Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.53; H, 6.21.

Diketone IX gave a red-violet enol test with ferric chloride. Oxidation of IX with alkaline potassium permanganate gave phthalic acid in 76% yield.

Treatment of diketone IX with refluxing ethanolic hydrazine gave a good yield of pyrazole XI, m.p. 173.5–174° after recrystallization from benzene–hexane.

Anal. Calcd. for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21. Found: C, 78.30; H, 6.67; N, 15.22.

A sample of diketone IX was refluxed with aqueous sodium hydroxide under a nitrogen atmosphere to give β-tetralone, which was isolated as its semicarbazone, m.p. 191–192° after three recrystallizations from ethanol, lit.[20] m.p. 193–194°. The odor of acetic acid could be detected in the acidified hydrolysate. When the hydrolysis was not conducted in a nitrogen atmosphere, the blue-black color, characteristic of the base-catalyzed air oxidation of β-tetralone,[21] was detected.

2-(*o*-Chlorobenzyl)-1,3-butanedione (XII).—To a cooled solution of 1.0 mole of sodium ethoxide (prepared from 23 g. of sodium) in 500 ml. of absolute ethanol was added a mixture of 172 g. (0.94 mole) of 4-(*o*-chlorophenyl)-2-butanone[12] and 80.0 g. (1.08 moles) of ethyl formate.[13] The solution was stirred at room temperature for 16 hr. Ethanol was removed under reduced pressure. To the residue was added ice–water, followed by 100 ml. of hydrochloric acid, and finally 500 ml. of ether. Crystals of XII (74 g., m.p. 120–122°) formed in the mixture, and were removed by filtration. The ethereal layer of the filtrate was separated and evaporated to a small volume to give an additional 42 g. of XII, m.p. 107–117°. The total yield of 2-(*o*-chlorobenzyl)-1,3-butanedione (XII) was 116 g. (58%). Recrystallization from methanol afforded crystals, m.p. 122–123°.

Anal. Calcd. for $C_{11}H_{11}ClO_2$: C, 62.76; H, 5.26; Cl, 16.83. Found: C, 62.69; H, 5.08; Cl, 17.04.

The green copper chelate of XII, m.p. 202–203° after recrystallization from benzene, was prepared by treatment with aqueous cupric acetate.

Anal. Calcd. for $C_{22}H_{20}Cl_2O_4Cu$: C, 54.72; H, 4.18; Cl, 14.69; Cu, 13.16. Found: C, 55.06; H, 4.10; Cl, 15.00; Cu, 13.46.

Formation of Binaphthol XV from XII.—To a solution of 13.2 g. (0.063 mole) of β-ketoaldehyde XII in 125 ml. of liquid ammonia and 125 ml. of anhydrous ether was added 0.264 mole of potassium amide (prepared from 10.3 g. of potassium) in 300 ml. of liquid ammonia. After 1 hr., ammonium chloride was added to the dark green solution to neutralize excess base and the ammonia was evaporated. The residue was extracted with dilute hydrochloric acid and ether. The ethereal solution was separated and evaporated. The residual solid was washed with benzene to leave 3.1 g. (29%) presumably of 2,2′,α,α′-tetrahydroxy-3,3′-dimethyl-1,1′-binaphthyl (XV), m.p. 216°, and m.p. 231–232° after chromatography on silica gel and recrystallization from ethyl acetate.

Anal. Calcd. for $C_{22}H_{18}O$: C, 75.84; H, 5.79; mol. wt., 346. Found: C, 76.03, 75.94; H, 5.07, 5.08; mol. wt., 356.[22]

This compound gave an enol test with ethanolic ferric chloride, but neither a copper chelate nor a pyrazole could be prepared.

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[20] N. M. Przhiyalgovskaya, L. N. Lavrisheva, and V. N. Belov *J. Gen. Chem. USSR*, **27**, 1349 (1957).

[21] J. W. Cornforth, R. H. Cornforth, and R. Robinson, *J. Chem. Soc.*, 689 (1942).

[22] The molecular weight was determined at 37° in acetone solution employing a Mechrolab osmometer.

Benzylation and Dehydrogenation of 3-Phenylindan-1-one through Its α,β-Dicarbanion. Synthesis of 3-Phenylindenone[1]

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3-Phenylindan-1-one (I) underwent a twofold acid–base reaction with two molecular equivalents of sodium amide in liquid ammonia to form α,β-disodio salt II, which underwent alkylation with benzyl chloride to give β-benzyl derivative III. The monosodio salt of I was benzylated to afford the α-benzyl derivative V. III was reduced to give 1-benzyl-1-phenylindane. Dehydrogenation of I through its disodio salt II was effected with 2,3-dibromo-2,3-dimethylbutane to form 3-phenylindenone. Similar dehydrogenations of 2,3-diphenylindanone and 2,3,3-triphenylpropionitrile were effected through their dicarbanions to yield 2,3-diphenylindenone and 2,3,3-triphenylacrylonitrile, respectively. Possible mechanisms for this new method of dehydrogenation are mentioned.

Since 3-phenylindan-1-one (I) has not only α-hydrogens but also a β-hydrogen activated by two aryl groups, it might be expected to undergo a twofold acid–base reaction with sodium amide in liquid ammonia to form α,β-disodio salt II. This was realized as demonstrated not only by production of a deep red color like that of the diphenylmethide ion[2] but also by alkylation with a molecular equivalent of benzyl chloride to form β-benzyl derivative III in 73% yield (Scheme A).

Similar to the benzylation of sodium diphenylmethide in liquid ammonia,[2] that of disodio salt II was rapid as indicated by immediate discharge of the red color by the equivalent of halide.

That the conversion of I to II as represented in Scheme A was essentially complete was indicated not only by the high yield of III but also by the lack of formation of an isolable amount of stilbene, some of which would probably have been produced had there been an appreciable amount of amide ion present in the equilibrium.[3]

Although disodio salt II was generally prepared by addition of I to the reagent, the inverse addition procedure was also employed to show the intermediate formation of monosodio salt IV. Thus, when sodium amide in liquid ammonia was added slowly to I in ether the yellow-brown color of IV persisted until slightly more than a molecular equivalent had been added; then the red color of II became evident and deepened until addition of the second equivalent of the base was complete.

The product from the benzylation of II was shown *not* to be the possible α-benzyl derivative V, which was prepared from monosodio salt IV and benzyl chloride in diglyme (β,β′-dimethoxydiethyl ether) at 100°. Incidentally, IV failed to afford an isolable amount of

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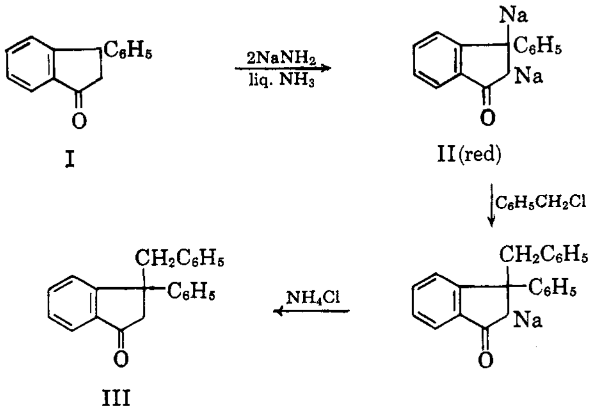
[1] Supported by the National Science Foundation Grant No. G 14527.

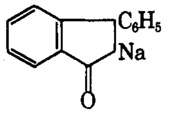
[2] C. R. Hauser and P. J. Hamrick, *J. Am. Chem. Soc.*, **79**, 3142 (1957).

[3] The stilbene would have arisen through self-alkylation of the benzyl chloride; see C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *ibid.*, **78**, 1653 (1956).

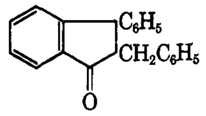
SCHEME A



V with benzyl chloride in liquid ammonia during an hour. This is not surprising since benzylation of potassioacetophenone has been observed to be very slow in this medium (−33°).[4]

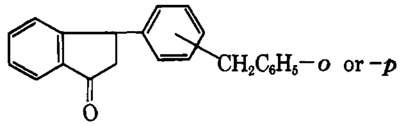


IV



V

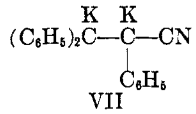
The assignment of structure III to the product obtained from benzylation of II was supported by its nuclear magnetic resonance spectrum[5] which showed, beside the aromatic multiplet resonance, a singlet at τ 6.58 and an unperturbed AB quartet at τ 7.16 (J = 18 c.p.s.). The integrated peak area ratio for the singlet to the quartet is 1:1. The rather large spin–spin coupling constant for the AB system indicates that this coupling is of the *geminal* rather than the *vicinal* type. The band at τ 6.58 was assigned to the β-benzyl protons of III and the quartet at higher frequency to the α-methylene protons.[6] In agreement with structure III the resonance frequency of one of these latter protons was increased by the shielding effect of the β-phenyl substituent.[7] This spectrum is incompatible with V or the *o*- or *p*-benzyl derivatives VI, which appear to be the only other possible structures for the benzylation product of II.



VI

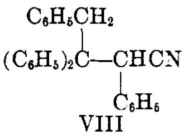
As anticipated, Clemmensen reduction of β-benzyl derivative III afforded a hydrocarbon, which was presumably 1-benzyl-1-phenylindane (66%).

The formation of α,β-disodio salt II and its benzylation at the β-position to give III (Scheme A) is similar to the previously observed formation of α,β-dipotassio salt VII and its benzylation to afford VIII.[8]



$(C_6H_5)_2\overset{K}{C}-\underset{C_6H_5}{\overset{K}{C}}-CN$

VII

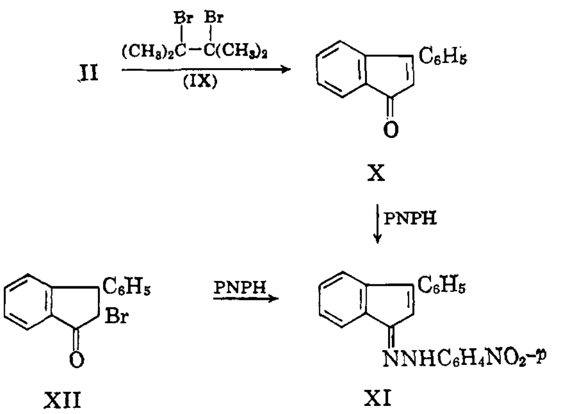


$(C_6H_5)_2\underset{C_6H_5}{\overset{C_6H_5CH_2}{C}}-CHCN$

VIII

Next, 3-phenylindan-1-one (I) was dehydrogenated through its disodio salt II to form 3-phenylindenone (X) in 40–50% yield. This was accomplished with 2,3-dibromo-2,3-dimethylbutane (IX), which was presumably converted to 2,3-dimethylbutene.[9] The infrared spectrum of the crude product X showed bands at 1713 and 1621 cm.$^{-1}$ which may be ascribed to the cyclopentadienone[10] and the conjugated olefinic groups,[11] respectively. Because of its susceptibility to oxidation, X was isolated as its *p*-nitrophenylhydrazone XI. The over-all yield of XI from I was 37–46%. The structure of XI was established by an independent synthesis from α-bromo ketone XII[12] and *p*-nitrophenylhydrazine (PNPH) as described previously[13] (Scheme B).

SCHEME B



That the product obtained in the reaction of disodio salt II with dibromide IX was not the possible α-bromo ketone XII (see Scheme B) was shown by negative Lassaigne and Beilstein tests for halogen and by comparison of the infrared spectra of the two compounds.

Although the conversion of α-bromo ketone XII to *p*-nitrophenylhydrazone XI involved dehydrobromination, attempts to effect dehydrobromination of XII to form X by means of aqueous sodium acetate and of aqueous or alcoholic potassium hydroxide were unsatisfactory; apparently X was unstable towards the latter reagent.

The present method of synthesis of unsaturated ketone X appears to be superior to an earlier method involving cyclization and dehydration of β-hydroxy ester XIII, which has been reported to afford X in extremely poor yield.[14] No analysis was given.[14] Several attempts by us to prepare X from XIII were unsatisfactory apparently because the conditions that appeared to be required for cyclization converted X to truxones XIV (see Experimental).

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(4) C. R. Hauser and T. A. Mashburn, *J. Org. Chem.*, **26**, 1795 (1961).

(5) We are indebted to Dr. Walter L. Meyer, Dept. of Chemistry, Indiana University, Bloomington, Ind., for this spectrum.

(6) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 57.

(7) See ref. 6, p. 125.

(8) C. R. Hauser, T. M. Harris, and T. G. Ledford, *J. Am. Chem. Soc.*, **81**, 4099 (1959).

(9) K. Ziegler and B. Schnell, *Ann.*, **437**, 227 (1924).

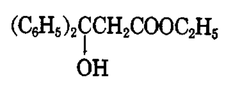
(10) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 148.

(11) L. J. Bellamy, *ibid.*, p. 35.

(12) R. Weiss and S. Luft, *Monatsh.*, **48**, 337 (1927).

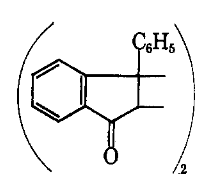
(13) K. von Auwers and R. Hugel, *J. prakt. Chem.*, **143**, 157 (1935).

(14) R. de Fazi, *Gazz.*, **49**, 253 (1919).



$$\underset{\text{OH}}{(C_6H_5)_2\overset{}{C}}CH_2COOC_2H_5$$

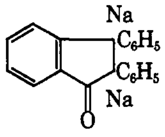
XIII



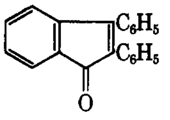
XIV

However, the recent method of Blomquist and Moriconi[15] involving dehydrogenation of I with selenium dioxide furnishes another satisfactory method. As in our case, these workers isolated X as a derivative (semicarbazone).

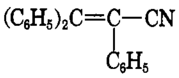
To show that the present method is quite general, 2,3-diphenylindanone and 2,3,3-triphenylpropionitrile were dehydrogenated similarly through their dialkali salts XV and VII to form XVI and XVII, respectively. Although the yields were good (70%), other satisfactory methods are available for XVI[16] and XVII.[17]



XV



XVI



$$(C_6H_5)_2C{=}\underset{C_6H_5}{C}{-}CN$$

XVII

In Table I are summarized the yields of X, XVI, and XVII that were obtained from α,β-dicarbanions on varying the metallic cation and mode of addition. The best of these yields were essentially duplicated in other runs. In dehydrogenation of I, two molecular equivalents of dibromide IX affected a better yield than one equivalent, though slightly more than one may have been equally satisfactory. In the two other dehydrogenations, only one equivalent of IX was used. Table I shows that the metallic cation and the mode of addition influence considerably the yields of products.

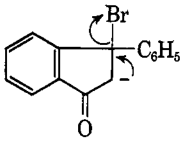
TABLE I

DEHYDROGENATIONS THROUGH α,β-DICARBANIONS BY DIBROMIDE IX[a]

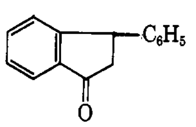
α,β-Dicarbanion	Metallic cation	Mode of addition	Unsaturated product	Yield, %
II	Na	Inverse	X	40–50
II	Na	Direct	X	0
II[b]	K	Inverse	X	*ca.* 10
XV	Na	Direct	XVI	70
XV	Na	Inverse	XVI	35
XV[b]	K	Direct	XVI	17
VII	K	Direct	XVII	70
VII[c]	Na	Direct	XVII	40
VII[c]	Na	Inverse	XVII	Trace

[a] Only the experiment that afforded the highest yield of each unsaturated product is described in Experimental. [b] Dipotassio salt. [c] Disodio salt.

Two mechanisms appear possible for the conversion of α,β-dicarbanions to the unsaturated products. One would involve displacement on the bromine of IX by the dicarbanion to form, for example, XVIII, which undergoes elimination to give X. The other would involve the intermediate formation of an ion radical, for example, XIX by displacement of one electron on the bromine of IX by the dicarbanion. Recent papers have described displacement on the halogen of certain halides by diphenylmethide ion,[18] and the formation, in equilibrium, of ion radicals when 1,2-dicarbanions are present with the corresponding unsaturated compounds.[19]



XVIII



XIX

Experimental[20]

3-Phenylindan-1-one (I).—This compound was prepared from 3,3-diphenylpropionic acid[21] by cyclization of its acid chloride with aluminum chloride.[22]

Conversion of I to α,β-Disodio Salt II.—To a stirred suspension of 0.05 mole of sodium amide in 200 ml. of commercial, anhydrous liquid ammonia[23] was added, during 5 min., 5.2 g. (0.025 mole) of 3-phenylindan-1-one (I) in 30 ml. of dry ether. After stirring for 45 min., the resulting dark red solution was assumed to contain 0.025 mole of α,β-disodio salt II.

Benzylation of II to Form β-Benzyl Derivative III.—To the stirred solution of 0.025 mole of α,β-disodio salt II (see above) was added, during 5 min., 3.2 g. (0.025 mole) of benzyl chloride in 30 ml. of dry ether. The red color of II was discharged immediately. After 30 min., 1.35 g. (0.025 mole) of ammonium chloride was added, and the ammonia evaporated as 200 ml. of ether was added. The resulting ethereal suspension was shaken with water, and the layers were separated. The ethereal layer was dried over anhydrous magnesium sulfate, and the solvent removed. The residue was recrystallized from 95% ethanol to give 5.4 g. (73%) of 3-benzyl-3-phenylindanone (III) as colorless cubes, m.p. 115–116°. Its infrared spectrum (as Nujol mull) showed principal bands at 700, 707, 754, 760, 771, 1240, and 1700 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.45; H, 6.15.

Reduction of 0.45 g. of III by refluxing it with 3.5 g. of amalgamated zinc and 10 ml. of aqueous–ethanolic concentrated hydrochloric acid for 9 hr. (further portions of the acid being added)[24] afforded 0.28 g. (66%) of 1-benzyl-1-phenylindane, m.p. 88–88.5° (recrystallized from 95% ethanol). Its infrared spectrum showed principal bands at 702, 748, 760, 775, 1082, 1447, 1455, 1497, and 3050 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{20}$: C, 92.92; H, 7.09. Found: C, 93.05; H, 7.17.

Benzylation of Monosodio Salt IV to Form α-Benzyl Derivative V.—To a stirred suspension of 0.03 mole of sodium amide in 150 ml. of liquid ammonia was added 6.24 g. (0.03 mole) of 3-phenylindan-1-one (I) in 25 ml. of dry ether. The resulting yellow-brown solution of monosodio salt IV was stirred for 15 min. The ammonia was evaporated as 150 ml. of dry diglyme was added, followed by 3.81 g. (0.03 mole) of benzyl chloride in 30 ml. of dry ether. After heating on the steam bath for 1.5 hr. and cooling, the reaction mixture was shaken with water. Ether was added, and the layers were separated. The organic layer was dried, and the ether was removed. The black, oily residue was chromatographed on alumina to give 1.52 g. (17%) of 2-benzyl-3-

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[15] A. T. Blomquist and E. J. Moriconi, *J. Org. Chem.*, **26**, 3761 (1961).

[16] C. F. Koelsch, *J. Am. Chem. Soc.*, **56**, 1337 (1934).

[17] S. Wawzonek and E. M. Smolin, *Org. Syn.*, **31**, 52 (1951).

[18] C. R. Hauser, W. G. Kofron, W. R. Dunnavant, and W. F. Owens, *J. Org. Chem.*, **26**, 2627 (1961).

[19] G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **84**, 4155 (1962).

[20] Analyses were by Galbraith Laboratories, Knoxville, Tenn. Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected. Infrared spectra were determined with a Perkin-Elmer Infracord by the potassium bromide pellet method except where noted. The n.m.r. spectrum was obtained from dilute solution in carbon tetrachloride with tetramethylsilane as internal standard using a Varian A-60 spectrometer.

[21] K. von Auwers and E. Auffenberg, *Ber.*, **52**, 92 (1919).

[22] P. Pfeiffer and H. L. de Waal, *Ann.*, **520**, 185 (1935).

[23] C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **8**, 122 (1954).

[24] E. Clemmensen, *Ber.*, **47**, 681 (1914).

phenylindanone (V), m.p. 82–83° (recrystallized from 95% ethanol). Its infrared spectrum showed principal bands at 698, 710, 740, 760, 1222, 1492, 1605, 1702, 2915, and 3030 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.68; H, 6.17.

Dehydrogenation of I through Disodio Salt II to Form X.—To a stirred solution of 24.4 g. (0.1 mole) of 2,3-dibromo-2,3-dimethylbutane (IX)[25] in dry ether was added, during 30 min., a solution of 0.05 mole of disodio salt II in 200 ml. of liquid ammonia. The red color of II was discharged immediately, but the reaction mixture soon darkened. The resulting brown mixture was stirred for 30 min., and the ammonia was replaced by ether. The resulting yellow-green suspension was filtered, and the solvent was removed from the filtrate. The residue was placed immediately on an alumina column. The column was eluted immediately[26] with hexane to remove the excess dibromide IX, and then with 20% benzene–hexane to remove 3-phenylindenone (X), which was obtained as a yellow-orange oil on evaporation of the solvent, yielding 4.1–5.2 g. (40–50%). Its infrared spectrum (liquid film) showed principal bands at 693, 752, 765, 1621, and 1713 cm.$^{-1}$. Compound X produced an emerald green color with concentrated sulfuric acid.[14] Compound X (0.67 g.) was treated with 0.6 g. of *p*-nitrophenylhydrazine in ethanol–hydrochloric acid[27] at 40° for 45 min. to afford *p*-nitrophenylhydrazone XI in 90–92% yield. After recrystallization from acetonitrile, XI melted at 266–267°, lit.[13] m.p. 266–267°. Compound XI produced a blue color with aqueous sodium hydroxide.[13]

Anal. Calcd. for $C_{21}H_{15}N_3O_2$: C, 73.89; H, 4.43; N, 12.31. Found: C, 74.01; H, 4.56; N, 12.28.

Independent synthesis of XI was effected from 2-bromo ketone XII[12] and the *p*-nitrophenylhydrazine reagent.[27,13] The product had m.p. 266–267°, undepressed on admixture with a sample of XI prepared from X as described above. Infrared spectra of the two samples were identical.

Attempted Preparation of X from 3-Hydroxy Ester XIII.—A 0.3-g. sample of ethyl 3-hydroxy-3,3-diphenylpropionate (XIII)[28] was dissolved in 3 ml. of concentrated sulfuric acid to produce the emerald-green color indicative of the formation of 3-phenylindenone (X, see above) but, on standing 24 hr. at room temperature as described by de Fazi,[14] the color changed to brown. There was isolated only a white powder, m.p. 205–235° (recrystallized from 95% ethanol), which was presumably a mixture of α- and γ-diphenyltruxones, m.p. 253 and 224°, respectively.[29] Similar results were obtained with ester XIII and with the corresponding acid employing 96% sulfuric acid for 30 min. or 3 hr. and 90% sulfuric acid for 12 hr. When the ester was treated with 80% or 60% sulfuric acid for 12 hr., and with polyphosphoric acid for 3 or 12 hr., the emerald-green color failed to appear, and the only product isolated was 3-phenylcinnamic acid. When the acid corresponding to XIII was treated similarly, it was largely recovered.

Dehydrogenation of 2,3-Diphenylindanone to Form XVI.—2,3-Diphenylindanone was prepared in 60% yield from 2,3,3-triphenylpropionic acid[30] through its acid chloride, which was cyclized with aluminum chloride.[16,22] The product melted at 99–100°, lit.[16] m.p. 100–101°.

A dry, ethereal solution of 1.42 g. (0.005 mole) of 2,3-diphenylindanone was added dropwise to a stirred suspension of 0.01 mole of sodium amide in 150 ml. of liquid ammonia; the mixture was stirred for 30 min. To the resulting deep red solution containing XV was added, with stirring, a dry, ethereal solution of 1.22 g. (0.005 mole) of dibromide IX. After 60 min., the ammonia was replaced by ether, and the mixture was filtered. The solvent was removed from the filtrate, and the residue recrystallized from hexane to give 0.99 g. (70%) of 2,3-diphenylindenone (XVI) as red needles, m.p. 152–153°, lit.[31] m.p. 150–151°.

Dehydrogenation of 2,3,3-Triphenylpropionitrile to Form XVII.—2,3,3-Triphenylpropionitrile[8] (3.55 g., 0.0125 mole) was converted to its dipotassio salt VII,[32] which was treated with a molecular equivalent of dibromide IX essentially as described above for disodio salt XV. During the addition of IX, the red color of VII changed to intense purple, which faded to brown when the addition was complete. There was obtained 2.45 g. (70%) of 2,3,3-triphenylacrylonitrile (XVII), m.p. 165–166°, lit.[32] m.p. 165°.

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(25) This compound was prepared by bromination of 2,3-dimethylbutane, as described by A. V. Grosse and V. N. Ipatieff [*J. Org. Chem.*, **8**, 438 (1943)], and purified by chromatography on alumina.

(26) When the product was allowed to remain on the column overnight, the yellow-orange band became dark green and the yield of X was reduced considerably.

(27) Concentrated hydrochloric acid was added to a suspension of *p*-nitrophenylhydrazine (0.6 g.) in 95% ethanol until solution was achieved; then 5 drops more of the acid were added.

(28) W. R. Dunnavant, and C. R. Hauser, *J. Org. Chem.*, **25**, 503 (1960).

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The Reaction of Chloramine with Alkyl Sulfides[1]

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Organic sulfides react with chloramine to give a series of compounds having the probable general formula, $(R_2\overset{+}{S}NH\overset{-}{N}H)_2$, bis(iminodialkylsulfilimine) and its salts. It is postulated that a sulfiliminium salt is initially formed from sulfide and chloramine and then aminated by another mole of chloramine as is shown. The

$$R_2S + NH_2Cl \longrightarrow (R_2\overset{+}{S}\text{–}NH_2)\overset{-}{Cl} \xrightarrow{NH_2Cl} (R_2\overset{+}{S}\text{–}NH\overset{-}{N}H)_2HCl$$

labile hydrogen chloride can be removed completely by sublimation in the presence of sodium methylate to give the free base, $(R_2\overset{+}{S}NH\overset{-}{N}H)_2$. In solution and especially in the solid phase, this dimer is postulated as consisting of two betaine-type monomeric units held together in a six-membered ring by electrostatic attraction or by resonance stabilization. The monomer is capable of existence in the vapor phase.

Organic sulfides have, for many years, been known to react with aromatic N-chlorosulfonamides such as chloramine B and T to form sulfilimines.[2,3]

$$R_2S + p\text{-}CH_3C_6H_4SO_2NClNa \longrightarrow p\text{-}CH_3C_6H_4SO_2NSR_2 + NaCl$$

In a recent series of papers, Appel[4] described the preparation of similar compounds from chloramine, NH_2Cl, and O-aminosulfonic acid, NH_2OSO_3H.

$$R_2S + NH_2X \longrightarrow [R_2\overset{+}{S}NH_2]\overset{-}{X}$$

Previous to the publication of these studies, we treated sulfides with chloramine in the expectation of

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