at least 1.5%, would indicate that association of acid end-groups is not an appreciable factor at these concentrations. Polymer 8, with a more nearly equal number of amino and acid end-groups, also shows no appreciable deviation of $\ln \eta_r$ in Fig. 1, and its general viscosity characteristics are similar to those of no. 9, which is of similar molecular weight, but which has a high ratio of acid to amino end-groups. The dimeric acid did show a slight increase in $\ln \eta_r/c$ with increasing concentration, and the polymer of lowest molecular weight, no. 1, also showed a slight similar increase of this value at concentrations above 1.5%, whereas the higher polymers often showed a slight decrease. These phenomena would indicate some association of acid end-groups at higher concentrations in the cases of polymers with a high concentration of acid end-groups.

Summary

1. Polyamides of dilinoleic acid and ethylenediamine have been prepared with molecular weights from 2,200 to about 15,000.

2. The relationship of molecular weight to intrinsic viscosity can be expressed by the equation

$$[\eta] = 4.06 \times 10^{-3} M^{0.42}$$

3. The nature of this relationship, and the results of a study of the viscosities of mixtures of polymers indicate that the number average molecular weights of the polymers, as prepared, bear a constant ratio to the viscosity and the weight average molecular weights.

4. Except at higher concentrations with polymers of high acid values, association of terminal end-groups is not very significant.

MINNEAPOLIS, MINN. RECEIVED MAY 17, 1947

[CONTRIBUTION FROM THE THOMPSON LABORATORY OF THE PHILLIPS EXETER ACADEMY]

The Addition of Halogens to an Acetylenic Ketone

BY CHARLES L. BICKEL

Diaryl acetylenic ketones undergo many addition reactions; one of the simplest of these would appear to be the addition of the halogens. The halogenation of a diaryl acetylenic ketone has, however, been investigated in only one case—that of phenylbenzoylacetylene. Nef[1] obtained phenylbenzoylacetylene diiodide by the addition of iodine in ether solution. Later, Dufraisse[2] studied the addition of both bromine and iodine to phenylbenzoylacetylene and obtained phenylbenzoylacetylene dibromide, as well as the diiodide previously described by Nef.

Recent papers from this Laboratory describe the preparation of *o*-chlorophenylbenzoylacetylene,[3,4] a substance which can be obtained in excellent yield from simple starting materials. This acetylenic ketone crystallizes well from oily mixtures and can therefore be isolated more easily than the unsubstituted analogue. These facts suggested the present study of the action of the halogens on *o*-chlorophenylbenzoylacetylene.

Nef stated that an ethereal solution of phenylbenzoylacetylene easily absorbs iodine while Dufraisse stated only that an ethereal solution of the acetylene, treated with an ethereal solution of iodine, gives the iodine addition product. Neither author indicated that the reaction was sluggish. *o*-Chlorophenylbenzoylacetylene, on the other hand, gives no apparent reaction with iodine at room temperature. When a chloroform solution of iodine and the acetylene is heated, there is no evidence of reaction until the solvent has been completely evaporated. Further heating of the residual mixture of iodine and *o*-chlorophenylbenzoylacetylene gives a solid cake from which the iodine addition product can be isolated in good yield.

Although the melting point of phenylbenzoylacetylene diiodide has been variously reported,[1,2] there is no indication in the literature that the melting of this substance is attended by decomposition. *o*-Chlorophenylbenzoylacetylene diiodide, however, decomposes slowly at about 145° and rapidly at 172°, the temperature at which it appears to melt. The decomposition is a clean reaction, iodine and the original acetylenic ketone being the only products. In fact, the thermal decomposition of the diiodide provides the best method of analysis.

o-Chlorophenylbenzoylacetylene, like the unsubstituted analogue, reacts readily with bromine to give a dibromide, a substance which is stable at a temperature one hundred degrees above its melting point. The same dibromide is obtained by treating the diiodide with bromine.

In view of the successful addition of iodine and bromine to *o*-chlorophenylbenzoylacetylene, no difficulty was anticipated in the addition of chlorine. However, attempts to prepare the dichloride have so far met with no success. The acetylenic ketone is recovered unchanged when chlorine is bubbled through its chloroform solution, either at room temperature or at the boiling point of the solution, and even when a trace of iodine is added. When chlorine is bubbled through the molten acetylenic ketone, a red oil is obtained which has as yet given no solid products. Chlorine does not displace bromine from the di-

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(1) Nef, *Ann.*, **308**, 277 (1899).

(2) Dufraisse, *Ann. chim.*, **17**, 133 (1922).

(3) Bickel, THIS JOURNAL, **69**, 73 (1947).

(4) Bickel, *ibid.*, **69**, 2134 (1947).

bromide, the dibromide being recovered unchanged.

When chlorine is bubbled into a chloroform solution of the diiodide, iodine is liberated and a single crystalline product is obtained. The analysis of this substance indicates that only one of the iodine atoms of the diiodide has been displaced. This product presumably has the structure A-CI=CCl-B or A-CCl=CI-B, where A is the *o*-chlorophenyl group and B is the benzoyl group. Prolonged treatment of the diiodide with chlorine at a higher temperature gives a mixture of substances. The analytical results indicate that one component of this mixture is a saturated compound formed by the addition of chlorine to the monochloride described above, which may be tentatively assigned the structure A-CICl—CCl_2-B or A-CCl_2—CICl-B.

The author is indebted to the Marine Biological Laboratory of Woods Hole, Mass., for the chemicals needed in preparing the starting materials used in this problem and also for the use of the facilities of the Marine Biological Laboratory.

Experimental

o-**Chlorophenylbenzoylacetylene Diiodide.**—A suspension of 15 g. of *o*-chlorophenylbenzoylacetylene and 18.5 g. of iodine in 50 cc. of chloroform was heated until the solvent was completely removed. The residual solid cake was cooled, about 100 cc. of ether added and the solid cake pulverized, filtered and washed with ether. The ether solution, washed with sodium thiosulfate solution to remove excess iodine, gave 1.5 g. of the diiodide. The solid diiodide not dissolved by the ether weighed 26 g., a total yield of 89%.

o-Chlorophenylbenzoylacetylene diiodide is moderately soluble in chloroform and acetone, sparingly soluble in ether and very sparingly soluble in petroleum ether. It crystallizes as colorless needles from ether. When heated slowly, the diiodide begins to lose iodine at 140–145°; when heated rapidly, it appears to melt at about 172°. The diiodide was analyzed by heating a weighed sample in a platinum crucible at 160–170° until iodine was no longer liberated. The residue in the crucible solidified on cooling and melted at 94°, a mixed melting point proving it to be *o*-chlorophenylbenzoylacetylene.

Anal. Calcd. for $C_{15}H_9OClI_2$: $C_{15}H_9OCl$, 48.7; I, 51.3. Found: $C_{15}H_9OCl$, 49.0; I, 51.0.

o-**Chlorophenylbenzoylacetylene Dibromide. A. By the Action of Bromine on** *o*-**Chlorophenylbenzoylacetylene.**—Bromine was added to a solution of 5 g. of *o*-chlorophenylbenzoylacetylene in 20 cc. of chloroform until the color of free bromine was apparent, considerable heat being liberated. The chloroform was then boiled off and the solid residue was taken up in about 100 cc. of ether. The ether solution gave 7.1 g. of the dibromide, a yield of 85%.

B. By the Action of Bromine on the Diiodide.—Six grams of bromine was added to a suspension of 8 g. of the diiodide in 30 cc. of chloroform. Evaporation of the chloroform gave a solid product which was taken up in ether. The ether solution, washed with sodium thiosulfate solution, gave 3.5 g. of the dibromide described above, a 54% yield. The residual orange-red oil has as yet given no solid products.

o-Chlorophenylbenzoylacetylene dibromide is readily soluble in chloroform, moderately soluble in ether and sparingly soluble in petroleum ether. It crystallizes as colorless prisms from ether and melts at 142°, with no sign of decomposition up to 250°.

Anal. Calcd. for $C_{15}H_9OClBr_2$: C, 44.9; H, 2.3. Found: C, 44.8; H, 2.5.

The Action of Chlorine on the Diiodide.—Dry chlorine was bubbled into a suspension of 5 g. of the diiodide in 25 cc. of chloroform at room temperature. The color of free iodine appeared immediately and the diiodide rapidly went into solution. After about one hour the delivery of gas was discontinued and the solvent evaporated. The product, which solidified on cooling, was dissolved in ether and the free iodine removed with sodium thiosulfate. The ether solution gave 2.5 g. of massive, colorless prisms melting at 125–126°.

Anal. Calcd. for $C_{15}H_9OCl_2I$: C, 44.7; H, 2.3. Found: C, 44.3, 44.5; H, 2.5, 2.5.

In a second experiment, dry chlorine was bubbled into a suspension of 10 g. of the diiodide in 50 cc. of chloroform, heated to the boiling point. After about two hours the solvent was evaporated, the flow of gas being maintained throughout. The product, after the removal of the iodine, was a mixture from which was obtained about 3 g. of colorless prisms, melting at 172.5° after repeated recrystallization from ether.

Anal. Calcd. for $C_{15}H_9OCl_4I$: C, 38.0; H, 1.9. Found: C, 38.5; H, 2.2.

Summary

Iodine and bromine give addition products with *o*-chlorophenylbenzoylacetylene, the diiodide losing iodine near its melting point and regenerating the acetylenic ketone.

Attempts to prepare the dichloride of *o*-chlorophenylbenzoylacetylene were unsuccessful. Two substances formed by the action of chlorine on the diiodide are reported.

EXETER, NEW HAMPSHIRE RECEIVED AUGUST 23, 1947