tively polarized by hydrogen bonding with the basic nitrogen of another ring.[7]

Experimental[8]

Dimer of 1-Methyl-3-benzal-4-piperidone (I).—The following improved method was used for this product. To 1.13 g. of 1-methyl-4-piperidone and 1.06 g. of benzaldehyde in 2 ml. of 95% ethanol was added 0.3 g. of potassium hydroxide in 1 ml. of water. The solution was stirred and heated at 60–70° for four hours. The precipitate was filtered and triturated with water. When dried the light yellow solid weighed 1.47 g. (73%), m.p. 193–207°. Recrystallization from 95% ethanol afforded an analytical sample, m.p. 224–225°. The product I showed a strong tendency to form supersaturated solutions in ethanol, but recrystallization could be achieved by dissolution in a minimum of hot ethanol followed by distillation of about two-thirds of the ethanol. This product had the same analyses and its melting point was not depressed by a sample prepared in the earlier work;[2] mol. wt. (Rast) 408.

Hydrogenation of I.—To 2.01 g. of I was added 11.9 ml. of 0.839 N hydrochloric acid and 0.15 g. of Adams platinum oxide catalyst. The solution was shaken with hydrogen at 38 pounds pressure until two equivalents of hydrogen per mole of I had been absorbed (65 minutes). The solution was filtered to remove the catalyst and neutralized with sodium hydroxide to give a white solid with wide melting range (85–95°), which could not be narrowed by recrystallization; mol. wt. (Rast) 390.

Acetate of I.—To a mixture of 2.01 g. of I and 0.75 g. of fused sodium acetate under nitrogen were added 10 ml. of acetic anhydride. The mixture was heated at 110° with stirring for two hours, cooled and poured into 75 ml. of ice-water. After standing for one hour the aqueous solution was neutralized with sodium bicarbonate. The resulting fluffy, white precipitate was washed with water, dried, dissolved in ether and filtered. The ether solution was poured onto a 38-cm. column of Alcoa activated alumina F-20. Elution of ether–isopropyl alcohol solution (100–0.25) gave 1.3 g. of solid which was triturated with isopropyl ether and recrystallized from ethyl ether to give an analytical sample of the acetate of I; m.p. 170–172°.

Anal. Calcd. for $C_{28}H_{32}N_2O_3$: C, 75.64; H, 7.26. Found: C, 75.38; H, 7.10.

This acetate of I had an ultraviolet absorption maximum at 287 mμ (log ϵ 4.43) and molecular weight (Rast) 455. Further elution of the column with ether–isopropyl alcohol (10:1) gave 0.5 g. of an oil that failed to crystallize.

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[7] For examples of interaction between a nitrogen and a carbonyl group see N. J. Leonard, R. C. Fox, M. Oki and S. Chiavarelli, This Journal, **76**, 630 (1954).

[8] Spectra were determined with a Cary Ultraviolet Recording Spectrophotometer, model 11MS and a Baird Double Beam Infrared Recording Spectrometer, model B, fitted with a sodium chloride prism. Ultraviolet adsorption spectra were determined in ethanol. Infrared adsorption spectra were determined in a Nujol mull.

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Some Reactions with Chlorendic Anhydride[1]

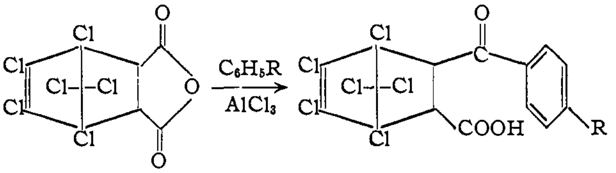
BY E. T. MCBEE AND W. R. DIVELEY[2]

RECEIVED JULY 21, 1954

In connection with other investigations in this Laboratory concerning hexachlorocyclopentadiene and its derivatives,[3-5] chlorendic anhydride was examined with respect to its behavior in the Friedel–Crafts reaction and toward aqueous ammonia.

If chlorendic anhydride is regarded as a substituted succinic anhydride, it can be expected to act as an acylating agent in the Friedel–Crafts reaction.[6] Its non-chlorinated analog, bicyclo-[2.2.1]5-heptene-2,3-dicarboxylic anhydride, however, does not react with benzene and aluminum chloride, whereas the corresponding saturated compound does.[7]

It has now been established that chlorendic anhydride reacts with benzene and toluene in the presence of aluminum chloride to give the expected keto acids in yields of 85–89%.



I II

The acids II (R = H, Me) can be esterified but fail to cyclize on heating with concentrated or fuming sulfuric acid, which was also observed in the case of the analogous 3-benzyl-norcamphane-2-carboxylic acid.[7]

The crystalline imide of chlorendic acid may be prepared in excellent yield by the reaction of chlorendic anhydride with aqueous ammonia at room temperature.

Experimental[8]

Chlorendic Anhydride.—Commercial chlorendic anhydride[9] was purified by refluxing with acetyl chloride for 2 hours immediately before use. After cooling the mixture was filtered with suction, washed twice with anhydrous ether and warmed briefly on a steam-bath to remove residual ether.

3-Benzoyl-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]5-heptene-2-carboxylic Acid.—Chlorendic anhydride (37.1 g., 0.1 mole) was dissolved in 150 ml. of dry, thiophene-free benzene. To this solution was added all at once 38.5 g. (0.29 mole) of pulverized aluminum chloride. An immediate exothermic reaction was controlled by cooling. After the reaction had subsided, the mixture was refluxed gently for one hour. After cooling, the mixture was hydrolyzed by cautious addition, with stirring, of 50 ml. of water, followed by 100 ml. of 10% hydrochloric acid. The mixture was allowed to stand overnight and steam distilled to remove the benzene. The solid, which remained in the residue, was filtered with suction and digested with two 400-ml. portions of boiling water. The remaining tan solid was decolorized with Norit and crystallized from benzene. Drying of the crude, m.p. 187–192°, at 130° and recrystallizing from the same solvent gave colorless prisms, m.p. 196–197°, yield 85%.

Anal. Calcd. for $C_{15}H_8O_3Cl_6$: C, 40.09; H, 1.78; neut. equiv., 449. Found: C, 40.12; H, 2.07; neut. equiv., 446.

Ethyl Ester.—On esterification with ethanol and sulfuric acid, the acid was converted to the ethyl ester, m.p. 80–81°.

Anal. Calcd. for $C_{17}H_{12}Cl_6O_3$: C, 42.80; H, 2.53. Found: C, 42.74; H, 2.21.

1,4,5,6,7,7-Hexachloro-3-(*p*-toluyl)-bicyclo[2.2.1]5-heptene-2-carboxylic Acid.—The analogous reaction of 37.1 g. (0.1 mole) of chlorendic anhydride, 150 ml. of toluene and

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[1] The simple name "chlorendic anhydride" for 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]5-heptene-2,3-dicarboxylic anhydride conforms to the International system of nomenclature and to the system of Patterson and Capell in the "Ring Index" (*Chem. Eng. News*, **32**, 873 (1954)).

[2] Abstracted from the doctoral thesis of W. R. Diveley, Purdue University, 1952.

[3] E. T. McBee and C. F. Baranauckas, *Ind. Eng. Chem.*, **41**, 806 (1949).

[4] J. S. Newcomer and E. T. McBee, This Journal, **71**, 946, 952 (1949).

[5] E. T. McBee, H. Rakoff and R. K. Meyers, *ibid.*, **77**, in press.

[6] R. Adams, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 229.

[7] M. S. Morgan, R. S. Tipson, A. Lowy and W. E. Baldwin, This Journal, **66**, 404 (1944).

[8] All temperatures are uncorrected.

[9] The authors are indebted to the Hooker Electrochemical Company for a generous supply of this anhydride.

35.0 g. (0.26 mole) of aluminum chloride was heated at 80° for one hour after the exothermic reaction had ceased. The reaction product, which was worked up in the same way, consisted of colorless prisms, m.p. 207–208° (from benzene), yield 89%.

Anal. Calcd. for $C_{16}H_{10}Cl_6O_3$: C, 41.47; H, 2.16; neut. equiv., 463. Found: C, 41.75; H, 2.24; neut. equiv., 462.

Ethyl ester: colorless platelets from aqueous ethanol, m.p. 113–114°.

Anal. Calcd. for $C_{18}H_{14}Cl_6O_3$: C, 44.02; H, 2.87. Found: C, 44.19; H, 2.75.

1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]5-heptene-2,3-dicarboximide.—An excess of concentrated ammonia was slowly added with stirring to 17.1 g. (0.1 mole) of powdered chlorendic anhydride. A vigorous exothermic reaction occurred when the reactants were mixed. The mixture was allowed to stand overnight, 200 ml. of water was added and a small amount of unchanged acid removed by filtration. The filtrate was acidified with sulfuric acid and the precipitated imide was filtered with suction and crystallized from aqueous ethanol, colorless plates, m.p. 279–280°, yield 95%.

Anal. Calcd. for $C_{15}H_8Cl_6NO_3$: C, 29.19; H, 0.81; N, 3.78. Found: C, 29.12; H, 1.04; N, 3.85.

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Photoinitiated Diradical Polymerization of Methyl Methacrylate

BY W. E. MOCHEL, J. L. CRANDALL AND J. H. PETERSON

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Benzoin has been known for some years to be an effective photoinitiator for vinyl polymerization,[1] but the mechanism has remained unknown. It has been shown that although simple ethers of benzoin are effective photoinitiators,[2] oximes, in which the carbonyl function is changed, are generally ineffective. This evidence supports a hypothesis that the carbonyl group is the active group of benzoin and that modifications involving the hydroxyl do not change the activity significantly. To obtain information about how the benzoin derivatives are combined in the polymer resulting from photoinitiated polymerization, carbon-14 tagged benzoin methyl ether was used for a study of the photopolymerization of methyl methacrylate. Methyl methacrylate was selected as a subject monomer because the amount of chain transfer involved is lower than with many other monomers.[3]

Polymer prepared by photoinitiation with benzoin methyl ether tagged with carbon-14 in the methyl group was washed to free it of uncombined initiator and its molecular weight determined by viscosity measurements in benzene. The viscosity–molecular weight relationship of Baxendale, Bywater and Evans,[4] was used to calculate molecular weight of the polymer. It is recognized that the molecular weight obtained by this means is a viscosity average, but the final conclusions are not altered significantly by use of calculated number average molecular weights (assuming $\bar{M}_n = 0.7\,\bar{M}_v$).

The radioactivity of the polymer after precipitation two and three times was determined by combustion and count in an internal gas-flow type counter. The figures obtained after successive precipitations indicated that uncombined benzoin methyl ether had been removed. The effectiveness of reprecipitation for removal of benzoin methyl ether was further checked by examination of polymethyl methacrylate made by a thermally-initiated polymerization in the presence of tagged benzoin methyl ether. Such polymer after two precipitations did not retain significant activity, indicating that the uncombined benzoin methyl ether was removed readily by the precipitation technique used and that there was no significant amount of free radical chain transfer with the benzoin methyl ether, which would have resulted in its combination in the polymer.

Three polymerizations using different amounts of benzoin methyl ether produced polymers containing an average of 12.3 to 14.7 benzoin methyl ether residues per polymer molecule (see Table I). These are average values; no corrections were made for thermal polymerization of the monomer and the molecular weight distribution of the polymer was not measured.

TABLE I

PHOTOINITIATION WITH LABELED BENZOIN METHYL ETHER

No.	MMA, g.	BME,[a] g.	Time, min.	Polymer, g.	Radioassay,[b] % BME	$[\eta]$[c]	$\bar{M}_v$[d]	BME/polymer mol.
1	7.70	0.0098	20	0.1248	1.10	0.92	252,000	12.3
2	7.68	.0201	30	.2645	1.41	.81	213,000	13.2
3	7.83	.0298	30	.2475	1.53	.82	218,000	14.7

[a] Labeled benzoin methyl ether. [b] BME retained in polymer after third reprecipitation. [c] Mean of $(\ln \eta_{rel})/c$ and η_{sp}/c in benzene at $c = 0.1$ g./100 ml. [d] From $M = 2.81 \times 10^5\,[\eta]^{1.32}$.

Although the values for molecular weight are not precisely correct, the values obtained show that there are several initiator fragments combined per polymer molecule on the average. This result may be interpreted either by means of a polymerization mechanism involving diradical initiation and termination by mutual combination or by copolymerization of methyl methacrylate with light-activated benzoin methyl ether. Neither interpretation is entirely satisfactory. The measured molecular weights appear to agree within experimental error with values calculated from reported rate constants and monoradical initiation.[3,5] Furthermore, there appears to be a square-root dependence of the polymerization rate on concentration of the benzoin methyl ether.

Benzoin, a photoinitiator similar to benzoin methyl ether, shows a relatively long-lived low-temperature phosphorescence (half-life 0.024 sec.)[6] indicative of triplet state diradicals.[7] Quantum

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(1) C. L. Agre, U. S. Patent 2,367,661 (January 23, 1945).

(2) M. M. Renfrew, U. S. Patent 2,448,828 (September 7, 1948).

(3) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **71**, 497 (1949).

(4) J. H. Baxendale, S. Bywater and M. G. Evans, *J. Polymer Sci.*, **1**, 237 (1946).

(5) B. R. Chinmayanadam and H. W. Melville, *Trans. Faraday Soc.*, **50**, 73 (1954).

(6) Unpublished measurement of Dr. J. C. Rowell of this Laboratory.

(7) G. N. Lewis and M. Kasha, THIS JOURNAL, **66**, 2100 (1944).