ether (bp 60–90°) eluted 3.8 g (92%) of *o*-azidodiphenylmethane.

Anal. Calcd for $C_{13}H_{11}N_3$: C, 74.61; H, 5.30; N, 20.09. Found: C, 74.84; H, 5.37; N, 19.96.

Decomposition of *o*-Azidodiphenylmethane. A.—To 150 ml of decalin preheated to 160°, 4.5 g of *o*-azidodiphenylmethane was added. After 5 hr at 160–165°, all gas evolution had ceased. A total of 480 ml of gas at standard conditions were collected (theoretical, 475 ml). The solvent was removed at <5-mm pressure. The residue was dissolved in a mixture of benzene and petroleum ether and put on an alumina chromatographic column. Petroleum ether eluted the first fraction. This fraction yielded 1.6 g (41%) of *o*-aminodiphenylmethane upon distillation. No other products were isolated.

B.—A solution of 2.0 g of *o*-azidodiphenylmethane in 100 ml of 1,2,4-trichlorobenzene was heated to 160° and maintained at this temperature for 4 hr. The solvent was removed at <5-mm pressure, and the residue subjected to steam distillation. The steam distillate was extracted twice with 150 ml of ether. The etheral extracts were dried with sodium sulfate. Removal of the ether at reduced pressure left 1.1 g (66%) of crude azepino-[2,1-*a*]-11H-indole (I), mp 80–87°. This solid was recrystallized from hexane to yield white crystals, mp 91°. An analytical sample was sublimed at 80° (0.1 mm), mp 91–91.5°.

Anal. Calcd for $C_{13}H_{11}N$: C, 86.15; H, 6.12; N, 7.73. Found: C, 86.05; H, 6.20; N, 7.62.

1,2,3,4,5-Pentahydroazepino[2,1-*a*]indole (II).—A solution of 0.8 g of I in 200 ml of ethanol was catalytically hydrogenated with 0.4 g of 10% palladium on charcoal on a Parr shaker. The sample was filtered free of catalyst, and the solvent was removed at reduced pressure. The solid residue was recrystallized from a hexane–cyclohexane mixture to yield 0.65 g (79.5%) of 1,2,3,4,5-pentahydroazepino[2,1-*a*]indole, mp 82–88°. An analytical sample was prepared by sublimation at 80° (0.1 mm) to yield white crystals, mp 88°.

Anal. Calcd for $C_{13}H_{15}N$: C, 84.27; H, 8.16; N, 7.56. Found: C, 84.29; H, 8.00; N, 7.59.

Registry No.—I, 17691-63-3; II, 17691-64-4; *o*-azidodiphenylmethane, 17691-65-5.

Acknowledgments.—The authors are deeply indebted to Dr. L. Schieler and Professor P. A. S. Smith for their helpful interest in this work and to Mr. S. Hotta for spectral measurements and valuable preparative assistance.

Synthesis of New Chlorine-Substituted Derivatives of 2-Tetralone[1,2]

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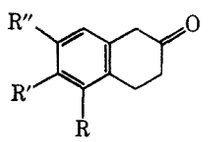
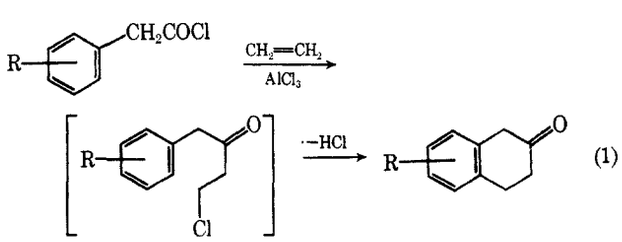
2-Tetralones containing one or more chlorine substituents on the aromatic ring have not been described in the chemical literature to date. Such compounds are of interest, in this laboratory, as points of departure for the synthesis of various chlorine-substituted condensed ring systems of potential biological interest. In the present Note, we should like to report the preparation of 6-chloro-2-tetralone (**1**), 7-chloro-2-tetralone (**2**), 5,7-dichloro-2-tetralone (**3**), and 6,7-dichloro-2-tetralone (**4**) *via* the Darzens reaction,[3] as modified by Burckhalter and Campbell.[4]



1, R = R″ = H; R′ = Cl
2, R = R′ = H; R″ = Cl
3, R = R″ = Cl; R′ = H
4, R = H; R′ = R″ = Cl

Methods of synthesis of 2-tetralone and its substituted analogs have been reviewed recently.[5] The approach favored by most workers during the past 25 years has involved reduction of substituted 2-methoxynaphthalene derivatives with sodium in alcohol. Catalytic, electrolytic, and sodium–liquid ammonia reductions have also been reported. This general plan appeared to be unsuitable for the synthesis of chlorinated 2-tetralones because of (1) the possibility of base-catalyzed dehalogenation, and (2) the relative inaccessibility of the required 2-methoxynaphthalene intermediates. Multistep sequences have been devised to transform substituted 1-tetralones into the corresponding 2-tetralones. However, such methods offer no particular advantage in this case because chlorinated 1-tetralones are themselves not readily obtained. The condensation of substituted phenylacetyl chlorides with ethylene under the influence of aluminum chloride (eq 1), according to the convenient



(1)

one-step procedure of Burckhalter and Campbell,[4] appeared to be an attractive alternative to the use of preformed naphthalene precursors. 2-Tetralones containing alkyl substituents in the saturated ring were prepared as early as 1947 by this approach in a two-step procedure.[6] However, little work has been done to define either the precise mechanism or the synthetic scope of this interesting reaction.

(1) This investigation was supported in part by Research Contract DA-49-193-MD-3008 from the U. S. Army Medical Research and Development Command, Office of the Surgeon General, and by Research Career Development Award K3-CA-22,151 from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service. This is publication number 342 from the Army Research Program on Malaria.

(2) Presented in part before the Division of Medicinal Chemistry at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 4, 1968.

(3) L. F. Fieser and M. Fieser, "Topics in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1963, p 548.

(4) J. H. Burckhalter and J. R. Campbell, *J. Org. Chem.*, **26**, 4232 (1961).

(5) V. F. Schner and N. M. Przhiyalgovskaya, *Russ. Chem. Rev.*, **35**, 523 (1966).

(6) J. Colonge and J. Chambion, *Compt. Rend.*, **224**, 128 (1947); J. Colonge and J. Chambion, *Bull. Soc. Chim. Fr.*, 1002 (1947).

The substituted phenylacetic acids employed in this work were all known previously[7-9] and were prepared essentially according to the literature, with the exception of 3,5-dichlorophenylacetic acid, which we chose to prepare *via* 3,5-dichlorobenzyl chloride instead of 3,5-dichlorobenzyl bromide as reported.[8] The bromide is less accessible than the chloride and is inconvenient to use on a large scale because of its strong lachrymatory properties. Condensation of the acid chlorides with ethylene was conducted essentially as described by Burckhalter and Campbell,[4] except that the reaction was allowed to proceed overnight in order to compensate for the expected deactivating effect of halogen substituents.

p-Chlorophenylacetyl chloride and 3,5-dichlorophenylacetyl chloride gave single products **1** and **3**, respectively, upon reaction with ethylene. Reaction with 3,4-dichlorophenylacetyl chloride produced only one of the two possible 2-tetralone derivatives, as evidenced by glpc analysis. The nmr spectrum of this compound showed two isolated singlets at τ 2.76 and 2.86, in agreement with the 1,4 aromatic proton substitution pattern in structure **4**. The sterically less favored isomer, 5,6-dichloro-2-tetralone, would be expected to show a pair of doublets corresponding to 1,2 aromatic proton substitution. The reaction of *m*-chlorophenylacetyl chloride, on the other hand, was found to be somewhat less selective than that of the 3,4-dichloro analog. Glpc analysis of material purified by routine vacuum distillation revealed the presence of two products, in the ratio of approximately 3:1. The nmr spectrum of the mixture likewise indicated that one isomer, presumably **2**, was preponderant. A strong singlet at τ 6.56 was observed, which was assigned to the $ArCH_2CO$ protons in **2**. A small second peak at τ 6.53 was also seen, which was assumed to be caused by the presence of a minor quantity of 5-chloro-2-tetralone.

On the basis of the failure of *p*-nitrophenyl- and diphenylacetyl chloride to yield substituted 2-tetralones, Burckhalter and Campbell[4] proposed that electron-withdrawing substitution in the aromatic ring retards the reaction by hindering ionization to an intermediate carbonium ion–aluminum chloride complex of unspecified structure. In the present investigation, the condensation of mono- and dichlorophenylacetyl chlorides with ethylene has been found to proceed in yields averaging 55–60%. The yields do not differ greatly from the values given for 2-tetralone (75%) and 6-methoxy-2-tetralone (56%), the only 2-tetralone derivatives reported by Burckhalter and Campbell. Thus our data suggest that electron-withdrawing halogen substituents may retard the condensation to a small extent. However, as with other Friedel–Crafts reactions involving halogen-substituted aromatic compounds,[10] the effect is not strong enough to negate the obvious preparative advantages of this reaction.

(7) R. C. Elderfield and K. L. Burgess, *J. Amer. Chem. Soc.*, **82**, 1975 (1960).

(8) M. B. Pybus, R. L. Wain, and F. Wightman, *Ann. Appl. Biol.*, **47**, 593 (1959); *Chem. Abstr.*, **54**, 12052 (1960).

(9) (a) S. Chiavarelli and M. A. Jorio, *Gazz. Chim. Ital.*, **86**, 1054 (1956); *Chem. Abstr.*, **52**, 3832 (1958).

(10) For a discussion of the Friedel–Crafts alkylation of aromatic compounds with alkyl halides, see F. A. Drahowzal in "Friedel–Crafts and Related Reactions," Vol. II, G. A. Olah, Ed., Interscience Publishers, New York, N. Y., 1964, Chapter 4.

Experimental Section[11]

Materials.—*p*-Chlorophenylacetonitrile and 3,5-dichlorobenzoic acid were purchased from Aldrich Chemical Co., Inc., Milwaukee, Wis. *m*-Chlorophenylacetonitrile and 3,4-dichlorobenzyl chloride were obtained from Columbia Organic Chemicals Co., Inc., Columbia, S. C., and from K & K Laboratories, Inc., Plainview, N. Y. *p*-Chlorophenylacetic acid, mp 104–106° (lit.[7] mp 106–106.5°), and *m*-chlorophenylacetic acid, mp 76–77° (lit.[7] mp 77–77.5°), were prepared from the corresponding nitriles in 94 and 71% yield, respectively, by hydrolysis with a refluxing mixture of aqueous acetic and sulfuric acids as prescribed in the literature.[7] *p*-Chlorophenylacetyl chloride, bp 94° (0.5 mm) [lit.[12] bp 119° (14 mm)], and *m*-chlorophenylacetyl chloride, bp 87–88° (0.25 mm) [lit.[12] bp 121° (17 mm)], were obtained by reaction of the acids with excess thionyl chloride on the steam bath, the yields of distilled acid chlorides being 76 and 58%, respectively. 3,4-Dichlorophenylacetonitrile, bp 130–135° (0.5–1.0 mm) [lit. bp 150–151° (6 mm),[9] 167–169° (15 mm)[13]], was synthesized in 88% yield by treatment of the benzyl chloride derivative with sodium cyanide in refluxing aqueous ethanol.[9] Hydrolysis of the nitrile with the standard aqueous acetic–sulfuric acid reagent[7,9] afforded 3,4-dichlorophenylacetic acid, mp 79–85° (lit.[9] mp 84°), in 81% yield. Overnight reaction of the crude acid with thionyl chloride in refluxing benzene gave a 77% yield of 3,4-dichlorophenylacetyl chloride, bp 123–126° (0.5–1.0 mm). The acid chlorides were used as soon as possible after distillation, in order to minimize decomposition during storage.

6-Chloro-2-tetralone (1).—A solution of *p*-chlorophenylacetyl chloride (46 g, 0.24 mol) in carbon disulfide (500 ml) was added dropwise with vigorous mechanical stirring to a suspension of anhydrous aluminum chloride (61.2 g, 0.46 mol) in carbon disulfide (700 ml) at 5°. When addition was complete, ethylene gas was introduced through a sintered-glass inlet tube for a period of 5 hr, with the temperature being kept at 5–10°. The mixture was stirred overnight at room temperature, and then poured into a large beaker of crushed ice. The aqueous layer was separated and washed with dichloromethane (two 900-ml portions). The dichloromethane extracts and carbon disulfide layer were combined, dried, and concentrated to dryness under reduced pressure. The dark oily residue was treated with a solution of sodium bisulfite (100 g) in water (180 ml) and ethanol (60 ml), and the mixture was shaken vigorously and allowed to stand overnight.[14] The crystalline bisulfite adduct was filtered, washed with alcohol, and rinsed with ether to yield 66.5 g (97%). The bisulfite adduct was suspended in water (350 ml), and sodium carbonate (80 g) was added. The basic mixture (pH 9) was stirred for 3 hr, and then extracted with ether (three 250-ml portions). The combined ether extracts were washed with 1 *N* hydrochloric acid (90 ml), rinsed to neutrality with water, dried, and evaporated to dryness: yield 30 g (70%); mp 60–62.5°; ν_{max}^{KCl} 1720 cm^{-1} (C=O); positive "tetralone blue" test.[4,15] The analytical sample, prepared in a separate small-scale run, had mp 68–70°.

Anal. Calcd for $C_{10}H_9ClO$: C, 66.49; H, 5.02; Cl, 19.63. Found: C, 66.30; H, 5.04; Cl, 19.64.

The **semicarbazone** of 1 had mp 195–197° (EtOH).

(11) Ultraviolet spectra were measured with Cary Model 11 and Model 15 spectrophotometers. Infrared spectra were taken in potassium chloride disks with a Perkin-Elmer Model 137B double-beam recording spectrophotometer. Nmr spectra were determined in carbon tetrachloride solution on a Varian A-60 instrument, with tetramethylsilane as the internal reference. Glpc analyses were performed on an F & M Model 720 instrument, using 6 ft × 1/4 in. 10% silicone rubber (SE-30) columns and helium as the carrier gas. Analytical samples were dried over phosphorus pentoxide at 70–100° (0.05 mm). Melting points were measured in Pyrex capillary tubes in a modified Wagner–Meyer apparatus [E. C. Wagner and J. F. Meyer, *Ind. Eng. Chem., Anal. Ed.*, **10**, 584 (1938)] at a heating rate of 2°/min and are corrected wherever possible. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

(12) P. D. Bartlett and C. Rüchardt, *J. Amer. Chem. Soc.*, **82**, 1756 (1960).

(13) S. Chiavarelli and M. A. Jorio, German Patent 1,109,700 (June 29, 1961); *Chem. Abstr.*, **56**, 12802 (1962).

(14) M. D. Soffer, M. P. Bellis, H. E. Gellerson, and R. A. Stewart, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 904.

(15) (a) H. W. Wanzlich, M. Lehmann-Hrochler, and S. Mohrmann, *Ber.* **90**, 2521 (1957); (b) A. C. Baillie and R. H. Thomson, *J. Chem. Soc.*, 2184 (1966). In this test an alcoholic solution of the compound is basified with dilute sodium hydroxide and shaken vigorously; the appearance of a deep blue color indicates a 2-tetralone.

Anal. Calcd for $C_{11}H_{12}ClN_3O$: C, 55.58; H, 5.09; Cl, 14.92; N, 17.68. Found: C, 55.57; H, 5.08; Cl, 14.69; N, 17.37.

7-Chloro-2-tetralone (2).—The procedure described above for the synthesis of **1** was repeated with *m*-chlorophenylacetyl chloride. Vacuum distillation was used to purify the oily ketone recovered after base treatment of the crystalline bisulfite adduct: yield 47%; bp 145° (0.6 mm); mp 43–46° (solid formed in the receiver); ν_{max}^{KCl} 1720 cm^{-1}. Analysis of this material by glpc (150°)[11] showed two peaks with retention times of 3.6 and 6.4 min, respectively. The ratio of peak areas was approximately 3:1. The nmr spectrum indicated the presence of two compounds in unequal proportions. The principal isomer, assumed to be **2**, showed a singlet at τ 6.56 ($ArCH_2CO$). A smaller singlet at τ 6.53 was also observed, suggesting the probable presence of some 5-chloro-2-tetralone.

Anal. Calcd for $C_{10}H_9ClO$: C, 66.49; H, 5.02; Cl, 19.63. Found: C, 66.66; H, 5.28; Cl, 19.93.

5,7-Dichloro-2-tetralone (3).—3,5-Dichlorobenzoic acid was reduced in 78% yield with lithium aluminum hydride in refluxing ether,[16] with formation of 3,5-dichlorobenzyl alcohol, mp 78° (lit.[16] mp 78–79°). A mixture of this alcohol (125 g, 0.71 mol) and thionyl chloride (113 g, 0.95 mol) was refluxed 3 hr to give 94 g (68%) of 3,5-dichlorobenzyl chloride,[17] bp 83° (1.8 mm) [lit. bp 60° (0.35 mm),[16] 115–123° (10 mm)[18]]. To a stirred suspension of sodium cyanide (13 g, 0.27 mol) in dry dimethyl sulfoxide (50 ml) was added dropwise under nitrogen at 50° a solution of the above benzyl chloride (45 g, 0.23 mol) in dry dimethyl sulfoxide (150 ml). After being stirred overnight at room temperature, the mixture was diluted with water (400 ml), and extracted with chloroform (three 300-ml portions). The combined extracts were washed with water (100 ml), dried, and evaporated to dryness. Distillation of the residue gave 28 g (66%) of 3,5-dichlorophenylacetonitrile, bp 101–103° (0.1 mm) [lit.[8] bp 165–168° (17 mm)]. The dinitrile was heated for 6 hr under reflux with a mixture of concentrated sulfuric acid (28 ml), glacial acetic acid (28 ml), and water (28 ml). The hydrolysis mixture was cooled, and the precipitate was filtered and washed thoroughly with ice-cold water to give 24 g (78%) of 3,5-dichlorophenylacetic acid, mp 110–112° (lit.[8] mp 112–115°). This acid (139 g, 0.68 mol) was allowed to react overnight with thionyl chloride (100 g, 0.84 mol) in refluxing benzene (200 ml). Removal of the solvent and unreacted thionyl chloride under reduced pressure and distillation of the residue gave 99 g (66%) of 3,5-dichlorophenylacetyl chloride, bp 114–118° (2 mm).[19] The general procedure used in the preparation of **1** was repeated with this acid chloride to give a 58% yield (best run) of **3**: mp 76–78°; ν_{max}^{KCl} 1730 cm^{-1} (C=O); positive "tetralone blue" test.

Anal. Calcd for $C_{10}H_8Cl_2O$: C, 55.84; H, 3.75; Cl, 32.97. Found: C, 56.04; H, 3.97; Cl, 33.10.

The **2,4-dinitrophenylhydrazone** of **3** had mp 172.5–174° (EtOH).

Anal. Calcd for $C_{16}H_{12}Cl_2N_4O_4$: C, 48.12; H, 3.06; Cl, 17.94; N, 14.17. Found: C, 48.44; H, 3.29; Cl, 18.03; N, 14.01.

6,7-Dichloro-2-tetralone (4).—The general procedure used for the synthesis of **1** was repeated with 3,4-dichlorophenylacetyl chloride to give a 58% yield (best run) of **4**. Glpc analysis (200°)[11] showed a single peak with a retention time of 4.75 min. For microanalysis, a portion of the crude crystalline product was recrystallized from 1:2 carbon tetrachloride–petroleum ether (bp 60–80°): mp 97–98°; ν_{max}^{KCl} 1720 cm^{-1}.

Anal. Calcd for $C_{10}H_8Cl_2O$: C, 55.84; H, 3.75; Cl, 32.97. Found: C, 55.57; H, 3.80; Cl, 32.87.

The **semicarbazone** of **4** had mp 224–225° (EtOH).

Anal. Calcd for $C_{11}H_{11}Cl_2N_3O$: C, 48.55; H, 4.08; Cl, 26.06; N, 15.44. Found: C, 48.72; H, 4.16; Cl, 26.34; N, 15.16.

Registry No.—**1**, 17556-18-2; **1** semicarbazone, 17605-22-0; **2**, 17556-19-3; **3**, 17556-20-6; **3** 2,4-dinitrophenylhydrazone, 17556-21-7; **4**, 17556-22-8; **4** semicarbazone, 17556-23-9; 2-tetralone, 530-93-8.

(16) R. Fuchs and D. M. Carlton, *J. Amer. Chem. Soc.*, **85**, 104 (1963).

(17) 3,5-Dichlorobenzyl chloride has also been prepared from the alcohol by reaction with phosphorus pentachloride [F. Asinger and G. Lock, *Monatsh. Chem.*, **62**, 344 (1933)], and also from 3,5-dichlorotoluene by direct photocatalytic chlorination at 180° (see ref 18).

(18) British Patent 923,128 (April 10, 1963); *Chem. Abstr.*, **60**, 1048 (1964).

(19) A 79% yield of acid chloride was obtained in a subsequent experiment, in which the acid was added in small portions to an equal weight of thionyl chloride on the steam bath, and the mixture was refluxed for 3 hr.

Base-Catalyzed Conversion of Thiolcarbonate Esters into Sulfides. Reactions of Xanthate Esters

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Thiolcarbonate and xanthate esters are well known to be readily solvolized by protonic solvents under basic conditions,[1] but little is known of their base-catalyzed reactions under aprotic conditions. This Note described our study of such reactions of representative thiolcarbonates and xanthates.

Thiolcarbonate esters.—We have found that certain aprotic Lewis bases strongly catalyze conversion of thiolcarbonates into sulfides with loss of CO_2. In favorable cases, the reaction goes under mild conditions in quantitative yields. For example, liquid O-methyl-S-phenyl thiolcarbonate (**1**) is converted into methyl phenyl sulfide (**2**) and CO_2 in high yield at 35° by solutions containing fluoride ion (eq 1). Without a catalyst **1** is thermally stable to about 180°, where slow (0.25%/hr) conversion into **2** occurs (eq 2). An analogous reaction of cyclic ethylene thiolcarbonate was reported to give ethylene sulfide.[2]

$$\underset{\mathbf{1}}{C_6H_5S\overset{\overset{O}{\|}}{C}OCH_3} \xrightarrow[35°,\ 64\ hr]{Et_4N^+F^-,\ MeCN} \underset{\mathbf{2}\ (97\%)}{C_6H_5SCH_3} + CO_2 \quad (1)$$

$$\mathbf{1} \xrightarrow[180°,\ 64\ hr]{neat} \mathbf{2}\ (12\%) + CO_2 \quad (2)$$

A number of bases were tested as catalysts for conversion of **1** into **2** in nitrobenzene (Table I). Mixtures of solvent, **1**, and catalyst in a 40:10:1 ratio by weight was heated at 85 ± 1° for 1.0 hr. Yields were estimated by nmr analysis.

TABLE I

CATALYSTS FOR CONVERSION OF 1 INTO 2

Catalyst	Conversion, %	Catalyst	Conversion, %
$Et_4N^+F^-$	100	$(Me_2NCH_2^-)_2$	100
$Bu_4N^+Br^-$	9	Pyridine	52
Et_3P	99	Quinoline	2
$(C_8H_{17})_3P$	94	Imidazole	2
$(C_6H_5)_3P$	18	$(C_6H_5)N{=}N(C_6H_5)$	Trace
Et_3N	100	$(C_6H_5)_3PS$	Trace
$(C_6H_5)CH_2NMe_2$	86	None	Trace

These data show that tertiary phosphines, tertiary amines, and soluble fluorides are good catalysts. Similar tests at 35° revealed that fluoride ion is far more active than pyridine; fluoride appears to be the best catalyst for difficult cases. Trioctylphosphine is also a useful catalyst, being nonvolatile, easily handled, and

(1) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. IV, Chemical Publishing Co., Inc., New York, N. Y., 1962, pp 137, 165–167.

(2) (a) D. D. Reynolds, *J. Amer. Chem. Soc.*, **79**, 4951 (1957). (b) D. D. Reynolds, U. S. Patent 2,828,318 (1958); *Chem. Abstr.*, **52**, 14651*f* (1958).