which may have contained some phenylacetaldehyde (XIX), while from the later eluates, 394 mg. (56%) of cholestan-3-one (IX) was isolated.

Desulfurization of Spiro-(5-phenyl-1,3-oxathiolane-2,3′-cholestane) (XX).—A sample (0.82 g.) of this hemithioketal was desulfurized on the same day and under exactly the same conditions as described for its isomer XVII. The steam distillate again was divided into two equal portions; one of them, after treatment with 2,4-dinitrophenylhydrazine, led to 27 mg. (12%) of acetophenone (XXI) 2,4-dinitrophenylhydrazone, m.p. 247–249°. The second portion was transformed into its 3,5-dinitrobenzoate yielding 87 mg. (35%) of phenylmethylcarbinol (XXII) 3,5-dinitrobenzoate, m.p. 94–95°, $[\alpha]^{25}_{D}$ +7° (c 0.9).[13] As pointed out in the discussion, this rotation could not be obtained reproducibly and in one run the product was found to be optically inactive. Chromatography of the non-volatile portion gave 0.409 g. (67%) of pure cholestan-3-one (IX).

Spiro-(5-diphenylmethyl-1,3-oxathiolane-2,3′-cholestane) (XXIII).—A mixture of 10.0 g. each of cholestan-3-one (IX), 1,1-diphenyl-3-mercaptopropan-2-ol (IV), freshly fused zinc chloride and anhydrous sodium sulfate in 70 cc. of dioxane was shaken for 2 days and then allowed to stand at room temperature for an additional day. Dilution with ether, washing with water and 10% sodium carbonate solution, drying and evaporation left a residue which on successive concentration of its acetone solution gave three crystalline fractions (A, B and C).

Fraction A (4.1 g., m.p. 173–180°) was recrystallized several times from chloroform–methanol (2.93 g. (needles) to constant m.p. 193–194°, $[\alpha]^{28}_{D}$ +60°).

Anal. Calcd. for $C_{42}H_{60}OS$: C, 82.30; H, 9.87. Found: C, 82.04; H, 9.94.

Fraction B (3.3 g., m.p. 162–165°) was recrystallized three times from acetone; yield 1.67 g., m.p. 172–173° (needles), $[\alpha]^{25}_{D}$ −9.7°.

Anal. Calcd. for $C_{42}H_{60}OS$: C, 82.30; H, 9.87. Found: C, 82.15; H, 9.83.

Fraction C (3.6 g., m.p. 130–135°) crystallizes as prisms from acetone; yield 1.22 g., m.p. 70–80° then resolidifying and melting at 152–153°, $[\alpha]^{25}_{D}$ +2.8°.

Anal. Calcd. for $C_{42}H_{60}OS$: C, 82.30; H, 9.87. Found: C, 82.60; H, 10.17.

The infrared spectra (nujol mulls) of all three isomers showed distinct differences in the fingerprint region.

Desulfurization of Spiro-(5-diphenylmethyl-1,3-oxathiolane-2,3′-cholestane) (XXIII).—W-2 Raney nickel catalyst (20 g., 3 days old) was refluxed with stirring for 1 hour with 250 cc. of ethyl methyl ketone, 2.0 g. of isomer A (m.p. 193–194°) of the hemithioketal XXIII was added and refluxing was continued with stirring for 24 hours. When the reaction was carried out in acetone solution, up to 80% of the hemithioketal was recovered.

The catalyst was filtered, the solvent was removed and the residue was chromatographed in 36 fractions over 30 g. of Merck acid-washed alumina. The first 23 fractions, eluted with petroleum ether, furnished 975 mg. (78%) of cholestan-3-one (IX), m.p. 126–127°, while from the petroleum ether–benzene (1:1) eluates, 20 mg. (2%) of cholestan-3β-ol (VIII), m.p. 138–139°, was obtained. The last 6 fractions, eluted with benzene, were combined and treated in pyridine solution with 3,5-dinitrobenzoyl chloride in the usual fashion. Crystallization from hexane gave 676 mg. (52%) of needles of the 3,5-dinitrobenzoate of (+)1,1-diphenylpropan-2-ol (V), m.p. 154.5–155°, $[\alpha]^{25}_{D}$ −46.1° (c 1.4), unchanged after three recrystallizations ($[\alpha]^{25}_{D}$ −46.8°).

Anal. Calcd. for $C_{22}H_{18}N_2O_6$: C, 65.02; H, 4.46. Found: C, 64.78; H, 4.36.

A sample (400 mg.) of the 3,5-dinitrobenzoate was refluxed for 2 hours with 300 cc. of 5% methanolic potassium hydroxide and the (+)1,1-diphenylpropan-2-ol was crystallized three times from pentane, the melting point changing only by 1°; prisms, m.p. 57.5–58°, $[\alpha]^{25}_{D}$ +5.8° (c 2.1).

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.92; H, 7.64.

Desulfurization of 1.0 g. of isomer C (m.p. 152–153°) of the hemithioketal XXIII under precisely the same conditions yielded 80% of cholestan-3-one and 380 mg. (57%) of the 3,5-dinitrobenzoate of (−)1,1-diphenylpropan-2-ol (V), m.p. 154.5–155°, $[\alpha]^{25}_{D}$ +44° (c 1.7). Admixture with the above antipode lowered the m.p. to 129–130°, corresponding to the melting point of the racemic derivative which had been prepared independently.

Anal. Calcd. for $C_{22}H_{18}N_2O_6$: C, 65.02; H, 4.46. Found: C, 65.25; H, 4.57.

Saponification as described above followed by recrystallization from pentane yielded prisms of (−)1,1-diphenylpropan-2-ol, m.p. 57.5–58°, $[\alpha]^{25}_{D}$ −5.8° (c 2.6).

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.56; H, 7.63.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Azo Compounds. XV. Biradical Sources. The Synthesis and Decomposition of Large Membered Ring Azo Compounds[1]

BY C. G. OVERBERGER AND MILTON LAPKIN[2]

RECEIVED MARCH 28, 1955

The cyclic bis azo compounds VI (n = 8,10) have been prepared and characterized. A study of the decomposition of VI, n = 8, in xylene at 120° resulted in the isolation and characterization of VII, a twenty-membered carbon ring. From the rate data obtained, it is suggested that both azo linkages in VI, n = 8, do not decompose at exactly the same rate. Decomposition of VI, n = 8, in styrene gave no polystyrene under conditions in which a similar radical derived from a linear azo compound produced polymer. Thus, it is clear that biradical propagation cannot take place even under these favorable conditions.

We have initiated a study of the properties of moderately active biradicals in solution. A principal difficulty encountered in such a study has been the availability of biradical sources. There are numerous examples in the literature of organic compounds which are reported to contain two unpaired electrons in the triplet state. For the most part, however, these are either of the very stable triphenylmethyl type or very unstable biradicals suggested as intermediates in gas phase decompositions. It is impossible in an article of this type to review adequately the background but a compilation of references seems pertinent. One of the first compounds reported which showed some

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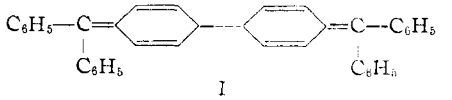
[1] Presented in part before the Polymer Division at the 126th Meeting of the American Chemical Society, New York, September 12–17, 1954. This is the 15th in a series of papers concerned with the preparation and decomposition of azo compounds. For the 14th paper in this series, see C. G. Overberger and B. F. Marks, THIS JOURNAL, **77**, 4104 (1955).

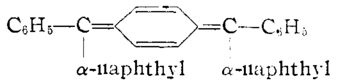
[2] This paper comprises a portion of a thesis presented by Mr. M. Lapkin in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

properties of a biradical, (p,p'-phenylene-bis-diphenylmethyl (named as a biradical, although it exists in quinoid form), was obtained by Thiele in 1904.[3]

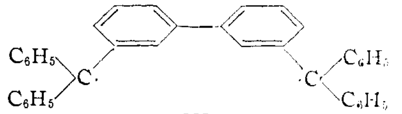
Muller and co-workers[4] in a series of papers demonstrated that stable biradicals exist in a number of cases (III) and that several of the compounds which previously had been thought to exist as biradicals were actually largely diamagnetic[5] (I, II). More recent work utilizing paramagnetic resonance techniques has suggested that compounds of type I and others may be paramagnetic to a very slight extent[6] *i.e.*



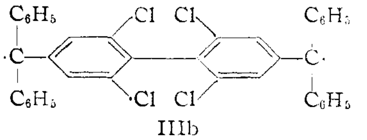
I



II

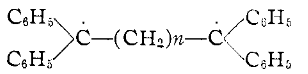


IIIa



IIIb

Wittig and co-workers[7] reported the effect of ring size on association or ring formation of the stable triarylmethane type of biradical. They attributed the radical dissociation of the hexasubstituted ethanes to the space occupied by, and the electrochemical character of, the substituents, and suggested that in strained ring systems there should be forces which also tend to increase the carbon bond distances and lead to dissociation to give biradicals. They prepared materials of different chain lengths of structure IV, and showed that when n was 1 or 2 the material was unassociated and had the chemical properties of a radical source.



$(C_6H_5)_2\dot{C}-(CH_2)_n-\dot{C}(C_6H_5)_2$

IV

A substantial amount of work has been reported on the transitory formation of biradicals, largely in the gas phase.[8]

A more recent development is concerned with the possibility of biradical initiation and biradical propagation in vinyl polymerization. The possible existence of biradicals in a vinyl polymerization was first discussed from a theoretical viewpoint by a number of workers.[9] Recent work both theoretical and experimental[10] has demonstrated the improbability of biradical propagation although the question of whether biradical initiation can occur has not been resolved.

The results indicated self termination or transfer of the biradicals within a short period of time, although the question whether any small ring polymer was actually formed by biradical initiation with a catalyst has not been answered. In a recent paper by Russell and Tobolsky[10f] concerned with the photolysis in methyl methacrylate of a cyclic disulfide, 1,4,5-oxadithiacycloheptane, as a source of biradicals, it was demonstrated that biradical propagation does not occur. From the ultraviolet spectrum of the solution, some indication was obtained that the biradical had reacted with at least one monomer unit before recombination since a loss of disulfide concentration was noted.

Recent workers[11] have reported the preparation of polymeric azo compounds[11a] and cyclic peroxides[11b,c] as catalysts for radical polymerization. However, no evidence to show whether polymerization did occur by biradical propagation is reported, or even whether the catalyst actually decomposed to give biradicals.

Cyclic azo compounds which would decompose at moderate temperatures to give biradicals seemed attractive for a number of reasons. The mechanism of decomposition of several types of linear azo compounds has been studied in detail by a number of investigators[12] so that background material was available.

The decompositions of azo compounds are usually capable of careful kinetic analysis as well as convenient product analysis. In particular, we desired a compound in which the competing reaction of cyclization would be minimized, that is a ring size which would be more difficult to form than conventional 5-, 6- or 7-membered rings. This would

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[3] J. Thiele and H. Balhorn, *Ber.*, **37**, 1463 (1904).

[4] (a) E. Muller and I. Muller-Rodloff, *Ann.*, **517**, 134 (1935); (b) E. Muller and I. Muller-Rodloff, *Ber.*, **68B**, 1276 (1935); (c) E. Muller and H. Neuhoff, *ibid.*, **72B**, 2063 (1939); (d) E. Muller and E. Tietz, *ibid.*, **74**, 807 (1941); (e) E. Muller and H. Pfanz, *ibid.*, **74**, 1051 (1941); (f) 1075 (1941); (g) E. Muller and E. Hertel, *Ann.*, **555**, 157 (1944).

[5] (a) A. E. Tschitschibabin, *Ber.*, **40**, 1810 (1907); (b) G. Wittig and W. Weiner, *Ann.*, **483**, 144 (1930); (c) S. Allard, *Compt. rend.*, **199**, 423 (1934); (d) W. Schlenk and M. Brauns, *Ber.*, **48**, 716 (1940); (e) E. Clar, *ibid.*, **65**, 503 (1932); (f) A. Schonberg, *Trans. Faraday Soc.*, **32**, 514 (1930); (g) C. Dufraisse and A. Etienne, *Compt. rend.*, **201**, 280 (1935).

[6] C. A. Hutchison, Jr., A. Kowalsky, R. A. Pastor and G. W. Wheland, *J. Chem. Phys.*, **20**, 1485 (1952).

[7] (a) G. Wittig and M. Leo, *Ber.*, **62B**, 1405 (1929); (b) **61B**, 854 (1928); (c) G. Wittig and F. von Lupin, *ibid.*, **61B**, 1627 (1928).

[8] (a) L. S. Kassel, *J. Chem. Phys.*, **1**, 749 (1933); (b) C. E. H. Bawn and R. F. Hunter, *Trans. Faraday Soc.*, **34**, 608 (1938); (c) C. E. H. Bawn and W. J. Dunning, *ibid.*, **35**, 185 (1939); (d) C. E. H. Bawn and J. Milsted, *ibid.*, **35**, 889 (1939); (e) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1521 (1938); (f) O. D. Saltmarsh and R. G. W. Norrish, *ibid.*, 455 (1935); (g) M. Szwarc, *J. Polymer Sci.*, **6**, 319 (1951).

[9] (a) C. D. Hurd, *Ind. Eng. Chem.*, **26**, 50 (1934); (b) H. Dostal and H. Mark, *Trans. Faraday Soc.*, **32**, 54 (1936); (c) P. J. Flory, THIS JOURNAL, **59**, 241 (1937).

[10] (a) R. N. Haward, *Trans. Faraday Soc.*, **46**, 204 (1950); (b) B. H. Zimm and J. K. Bragg, *J. Polymer Sci.*, **9**, 476 (1952); (c) D. H. Johnson and A. V. Tobolsky, THIS JOURNAL, **74**, 938 (1952); (d) K. E. Russell and A. V. Tobolsky, *ibid.*, **75**, 5052 (1953); (e) F. R. Mayo, *ibid.*, **75**, 6133 (1953); (f) K. E. Russell and A. V. Tobolsky, *ibid.*, **76**, 395 (1954).

[11] (a) J. W. Hill, U. S. Patent 2,556,876 (1951); (b) H. F. Park, U. S. Patent 2,620,330 (1952); (c) H. F. Park, U. S. Patent 2,664,416 (1953).

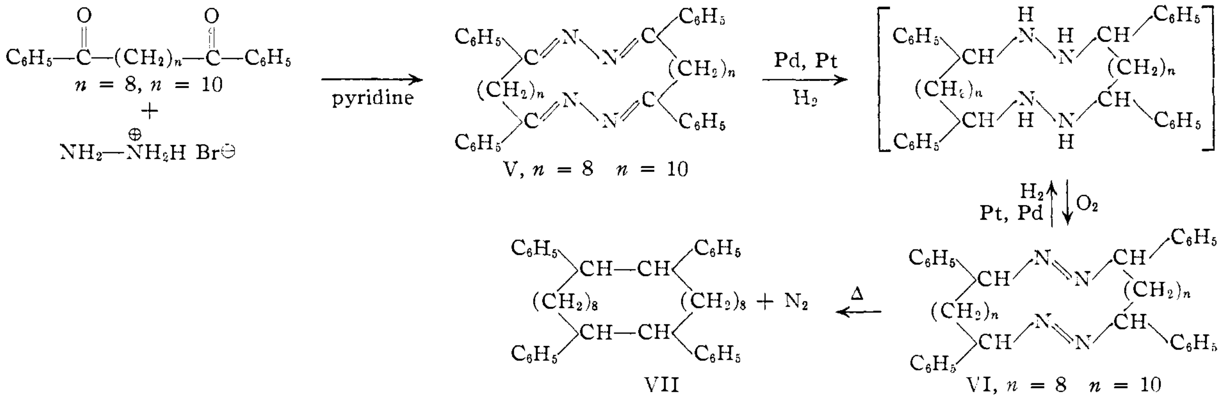
[12] (a) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, THIS JOURNAL, **71**, 2661 (1949); (b) S. G. Cohen, S. J. Groszos and D. B. Sparrow, *ibid.*, **72**, 3947 (1950); (c) S. G. Cohen and C. H. Wang, *ibid.*, **75**, 5504 (1953).

enable the initial product to at least be able to effect biradical initiation unless a very large cage effect was operative. Unfortunately, a 24-membered ring azo compound was obtained rather than the initially desired 12-membered ring compound.

This paper will describe the preparation of 3,12,15,24-tetraphenyl-1,2,13,14-tetraaza-1,13-cyclotetracosatetradiene (VI, $n = 8$) a 24-membered cyclic azo compound and the corresponding 28-membered ring cyclic azo compound VI, $n = 10$. The decomposition of VI, $n = 8$, in an inert solvent and in styrene also is reported.

A. Preparation of Azo Compounds

Discussion.—The cyclic azo compounds were prepared as shown in the following outline. The diketones were prepared from the appropriate dibasic acid chlorides and benzene by a typical Friedel and Crafts acylation procedure. Treatment of the diketone with hydrazine under very specific reaction conditions gave cyclic azine V.



The diketone was treated initially with hydrazonium bromide in dimethylformamide solution. The resulting hydrazone was found to be stable only in solution and could not be isolated. Dimethylformamide was the only solvent available which would dissolve both the diketone and the hydrazonium salt. After thorough mixing of the reactants the solution was diluted further with ethanol and added to refluxing ethanol containing pyridine under conditions of high dilution which gave a 22% yield of the cyclic azine (V, $n = 8$). Dilution was important and yields decreased as the concentration of reactants increased. The molecular weight of V, $n = 8$, was determined carefully by a number of methods, including the use of a Swietoslawski differential ebulliometer[13] and the Signer–Barger method of isopiestic analysis,[14] the latter procedure being used at room temperature. No differences in molecular weight are noted either in benzene or acetone and it seems clear that V, $n = 8$, is not an associated 12-membered ring. The infrared spectrum of V, $n = 8$, was shown to be identical when compared at room temperature and from 40–70° which was further evidence against association. V, $n = 8$, could be prepared by initial reaction of the diketone directly with the hydrazonium salt without preformation of the alleged hydrazone, although the yields were generally lower by this procedure. The other product obtained in the reaction was polymeric and was not characterized further. Presumably in the equilibrium mixture present in the dilution reaction the 24-membered ring is more stable than the 12-membered ring probably due to steric factors. It was noted that if the azine was allowed to stand in base over a period of time the yield decreased and polymer formation increased. The structure of the azine V was demonstrated by analysis, quantitative hydrogenation and by both infrared and ultraviolet absorption spectra. The infrared spectrum was very similar to that of a model linear azine, from propiophenone $C_6H_5\text{-}(C_2H_5)\text{-}C{=}NN{=}C(C_2H_5)C_6H_5$, with a characteristic C=N stretching frequency at 6.23 μ.[15] The spectrum of the 28-membered azine was identical with the 24-membered azine. The ultraviolet absorption spectrum shows a $\lambda_{max.}$ 272 mμ, ϵ_{max} 17,600, which is characteristic of an azine group of this type.[16,17] V, $n = 10$, was prepared under conditions similar to those reported for the 24-membered ring azine.

Hydrogenation in acidic solvents which has been used for the reduction of azines[18] was not suitable

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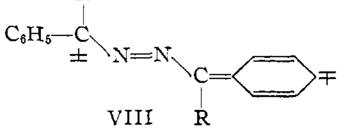
[13] W. Swietoslawski, "Ebulliometric Measurements," Reinhold Publ. Corp., New York, N. Y., 1945; W. E. Barr and V. J. Anhorn, *Instruments*, **20**, 822 (1947).

[14] E. P. Clark, *Ind. Eng. Chem., Anal. Ed.*, **13**, 820 (1941).

[15] P. D. Pickard and G. W. Polly, THIS JOURNAL, **76**, 5169 (1954).

[16] L. N. Ferguson and T. C. Goodwin, *ibid.*, **71**, 633 (1949).

[17] E. R. Blout, V. Eager and M. Gofstein, *ibid.*, **68**, 1983 (1946). The presence of one maximum in the ultraviolet absorption spectrum of V, $n = 8$, is in agreement with the conclusions drawn by Blout and co-workers in their examination of the ultraviolet absorption spectra of various aldazines and ketazines. They found that the effect of α-alkyl substitution in benzalazine was to shift the absorption maximum toward shorter wave lengths. Blout pointed out that the α,α'-dialkyl substituted benzalazines were made up of two absorbing units, the first the linear benzalazine structure which would be present only in a planar molecule, and the second is a structure absorbing at shorter wave lengths (about 270 mμ) which is probably associated with forms such as VIII, where one of the benzene rings is in a plane different from the other due to the effect of the α-alkyl group. These two absorbing units were found by Blout to occur in propiophenone azine which has a maximum at 270 mμ, and an inflection at ~295 mμ which probably was due to the transitions of the planar form. We found no inflection in the absorption spectrum of the cyclic azine where a planar structure would be impossible.



VIII

[18] H. L. Lochte, J. R. Bailey and W. A. Noyes, *ibid.*, **43**, 2597 (1921).

here because of ease of hydrolysis. Furthermore, it was necessary to use very pure azine for the hydrogenation to proceed successfully, an observation also made by Schulze and Lochte[19] in their reduction of a number of azines. Hydrogenation was only successful when a mixed catalyst was used composed of platinum oxide and palladium-on-charcoal. The product isolated from the reduction was not the expected hydrazine but rather the azo compound VI due to the ease of air oxidation of the intermediate hydrazine. Attempts to isolate the hydrazine in an inert atmosphere were unsuccessful due to the extreme rapidity of oxidation. The azo compound VII, $n = 8$, could be hydrogenated quantitatively over 10% palladium-on-charcoal and platinum oxide catalyst; however again oxidation during isolation occurred and the product isolated from the reduction was identical with the starting material. A picrate of the unstable hydrazine was isolated and characterized by performing the initial isolation procedure in an inert atmosphere. The azo compound VI did not form a picrate. The ultraviolet absorption spectrum was almost identical with that of the linear azo compound $C_6H_5CH(C_2H_5)N{=}NCH(C_2H_5)C_6H_5$[12b] and showed an absorption peak, λ_{max} 355 mμ, log ϵ_{max} 2.1. The infrared spectrum was very similar to that of the linear compound and devoid of any NH frequencies in the 3 μ area. The azo linkage would be expected to absorb in the 6.0 μ region in analogy with C=N and C=C, although it would likely be weak unless conjugated and might be absent in symmetrical structures.[20] No absorption in this region for both the cyclic or linear azo compounds appeared characteristic of the N=N group and if it does exist it must be very weak or possibly masked by the phenyl absorption.

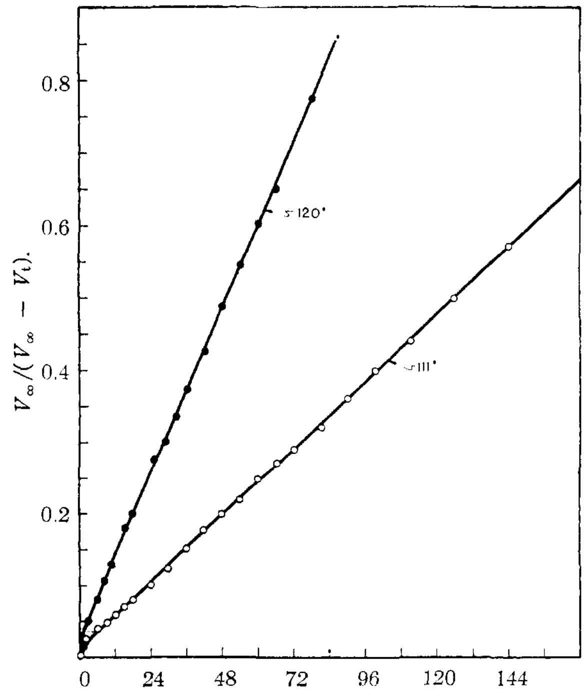


Fig. 1.—Decomposition of the cyclic azo compound, VI, $n = 8$.

The preparation of 1,10-diphenyl-1,10-decanediol and the corresponding dibromide which were starting materials for an unsuccessful synthesis are described in the Experimental section. The reduction of propiophenone azine with sodium amalgam and the isolation of the oxalate of the hydrazine ($C_6H_5CH(C_2H_5)NH{-}NH_2$) resulting from the hydrolysis of the half-reduced azine, the hydrazone, also is described.

The decomposition of VI, $n = 8$, was carried out in xylene at 120° with larger quantities than were used in the kinetic experiments in order to isolate and characterize the products. Although purification was difficult, compound VII, a 20-membered ring, was isolated in 72% yield and characterized.

The product did not decolorize potassium permanganate and no C=C frequency was found in the infrared spectrum in the 10.35 μ region. Attempted synthesis of VII by four separate synthetic methods involving high dilution failed. The initial diketone was isolated in low yield when VII was oxidized with chromic acid. A refluxing solution of iodine in xylene was decolorized[21] when a solution of VI, $n = 8$, was added, but no diiodide could be isolated.

B. Kinetic Measurements

I. **Procedure.**—The procedure for measuring rates of decomposition has been described previously.[12a,22]

II. **Results.**—The rate of decomposition of the cyclic azo compound VI, $n = 8$, as measured by nitrogen evolution at 119.8 and 110.8° in xylene, was found to be 2.2×10^{-4} and 8.9×10^{-5} sec.$^{-1}$, respectively. The energy of activation as calculated from these values was 30.2 kcal./mole. In Fig. 1 a plot of ln $V_\infty/(V_\infty - V_t)$ *vs.* time is reproduced for one of the experimental runs and is an example of the general accuracy of the determination. It will be noted that the plot is not an exact first-order plot. A rate has been determined from the more straight line portion of the curve after the initial rate. The reason for this discrepancy is discussed in the section to follow.

III. **Discussion.**—The calculated rate of decomposition was determined from the slope of the line in Fig. 1. The line does not pass through the origin because there was an apparent higher initial rate during the first five minutes of decomposition which could be duplicated. The presence of apparent induction periods was one of the experimental difficulties found by other workers[12a] for this method of kinetic analysis; it appears, therefore, that the initial rapid rate is not due to experimental error and we are investigating this question in more detail. Primary decomposition

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[19] W. A. Schulze and H. L. Lochte, THIS JOURNAL, **48**, 1030 (1926).

[20] L. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 229.

[21] M. C. Ford and W. A. Waters, *J. Chem. Soc.*, 1851 (1951).

[22] (a) C. G. Overberger and M. B. Berenbaum, THIS JOURNAL, **73**, 2618 (1951); (b) **73**, 4883 (1951); (c) C. G. Overberger, H. Biletch, A. B. Finestone, J. Lilker and J. Herbert, *ibid.*, **75**, 2078 (1953); (d) C. G. Overberger, W. F. Hale, M. B. Berenbaum and A. B. Finestone, *ibid.*, **76**, 6185 (1954).

should produce a biradical with the resultant formation of a linear azo linkage which should decompose at a slower rate than the cyclic azo linkage. It has been shown, however, that intramolecular coupling of the radicals occurs at least 72% of the time and since the rate of combination of the unstable biradical undoubtedly would be faster than the rate of decomposition of a second azo linkage, a 22-membered ring intermediate would be one explanation.

Although consideration of molecular models indicates a strain-free molecule with both azo groups *trans*, the most stable thermodynamic structure of an azo compound,[23] it is not certain that one of the azo linkages is not *cis* in the initial cyclic material. The azo compound isolated (VI, $n = 8$) as a crystalline solid represents one specific stereoisomer since geometric isomerism can exist and the decomposition pattern may represent the influence of different configurations near each azo linkage.

The value of k was similar to the rate of decomposition of the azo compound from propiophenone, whose rate at 120° was 2.1×10^{-4} sec.$^{-1}$, calculated from the data of Cohen, *et al.*[12b]

C. Polymerization

I. **Procedure.**—Styrene was washed with sodium hydroxide solution until both layers were colorless, then with distilled water until neutral, dried over anhydrous magnesium sulfate, and distilled in a nitrogen atmosphere under reduced pressure. It then was kept at Dry Ice temperatures until ready for use when it was redistilled. The pure styrene was weighed into glass tubes and degassed until there was no longer any dissolved air present. The tubes were then sealed and placed in a constant temperature bath for the desired period, removed, cooled rapidly to room temperature, the material dissolved in methyl ethyl ketone and precipitated by addition to methanol. The precipitated polystyrene was washed well with additional methanol and dried in a vacuum oven to constant weight.

II. **Results.**—Table I presents the results obtained from the thermal polymerization of pure styrene, styrene and the cyclic azo compound VI, $n = 8$, and styrene with the linear azo compound $C_6H_5(C_2H_5)CHN{=}NHC(C_2H_5)C_6H_5$. The values obtained for % conversion clearly show that initiation by the cyclic azo catalyst was extremely inefficient for the propagation of a growing polymer chain. The rate of decomposition of propiophenone azo compound was slightly less than the rate of decomposition of the cyclic azo compound at 100° so that the poor catalyst activity of the cyclic compound should not be due to a deficiency of radicals. Haward[10a] discussed the role of biradicals in a polymerizing medium on a statistical basis and concluded that biradicals will be terminated chiefly by intramolecular reaction as opposed to termination involving radicals of two different chains. Zimm and Bragg[10b] also discussed the possible reactions of biradicals from a theoretical standpoint and concluded that biradical propagation to give high polymeric material should constitute a very small portion of any polymerization process with the resultant formation of low molecular weight rings. These calculations were based, however, on the thermal polymerization of pure styrene and may not represent the case of a polymerization induced by biradicals from an added catalyst. The lack of reactivity of the cyclic azo catalyst probably was due to two factors: self termination to form small rings resulting after a few units of styrene were added which is indicated by the small increase in polymer formation with added catalyst, and recombination of the primary biradical being sufficiently rapid to become diffusion controlled to the extent that some of the radical pairs never become separated. We are endeavoring to study these possibilities in greater detail.

TABLE I

POLYMERIZATION OF STYRENE WITH THE 24-MEMBERED CYCLIC AZO CATALYST, VI, $n = 8$

Catalyst, mole, %	Temp., °C.	Time, hr.	Polymer yield, %
0.0	60.4	26.5	1.8
.065	60.4	20.0	2.7
.0	80.0	8.0	4.7
.189	80.0	8.0	6.2
.0	98.2	1.0	2.2
.297	98.2	1.0	4.6
Propiophenone azo catalyst,			
0.725	98.2	1.0	30.2

Experimental[24]

Preparation of the 24-Membered Ring Azine, 3,12,15,24-Tetraphenyl-1,2,13,14-tetraaza-2,12,14,24-cyclotetracosatetraene.—After a large number of initial experiments it was found that the procedure discussed below gave the highest yield. Solutions of 32 g. (0.1 mole) of 1,10-diphenyl-1,10-decanedione,[25,26] m.p. 94–96°, 75% (prepared from sebacoyl dichloride)[27] in 550 ml. of dimethylformamide, and 11.2 g. (0.01 mole) of hydrazonium bromide[28] (from 85% hydrazine hydrate and 48% aqueous hydrobromic acid, m.p. 86.5–88.5°, 85%) in 350 ml. of dimethylformamide (both solutions initially were warmed separately to dissolve the materials) were mixed together and allowed to shake for two days until homogeneous, and then to stand for an additional three days (solution A). The monohydrazone hydrobromide of the diketone, which is the product which probably forms during the shaking period, was stable only in solution, since attempts to isolate the hydrazone by evaporation or distillation of the solvent resulted in every case in the isolation of a yellow crystalline material of polymeric character which did not contain bromine.

To 7.5 l. of ethanol and 300 ml. of pyridine was added solution A further diluted with 2.1 l. of ethanol, over a period of five days, with continuous reflux and vigorous stirring. It is desirable to dissolve aliquot portions of A in the ethanol only as needed, since precipitation of yellow polymeric material takes place if the solution stands over an extended period of time. The reaction mixture, after addition is complete, was refluxed with stirring for two additional days and the solvent then was removed under vacuum to a volume of 1.5 l. This solution then was poured, with stirring, into 2.5 kg. of ice-water and a yellow waxy solid separated. The precipitate was removed by filtration with the aid of Filter-cel, washed well with water, and then washed twice with cold methanol and twice with hot methanol. The product then was crystallized from ether with Norite. It was important to crystallize fractionally at this point; material was collected only as long as a further decrease in the volume of the ether resulted in precipitation of crystalline material. When a further decrease in the volume of the filtrate resulted in the formation of an oil, the remaining ether was removed, the oil allowed to dry for

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[23] A. C. Freeman and R. J. W. LeFevre, *J. Chem. Soc.*, 415 (1951); R. J. W. LeFevre and C. V. Worth, *ibid.*, 1814 (1951).

[24] All melting points are corrected.

[25] N. Auger, *Ann. chim. phys.*, [6] **22**, 363 (1891).

[26] J. K. Simons, U. S. Patent, 2,396,893, March, 1946.

[27] T. Lieser and K. Macura, *Ann.*, **548**, 226 (1941).

[28] E. C. Gilbert and A. W. Cobb, THIS JOURNAL, **57**, 39 (1935).

several hours in an air current, the process of washing with methanol repeated, and the material then was fractionally crystallized from acetone with Norite. All crystalline material obtained then was recrystallized two times from acetone and once from ether, washing with hot methanol after each recrystallization, to give 7 g. (22%) of light yellow azine, m.p. 146.0–147.0°. Two further recrystallizations from acetone gave an analytically pure sample, m.p. 146.5–147.5°.

Anal. Calcd.[29] for $C_{44}H_{52}N_4$: C, 82.95; H, 8.23; N, 8.79; mol. wt., 637. Found: C, 82.84; H, 8.38; N, 8.90; mol. wt., 648, acetone; 597, benzene (Swietoslawski differential ebulliometer)[13]; 627, butanone (ebullioscopic); 571, chloroform (Signer–Barger method).[14] The infrared spectrum was very similar to that of the linear compound $C_6H_5C(C_2H_5){=}NN{=}(C_2H_5)CC_6H_5$ with a characteristic C=N stretching frequency at 6.23 μ.[15] The ultraviolet absorption spectrum had a characteristic azine peak conjugated with phenyl at 272.5 mμ, ϵ_{max} 17,600.[16]

Hydrogenation of the Azine.—The purity of the azine had a profound effect upon the success of the hydrogenation. Unless pure material was used for the hydrogenation the reduction usually did not go to completion, and it was difficult to isolate any crystalline material from the reaction. The azine, 7 g. (0.011 mole), suspended in 200 ml. of ethanol to which 0.5 g. of platinum oxide and 0.5 g. of 10% palladium-on-charcoal had been added, absorbed four mole equivalents of hydrogen after being shaken for three hours at a temperature of 63°, and at a pressure of 3 atm. Reduction was unsuccessful when the individual catalysts were used alone. The solution became colorless after a successful reduction and the change in color indicated that the reduction had proceeded to completion. The reaction was allowed to cool to about 45° and the catalyst removed by filtration. The purification of the product was simplified when care was taken to filter the solution from the catalyst before the system reached room temperature since the unstable, highly supersaturated solution easily deposited crystals. Cooling to ice temperatures resulted in the precipitation of 4.6 g. of white material. About 1.0 g. more of material can be recovered by decreasing the volume of filtrate by evaporation; total yield of crude product (80%). The product was purified by washing with hot methanol, and recrystallized from ether two times and petroleum ether (b.p. 30–60°) three times to give white crystals, m.p. 130–131° dec. It very slowly decomposes at room temperature.

Quantitative hydrogenation of the azine was carried out at atmospheric pressure. The bottle was heated by means of an attachable heating jacket and the reduction was carried out as described above except that the catalyst was pre-reduced and the shaking period was increased (10 to 20 hours). The azine absorbed 93% of the theoretical hydrogen required for reduction of the four azine linkages. The above material was not the expected hydrazine but rather the 3,12,15,24-tetraphenyl-1,2,13,14-tetraaza-1,13-cyclotetracosatetradiene containing two azo linkages, formed by oxidation of the hydrazine in air. The material contained no –NH– frequency in its infrared spectrum, and had a peak at 357 mμ in its ultraviolet spectrum indicative of an azo linkage of this type conjugated with phenyl.[12b,30]

The infrared ultraviolet spectra were very similar to that of the linear compound, $C_6H_5CH(C_2H_5)N{=}N(C_2H_5)CH{-}C_6H_5$.

Anal. Calcd. for $C_{44}H_{56}N_4$: C, 82.45; H, 8.81; N, 8.74; mol. wt., 641. Found: C, 82.72, 82.19; H, 9.01, 9.12; N, 8.94, 9.03; mol. wt., 611, chloroform; 574, carbon tetrachloride (Signer–Barger method).

The Picrate of the Hydrazine. 3,12,15,24-Tetraphenyl-1,2,13,14-tetraazacyclotetracosatetraene.—As was indicated above, the hydrazine was unstable in air, and attempts to isolate the pure compound in an inert atmosphere were unsuccessful; therefore a salt of the hydrazine was prepared. Difficulty was encountered in isolating a salt, and a number of unsuccessful attempts were made with some inorganic and organic acids before success was achieved with picric acid. The azine VI, $n = 8$, 1.5 g. (0.0023 mole), suspended in 40 ml. of petroleum ether (b.p. 60–68°) containing 0.3 g. of platinum oxide and 0.3 g. of 10% palladium-on-charcoal was hydrogenated at room temperature at 3 atm. for several minutes to pre-reduce the catalyst. The mixture then was heated to 60° and hydrogenated for six hours to give a colorless solution. To this was added a solution of 3.0 g. (0.013 mole) of picric acid in 300 ml. of absolute ether; the entire operation was performed in a nitrogen atmosphere. Nitrogen had been bubbled through the ether solution of picric acid previously. The solution was stoppered and allowed to stand for 12 hours. It was then filtered and reduced to one-half its volume. A small amount of oil was present which was removed by decantation.

The decanted solution was allowed to evaporate to dryness, leaving a dark red waxy solid which was washed well with ethanol leaving undissolved 0.2 g. (0.8%) of yellow solid. The material was crystallized from an acetone-ethanol solution, the solvent dissolved in an acetone–benzene solution. Removal of the solvent gave an oil which crystallized upon addition of a small amount of ethanol with scratching. This solid was washed with cold ethanol, then warm ethanol and finally benzene to give yellow crystals, m.p. 164.5–165.5° dec.

Anal. Calcd. for $C_{56}H_{66}N_{10}O_{14}$: C, 60.97; H, 6.03; N, 12.70. Found: C, 61.03; H, 5.87; N, 12.79.

The azo compound VI, $n = 8$, did not form a picrate when treated with picric acid under similar conditions.

Quantitative Hydrogenation of the Azo Compound.—To a semi-micro hydrogenator containing 0.4 g. of platinum oxide and 0.3 g. of 10% palladium-on-charcoal catalyst pre-reduced in 20 ml. of ethanol, was added 0.1620 g. (0.00025 mole) of azo compound. In 10 hours, the material absorbed 102% of the theoretical moles of hydrogen. The catalyst was removed and washed with ether and the filtrate concentrated to a small volume and cooled. Oxidation during isolation occurred and the azo compound was recovered, m.p. 128.5–132°. A mixed melting point with the starting material, m.p. 131–132°, melted at 129–132°.

1,12-Diphenyl-1,12-dodecanedione.—1,10-Decanedicarboxylic acid[31] (from 1,10-dibromodecane, m.p. 121–124.5°, 50%), 42.5 g. (0.18 mole), was refluxed with 66 g. (0.5 mole) of thionyl chloride for three hours according to the method previously described.[25] The excess thionyl chloride then was distilled under vacuum to give 47 g. of the crude 1,10-decanedicarboxylic acid chloride. It decomposed readily on distillation, b.p. 162° (1.6 mm.), d^{30}_4 1.0069, and hydrolyzed readily in moist air. A suspension of 60 g. (0.45 mole) of aluminum chloride and 500 ml. of dry benzene was prepared. To the rapidly stirring mixture was added 43 g. (0.16 mole) of the crude acid chloride over a period of 30 minutes, while the flask was cooled by means of an ice-bath. The surrounding ice then was removed, and stirring was continued until the evolution of hydrogen chloride had ceased—about two hours. The contents of the vessel then were poured slowly and with constant stirring into a mixture of 200 g. of ice and 60 ml. of concentrated hydrochloric acid. Sufficient benzene then was added to dissolve any white precipitate that was present, the benzene layer was separated and washed, first with a dilute solution of sodium carbonate and then with water. Care should be taken in washing with the sodium carbonate solution to have sufficient benzene present, otherwise precipitation of diketone occurs on addition of the carbonate. The benzene solution then was concentrated to a small volume and allowed to cool to give 39 g. (68%) of the crude 1,10-dibenzoyldecane, m.p. 86–91°. An analytically pure sample was obtained by washing the material through a column of activated alumina using chloroform as the solvent, and successively recrystallizing the material from ethanol, methanol and ether to give white crystals, m.p. 98.0–99.0°.

Anal. Calcd. for $C_{24}H_{30}O_2$: C, 82.23; H, 8.63. Found: C, 82.27; H, 8.55.

Preparation of the 28-Membered Ring Azine, 3,14,17,28-Tetraphenyl-1,2,15,16-tetraaza-2,14,16,28-cyclooctacosatetraene.—This azine was prepared according to the directions given for the 24-membered azine. From the solution of 7 g. (0.02 mole) of 1,12-diphenyl-1,12-dodecanedione and 2.26 g. (0.02 mole) of hydrazonium bromide in 400 ml. of dimethylformamide, further diluted with 1 l. of ethanol and then added to 2.5 l. of ethanol containing 150 ml. of pyridine, was obtained 1.85 g. (26%) of crude azine. Recrystallizations from acetone and ether and washing with hot

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(29) Analyses by Dr. K. Ritter, Zurich, Switzerland; Dr. F. Schwarzkopf, New York, N. Y.; Dr. H. S. Clark, Urbana, Ill.

(30) G. Fedor and P. Szarvas, *Ber.*, **76B**, 334 (1943).

(31) P. Chuit, *Helv. Chim. Acta*, **9**, 264 (1926).

methanol before each crystallization, gave very light yellow crystals, m.p. 108.0–109.5°.

Anal. Calcd. for $C_{48}H_{60}N_4$: C, 83.22; H, 8.73; N, 8.09; mol. wt., 693. Found: C, 83.10; H, 8.59; N, 8.19; mol. wt., 650 (camphor).

The infrared spectra of the 24- and the 28-membered ring azines were identical.

Preparation of the 28-Membered Ring Azo Compound.—This azo compound was prepared according to the directions given for reduction of the 24-membered ring azine. From 3.12 g. (0.0045 mole) of azine there was obtained a yellow oily solid after evaporation of solvent, which gave 0.8 g. (25%) of crude crystalline material on washing with a small amount of ether. The product was recrystallized twice from acetone and then ether to give white crystals, m.p. 129.0–131.0° dec. It decomposed slowly at room temperature.

Anal. Calcd. for $C_{45}H_{64}N_4$: C, 82.70; H, 9.26; N, 8.04. Found: C, 82.90; H, 9.05; N, 8.26.

The infrared spectra of the 24- and 28-membered ring azo compounds were essentially identical.

Lithium Aluminum Hydride Reduction of 1,10-Diphenyl-1,10-decanedione.—To 11.2 g. (0.4 mole) of lithium aluminum hydride in 640 ml. of anhydrous ether was added with stirring a solution of 75 g. (0.23 mole) of 1,10-diphenyl-1,10-decanedione in 350 ml. of tetrahydrofuran over a period of 2 hours. The reaction mixture then was stirred for an additional 30 minutes before the excess hydride was destroyed with ethanol followed by water. The mixture was filtered from the hydroxides and the solvent removed to give 56 g. of the white crystalline alcohol. The precipitate of hydroxides then was washed well with hot benzene to give, upon removal of the solvent, 10 g. more of alcohol, total yield, m.p. 64–67° (85%) (70–72°, prepared from the diketone, sodium and alcohol).[32]

1,10-Diphenyl-1,10-dibromodecane.—Dry hydrogen bromide was passed through a suspension of 20.5 g. (0.64 mole) of the 1,10-diphenyl-1,10-decanediol partly dissolved in 100 ml. of dry benzene for four hours, the reactant being kept at a temperature of 15–20° during the reaction period. All of the diol had gone into solution after the first hour. The weight of the flask remained constant during the last hour. The benzene solution was washed with water, and then three times with a saturated solution of sodium bisulfate until the solution had turned colorless. The solution was dried over potassium carbonate, the benzene then was removed and the oil that remained was crystallized from ether with cooling in a Dry Ice–acetone-bath with vigorous stirring during the crystallization period to prevent caking of the material to give 19 g. (67%) of white solid which must be thoroughly sucked free from solvent as rapidly as possible to prevent the material from melting. An analytical sample was prepared by recrystallizing the product twice from ether and once from a petroleum ether (b.p. 28–38°)-ethanol solution, cooling and stirring as described above after each crystallization, to give white crystals, m.p. 40 0–43.5°.

Anal. Calcd. for $C_{22}H_{28}Br_2$: C, 58.42; H, 6.23; Br, 35.34. Found: C, 58.62; H, 6.20; Br, 35.35.

Preparation of Structurally Similar Compounds.—In order to compare the infrared absorption spectra of linear compounds of similar structure with the cyclic ones, the propiophenone azine, the corresponding hydrazine and azo compounds were prepared according to the directions of Cohen, *et al.*[12b] Samples of the azine and azo compounds were recrystallized from ethanol and their infrared absorption spectra were obtained.

Reduction of Propiophenone Azine with Sodium Amalgam.—To a refluxing solution of 10 g. (0.04 mole) of propiophenone azine in 65 ml. of ethanol which was stirred while continuously flushed with nitrogen, was added over a period of 1.25 hours, 130 g. (0.13 mole) of 2% sodium amalgam.[33] The color of the solution changed from a deep orange to a very light yellow. The solution was heated for an additional 30 minutes and stirred for one hour longer. All the operations described below were performed in a nitrogen atmosphere until formation of the salt. A portion of the solution was poured into 800 ml. of water (previously flushed with nitrogen) and the resulting precipitate was filtered to give a small amount of waxy solid. This was dissolved in ethanol and a saturated solution of anhydrous oxalic acid in ethanol was added. On standing, 1.5 g. of a white precipitate formed. This was recrystallized from ethanol, washed twice with ether, and recrystallized twice more from ethanol to give white crystals of the oxalate of propiophenone hydrazine (probably formed by hydrolysis of the propiophenone hydrazone) and formation of the oxalate, m.p. 129.0–130.0° dec.

Anal. Calcd. for $C_{11}H_{16}N_2O_4$: C, 54.98; H, 6.71; N, 11.66. Found: C, 54.84; H, 6.65; N, 11.66.

Decomposition Products. Formation of a 20-Membered Cyclic Hydrocarbon.—To 100 ml. of xylene in a flask with a nitrogen inlet and a stirrer to which nitrogen was continuously introduced, was added 12.0 g. of 24-membered cyclic azo compound and the material allowed to decompose for 20 hours. The xylene then was removed in a current of air and the yellow waxy material which remained was placed in a small column and distilled. A small amount of material was collected below 290° (0.35 mm.). The material which distilled at 299–312° (0.35 mm.) was collected, the major portion distilling at 312° (0.35 mm.) to give 8.45 g. of a light yellow viscous material. This was dissolved in petroleum ether (b.p. 28–38°) leaving 300 mg. (2.7%) of solid, m.p. 107–120°. This product was purified but not characterized.

The petroleum ether solution from the above procedure was passed through a column of activated alumina with 800 ml. of petroleum ether as the eluent to give 7.9 g. (72%) of a colorless glassy material, $n^{25}\mathrm{D}$ 1.5620, which did not decolorize permanganate and analyzed correctly for a 20-membered cyclic hydrocarbon.

Anal. Calcd. for $C_{44}H_{56}$: C, 90.35; H, 9.65; mol. wt., 585. Found: C, 90.49, 90.13; H, 9.66, 9.88; mol. wt., 550, 556, butanone (ebullioscopic).

Oxidation of the Cyclic Hydrocarbon.—A mixture of 1.3 g. of VII, 45 ml. of glacial acetic acid, 10 g. of potassium hydrogen sulfate and 5 g. of chromium(VI) oxide was refluxed for 16 hours. The potassium hydrogen sulfate was removed from the reaction mixture by filtration, the filtrate made slightly basic with sodium carbonate, and extracted several times with methylene chloride and then ether. The organic extracts were dried over magnesium sulfate, the solvent removed and the oil which remained was recrystallized from methanol with Norite to give 0.07 g. (5%) of a white solid, m.p. 94–96°, which did not depress the m.p. of an authentic sample of 1,10-diphenyl-1,10-decanedione. Its infrared spectrum was similar to that of the authentic sample.

The water layer from the above extraction was acidified with nitric acid and extracted with ether. The ether extract was dried over magnesium sulfate and the solvent removed to give a waxy solid which was recrystallized from water with Norite to give 0.35 g. (32%) of white product that did not depress the m.p. of an authentic sample of benzoic acid.

Spectra.—A Perkin-Elmer model 21 double beam recording spectrophotometer was employed with a NaCl prism to study the 2–15 μ range. The ultraviolet absorption spectra were determined with a Beckman quartz ultraviolet spectrophotometer in purified ethanol as a solvent.

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[32] W. Borsche and J. Wollemann, *Ber.*, **44**, 3185 (1911).

[33] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 418.