successfully converted to α,ω-diphenylpelargonic acid (X) in the same way, *via* the acrylic acid VII. Similarly, α,ω-diphenylcapric acid (XI) was prepared from α-phenyl-β-(5-γ-phenylpropyl-2-thienyl)acrylonitrile (V), the latter compound being synthesized from 5-γ-phenylpropyl-2-thenaldehyde.

In view of the ready availability of the thiophene aldehydes as intermediates, and despite the low over-all yields, the present method seems to offer a more convenient route to α,ω-diarylated higher fatty acids than the routine malonic syntheses.

EXPERIMENTAL

Preparation of intermediates. 2-Benzyl- and 2-β-phenylethylthiophene were prepared by applying the Huang-Minlon modification[7] of the Kishner-Wolff reaction to 2-benzoyl- and 2-phenacetylthiophene. 2-β-Phenylpropionylthiophene, prepared by a stannic chloride-catalyzed Friedel-Crafts reaction of β-phenylpropionyl chloride with thiophene,[8] was similarly reduced to 2-γ-phenylpropylthiophene,[3] a pale yellow oil, b.p. 288–289°, n_D^{19} 1.5798; the yield of the reduction was 60%.

Formylation of these arylalkylthiophenes was effected by means of dimethylformamide and phosphorus oxychloride; *5-γ-phenylpropyl-2-thenaldehyde* thus prepared was a pale yellow oil, b.p. 222–225°/19 mm. (69% yield).

Anal. Calcd. for $C_{14}H_{14}OS$: C, 73.0; H, 6.1. Found: C, 72.8; H, 6.2.

α-Phenyl-β-(5-benzyl-2-thienyl)acrylic acid (VI). The hydrolysis of the corresponding nitrile[9] was effected either by prolonged heating (72 hr.) with a solution of sodium hydroxide in propanol or butanol, or, more rapidly and with similar yields, by the sulfuric acid method. Acid VI crystallized from ethanol in shiny, colorless leaflets, m.p. 139°; yield: 55–65%.

Anal. Calcd. for $C_{20}H_{16}O_2S$: C, 75.0; H, 5.0. Found: C, 74.9; H, 5.0.

α,ω-Diphenylcaprylic acid (IX). To a solution of the foregoing acid (4 g.) in a 10% aqueous solution of sodium hydroxide heated on a water bath, a large excess of Raney alloy of nickel and aluminum (20 g.) was added in small portions with stirring, and heating was continued for a further thirty minutes. After cooling, the precipitate of nickel was filtered off and washed several times with hot water; the filtrate was acidified with hydrochloric acid, the reduction product taken up in benzene, the benzene solution washed with water then dried over sodium sulfate, and the solvent removed. The residue was recrystallized several times from petroleum ether, giving colorless prisms, m.p. 65°; yield: 74%.

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.1; H, 8.1. Found: C, 81.0; H, 8.0.

α-Phenyl-β-(5-β-phenylethyl-2-thienyl)acrylonitrile (IV). An equimolar mixture of 5-β-phenylethyl-2-thenaldehyde and benzyl cyanide in ethanol was shaken for a few minutes with a few drops of 20% aqueous sodium hydroxide; the oily precipitate which formed on dilution with water, solidified on standing in the refrigerator. Recrystallization from ethanol afforded an 87% yield of shiny, yellowish prisms, m.p. 111°.

Anal. Calcd. for $C_{21}H_{17}NS$: C, 80.0; H, 5.4. Found: C, 80.2; H, 5.5.

α-Phenyl-β-(5-β-phenylethyl-2-thienyl)acrylic acid (VII). Obtained in 55% yield by hydrolysis of the foregoing nitrile, this acid crystallized from ethanol in fine, colorless prisms, m.p. 179°.

Anal. Calcd. for $C_{21}H_{18}O_2S$: C, 75.4; H, 5.4. Found: C, 75.2; H, 5.4.

α,ω-Diphenylpelargonic acid (X). This acid, obtained in 70% yield, crystallized from methanol in fine, colorless prisms, m.p. 92°.

Anal. Calcd. for $C_{21}H_{26}O_2$: C, 81.3; H, 8.4. Found: C, 81.4; H, 8.4.

α-Phenyl-β-(5-γ-phenylpropyl-2-thienyl)acrylonitrile (V). This nitrile, prepared in 76% yield, crystallized from ethanol in shiny, yellowish leaflets, m.p. 59°.

Anal. Calcd. for $C_{22}H_{19}NS$: C, 80.2; H, 5.8. Found: C, 80.3; H, 5.9.

α-Phenyl-β-(5-γ-phenylpropyl-2-thienyl)acrylic acid (VIII). This acid (obtained in 65% yield by acid hydrolysis and in 40% yield by alkaline hydrolysis) crystallized from ethanol in fine, colorless prisms, m.p. 148°.

Anal. Calcd. for $C_{22}H_{20}O_2S$: C, 75.9; H, 5.7. Found: C, 75.7; H, 5.8.

α,ω-Diphenylcapric acid (XI). Obtained in 63% yield, this acid crystallized from methanol in shiny, colorless leaflets, m.p. 80°.

Anal. Calcd. for $C_{22}H_{28}O_2$: C, 81.5; H, 8.6. Found: C, 81.5; H, 8.8.

THE RADIUM INSTITUTE
UNIVERSITY OF PARIS
PARIS V^e, FRANCE

---

[7] Huang-Minlon, *J. Am. Chem. Soc.*, **67**, 2478 (1945).

[8] N. P. Buu-Hoï, N. Hoán, and N. D. Xuong, *J. Chem. Soc.*, 3499 (1951).

[9] *Cf.* N. P. Buu-Hoï and J. Lecocq, *J. Chem. Soc.*, 641 (1947).

Decomposition of Phenylazotriphenylmethane in the Presence of Triphenylmethyl

JOHN F. GARST AND GEORGE S. HAMMOND

Received May 27, 1957

Whether the thermal decomposition of unsymmetrical azoalkanes and arylazoalkanes proceeds with simultaneous cleavage of the two carbon-nitrogen bonds or with the cleavage of only one of these, followed by the other, is not known with certainty. Rampsberger,[1] considering the reactivities of azomethane, isopropylazomethane, and azoisopropane, has argued that the cleavage is of the former type, since each substitution of isopropyl for methyl results in an almost equal decrease in activation energy. Cohen and Wang[2] have argued similarly concerning the variations of activation energies among the compounds azomethane, azodiphenylmethane, azoisopropane, azo-α-phenyl-ethane, azodiphenylmethane, azoisopropane, azo-α-phenylethane, phenylazodiphenylmethane, and phenylazotriphenylmethane, but pointed out that such arguments apply only to the fragmentation of the symmetrical compounds. The latter authors suggest that reaction 1 may account for the lack of production of triphenylmethane

$$\mathrm{Ph{-}N{=}N{-}CHPh_2 \longrightarrow Ph{-}N{=}N\cdot + \cdot CHPh_2} \qquad (1)$$

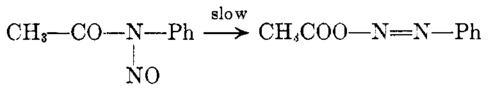
---

[1] H. C. Rampsberger, *J. Am. Chem. Soc.*, **49**, 912, 1495 (1927); **50**, 714 (1928); **51**, 2134 (1929).

[2] S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **77**, 2457, 3628 (1955).

when phenylazodiphenylmethane is decomposed in decalin. The phenylazo radical might live long enough to diffuse from the neighborhood of its partner radical before it loses nitrogen; the phenyl radical would then attack solvent at a rate with which the reaction between phenyl and diphenylmethyl radicals could not compete. They applied a similar argument to the lack of formation of tetraphenylmethane in quantity in decompositions of phenylazotriophenylmethane, though there is a possibility in this case that a steric factor causes a relatively high activation energy for the phenyl-triphenylmethyl reaction.

DeTar and Scheifele[3] have isolated azobenzene from the decomposition of *N*-nitrosoacetanilide in benzene and have estimated the yield at 6%. The possibility exists that the azobenzene was an impurity in the N-nitrosoacetanilide, which is difficult to obtain and keep in a pure state, but it may also have arisen from such sequences as:



$$\mathrm{CH_3{-}CO{-}\underset{\substack{|\\ NO}}{N}{-}Ph \xrightarrow{\text{slow}} CH_3COO{-}N{=}N{-}Ph} \quad (2)[4]$$

$$\mathrm{CH_3COO{-}N{=}N{-}Ph \xrightarrow{\text{fast}} CH_3COO\cdot + Ph{-}N{=}N\cdot} \quad (3)[4]$$

$$\mathrm{Ph{-}N{=}N\cdot + PhH \xrightarrow{(R\cdot)} Ph{-}N{=}N{-}Ph\ (+RH)} \quad (4)$$

or

$$\mathrm{Ph{-}N{=}N\cdot \longrightarrow Ph\cdot + N_2} \quad (5)$$

$$\mathrm{Ph{-}N{=}N\cdot + Ph\cdot \longrightarrow Ph{-}N{=}N{-}Ph} \quad (6)$$

Davies, Hey, and Williams[5] have recently studied the rates of decomposition of a number of arylazotriphenylmethanes in various solvents. They noted that Wieland, Ploetz, and Indest[6] found incomplete nitrogen evolution from the decomposition of benzoylazotriphenylmethane, and that the products included a small amount of benzoylhydrazine. Davies, Hey, and Williams pointed out that this argues strongly for a primary dissociation to the benzoylazo radical and the triphenylmethyl radical. Consideration of the reactivities of azobenzene, benzoylazobenzene, and azodibenzoyl led them to the conclusion that the phenyl-nitrogen bond is stronger than the benzoyl-nitrogen bond. Thus, they consider that phenylazotriphenylmethane probably decomposes by fission of the triphenylmethyl-nitrogen bond. They were able to present a rationalization of the variation of decomposition rates of substituted phenylazotriphenylmethanes by considering the effects of substituents on the stability of the substituted phenylazo radicals. Cohen and Wang[7] were able to rationalize the substituent effect on the assumption that decomposition led directly to substituted phenyl radicals, nitrogen, and triphenylmethyl by considering the effect of the substituent on the relative stabilities of the azo compounds.

Suitably active radical scavengers could trap the phenylazo radical if it is formed. Davies, Hey, and Williams[5] have found that iodine does not effect the rate of decomposition of phenylazotriphenylmethane in toluene. Iodine would probably not slow the rate of nitrogen evolution even if it did trap the phenylazo radical momentarily, because the resultant diazoiodide would probably decompose to yield nitrogen at a faster rate than the original source. On the other hand, triphenylmethyl, if added in gross quantities, *might* react with the phenylazo radical to produce phenylazotriphenylmethane, which decomposes at a moderate rate.[5,7–9] Thus, the presence of triphenylmethyl in a decomposing solution of *N*-nitrosoacetanilide or phenylazotriphenylmethane might slow the rate of nitrogen evolution from these compounds. *N*-nitrosoacetanilide was found to react with triphenylmethyl in another fashion,[10] so the rate of nitrogen evolution could not be measured. The rates of nitrogen evolution from phenylazotriphenylmethane in chlorobenzene were measured at 50.00 ± 0.05° and at 27.00 ± 0.05° in the absence and presence of added triphenylmethyl and were found to be independent of the presence of triphenylmethyl. These observations *do not constitute a proof of a synchronous cleavage* of the two C—N bonds but do *indicate*[11] that the phenylazo radical, if it exists, has a rather short lifetime.

EXPERIMENTAL

Phenylazotriphenylmethane was prepared by the method of Cohen and Wang.[7] Chlorobenzene was washed with concentrated sulfuric acid, sodium hydroxide solution, and distilled water. It was then dried over magnesium sulfate and distilled through a 2.5-foot glass helices-packed column. A constant boiling middle fraction was used in these experiments. A solution of triphenylmethyl in chlorobenzene was prepared freshly for each run according to the procedure of Hammond, Ravve, and Modic,[12] using 6 g. triphenylchloromethane, 20 g. mercury, and 50 ml. chlorobenzene. The solutions were not assayed for triphenylmethyl but previous

---

(3) D. F. DeTar and H. J. Scheifele, Jr., *J. Am. Chem. Soc.*, **73**, 1442 (1951).

(4) R. Huisgen and G. Horeld, *Ann.*, **562**, 137 (1949); D. F. DeTar, *J. Am. Chem. Soc.*, **73**, 1446 (1951).

(5) G. L. Davies, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 4397 (1956).

(6) H. Wieland, T. Ploetz, and H. Indest, *Ann.*, **532**, 166 (1937).

(7) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **75**, 5504 (1953).

(8) D. H. Hey, *J. Chem. Soc.*, 1966 (1934).

(9) M. G. Alder and J. E. Leffler, *J. Am. Chem. Soc.*, **76**, 1425 (1954).

(10) Unpublished results from this laboratory.

(11) The indication is subject to assumption, alluded to above, that the reaction of the two radicals would regenerate the azo compound rather than giving some other product. We know of no direct evidence which bears on this question. Our results of course have no bearing upon the chemistry of possible cage effects of the decomposition.

(12) G. S. Hammond, A. Ravve, and F. Modic, *Anal. Chem.*, **24**, 1373 (1952).

experience in this laboratory indicates that the yield in such a preparation is 70 ± 10%.[13]

Kinetic measurements were by nitrogen evolution using the apparatus described previously.[14] For the 50.00 ± 0.05° (measured by a National Bureau of Standards calibrated thermometer) runs, approximately 3×10^{-2} M solutions of phenylazotriphenylmethane in chlorobenzene or in the chlorobenzene solution of triphenylmethyl prepared as above were used.

Volume measurements were made over 4- to 8-hr. periods, final volumes being read after 24 hr., or after heating the reaction vessels to 70–80° for 30 min., then cooling to 50°. The data gave good straight line plots in $\ln V_\infty/(V_\infty - V)$ *vs.* time. The same line was obtained both in the presence and absence of added triphenylmethyl. The observed first order rate constant was 0.88×10^{-2} min.$^{-1}$ Alder and Leffler[9] report 1.00×10^{-2} min.$^{-1}$ at 322.9° K. Their measurements were spectrophotometric. When oxygen was bubbled through the solution containing added triphenylmethyl after all the azo compound had been decomposed, ditriphenylmethyl peroxide (m.p. 184–185° uncorr.; lit, 185–186°) precipitated. The amount of peroxide was considerable but the weight was not recorded. For runs at 27.00 ± 0.05° approximately 2×10^{-1} M solutions of phenylazotriphenylmethane were used. These runs were followed for about 8 hr. (approximately one fourth of one half-life), then the temperature of the reaction vessel was raised to 70–80° for 30 min. The vessel and contents were cooled to 27° and final volumes were read. A plot of $\ln V_\infty/(V_\infty - V)$ *vs.* time gave reasonably straight lines corresponding to $k = 3.6 \times 10^{-4}$ min.$^{-1}$ (Alder and Leffler[9] report $2.14\text{–}2.38 \times 10^{-4}$ min.$^{-1}$) in both the presence and absence of added triphenylmethyl. However, at times greater than 400 min. deviations from linearity occurred, but these were identical in the absence and presence of added triphenylmethyl.

Acknowledgments. We are indebted to the National Science Foundation for a predoctoral fellowship held by John F. Garst and additional collateral support through a research grant. Many thanks are due to Dr. S. K. Liu for his assistance in the use of the apparatus for kinetic measurements.

CHEMICAL LABORATORY
IOWA STATE COLLEGE
AMES, IOWA

---

[13] G. S. Hammond and F. J. Modic, unpublished studies.

[14] C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, **72**, 3233 (1955).

Cyanamide Derivatives (LIV).[1] Cyanoformamidine and Its Reactions

KOZO SHIRAI, KEIJIRO ODO, AND KIICHIRO SUGINO

Received May 29, 1957

In previous work[2] it was found that cyanamide reacts in ethanol solution with the reduction product of guanidine in the presence of free guanidine to produce formoguanamine (III).

A study of the mechanism of this reaction, which is now reported, has shown that this reduction product of guanidine is formamidine (I) and that it reacts with cyanamide to give cyanoformamidine (II). This latter compound, which is formed in nearly quantitative yield from cyanamide and I, was characterized by its analysis and hydrolysis by dilute sulfuric acid to urea, formic acid, and ammonium sulfate.

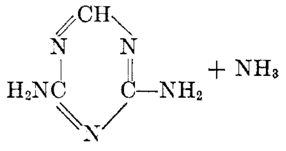
$$\mathrm{NH_2C(NH)NH_2} \xrightarrow{[H]} \underset{\mathrm{I}}{\mathrm{NH_2CH{=}NH}} + \mathrm{NH_3}$$

$$\mathrm{NCNH_2} + \mathrm{I} \longrightarrow \underset{\mathrm{II}}{\mathrm{NCNHCH{=}NH}} + \mathrm{NH_3}$$

$$\mathrm{II} + 3\mathrm{H_2O} \longrightarrow \mathrm{H_2NCONH_2} + \mathrm{HCOOH} + \mathrm{NH_3}$$

Cyanoformamidine (II) is a neutral substance, m.p. 137–138°. It is shown to be the intermediate in the formation of formoguanamine (III)[2] by the fact that it reacts readily with guanidine in ethanol solution at 70° to give III in 72% yield. The reaction mechanism thus established invalidates the one suggested earlier.[2]

$$\mathrm{NCNHCH{=}NH} + \mathrm{NH_2C(NH)NH_2} \longrightarrow$$



III

EXPERIMENTAL[3]

Isolation of formamidine (I). To a solution of 19.1 g. (0.2 mole) thoroughly dried guanidine hydrochloride in 100 cc. absolute ethanol was added 4.6 g. (0.2 mole) of clean sodium cuttings piece by piece with agitation, keeping the temperature at 15–25°. After separating the precipitated sodium chloride, 45.8 g. (0.2 mole) picric acid dissolved in 200 cc. of hot methanol was added and the precipitate was filtered off while hot. This amounted to 53 g. and consisted mainly of guanidine picrate. Then, by cooling the filtrate, 4.4 g. crude formamidine picrate, m.p. 227°, was obtained; 0.7 g. of the same picrate (purity, a little less) was recovered by subsequent evaporation of the mother liquor. A hot water extract of the crude guanidine picrate gave 2.3 g. formamidine picrate, m.p. 237°. The combined picrate was recrystallized from hot water. Yield 6.7 g. (24%), m.p. 246–247°. Formamidine hydrochloride derived from the picrate melts at 78°.

Cyanoformamidine (II). An ethanolic solution of free formamidine was prepared by treating 7.95 g. (0.1 mole) formamidine hydrochloride with an equivalent amount of sodium ethylate in 50 cc. ethanol. After separating sodium chloride, 4.20 g. (0.1 mole) cyanamide was added to the solution. During this procedure, cooling in an ice bath was necessary to avoid the decomposition of formamidine. Crystals began to separate from the ice-cooled mixture. It was then heated for 2 hr. at 50–75° to evolve ammonia and

---

[1] Part LIII, *J. Org. Chem.*, **22**, 1715 (1957).

[2] K. Odo, K. Shirai, and K. Sugino, *Bull. Chem. Soc. Japan*, **28**, 614 (1955).

[3] All melting points are uncorrected.