[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Studies Related to Pyracene. An Improved Synthesis[1,2]

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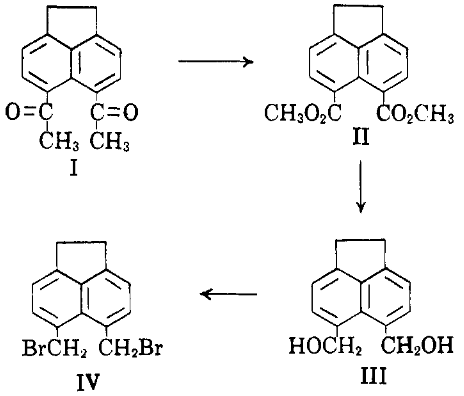
Formation of a second carbocyclic five-membered *peri*-ring on naphthalene has been attempted by several reactions not involving direct substitution on the naphthalene nucleus. The results are consistent with the concept that there is a definite increase in the distance between the 5- and 6-carbon atoms in acenaphthene as compared to the 1- and 8-carbons in naphthalene. An improved synthesis of pyracene has been achieved which is considerably shorter than the previous one.

In the previous paper[3] describing the first synthesis of pyracene (IX) it was noted that acenaphthenone could be prepared by the usual Friedel-Crafts ring closure but the corresponding cyclization of 5-acenaphtheneacetic acid (or derivatives) could not be realized. From considerations of the reported bond lengths and bond angles of the *peri*-ring in acenaphthene[4] it was thought that the strain in the molecule could cause an increase in the distance between the 5- and 6-positions and thus account for the observed results.

Further consideration of the problem led to the theorization that a particular distance between the 5- and 6-positions which would not permit direct electrophilic substitution would still allow ring closure by a reaction involving only the aliphatic carbons. The success of such a scheme would provide a most convenient route to pyracene not involving a dehydrogenation step. Bergmann and Szmuszkovicz[5] had found that acenaphthene could be prepared in high yield from 1,8-bis(bromomethyl)naphthalene and this method seemed well suited to the authors' purpose.

A necessary intermediate, 5,6-diacetylacenaphthene (I), had been prepared by Dziewouski and Spirer[6] by a Friedel-Crafts reaction of acenaphthene and acetic anhydride but no yields were reported. In this laboratory their procedure gave a small amount of diketone and a large amount of carbonaceous material. An alternate procedure[7] specifying acetyl chloride was modified (a large excess of the acyl halide was used) and a 59% yield of product was obtained. Oxidation of the diketone with potassium hypochlorite gave 5,6-acenaphthenedicarboxylic acid in good yield. This acid was difficult to purify and was also insoluble in the solvents usually employed for lithium aluminum hydride reductions. Accordingly, the impure acid was treated with diazomethane and the resulting diester (II) reduced to 5,6-bis(hydroxymethyl)acenaphthene (III). The desired dibromo derivative (IV) was readily obtained by treatment of the diol with phosphorus tribromide in the presence of pyridine.



Two methods for the cyclization of the dibromide were investigated. Treatment with phenyllithium according to the procedure of Bergmann and Szmuszkovicz[5] gave only yellow polymeric material. Similar results were obtained when an ethanolic solution of the dibromide was added to a suspension of zinc dust in the same solvent. These observations may be an indication that the activation energy for the cyclization of 5,6-bis(bromomethyl)acenaphthene is higher than that of 1,8-bis(bromomethyl)naphthalene due to the increased distance between the atoms concerned. No definite conclusion on this point is possible since it is not known whether the process is kinetically or thermodynamically controlled and, also, the reactions leading to polymerization may not be the same for both cases.

A final attempt to achieve the pyracene structure through this series was made on the diester (II). Subjecting this compound to conditions for the acyloin condensation as described by Le Clercq[8] resulted in a 92% recovery of starting

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(1) From the Ph.D. thesis of Robert G. Anderson.

(2) Support for a part of this work by contract DA-04-200-ORD-235 with the Office of the Ordnance Research, U. S. Army, is gratefully acknowledged.

(3) A. G. Anderson, Jr. and R. H. Wade, *J. Am. Chem. Soc.*, **74**, 2274 (1952).

(4) The values for the aliphatic carbon-carbon bond distance and aliphatic bond angle have subsequently been reduced from 1.8 Å. to 1.64 ± 0.04 Å. and from 114° to 101°, respectively [A. I. Kitaigordoskii, *J. Phys. Chem.* (*U.S.S.R.*), **23**, 1036 (1949)]. The departure from normal values is still such as to indicate the presence of considerable strain.

(5) E. D. Bergmann and J. Szmuszkovicz, *J. Am. Chem. Soc.*, **75**, 2760 (1953).

(6) K. Dziewouski and J. Spirer, *Bull. Intern. Acad. polon. sci.*, **1931A**, 231.

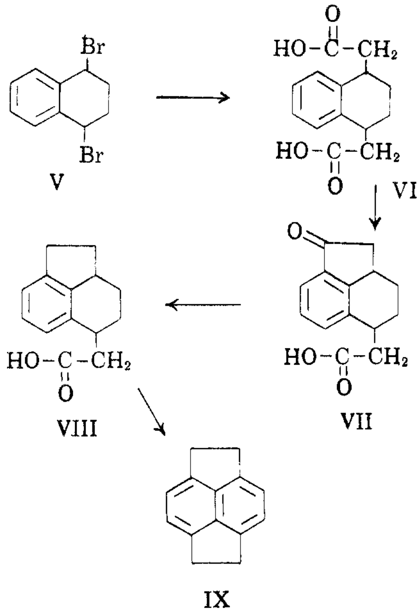
(7) K. Fleischer and P. Wolff, *Ber.*, **53**, 925 (1920).

(8) G. M. Le Clercq, Ph.D. thesis, University of Washington, 1956.

material and a small amount of a high-melting substance which could not be identified.

As the original synthesis of pyracene[3] was quite long and included some steps which were not adaptable to relatively large amounts, a new route was desirable. Of necessity the formation of the fourth ring had to involve a structure with only a benzene ring unsaturated and, since success had been had with 2a,3,4,5-tetrahydro-5-acenaphtheneacetic acid (VIII), an improved means of preparing this intermediate was sought and achieved.

Bromination of tetralin with *N*-bromosuccinimide gave 1,4-dibromotetralin (V) in 54% yield. In agreement with Orazi and Salellas,[9] who prepared it by a similar procedure, we found that this compound eliminated hydrogen bromide and formed naphthalene when warmed either in the solid state or in a polar solvent. This prevented the use of the usual polar solvents in the next reaction and, therefore, a mixture of diethyl sodiomalonate and xylene was added to a solution of pure 1,4-dibromotetralin in zylene. Hydrolysis and decarboxylation of the tetraester product gave a 71% yield of 1,2,3,4-tetrahydro-1,4-naphthalenediacetic acid (VI). If the mode of addition was reversed (dibromide added to diethyl sodiomalonate) in the displacement reaction, very impure diacid (VI) was obtained and the yield was considerably lower (47%). The diacid melted over a range of several degrees even when analytically pure and this was attributed to the presence of more than one stereoisomer. The same property was noted for the subsequent compounds made from the diacid.



Cylization of VI to 1-keto-2a,3,4,5-tetrahydro-5-acenaphtheneacetic acid (VII) was readily accomplished (71%) with polyphosphoric acid or *via* the acid chloride by a Friedel-Crafts reaction (61%) with aluminum chloride. The infrared spectrum of the keto acid surprisingly showed only one carbonyl band. Presumably both carbonyl groups in this compound absorb at the same wave length (5.85μ). All attempts to effect the cyclization of the keto acid with concentrated sulfuric acid or polyphosphoric acid at 150° or to prepare the ethylene ketal were unsuccessful.

Reduction of VII by a modified Wolff-Kishner reaction afforded 90% of the desired acid (VIII). For the conversion of VIII to pyracene, ring closure of the acid was effected (80%) with polyphosphoric acid, rather than as originally[3] with aluminum chloride on the acid chloride, and, after Wolff-Kishner reduction of the keto group in the product, the tetrahydropyracene was dehydrogenated (81%) with a rhodium-on-alumina catalyst and benzene in place of the earlier method[3] with palladium-on-charcoal. Both of these changes resulted in cleaner products and higher yields than were obtained previously.

The total number of isolation steps in the synthesis of pyracene has been reduced from the 15 in the original procedure to seven and the over-all yield raised from 12% (from cinnamic acid)[3] to 15% (from tetralin).

EXPERIMENTAL[10,11,12]

5,6-Diacetylacenaphthene (I). The procedure of Fleischer and Wolff[7] was modified such that 308 g. (2.34 moles) of aluminum chloride was added in 10-g. portions with stirring over a period of 2 hr. to a warm (42°) solution of 154 g. (1 mole) of acenaphthene and 234 g. (3 moles) of acetyl chloride in 850 ml. of carbon disulfide. After approximately 6 hr. (at 42°) the evolution of hydrogen chloride had ceased and the complex in the cooled (0°) mixture was decomposed with ice and 10% hydrochloric acid. The collected black precipitate was continuously extracted with ethanol (24 hr.) and the extract treated several times with decolorizing carbon, dried over magnesium sulfate, and concentrated to dryness under reduced pressure. The yield of crude (m.p. 147–149°) product was 140 g. (59%). A portion recrystallized twice from ethanol melted sharply at 149°.[7] The infrared spectrum (Nujol mull) showed a strong band at 5.98 μ. The dioxime, recrystallized from toluene, melted at 196–197°.[7]

5,6-Acenaphthenedicarboxylic acid. To a warm (55°) aqueous solution of potassium hypochlorite, prepared from 24.15 g. (0.17 mole) of calcium hypochlorite,[13] was added dropwise with stirring a solution of 11.5 g. (0.05 mole) of 5,6-diacetylacenaphthene in 50 ml. of dioxane. After the exothermic reaction began the temperature was maintained at 60–70° by cooling. When the addition was complete (45 min.), a solution of potassium hypochlorite, prepared from

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(9) O. O. Orazi and J. F. Salellas, *Anales asoc. quim. argentina,* **38,** 12 (1950).

(10) Melting points were taken on a Fisher-Johns apparatus and are uncorrected.

(11) Qualitative ultraviolet absorption spectra were taken in ethanol on a Cary Model 11S recording spectrophotometer. Quantitative ultraviolet spectra were determined with a Beckmann Model DU spectrophotometer. Infrared spectra were measured by a Perkin Elmer Model 21 recording spectrophotometer with sodium chloride cells.

(12) Microanalyses were performed by B. Nist and C. H. Ludwig.

(13) M. S. Newman and H. L. Holmes, *Org. Syntheses,* **Coll. Vol. II,** 428 (1943).

12.07 g. (0.09 mole) of calcium hypochlorite, was added and the mixture warmed (60–70°) for 6 hr. After the mixture was cooled and a small amount of gray solid separated, a solution of 10 g. of sodium bisulfite in 40 ml. of water was added and the resulting solution acidified with concentrated hydrochloric acid. The glutinous acid formed was separated, washed with water, and dried (vacuum oven at 80°) to yield 9.7 g. (81%) of product sufficiently pure for conversion to the diester. Treatment (several times) of an aqueous basic solution of the crude acid with Norite gave, on acidification and drying, tan crystalline material, m.p. 290–296°, which had a neutral equivalent of 122 (calcd. 121). The reported melting point is 293–294°.[14]

Dimethyl 5,6-acenaphthenedicarboxylate (II). A dichloromethane solution (200 ml.) of diazomethane from the reaction of 10 g. (0.013 mole) of *N*-nitroso-*N*-methylurea, 110 g. of potassium hydroxide, and 100 ml. of water, was dried over potassium hydroxide pellets and then added in portions to a cold (0°) suspension of 3.1 g. (0.0128 mole) of 5,6-acenaphthenedicarboxylic acid in 60 ml. of dichloromethane. The mixture was allowed to stand for 8 hr. in an ice bath and then 12 hr. at room temperature. The solvent was then removed (air stream) and a solution of the tan residue in benzene washed with 5% sodium bicarbonate and then water. Removal of the solvent from the dried (magnesium sulfate) solution gave 2.1 g. (59%) of crude diester, m.p. 138–141°. A portion sublimed *in vacuo* and recrystallized twice from methanol melted at 140–141°.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.88; H, 5.23.

5,6-Bis(hydroxymethyl)acenaphthene (III). To a cold (0°) mixture of 0.13 g. (0.0022 mole) of lithium aluminum hydride and 15 ml. of dry tetrahydrofuran was added dropwise with stirring a solution of 0.6 g. (0.0022 mole) of dimethyl 5,6-acenaphthenedicarboxylate in 15 ml. of dry tetrahydrofuran. The reaction mixture was allowed to warm to room temperature, heated under reflux for 1 hr., and cooled to 0°. After destroying excess hydride by adding 25 ml. of ethyl acetate and removing the solvent (reduced pressure), the gray solid complex was decomposed with 75 ml. of a 20% Rochelle salt solution and the resulting suspension washed with several portions of ether. Removal of the solvent from the dried (magnesium sulfate) ether solution yielded 0.34 g. (72%) of the diol, m.p. 130–135°. A portion recrystallized from ethyl acetate and sublimed *in vacuo* melted at 141–142°.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.58. Found: C, 78.49; H, 6.27.

5,6-Bis(bromomethyl)acenaphthene (IV). A mixture of 0.5 g. (0.0023 mole) of the above diol (III), a few drops of pyridine, and 75 ml. of benzene was heated under reflux until most of the diol had dissolved. Phosphorus tribromide (2.48 g., 0.0092 mole) was then added dropwise with stirring to the cooled (0°) solution. After maintaining the resulting white suspension at 55° for 2 hr., then cooling it to 0°, 30 ml. of water was added and the separated organic layer washed with 5% sodium bicarbonate and water. The solvent was removed under reduced pressure from the dried (magnesium sulfate) solution and the residue of product, m.p. 154–160°, found to be 0.63 g. (80%). A portion recrystallized twice from hexane melted at 160–162°.

Anal. Calcd. for $C_{14}H_{12}Br_2$: C, 49.44; H, 3.56; Br, 47.00. Found: C, 49.44; H, 4.00; Br, 46.82.

1,4-Dibromotetralin (V). The procedure used was a modification of those described by Orazi[9] and by Barnes.[15] A mixture of 132 g. (1.0 mole) of tetralin, 356 g. (2.0 moles) of *N*-bromosuccinimide, 2 liters of anhydrous carbon tetrachloride, and a few grains of benzoyl peroxide was brought to reflux in a 5-l. flask equipped with two Allihn condensers. After the vigorous reaction which ensued, and which was moderated by cooling with tap water, had subsided, the straw-colored mixture was refluxed for an additional 30 min., the succinimide then separated from the cooled contents of the flask, and the red filtrate concentrated to dryness (reduced pressure) under an inert atmosphere. The yield of crude dibromide, m.p. 89–93°, was 174 g. (60%). Two recrystallizations from sodium-dried hexane yielded 157 g. (54%) of pure product, m.p. 94–95°.[9] The dibromide slowly decomposed with the evolution of hydrogen bromide on standing at room temperature. This process was slowed by storage in the dark at 0° under a nitrogen atmosphere. The dibromide could be converted to naphthalene by refluxing in 95% ethanol for 30 min.

Anal. Calcd. for $C_{10}H_{10}Br_2$: C, 41.39; H, 3.47. Found: C, 41.54; H, 3.61.

1,2,3,4-Tetrahydro-1,4-naphthalenediacetic acid (VI). Under anhydrous conditions 480 g. (3.0 moles) of redistilled diethylmalonate was added slowly to a stirred mixture of 23 g. (1 mole) of molten sodium and 1300 ml. of dry xylene. The solution which was formed was added dropwise with stirring over a period of 1 hr. to a refluxing solution of 104 g. (0.36 mole) of 1,4-dibromotetralin in 650 ml. of dry xylene. The reaction mixture was heated under reflux for an additional hour and then washed with water until the washings were colorless. The organic portion was dried (magnesium sulfate) and the xylene and excess diethyl malonate then removed by distillation under reduced pressure. No attempt was made to purify the red oil (130 g.) which remained and which was presumed to be mostly tetraethyl 1,2,3,4-tetrahydro-1,4-naphthalenedimalonate.

The crude tetraester was refluxed with 303 g. (5.4 moles) of potassium hydroxide, 303 ml. of water, and 330 ml. of ethanol for 5 hr., and then most of the ethanol was removed by distillation. After the addition of 300 ml. of water and extraction with three 200-ml. portions of ether, the aqueous solution was acidified and the small amount of brown viscous material which formed separated by filtration. The aqueous solution was then extracted with an equal volume of ether for 24 hr. in a liquid-liquid extractor, the ether extract dried (magnesium sulfate), and the solvent removed. All attempts to purify the tan oil (93 g.), assumed to be crude 1,2,3,4-tetrahydro-1,4-naphthalenedimalonic acid, which remained were unsuccessful.

Heating the acidic oil at 140° for 30 min. and then at 180° until the evolution of carbon dioxide had ceased (20 min.) gave a brown oil which was taken up in 400 ml. of the 10% aqueous potassium hydroxide. The solution was washed with several portions of ether, treated with Norite, and then acidified by the dropwise addition of 100 ml. of concentrated hydrochloric acid without stirring. After being swirled gently, the milky solution was allowed to stand overnight. The tan crystalline diacid which formed amounted to 63 g. (71%) after being dried at 50° in a vacuum oven and melted at 156–163°. This material was used in the next step. Recrystallization of a portion three times from toluene and then sublimation at 180° (0.5 mm.) gave material which melted at 166–69°, and thus apparently was predominantly one isomer, and had a neutral equivalent of 240 (calcd. 248).

Anal. Calcd. for $C_{14}H_{10}O_4$: C, 67.73; H, 6.50. Found: C, 67.73; H, 6.58.

1-Keto-2a,3,4,5-tetrahydro-5-acenaphtheneacetic acid (VII). *Method A*. A mixture of 50 g. (0.2 mole) of finely powdered tetrahydro-1,4-naphthalenediacetic acid as isolated above and 500 g. of polyphosphoric acid[16] was warmed at 70–80° for 40 min.[17] with stirring under anhydrous conditions. The deep red solution was poured into 2 l. of cold water and, after 10–12 hr., the brown precipitate which formed was

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[14] M. Freund and K. Fleischer, *Ann.*, **399**, 182 (1913).

[15] R. A. Barnes, *J. Am. Chem. Soc.*, **70**, 145 (1948).

[16] Kindly provided by the Victor Chemical Works, Chicago, Ill.

[17] If the temperature was above 80°, or at 70–80° for longer than the optimum 40 min., predominantly tars were formed. If the temperature was maintained at 60° or below, mostly starting material was isolated.

separated and dissolved in ether. The ethereal solution was extracted with 10% aqueous potassium hydroxide until a portion of the extracts gave no precipitate when acidified.[18] Treatment of the basic extract with Norite and then acidification with 10% hydrochloric acid gave a tan oil which solidified on standing. The isolated solid material was dried in a vacuum oven at 50° and then weighed 33 g. (72%) and melted at 132–155°.

Method B. A mixture of 9 g. (0.036 mole) of the tetrahydro-1,4-naphthalenediacetic acid and 52 ml. of thionyl chloride was warmed carefully until the evolution of sulfur dioxide had ceased (15 min.). After removal of the excess thionyl chloride *in vacuo,* a solution of the residual acid chloride in 100 ml. of redistilled nitrobenzene was added with stirring over a period of 2 hr. to a cold (0°) solution of 19 g. (0.145 mole) of anhydrous aluminum chloride in 300 ml. of nitrobenzene. After standing for 10–12 hr. in a refrigerator, the dark red complex was hydrolyzed with ice and 10% hydrochloric acid. The organic layer was washed with several portions of 15% hydrochloric acid and then with 5% potassium hydroxide until a portion of the aqueous extract gave no precipitate when acidified. The basic solution was worked up as described in Method A to yield 5.1 g. (61%) of the crude keto acid, m.p. 132–156°. Treatment of the solution of a portion in 10% aqueous alkali several times with Norite followed by isolation as before and recrystallization from ethanol yielded colorless crystals, m.p. 140–156°. The wide range of melting point was attributed to the presence of more than one stereoisomer.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.02; H, 6.50. Found: C, 72.75; H, 6.58.

2a,3,4,5-Tetrahydro-5-acenaphtheneacetic acid (VIII). A modified Wolff-Kishner reduction of 7.1 g. (0.03 mole) of the keto acid with 35 ml. of 99% hydrazine hydrate, 28 ml. of ethanol, 35 ml. of diethylene glycol, and 3.3 g. of potassium hydroxide was carried out according to the procedure previously described[3] except that the crude product was not chromatographed. The oil obtained solidified on standing to yield 6 g. (90%) of material which melted at 89–96°. Recrystallization of a portion twice from petroleum ether afforded a product which melted at 99–101°[3] and apparently was predominantly the less soluble isomer. The ultraviolet and infrared absorption spectra of the recrystallized material were identical to those of a known sample.

2a,3,4,4a-Tetrahydro-1-pyracenone. Cyclization of 5.5 g. (0.025 mole) of the above tetrahydroacenaphtheneacetic acid by treatment with 50 g. of polyphosphoric acid[16] was effected as described above for the preparation of 1-keto-2a,3,4,5-tetrahydro-5-acenaphtheneacetic acid (VII). The reddish brown solution obtained was poured into cold water and the mixture stirred for 2 hr. at room temperature. The separated precipitate was dissolved in ether and the ether solution washed with 5% sodium bicarbonate, water, and saturated sodium chloride solution and then dried over magnesium sulfate. Removal of the solvent under reduced pressure left 3.9 g. (80%) of crude product. After one recrystallization from 70–90° ligroin followed by sublimation *in vacuo,* 3.0 g. (61%) of the ketone was obtained as colorless needles, m.p. 96–100°,[3] having ultraviolet and infrared absorption spectra identical to those of a known sample A small amount of starting material was recovered from the bicarbonate washes.

Pyracene (IX). The above tetrahydro-1-pyracenone was converted to 2a,3,4,4a-tetrahydropyracene as previously described.[3] A mixture of 0.24 g. (0.0013 mole) of the tetrahydropyracene, 15 ml. of anhydrous benzene, and 0.1 g. of 5% rhodium-on-alumina catalyst[19] was heated in a sealed tube at 290 ± 10° for 18 hr. in a rocker-type autoclave packed with glass wool and charged with 90 ml. of benzene. Separation of the catalyst and concentration of the filtrate yielded 0.19 g. (81%) of pyracene, m.p. 210–215°. A portion recrystallized from benzene melted at 215–216°[3] and gave no depression of melting point when mixed with a known sample.

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[18] A small amount of yellow, base insoluble material from the ether solution was isolated. It gave a positive reaction with 2,4-dinitrophenylhydrazine but could not be identified as the diketone resulting from cyclization of both carboxyl side chains.

[19] Baker and Company, Inc., Newark 5, N. J.

[CONTRIBUTION FROM THE RAHWAY RESEARCH LABORATORY OF THE METAL & THERMIT CORP.]

Preparation of Some Vinylsilanes with Vinylmagnesium Chloride[1]

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Tetravinylsilane, trivinylmethylsilane, trivinylphenylsilane, trivinylsilane, dibutyldivinylsilane, dimethyldivinylsilane, diphenyldivinylsilane, trimethylvinylsilane, and triphenylvinylsilane have been prepared by the reaction of vinylmagnesium chloride with appropriate silicon chlorides.

The development of the new intermediate, vinylmagnesium chloride, in this laboratory[2] has made possible the direct synthesis of organosilanes containing more than one vinyl group. In order to ascertain the utility of vinylmagnesium chloride, a group of nine organosilanes was prepared.

The development of the synthesis of tetravinylsilane involved the preparation of this compound in several solvent systems. The basic reaction of vinylmagnesium chloride in tetrahydrofuran with silicon tetrachloride in a solvent was used in all preparations. The solvents used were tetrahydrofuran, heptane, and benzene. The yields of tetravinylsilane ranged from 40% to 60%. Finally, as more was learned about the physical properties of tetravinylsilane, pentane was used as it was

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[1] This paper was presented before the 130th meeting of the AMERICAN CHEMICAL SOCIETY at Atlantic City, N. J., Sept. 1956.

[2] H. E. Ramsden, J. R. Leebrick, S. D. Rosenberg, E. H. Miller, J. J. Walburn, A. E. Balint, and R. Cserr, unpublished results. S. D. Rosenberg, A. J. Gibbons, Jr., and H. E. Ramsden, *J. Am. Chem. Soc.,* **79,** 2137 (1957).