it from the paper by some independent means.

Acknowledgments.—The author wishes to acknowledge the valuable technical assistance contributed by Mr. E. H. Schaefer, Jr., and Mr. R. L. DeArmond.

[Contribution from the Institute of Polymer Research, Polytechnic Institute of Brooklyn]

Azo-bis Nitriles. IV.[1] The Preparation and Decomposition of Azo Nitriles Derived from p-Substituted Phenylacetones

By C. G. Overberger and Harry Biletch[2]

This work was undertaken in order to ascertain the effect of a phenyl group or a p-substituted phenyl group on the rate of decomposition of compounds of the type $(p\text{-}XC_6H_4CH_2(CH_3)C(CN)N=)_2$. The preparation of 1,2-disubstituted hydrazines from phenylacetone, p-chlorophenylacetone and p-nitrophenylacetone is described. In the latter two examples the reaction was carried out by the addition of hydrogen cyanide to the hydrazone $R(CH_3)C(CN)—NH—N=C(CH_3)R$ in the presence of traces of acid. The preparation and characterization of the corresponding azo compounds $R(CH_3)C(CN)—N=N—(CN)C(CH_3)R$ are described. The rates of decomposition of these azo compounds have been determined at 80.0° and have been found to be nearly identical. Their rates have been compared with previous decomposition data. The results are in accord with predictions based on molecular models. Effects due to hyperconjugation are apparently negligible. The dimeric coupled products $R(CH_3)C(CN)(CN)C(CH_3)R$ have been prepared and characterized.

Previous papers[1,3] have described the preparation and decomposition of aliphatic azo nitriles. Differences in the rate of decomposition of these aliphatic azo nitriles have been explained on the basis of steric and polar factors.[1,3] This paper will describe the preparation and decomposition of the azo compounds derived from phenylacetone, p-chlorophenylacetone and p-nitrophenylacetone. In particular, we were interested in obtaining information about the effect of hyperconjugation involving hydrogen atoms in the transition state on the rate of decomposition.

A. Preparation of Azo Compounds

I. Discussion.—The azo compound from phenylacetone was prepared as described previously. This azo compound has recently been reported by Alderson and Robertson.[4] They prepared the hydrazine precursor by the addition of hydrogen cyanide under pressure to the corresponding azine. The 1,2-disubstituted hydrazines from p-chlorophenylacetone and p-nitrophenylacetone were prepared by the addition of hydrogen cyanide to the hydrazone $R(CH_3)C(CN)NH—C=C(CH_3)R$ in excess liquid hydrogen cyanide at room temperature in high yield, in the presence of traces of hydrochloric acid. The hydrazones were prepared according to a procedure previously used to prepare 1,2-disubstituted hydrazines, namely, reaction of the ketone with cyanide ion and hydrazine, the hydrazone representing the addition of only one cyano group.

Improved procedures for the preparation of p-chlorophenylacetone and p-nitrophenylacetone are described in the experimental section. The dimeric coupled products $R(CH_3(C(CN)(CN)C-(CH_3)R$ resulting from the decomposition of the

azo compounds have been prepared and characterized.

Experimental[5]

1,2-Di-2-(1-phenyl-2-cyano)-propylhydrazine.—Phenylacetone was prepared according to the procedure given in reference 6. The substituted hydrazine was prepared by a procedure similar to that described by reference 3a and Thiele and Heuser.[7] From 50 g. (0.37 mole) of phenylacetone, 29.5 g. (0.23 mole) of hydrazine sulfate and 20.7 g. (0.42 mole) of sodium cyanide, dissolved in 120 ml. of water and 180 ml. of ethanol, there was obtained on shaking for seven days at room temperature, a white slurry. To this was added 150 ml. of ether to give 29 g., m.p. 147–149° (dec.) of product. From the ether layer was recovered an additional 4 g. of crude product, total yield (54%). Successive recrystallizations from ether gave an analytical sample, m.p. 147–149° (dec.) (142°, from addition of hydrogen cyanide to azine, 44%).[4]

Anal. Calcd. for $C_{20}H_{22}N_4$: N, 17.61. Found: N, 17.72.

2,2'-Azo-bis-2-benzylpropionitrile.—The procedure was similar to that described by references 3a and 7. The crude 2,2'-azo-bis-2-benzylpropionitrile was recrystallized from ether without heating by adding enough petroleum ether (b.p. 28–39°) to the dry, colorless ether solution until it was just cloudy and allowing the solution to stand in the ice-box, 3.5 g. (70%), m.p. 82–84°, white needles (80–82° dec., no yield).[4]

Anal. Calcd. for $C_{20}H_{20}N_4$: N, 17.72. Found: N, 17.82.

sym-Dibenzyldimethylsuccinonitrile. A.—One gram (0.0031 mole) of the azo compound was heated in the dry state at 100° for 5 hours. An almost quantitative yield of the dinitrile was obtained. Recrystallization from a benzene–petroleum ether (b.p. 28–39°) mixture gave 0.73 g. (79%) m.p. 203–204°.

B.—The toluene which was employed as the solvent in the kinetic experiments was removed and the dinitrile recrystallized as indicated above. From 0.95 g. of the azo compound, 0.4 g. of pure dinitrile was obtained, as white feathery crystals, m.p. 203–204°, mixed m.p. 203–204°.

Anal. Calcd. for $C_{20}H_{20}N_2$: N, 9.72. Found: N, 9.61.

α-p-Chlorophenylacetoacetonitrile.—p-Chlorobenzyl cyanide was prepared according to procedures described by reference 6 and reference 8, m.p. 30°, b.p. 100–101° (1

(1) For the third paper in this series, see C. G. Overberger and M. B. Berenbaum, This Journal, **73**, 2618 (1951).

(2) This paper comprises a portion of a thesis presented by Harry Biletch in partial fulfillment of the requirements for the Degree of Master of Science in the Graduate School of the Polytechnic Institute of Brooklyn.

(3) (a) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, This Journal, **71**, 2661 (1949); (b) F. M. Lewis and M. S. Matheson, *ibid.*, **71**, 747 (1949).

(4) W. L. Alderson and J. A. Robertson, U. S. Patent 2,469,358, May 10, 1949.

(5) All melting points are corrected. Analyses by Drs. Weiler and Strauss, Oxford, England; Mr. Pao-tung Huang and one of us, Polytechnic Institute of Brooklyn; Mr. H. S. Clark, Urbana, Illinois; Dr. F. Schwarzkopf, New York, N. Y.

(6) (a) R. Adams and A. F. Thal, "Organic Syntheses," Coll. Vol. I, second edition, John Wiley and Sons, Inc., New York, N. Y., p. 107; (b) P. L. Julian, J. J. Oliver, R. H. Kimball, A. B. Pike and G. D. Jefferson, *ibid.*, Coll. Vol. II, second edition, p. 487; (c) P. L. Julian and J. J. Oliver, *ibid.*, p. 391.

(7) J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).

mm.), 84% (m.p. 30°, b.p. 265–267°, 91%, crude yield).[3a] It was further characterized by hydrolysis to *p*-chlorophenyl-acetic acid according to the procedure of Strauss[9a] and Maxwell,[9b] m.p. 105–106°, 76% (105–106°, 78%).[8b] The procedure used to prepare α-*p*-chlorophenylacetoacetonitrile was similar to that for the preparation of α-phenylacetoacetonitrile except that different reaction conditions were employed and modifications in the isolation procedure were made. In 265 ml. of absolute ethanol was dissolved 21.7 g. (0.94 g. atom) of clean sodium. To this was added a solution of 111 g. (0.73 mole) of *p*-chlorobenzyl cyanide and 96 g. (1.09 moles) of dry ethyl acetate over a period of one-half hour while maintaining reflux. The reaction was allowed to proceed for 4 hours at the reflux temperature, then cooled to room temperature and allowed to stand for one day. At the end of this time most of the sodium salt of α-phenylacetoaceto-nitrile had precipitated as a white solid but to ensure complete precipitation, 300 ml. of dry ether was added and the reaction mixture allowed to stand for an additional 2 hours. The sodium salt was than treated as described in reference 6. Recrystallization from an ethanol–water mixture gave 81 g. (57%), m.p. 126–127°, of white product.

Anal. Calcd. for $C_{10}H_8ONCl$: N, 7.23. Found: N, 7.51.

p-**Chlorophenylacetone.**—The procedure was similar to that described for the preparation of phenylacetone. From 73 g. (0.38 mole) of α-*p*-chlorophenylacetoacetonitrile hydrolyzed in 110 ml. of concentrated sulfuric acid and decarboxylated in dilute sulfuric acid for 5 hours, was obtained 42 g. (67%), b.p. 100–101° (3 mm.), $n^{20}D$ 1.5328 of product as a faintly yellow liquid (11%, $n^{20}D$ 1.5452 prepared from chloroacetone and chlorobenzene).[10]

Anal. Calcd. for C_9H_9OCl: C, 64.09; H, 5.34. Found: C, 64.11; H, 5.18.

The semicarbazone was prepared conventionally,[11] white flakes, m.p. 188–189° (dec.) (188°).[10]

2-(1-*p*-**Chlorophenyl-2-cyanopropyl)-hydrazone of Methyl-*p*-chlorophenylacetone.**—The procedure was similar to that described for the preparation of 1,2-di-2-(1-phenyl-2-cyano)-propylhydrazine except that the hydrazone precipitates instead of the 1,2-disubstituted hydrazine. From 20.0 g. (0.12 mole) of *p*-chlorophenylacetone, 9.75 g. (0.075 mole) of hydrazine sulfate and 7.35 g. (0.15 mole) of sodium cyanide in a solution of 120 ml. of methanol and 80 ml. of water, shaken for 4 days at room temperature was obtained 18.3 g. (85%), m.p. 96–99°, of hydrazone. After recrystallization from an ether–petroleum ether (b.p. 28–39°) mixture, there was obtained 14.8 g. (69%), m.p. 103–104° (dec.) of product as white, rosette-shaped crystals.

Anal. Calcd. for $C_{19}H_{19}N_3Cl_2$: C, 63.34; H, 5.28; N, 11.66. Found: C, 63.09; H, 5.24; N, 11.65.

1,2-**Di-2-(1-*p*-chlorophenyl-2-cyano)-propylhydrazine.**— To 16.0 g. (0.044 mole) of the 2-(1-*p*-chlorophenyl-2-cyano-propyl)-hydrazone of *p*-chlorophenylacetone was added 60 ml. of liquid hydrogen cyanide and 2 drops of concentrated hydrochloric acid. The mixture was allowed to stand at room temperature in a well-stoppered flask for 7 days. The hydrogen cyanide was vaporized and 15.0 g. (94%), m.p. 136–138° (dec.) of the 1,2-disubstituted hydrazine was obtained after recrystallization from ether. An additional recrystallization from ether gave 12.1 g. (71%), m.p. 142° (dec.), of white plate-like crystals.

Anal. Calcd. for $C_{20}H_{20}N_4Cl_2$: C, 62.02; H, 5.21; N, 14.46. Found: C, 62.20; H, 5.18; N, 14.38.

2,2′-**Azo-bis-2-*p*-chlorobenzylpropionitrile.**—The procedure was similar to that described by references 3a and 7. From 4.2 g. (0.011 mole) of 1,2-di-2-(1-*p*-chlorophenyl-2-cyano)-propylhydrazine with slow bromine addition for 4 hours was obtained 4.1 g. of product. Recrystallization from an ether–petroleum ether (b.p. 28–39°) mixture gave 3.0 g. (71%), m.p. 90–91° (dec.), of the azo compound as white needles.

(8) (a) R. v. Walther and A. Wetzlich, *J. prakt. Chem.*, [2] **61**, 187 (1900); (b) R. v. Walther and L. Hirschberg, *ibid.*, [2] **67**, 377 (1903).

(9) (a) F. v. Strauss, *Ann.*, **393**, 317 (1912); (b) T. Maxwell, *Ber.*, **12**, 1764 (1879).

(10) T. M. Patrick, E. T. McBee and H. B. Haas, This Journal, **68**, 1135 (1946).

(11) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1948. p. 170.

Anal. Calcd. for $C_{20}H_{18}N_4Cl_2$: N, 14.54. Found: N, 14.57.

sym-**Di-*p*-chlorobenzyldimethylsuccinonitrile. A.**—From 0.50 g. (0.0013 mole) of 2,2′-azo-bis-2-*p*-chlorobenzylpropionitrile heated at 100° for 6 hours was obtained 0.40 g. (87%) of dinitrile after one recrystallization from a benzene–petroleum ether (b.p. 28–39°) mixture, m.p. 196–198°.

B.—The toluene from a kinetic experiment was removed and the dinitrile recrystallized from a chloroform–petroleum ether (b.p. 28–39°) mixture, m.p. 196–198°, mixed m.p. 196–198°.

Anal. Calcd. for $C_{20}H_{18}N_2Cl_2$: N, 7.84. Found: N, 7.71.

p-**Nitrophenylacetone.**—From 40 g. (0.22 mole) of *p*-nitrophenylacetic acid and 80 g. of purified thionyl chloride, there was obtained 44 g. of *p*-nitrophenylacetyl chloride, m.p. 45–47° (46–47°).[12] The excess thionyl chloride was removed to allow crystallization of the acid chloride.

The procedure followed was similar to that described by Walker and Hauser,[13] with modification. These workers did not prepare this compound. The magnesium salt of ethyl malonate was prepared according to the procedure of the above reference from 5.96 g. (0.24 g. atom) of dry magnesium, 38.4 g. (0.24 mole) of dry ethyl malonate in 28 ml. of alcohol and ether. The solution was cooled to room temperature and 44 g. (0.22 mole) of *p*-nitrophenylacetyl chloride in 300 ml. of dry ether was added over a half-hour period and the solution refluxed for an additional two hours. The crude condensate was obtained, hydrolyzed and decarboxylated as described in reference 13. The crude ketone was precipitated from the reaction mixture upon diluting with water and was removed by filtration and washed with two 50-ml. portions of water, 50 ml. of 5% sodium bicarbonate solution and 50 ml. of water. The ether solution was dried over anhydrous magnesium sulfate and the product recrystallized (yellow plates) from an ether–petroleum ether (b.p. 28–39°) mixture, 22.9 g. (58%), m.p. 62–63° (40%, based on acid chloride using same general procedure with sodium ethoxide from petroleum ether, 65°)[14a] (obtained from *p*-nitrobenzaldehyde and diazomethane, m.p. 62° and from *p*-nitrophenylacetaldehyde and diazomethane, m.p. 62°).[14b]

Anal. Calcd. for $C_9H_9O_3N$: N, 7.82. Found: N, 7.67.

The 2,4-dinitrophenylhydrazone was prepared conventionally.[15] Recrystallization from ethanol gave a light red powder, m.p. 185–186° (dec.).

Anal. Calcd. for $C_{15}H_{13}O_6N_5$: N, 19.49. Found: N, 19.80.

2-(1-*p*-**Nitrophenyl-2-cyanopropyl)-hydrazone of *p*-Nitrophenylacetone.**—The procedure used was similar to that previously described for *p*-chlorophenylacetone. From 12 g. (0.068 mole) of *p*-nitrophenylacetone, 4.12 g. (0.084 mole) of sodium cyanide, 5.20 g. (0.040 mole) of hydrazine sulfate dissolved in 120 ml. of water and 180 ml. of methanol and shaken for 7 days at room temperature, there was obtained 12.5 g. (97%), m.p. 114–117° (dec.) of the crude hydrazone. After one recrystallization from a chloroform–ether mixture, there was obtained 9.5 g. (74%), m.p. 123–124° (dec.) of pure product as light yellow cubes.

Anal. Calcd. for $C_{19}H_{19}O_4N_5$: C, 59.82; H, 5.02; N, 18.4. Found: C, 59.77; H, 4.91; N, 18.6.

1,2-**Di-2-(1-*p*-nitrophenyl-2-cyano)-propylhydrazine.**— To 7.0 g. (0.018 mole) of 2-(1-*p*-nitrophenyl-2-cyanopropyl)-hydrazone of *p*-nitrophenylacetone was added 30 ml. of liquid hydrogen cyanide and 2 drops of concentrated hydrochloric acid. The mixture was allowed to stand for 8 days at room temperature in a well-stoppered flask. The excess hydrogen cyanide was removed to give 7.3 g., m.p. 130–136° (dec.), of crude hydrazine. Successive recrystallization from a chloroform–ether solvent mixture and a methylene chloride–ether mixture gave 4.7 g. (64%), m.p. 154–155° (dec.), of product as a white powder.

Anal. Calcd. for $C_{20}H_{20}O_4N_6$: C, 58.82; H, 4.93; N, 20.6. Found: C, 58.62; H, 5.11; N, 20.8.

(12) E. v. Wedekind, *Ann.*, **289**, 378 (1896).

(13) H. G. Walker and C. R. Hauser, This Journal, **68**, 1386 (1946).

(14) (a) A. Zaki and Y. Iskander, *J. Chem. Soc.*, 55 (1943); (b) F. Arndt, B. Eistert and W. Ender, *Ber.*, **62**, 44 (1929).
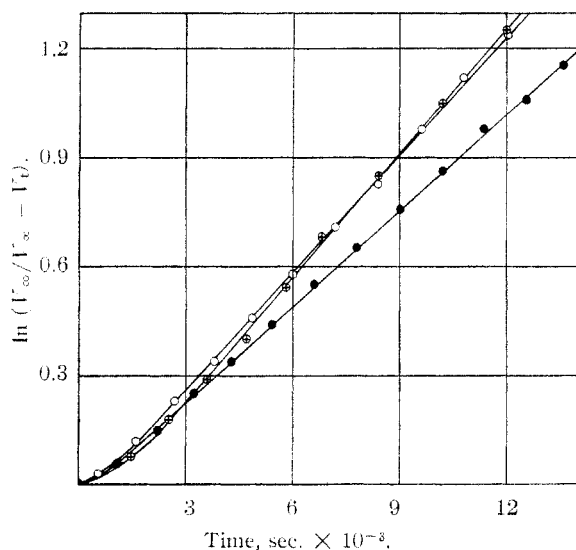
(15) Reference 11, p. 116.

Fig. 1.—Decomposition of azo nitriles in toluene: azo nitrile from *p*-chlorophenylacetone ●; azo nitrile from *p*-nitrophenylacetone ○; azo nitrile from phenylacetone ⊗.

2,2'-Azo-bis-2-*p*-nitrobenzylpropionitrile.—From 2.4 g. (0.006 mole) of 1,2-di-2-(1-*p*-nitrophenyl-2-cyano)-propylhydrazine after slow bromine addition for 5 hours was obtained 2.3 g. of crude product. Recrystallization from a methylene chloride–petroleum ether (b.p. 28–39°) mixture gave 1.6 g. (66%), m.p. 134° (dec.), of white tabular crystals.

Anal. Calcd. for $C_{20}H_{18}O_4N_6$: C, 59.11; H, 4.46; N, 20.69. Found: C, 59.35; H, 4.35; N, 20.68.

sym-Di-*p*-nitrobenzyldimethylsuccinonitrile.—From 0.96 g. of the crude dinitrile obtained by removal of the toluene from the kinetic experiments was obtained on recrystallization from a mixture of methylene chloride and petroleum ether (28–39°), 0.4 g., m.p. 268–270°, of product as a light yellow powder.

Anal. Calcd. for $C_{20}H_{18}O_4N_4$: N, 14.8. Found: N, 15.0.

B.   Kinetic Measurements

I.   Procedure.—The procedure for measuring rates of decomposition was essentially that described by Overberger, O'Shaughnessy and Shalit.[3a]

II.   Results.—The rates of decomposition of the compounds $R(CH_3)(CN)C$—N=N—$C(CN)(CH_3)R$, where $R = C_6H_5CH_2$—, *p*-$ClC_6H_4CH_2$—, and *p*-$NO_2C_6H_4CH_2$— as measured by nitrogen evolution are reported in Table I. Table I contains average rate constants for each compound for decompositions carried out in toluene at 80.0°. Previous work has shown that the effect of solvent and concentration on the rate of decomposition are negligible.[3a] In Fig. 1, plots of $ln\ V_\infty/V_\infty - V_t$ *vs.* time are reproduced for a typical experiment with each of the three azo compounds.

III.   Discussion of Results.—These results demonstrate that there is little or no effect of the group in the *p*-position of the benzene ring on the rate of decomposition of these azo compounds. They likewise show that the steric effect of the benzyl group in the compounds $C_6H_5CH_2(CH_3)$ $(CN)CN$=$NC(CN)(CH_3)CH_2C_6H_5$ is comparable

TABLE I

DECOMPOSITION RATES OF AZO NITRILES IN TOLUENE AT
80.0°: $(R)(CH_3)(CN)C$—N=N—$C(CN)(CH_3)(R)$

R	Azo nitrile, m.p., °C. (dec.)	k (sec.$^{-1}$ $\times$ 10^4)	No. of runs	Concn. range mole/liter	Average deviation
$C_6H_5CH_2$—	82–84	1.16	3	0.01886–0.03868	0.04
p-$ClC_6H_4CH_2$—	90–91	0.88	3	0.01786–.03380	.00
p-$NO_2C_6H_4CH_2$—	134	1.00	2	0.01724–.01872	.06

to that exhibited by a methyl group in 2,2'-azo-bis-isobutyronitrile.[16] Consideration of the Fisher–Hirschfelder molecular models on the basis of the steric explanation described in references 3a and 1 predict this result. There is no increased interaction between the two halves of the molecule ("F-strain") over that exhibited by 2,2'-azo-bis-isobutyronitrile.

It might be expected that any polar effect[17] of a group in the *p*-position would be very slight or negligible since the group cannot contribute to the transition state or the stability of the radical (A)

$$X\!-\!\!\left\langle\!\!\!\bigcirc\!\!\!\right\rangle\!\!-\!CH_2\!-\!\overset{\cdot}{C}(CN)CH_3$$

A
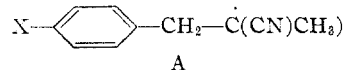
with any type of normal resonance. However, it was believed that hyperconjugation involving forms of the type below might contribute in addition to the normal type through the nitrile group because of the formation of a conjugated system which would include the *p*-substituent in its electron distribution. It was believed that this type

+ other forms including
nitrile group

+ other forms including
nitrile group
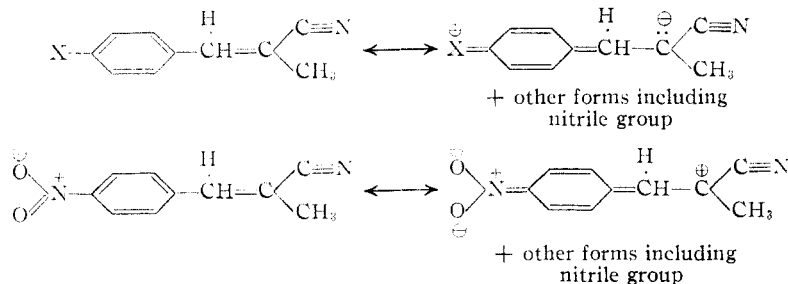
of compound represented a favorable case to demonstrate such an effect because of the conjugation produced in such a transition state. The lack of any apparent effect of the *p*-substituent on the rate even when the *p*-substituent is the nitro group as compared with hydrogen and chlorine, indicates that there is little difference between resonance of this type in the ground state and that involving the tertiary radical in the transition state.

A discussion of errors arising from this type of measurement was included in reference 3a.

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(16) Compare k = 1.60 sec.$^{-1}$ $\times$ 10^4 at 80.2° for 2,2'-azo-bis-isobutyronitrile; k = 1.03 sec.$^{-1}$ $\times$ 10^4 at 80.2° for the azo compound from methyl isopropyl ketone.

(17) S. G. Cohen, S. J. Groszos and D. B. Sparrow (THIS JOURNAL, **72**, 3947 (1950)) have recently demonstrated that polar factors are only of minor significance in decomposition of compounds of the type X-C_6H_4-CH(CH$_3$)N=N(CH$_3$)CH-H$_4$C$_6$-X where X = OCH$_3$, Cl, H. In this case more direct and significant polar effects might be anticipated.