyl chloride (4.8 g.) and water (15 cc.) after about half an hour of stirring at 0°. The precipitate was collected and sucked dry. Since it decomposed rapidly on standing it was used immediately without further purification or drying. For this reason, the amounts of this catalyst used were somewhat uncertain.

Attempts to prepare *p*- and *m*-nitrobenzoyl and 3,5-dinitrobenzoyl peroxides by the procedure described above for *p*-bromobenzoyl peroxide, using molecular equivalents of the reagents, yielded white powders which did not melt at 250°. These materials decomposed vigorously on ignition, leaving a white residue which dissolved in water to give an alkaline solution. These infusible substances were evidently the sodium salts of the peracids. For the two mono nitro derivatives, excellent yields of the peroxides were obtained, however, by using one-half the molecular equivalent of sodium peroxide (the theoretical amount). *p*-Nitrobenzoyl peroxide, obtained in 88% yield, melted at 155°[12] after recrystallization from toluene, taking care not to heat the solution above about 80°. *m*-Nitrobenzoyl

(9) Schulz and Husemann, *Z. physik. Chem.*, **B39**, 246 (1938).

(10) On the basis of this mechanism,[8] the chain length of peroxide-catalyzed addition polymerizations should be proportional to the monomer concentration and inversely proportional to the square root of the peroxide concentration.

(11) Analyses by L. G. Fauble, Mary S. Kreger, and Margaret McCarthy.

(12) Vanino and Uhlfelder, *Ber.*, **33**, 1047 (1900).

(13) Vanino and Uhlfelder[12] report the melting point as 152°.

TABLE I

SUMMARY OF EXPERIMENTAL DATA ON POLYMERIZATIONS IN THE PRESENCE OF SUBSTITUTED ACYL PEROXIDES

Peroxide catalyst	Concn., mole/l.	Monomer	Concn., mole/l.	Temp., °C.	Time. hrs.	Yield, %	Analyses, %	Average mol. wt. Cryoscopic[a]	Vis-cometric[b]	Approx. no. of fragments per polymer molecule
p-Bromobenzoyl-[c]	0.034	Styrene	0.28	80	5	80	5.72, 5.39 Br	3600	3200	2.54
Anisoyl-	.266	Styrene	.962	95	24	A. 20[d]	3.53 OCH₃	..	1350	..
						B. 64	6.40, 6.30 OCH₃	950	1300	1.94
Anisoyl-	.266	Styrene	.962	60	72	A. 60	2.24 OCH₃	..	1530	:
						B. ..				
Anisoyl-	.135	Styrene	.962	95	24	A. 44	2.11, 2.52 OCH₃	1000	1850	0.75
						B. 48	4.30 OCH₃	670	1200	.93
Anisoyl-	.066	Styrene	.962	95	24	A. 56	1.25 OCH₃	1100	2500	.44
						B. 28	2.14 OCH₃	..	1850	..
None	...	Styrene	.962	95	24	A. 52	..[e]	1720, 1550	8100, 8100	..
						B. none	..	..	..	..
Chloroacetyl-	ca. 0.15	Styrene	8.72	25	48	29	1.74 Cl[f]	2100	2480	1.03
Chloroacetyl-	ca. 0.15	Styrene	8.72	65	3	17	1.51 Cl[g]	4310	5060	1.84
Chloroacetyl-	ca. 0.15	Styrene	8.72	95	3	23	1.52 Cl[h]	2260	10,350	0.97
None	..	Styrene	8.72	95	3	10	..	..	64,300	..
Chloroacetyl-	ca. 0.15	Methyl methacry-	10	25[i,j]	12	84	0.315 Cl[k]	..	36,000	..
Chloroacetyl-	ca. 0.15	late	10	65	0.2	l	.482 Cl[m]	3710	7840	.50
Chloroacetyl-	ca. 0.10	Methyl methacry-	2.0	25[i]	12	50	.599 Cl[n]	5330	8000	.90
Chloroacetyl-	ca. 0.10	late	2.0	65[j]	12	70	1.34 Cl[o]	3650	2185	1.38

[a] The first cryoscopic (number average) molecular weight was measured using benzophenone as a solvent; the remainder using p-nitrotoluene, which proved very satisfactory. The experimental error for these measurements is approximately 10%. [b] The viscometric (weight average) molecular weights were calculated from the approximate Staudinger equation, mol. wt. $= \eta_{sp}/C_g.K_m$. The constant used for polystyrene was 2.6×10^{-4}, that for polymethyl methacrylate, 3.04×10^{-4}. The specific viscosities were measured at 20°, using tetralin as a solvent for polystyrene, chloroform for methyl methacrylate. [c] The solvent for this experiment was benzene. The solvent used in the other experiments was dioxane. [d] The samples A were precipitated from the reaction mixture (dioxane solution) by pouring into approximately three volumes of methanol. The lower molecular weight polymer was soluble in this mixture, so that the samples B were obtained only on the addition of approximately 10% of water. [e] Two methoxyl determinations indicated approximately 0.6% OCH₃ for this material. The source of this discrepancy is under investigation. [f] Anal. Calcd. for $ClCH_2(C_8H_8)_{20}$: C, 90.68; H, 7.65; Cl, 1.67; M.W., 2130. Calcd. for $ClCH_2(C_8H_8)_{20}O$: C, 90.01; H, 7.60; Cl, 1.65; M.W., 2150. Found: C, 90.12; H, 7.63. [g] Anal. Calcd. for $ClCH_2(C_8H_8)_{44}CH_2Cl$: C, 90.82; H, 7.66; Cl, 1.52; M.W., 4680. Found: C, 90.49; H, 7.67. [h] A sample of this polymer was further purified by dissolving in dioxane and precipitating with methanol. Anal. Calcd. for $ClCH_2(C_8H_8)_{90}CH_2Cl$: C, 91.55; H, 7.70; Cl, 0.75; M.W., 9470. Found: C, 91.54; H, 7.53; Cl, 1.05; M.W., 10,700 (visc.). [i] Experiments identical with these with the exception that the mixtures were kept at 5° yielded no polymer in a week. The catalyst was evidently preserved since on warming to room temperature, polymer was produced. [j] Experiments identical with these with the exception that no catalyst was added yielded no detectable amount of polymer. [k] Anal. Calcd. for $ClCH_2(C_5H_8O_2)_{100}O$: C, 59.77; H, 8.02; Cl, 0.353; M.W., 10,065. Found: C, 59.32; H, 8.10. [l] Within a few minutes after being warmed, this mixture reacted so vigorously that a considerable portion was lost. [m] Anal. Calcd. for $ClCH_2(C_5H_8O_2)_{60}$: C, 59.69; H, 8.02; Cl, 0.586; M.W., 6055. Found: C, 59.73; H, 8.08. [n] A sample of this polymer was further purified by dissolving in dioxane and precipitating with methanol. Anal. Calcd. for $ClCH_2(C_5H_8O_2)_{80}O$: C, 59.65; H, 8.02; Cl, 0.439; M.W., 8075. Found: C, 59.68; H, 8.38; Cl, 0.396; M.W., 8050 (visc.). [o] Anal. Calcd. for $ClCH_2(C_5H_8O_2)_{30}$: C, 59.41; H, 7.98; Cl, 1.16; M.W., 3055. Found: C, 59.36; H, 8.14.

peroxide, obtained in 90% yield, melted at 137–138°[12] after careful recrystallization from dioxane and alcohol.

The polymerization of styrene (1.5 g.) in the presence of p-bromobenzoyl peroxide (0.7 g.) was carried out in 50 cc. of benzene under reflux for five hours. The benzene was then evaporated nearly to dryness, the residue dissolved in dioxane and the polymer precipitated by addition of methyl alcohol. After three such reprecipitations the white, powdery polymer (ca. 1 g.) contained 5.72% bromine.

This polymer was refluxed with 20% potassium hydroxide for forty-eight hours, the polymer removed by filtration and the basic solution acidified strongly. No acidic material (p-bromobenzoic acid) could be isolated. The recovered polymer, reprecipitated from dioxane solution by adding methyl alcohol, gave the following analytical data.

Anal. Calcd. for $BrC_6H_4(C_8H_8)_{24}C_6H_4Br$: C, 87.14; H, 7.17; Br, 5.69; mol. wt., 2811. Calcd. for $BrC_6H_4CO_2(C_8H_8)_{24}CO_2C_6H_4Br$: C, 85.32; H, 6.94; Br, 5.52; mol. wt., 2900. Found: C, 86.95; H, 7.41; Br, 5.39 (5.72); mol. wt., 3600 ± 350 (cryoscopically), 3200 (viscometrically).

Experiments similar to the bromobenzoyl peroxide-catalyzed polymerization of styrene in benzene have been carried out for the anisoyl peroxide-catalyzed polymerization of styrene in dioxane, the chloroacetyl peroxide-catalyzed polymerization of styrene and the chloroacetyl peroxide-catalyzed polymerization of methyl methacrylate, without a solvent and in dioxane solution. The results of all the experiments are summarized in the table.

Attempts to polymerize styrene in the presence of m- and p-nitrobenzoyl peroxides failed, even under conditions

such that the styrene should have polymerized thermally. These peroxides thus actually acted as effective inhibitors of the polymerization. That this effect is due to the nitro group was established by addition of as little as 1-2% of nitrobenzene to reaction mixtures which would normally have yielded thermally- or benzoyl peroxide-catalyzed polystyrene. No polymer was obtained in either instance.[14]

Summary

The polymerization of styrene and of methyl

(14) Foord [*J. Chem. Soc*, 48 (1940)] has reported that nitro groups retard the thermal polymerization of styrene.

methacrylate in the presence of such catalysts as *p*-bromobenzoyl peroxide, anisoyl peroxide and chloroacetyl peroxide has yielded polymers with an average of from one-half to two and one-half fragments from the peroxide per polymer molecule. These observations are in complete accord with the suggestion that peroxides serve as catalysts for addition polymerization by decomposition to generate free radicals.

Branched-Chain Fatty Acids. I. Synthesis of 17-Methyloctadecanoic Acid

BY JAMES CASON

Although branched-chain fatty acids rarely occur in nature, there seems to be a special significance attached to those which do occur, such as the bile acids and the series of fatty acids isolated by Anderson and co-workers[1] from acid-fast bacteria. The acids isolated by Anderson are of both chemical and physiological interest, especially phthioic acid which induces in animals the development of typical tubercular lesions; yet very little is known concerning their structures except that tuberculostearic acid is probably 10-methyloctadecanoic acid.[2] Some evidence concerning the structure of phthioic acid has been published.[3] Determination of structure in this series is rendered rather difficult by lack of knowledge of the properties of pure synthetic branched-chain fatty acids. Fordyce and Johnson[4] have synthesized isostearic, isopalmitic and isomyristic acids, Spielman[2] has synthesized 10-methyloctadecanoic acid and Schneider and Spielman[5] have synthesized several 10-methyl and 2-methyl acids; however, in no case have several physical properties of an entire series of branched-chain acids been investigated. Since knowledge of this kind should be of help in deducing the structures of the naturally-occurring acids, the task of synthesizing the series of methyl-

(1) For references consult Anderson. *Physiol. Rev.*, **12**, 166 (1932); Anderson. *Chem. Reviews*, **29**, 225 (1941).
(2) Spielman. *J. Biol. Chem.*, **106**, 87 (1934).
(3) Spielman and Anderson. *ibid.*, **112**, 759 (1936); Wagner-Jauregg. *Z. physiol. Chem.*, **247**, 135 (1937); Robinson, *J. Chem. Soc.*, 505 (1940); Stenhagen and Ställberg. *J. Biol. Chem.*, **139**, 345 (1941).
(4) Fordyce and Johnson. THIS JOURNAL. **55**, 3368 (1933).
(5) Schneider and Spielman. *J. Biol. Chem.*, **142**, 345 (1942).

stearic acids has been inaugurated by the synthesis of 17-methyloctadecanoic acid.

Of the various methods which have been applied to building long aliphatic chains the reaction of an organometallic compound with the acid chloride of a half ester has proved especially satisfactory and in the present communication dialkyl cadmium compounds are shown to be quite useful for this purpose. Isononyl bromide, required for synthesis of 17-methyloctadecanoic acid, was conveniently prepared from isoamyl bromide by either of two methods. By use of the conventional reaction between a Grignard reagent and ethylene oxide isoamyl bromide may be converted to isoheptyl alcohol, and this in turn converted to its bromide and isononyl alcohol (IV). A more novel procedure begins with the reaction of di-isoamyl cadmium and β-carbomethoxypropionyl chloride (I) according to the method of Gilman and Nelson.[6] Such a reaction has previously been mentioned by Carter.[7] De Benneville[8] has reported a 30% yield of keto acid in the reaction between diphenyl cadmium and succinic anhydride; however, this yield is based on the anhydride and the yield calculated on the basis of the bromide used is only 12%. In the reaction between di-isoamyl cadmium and succinic anhydride the yield of 4-keto-7-methyloctoic acid was only 5-10% and the zinc compound gave no better results, so the use of the acid chloride (I) seems a definite advantage. When an effort

(6) Gilman and Nelson. *Rec. trav. chim.*, **55**, 518 (1936).
(7) Carter. *Iowa State Coll. J. Sci.*, **15**, 63 (1940).
(8) De Benneville. *J. Org. Chem.*, **6**, 462 (1941).