

lithium aluminum hydride, and was dried over molecular sieves.

**Kinetics.**—For the kinetic runs, the amine oxide monohydrate was accurately weighed into a clean, dry flask, and the desired solvent added from a volumetric pipet to give a solution 0.05 *M* in amine oxide. For runs made at 0°, 25° and 36°, the reactions were conducted in the same flasks placed in an appropriate water-bath, 2-ml. aliquots being removed and quenched with 10 ml. of water at proper times. For runs made at higher temperatures, 2-ml. aliquots were sealed in ampoules which were placed in appropriate oil-baths and withdrawn at the proper times, opened, and the reaction was quenched with 10 ml. of water. For those runs conducted in dry tetrahydrofuran, the solutions were prepared at -80°, and the water of hydration was removed with molecular sieves at that temperature. The solutions were then warmed to 0° or 25°. A minimum of 5 points was used for each kinetic run.

As an internal standard for quantitative analysis by gas chromatography, 5  $\mu$ l. of 2-phenyl-1-butene<sup>19</sup> was added to the aqueous quench mixture, and the olefin was extracted with 2 ml. of pure pentane. The pentane extract was submitted to gas chromatography, and the amount of each component relative to the internal standard estimated from the areas under the peaks. Synthetic mixtures were prepared which approximated the unknowns in each component, and the unknowns were corrected to the

known mixtures. Use of known mixtures demonstrated that results could be duplicated within 0.5% to an accuracy of  $\pm 2\%$ . The rate constants were calculated with the assumption that the maximum yield of olefin obtained in any of the runs with a given lot of amine oxide represented the maximum obtainable yield for that particular lot. Only one lot was employed for *erythro* material, while two lots were used for the *threo*-oxide. Duplicate runs were made on each lot in pure dimethyl sulfoxide at 52.4° to confirm the reproducibility of yields and rate constants. Only minor differences were observed in rate constants calculated this way and those based on the weight of the amine oxide hydrate employed.

The V.P.C. analysis was conducted as follows: After each aliquot of the reaction mixture was quenched with cold water, 4.7 mg. (5.0  $\mu$ l.) of 2-phenyl-1-butene was added as internal standard with a microliter syringe. The solution was then mixed thoroughly and extracted with 2 ml. of pure pentane. A 50- $\mu$ l. sample of this extract was then subjected to vapor phase chromatography with a Perkin-Elmer model 154C vapor fractometer using a 23%  $\gamma$ -methyl- $\gamma$ -nitropimelonitrile on firebrick column at 110° with helium at 15 p.s.i. as carrier gas. Control experiments with known mixtures of the three olefins were used to determine the proper factors for relating the relative peak area to composition of the mixtures.

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES, LOS ANGELES 24, CALIF.]

## Studies in Stereochemistry. XXXVI. Radical Anions as Neighboring and Electron Transfer Groups in Substitution-Reduction Reactions<sup>1</sup>

BY DONALD J. CRAM AND CECILE K. DALTON<sup>2</sup>

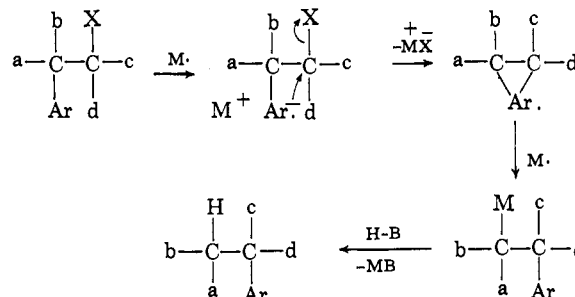
RECEIVED NOVEMBER 2, 1962

Examples have been found of reactions in which alkali metals transfer electrons to  $\beta$ -phenylalkyl methanesulfonates, and the aromatic radical anions generated act as neighboring groups in nucleophilic substitution-reduction reactions. Reaction of *threo*-2-phenyl-3-pentyl methanesulfonate with potassium in 1,2-dimethoxyethane gave hydrocarbon, 94% of which was 2-phenylpentane and 6% was 3-phenylpentane (product of phenyl migration). Treatment of *threo*-3-phenyl-2-pentyl methanesulfonate with sodium in liquid ammonia gave hydrocarbon, 75% of which was 3-phenylpentane and 3% was 2-phenylpentane (product of phenyl migration). Another type of reaction has been discovered in which alkali metals transfer electrons to 1-methoxy-2-(1-naphthyl)-ethane, the naphthyl group serving as an electron-transfer agent in reductive substitution of the methoxyl group. Treatment of 1,1-dideuterio-1-methoxy-2-(1-naphthyl)-ethane or 1,1-dideuterio-2-(1-naphthyl)-ethyl methanesulfonate with potassium in 1,2-dimethoxyethane gave 1-ethylnaphthalene deuterated only in the methyl group. In contrast, 1,1-dideuterio-2-(1-naphthyl)-ethyl *p*-toluenesulfonate when acetolyzed gave acetate in which deuterium was distributed equally in the two positions of the ethyl group. An ethylene naphthionium ion must have intervened in the solvolysis, but electron transfer occurred in the reductive substitution reaction without carbon participation.

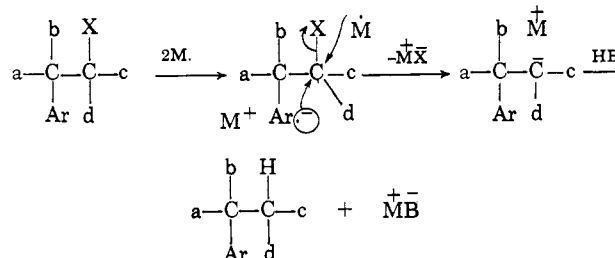
The ability of aryl groups to form ethylene phenonium ions as intermediates in solvolytic reactions has been well established,<sup>3</sup> as has the formation of a spiro-dienone from the anion of 2-(4-hydroxyphenyl)-ethyl bromide in a 1,3-elimination reaction.<sup>4</sup> These observations coupled with the fact that alkali metals transfer electrons to aromatic nuclei in the course of reduction<sup>5</sup> suggested that aryl radical anions might serve as neighboring groups in nucleophilic substitution-reduction reactions. Two general types of criteria might be used for detection of aryl involvement in reduction at saturated carbon: (1) If an aryl group migrates in the course of reduction (see formulas), it probably acts as a nucleophile in the process; one of a number of possible reaction schemes is formulated. (2) If the presence of an aryl group in the molecule is a condition for reductive substitution at saturated carbon, but no rearrangement occurs, aryl may serve as an electron transfer group without itself directly participating in displacement of the leaving group (see formulas for one of several possible mechanisms). In connection with the latter possibility, electron

transfers from one aromatic ring to a second in paracyclophanes,<sup>6</sup> diphenylmethane<sup>7</sup> and 1,2-diphenylethane<sup>7</sup> have been found to occur at very high rates.

Aryl radical anion participation in reductive substitution



Aryl electron transfer without direct participation



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(2) National Science Foundation Predoctoral Fellow, 1958-1959; du Pont Teaching Fellow, 1960-1961.

(3) (a) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3863, 3875 (1949); (b) **74**, 2129, 2159 (1952).

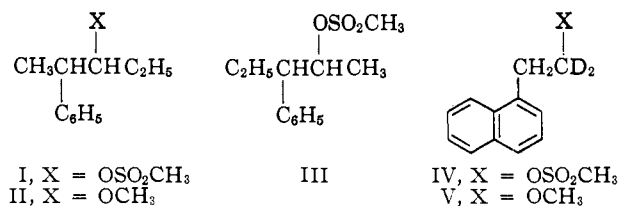
(4) S. Winstein and R. Baird, *ibid.*, **79**, 756 (1957).

(5) (a) C. A. Kraus, *Chem. Rev.*, **8**, 251 (1931); (b) A. J. Birch and H. Smith, *Quart. Rev. (London)*, **12**, 17 (1958).

(6) S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 6464 (1958).

(7) H. M. McConnell, *J. Chem. Phys.*, **35**, 503 (1961).

As a test of these possibilities, reactions of compounds I-V with potassium in 1,2-dimethoxyethane



were studied. These systems possess the advantages: (1) Skeletal rearrangement can be detected by examination of the hydrocarbon products. Rearrangement in reduction of I and II would produce 3-phenylpentane, and reductive rearrangement of III would provide 2-phenylpentane, both hydrocarbons being readily detected by vapor phase chromatographic methods. Reductive rearrangement of IV or V would provide 1-ethylnaphthalene deuterated at the  $\alpha$ -position, detectable by nuclear magnetic resonance techniques. (2) The phenyl and naphthyl groups differ greatly in their affinity for electrons. (3) The methanesulfonate and methoxide functions are far apart in their ability to serve as leaving groups.

### Results

Treatment of the methanesulfonate I with 2 gram atoms of potassium in dry 1,2-dimethoxyethane<sup>8</sup> gave good conversion to hydrocarbon, 94% of which was 2-phenylpentane (unrearranged) and 6% was 3-phenylpentane (rearranged). When small amounts of hydroxylic solvents were added to the medium, the base which was produced catalyzed elimination to give olefin. Reduction of methanesulfonate III with sodium in liquid ammonia produced a good yield of hydrocarbon, 75% of which was 3-phenylpentane (unrearranged), 3% was 2-phenylpentane (rearranged), 18% was olefin and 4% was not identified. Attempts to reduce II either with potassium in 1,2-dimethoxyethane or with sodium in liquid ammonia resulted in trivial amounts of reduction, even over a long period of time at both 25° and elevated temperatures.

Since naphthyl had not been examined as a neighboring group in a solvolysis reaction (possible model for reductive substitution), 1,1-dideuterio-2-(1-naphthyl)-ethyl *p*-toluenesulfonate was prepared by standard methods and acetylated. Acenaphthene, a possible product of naphthalene participation from the *peri*-position, was not detected in the product. The acetate produced was reduced to 2-(1-naphthyl)-ethanol, and the positions of the deuterium determined. Comparison of the nuclear magnetic resonance spectrum (n.m.r.) of this alcohol with that of authentic 1,1-dideuterio-2-(1-naphthyl)-ethane and that of non-deuterated alcohol indicated that the isotope was equally distributed between the two carbons of the side chain.

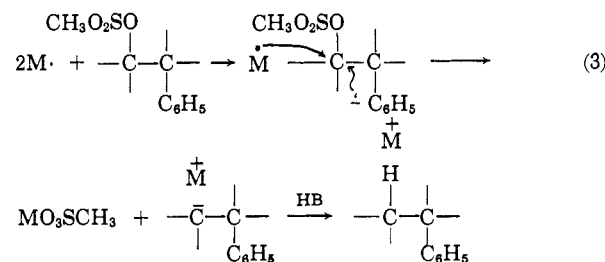
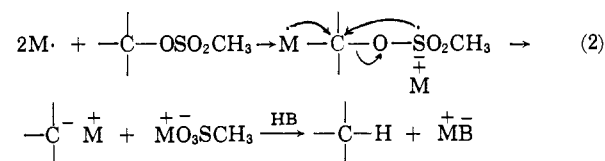
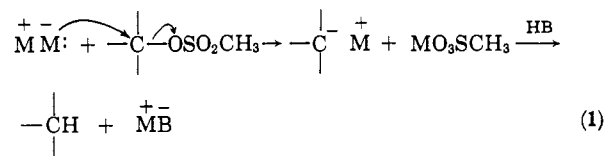
Reductive substitution of 1,1-dideuterio-1-methoxy-2-(1-naphthyl)-ethane (V) and of 1,1-dideuterio-2-(1-naphthyl)-ethyl methanesulfonate (IV) with 2 gram atoms of potassium in 1,2-dimethoxyethane readily produced 1-ethylnaphthalene in good yield at 0°. Comparison of the n.m.r. spectra of the samples of compound produced with that of authentic non-deuterated 1-ethylnaphthalene and of 1,1-dideuterio-2-(1-naphthyl)-ethane indicated that less than 5% deuterium scrambling had occurred during the reductive-substitution reactions of the ether and the methanesulfonate. As a control, acenaphthene was subjected

to the same conditions, and was found not to give 1-ethylnaphthalene.

### Discussion

**Phenyl Radical Anions as Neighboring Groups.**—Reductive substitution of the methanesulfonates of the phenylpentane systems I and III occurred with 4–6% phenyl migration as contrasted with acetolysis of 2-phenyl-3-pentyl and 3-phenyl-2-pentyl *p*-toluenesulfonates, which provided 40–60% rearrangement.<sup>3b</sup> In the solvolyses, most of the product involved phenonium ion intermediates. The question arises whether phenyl radical anions participated in displacement of the methanesulfonate group and whether bridged species intervened as discrete intermediates in the over-all reduction-substitution reaction, at least in that part of the reaction which resulted in rearranged product. Alternative possibilities will first be examined, along with a discussion of how unrearranged material is produced.

Three plausible general mechanisms can be written for the reaction which produces unrearranged material: (1) Two electrons might be donated by the alkali metal directly to saturated carbon in an S<sub>N</sub>2-like substitution reaction; a single electron transfer to produce a carbon radical as a first stage is considered unlikely. (2) An electron might be donated by the alkali metal to a d-orbital of sulfur, which in turn relays the electron to carbon simultaneously to a transfer of an electron from a second alkali metal atom to carbon. (3) An electron might be donated by the alkali metal to the benzene ring by the alkali metal, which in turn relays it to carbon of the side chain simultaneously to a transfer of an electron from a second alkali metal atom to carbon.



Conceivably rearrangement might occur after the carbon radical, or even after the organometallic compound, was formed. Both of these latter possibilities are highly unlikely. Others have demonstrated that 1,2-phenyl migrations to carbon radicals<sup>9</sup> or to carbon bonded to metal<sup>10</sup> occur only in systems widely different from those at hand. Furthermore, since ionization of secondary methanesulfonates does not

(9) For a summary, see D. J. Cram in M. S. Newman's "Steric Effects in Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1956, p. 283.

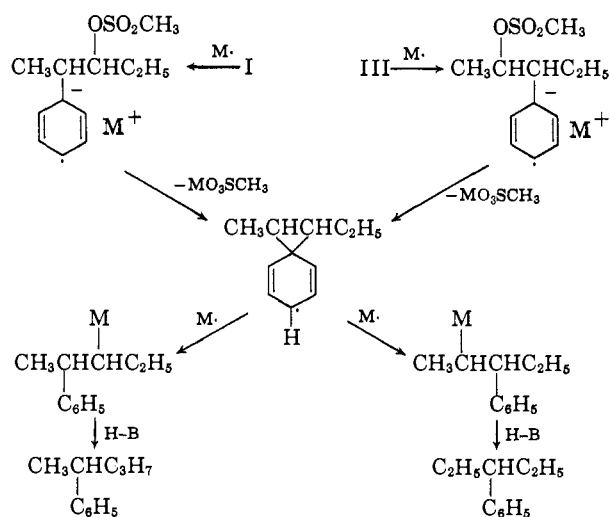
(10) H. E. Zimmerman and F. Smentowski, *J. Am. Chem. Soc.*, **79**, 5455 (1957); H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961).

(8) This solvent when completely dry has been reported [J. L. Down, B. Moore and G. Wilkinson, *J. Chem. Soc.*, 3767 (1959)] to dissolve small amounts of the alkali metals.

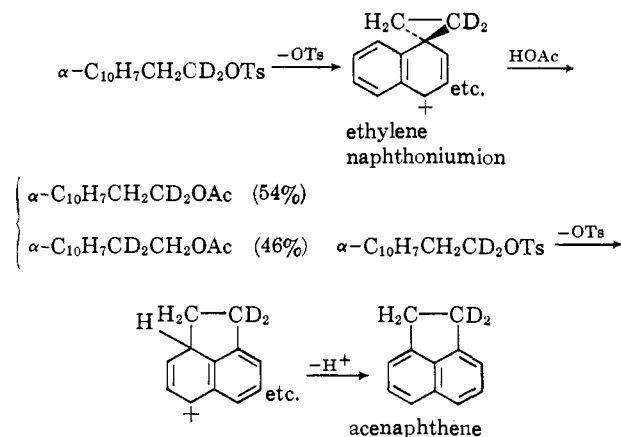
occur at 25° under basic conditions in 1,2-dimethoxyethane, reductive rearrangement could not have involved carbonium ions.

The most plausible mechanism for rearrangement is: The first stage involves a one-electron transfer from the alkali metal to the phenyl group, whose radical anion, as a powerful nucleophile, displaces the methanesulfonate group in a second stage to give a phenyl-bridged radical. This species in a third stage reacts with a second metal atom to give an organometallic compound, which abstracts a proton from the solvent to give reduction product. In such a scheme part of the bridged radical should open to give unrearranged and part rearranged organometallic compound, which in turn gives unrearranged and rearranged hydrocarbon. A small variation of this scheme would involve electron donation by metal to the bridged radical without ring opening, followed by ring opening and proton abstraction from the solvent.

Equivalent but less plausible mechanisms can be written in which the first stage involves donation of two electrons to the benzene ring to give a dianion, which goes to a bridged anion, and finally to rearranged product.



**Naphthonium Ions in Acetolysis.**—Unlike phenyl, the naphthyl group might aid in *solvolytic substitution reactions* from either of two positions: to produce an ethylene naphthonium ion, or to give a protonated acenaphthene. Since the bridged ion contains a plane



of symmetry, the deuterium label of the starting material should appear in the product of this ion, equally distributed between both carbon atoms of the side chain. The fact that essentially such deuterium distribution was observed in the acetate product pro-

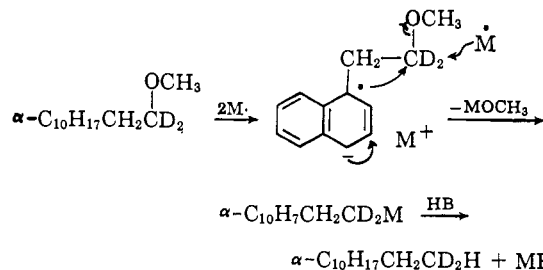
vides strong support for the ethylene naphthonium ion mechanism. The absence of acenaphthene in the product indicates the *peri*-position of the naphthalene nucleus never became involved in the reaction.

**Naphthyl as an Electron Relay Group.**—Reduction of 1,1-dideuterio-1-methoxy-2-(1-naphthyl)-ethane (V) with potassium in 1,2-dimethoxyethane occurred readily to give 1-ethylnaphthalene deuterated in the methyl group. No detectable rearrangement accompanied reduction. In contrast, *threo*-2-phenyl-3-methoxypentane (II) underwent reduction *extremely slowly*. The reactions were run in dimethoxyethane, which did not competitively destroy the potassium. These experiments demonstrate that the naphthyl group plays a necessary role in the reductive substitution of the ether linkage, and that phenyl also assists in reduction, but at a greatly reduced rate. Without these aryl groups, reduction of the ether linkages does not occur.

The absence of isotopic scrambling in reduction of V indicates that the 1-position of the naphthalene ring did not aid in displacement of the methoxide group. In the model solvolysis experiment, the 1-position of the naphthalene ring was exclusively involved in the reaction. It therefore seems improbable that the naphthyl radical anion formed from V could aid in displacement of the methoxyl group by covalent bond formation from either the  $\beta$ - or *peri*-carbon of the naphthalene nucleus. Furthermore, no products were obtained suggestive of such a reaction course.

The facts point to a mechanism which casts the naphthalene nucleus in the role of a group which transfers at least one electron from the alkali metal to the carbon atom attached to the methoxyl group. Since the electron is spread over the entire naphthalene nucleus (probably not uniformly), possibly no particular position is involved in the transfer. On the other hand, the process of electron transfer can be visualized as involving particular carbon atoms such as those of the  $\alpha$ - or *peri*-positions as the electron-donating sites of the naphthalene nucleus. In the transition state for the electron transfer, the electron in a sense would bond two nuclei. Such a bond would be different from a true  $\sigma$ -bond which would result from aryl participation in substitution.

Other investigators<sup>6,7</sup> have observed that electrons migrate intramolecularly from one benzene ring to a second across distances well in excess of 3 Å. between nuclei. The distance between the  $\alpha$ -carbon of the naphthalene nucleus and the carbon attached to the methoxyl group is approximately 2.5 Å. Thus the electron magnetic resonance spectral work<sup>6,7</sup> and the chemistry of this reduction-substitution reaction are consistent with one another. The fact that the phenyl group of II was less effective in the reduction than the naphthyl group of V is consistent with the much lower electron affinity of the phenyl group. An over-all mechanism consistent with all the facts is formulated.<sup>11</sup>

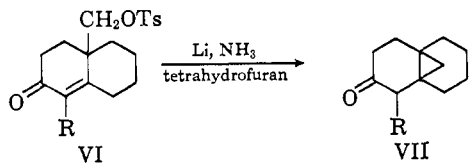


Reduction of methanesulfonate IV without rearrangement could have involved either the naphthal-

(11) Work is in progress designed to determine the scope and geometric requirements for reactions which involve electron relay processes.

ene ring or the sulfur of the sulfonate group as the electron transfer center.

To the authors' knowledge, the only previously published example of where a radical anion might have served as a neighboring group involved the conversion of VI to VII.<sup>12</sup>



### Experimental

**threo-2-Phenyl-3-pentyl Methanesulfonate (I).**—A solution of 1 ml. of dry pyridine, 0.323 g. of *threo*-2-phenyl-3-pentanol<sup>3</sup> and 0.275 g. of methanesulfonyl chloride was allowed to stand at 25° for 14 hr. The reaction mixture was shaken with a mixture of 20 ml. of 2*N* sulfuric acid and 40 ml. of 1:1 ether-pentane. The organic layer was washed with dilute sulfuric acid, water, dilute sodium hydroxide solution, water and was dried. Evaporation of solvent under vacuum gave a colorless oil, which was crystallized from pentane at -80°, m.p. 45.8–46.3°, wt. 0.422 g. (87%).

*Anal.* Calcd. for C<sub>12</sub>H<sub>18</sub>O<sub>3</sub>S: C, 59.47; H, 7.49. Found: C, 59.51; H, 7.33.

**threo-3-Phenyl-2-pentyl Methanesulfonate (III).**—Application of the above procedure to 1.03 g. of *threo*-3-phenyl-2-pentanol<sup>3</sup> gave a 60% yield of III, m.p. 45.3–45.8° (crystallized from pentane).

*Anal.* Calcd. for C<sub>12</sub>H<sub>18</sub>O<sub>3</sub>S: C, 59.47; H, 7.49. Found: C, 59.72; H, 7.46.

**threo-2-Phenyl-3-methoxypentane (II).**—Potassium metal (0.552 g.) was added to 100 ml. of benzene (dry to molecular sieves), and the mixture was heated to reflux under dry pure nitrogen. To this mixture was added 2.08 g. of *threo*-2-phenyl-3-pentanol,<sup>3</sup> and the resulting yellow-orange solution was heated at reflux with stirring for 4 hr. The mixture was cooled, and a solution of 2.48 g. of methyl iodide in 20 ml. of benzene was added dropwise. The mixture (heavy white precipitate) was stirred for 14 hr., and 100 ml. of water was added. The benzene layer was separated, the aqueous layer extracted with pentane, and the combined organic layers were washed with water and dried. Solvent was evaporated through a small fractionating column, and the residual oil was chromatographed on a column of 112 g. of alumina made up in pentane. Product was eluted with 1 l. of pentane, evaporation of which gave an oil which was flash-distilled at a pot temperature of 90° (0.4 mm.) to give 1.35 g. (60%) of ether II. Gas chromatography on 33% polyethylene glycol on firebrick at 125° and 15 p.s.i. (helium) detected only a single compound.

*Anal.* Calcd. for C<sub>12</sub>H<sub>18</sub>O: C, 80.82; H, 10.17. Found: C, 80.96; H, 10.39.

**1,1-Dideuterio-2-(1-naphthyl)-ethanol.**—To a stirred slurry of 4.85 g. of lithium aluminum deuteride and 50 ml. of dry ether under helium was added dropwise a solution of 27 g. of methyl 1-naphthylacetate<sup>13</sup> in 35 ml. of dry ether. The mixture was held at reflux for 14 hr., cooled to 0°, and mixed with cold dilute sulfuric acid. The aqueous layer was extracted with ether, and the combined ether extracts were washed with dilute sodium hydroxide solution, water, and were dried. Solvent was evaporated, and the crystalline residue was recrystallized from ether-pentane; wt. 22.42 g. (96%), m.p. 61–62°, literature<sup>14</sup> for 2-(1-naphthyl)-ethanol, 62°. Deuterium analysis by combustion and falling drop method gave 16.51 atom % excess deuterium, which corresponds to 1.99 atoms of deuterium per molecule.

A sample of 2-(1-naphthyl)-ethanol was prepared in 83% yield by lithium aluminum hydride reduction of 1-naphthylacetic acid; m.p. 58.0–59.5°, lit.<sup>14</sup> 62°.

**1,1-Dideuterio-1-methoxy-2-(1-naphthyl)-ethane (V).**—A solution of 3.76 g. of 1,1-dideuterio-2-(1-naphthyl)-ethanol in 200 ml. of dry benzene was treated with 1.89 g. of sodium hydride dispersed in mineral oil. The resulting gray slurry was stirred at reflux temperature for 12 hr., at the end of which time the mixture was cooled and 10 ml. of methyl iodide was added. The mixture was stirred at room temperature for 5 hr., and at reflux temperature for 12 hr. The flask was then cooled to 0° and cold water added cautiously. The benzene layer was washed with water, dried, filtered and evaporated. The residue was chroma-

tographed on 141 g. of alumina in a column packed in pentane. Impurities (V.P.C. criterion) were found in the first 500 ml. of pentane eluate, whereas V was eluted in the next 2.5 l. Pentane from these fractions was evaporated through a small column, and the residue was distilled at 109–110° at 0.23 mm. to give 2.62 g. (65%) of V. The infrared spectrum of this oil exhibited very strong bands at 8.69 and 9.00 μ characteristic of carbon-oxygen bonds, and medium bands at 4.61 and 4.82 μ characteristic of C-D bonds. Deuterium analysis by combustion and falling drop method gave 14.03 atom % excess deuterium, which corresponds to 1.97 atoms of deuterium per molecule.

Non-deuterated V, 1-methoxy-2-(1-naphthyl)-ethane, was also prepared, b.p. 103–104° (0.2 mm.).

*Anal.* Calcd. for C<sub>13</sub>H<sub>14</sub>O: C, 83.84; H, 7.57. Found: C, 83.56; H, 7.57.

**1,1-Dideuterio-2-(1-naphthyl)-ethyl *p*-Toluenesulfonate.**—From 0.362 g. of 1,1-dideuterio-2-(1-naphthyl)-ethanol and 0.732 g. of *p*-toluenesulfonyl chloride was prepared 0.547 g. (78%) of white crystals (ether-pentane) by the usual procedure; m.p. 58.5–59.5°.

The non-deuterated analog, 2-(1-naphthyl)-ethyl *p*-toluenesulfonate, was also prepared in 70% yield, m.p. 56.5–58.0°.

*Anal.* Calcd. for C<sub>19</sub>H<sub>18</sub>O<sub>3</sub>S: C, 69.91; H, 5.56. Found: 69.83; H, 5.85.

**1,1-Dideuterio-2-(1-naphthyl)-ethyl Methanesulfonate.**—From 1.36 g. of 1,1-dideuterio-2-(1-naphthyl)-ethanol and 1.32 g. of methanesulfonyl chloride by the usual method was obtained 1.48 g. (75%) of the sulfonate ester as colorless needles from ether-pentane; m.p. 82.0–82.5°. Deuterium analysis by combustion and falling drop method gave 13.97 atom % excess deuterium, which corresponds to 1.96 atoms of deuterium per molecule.

**1,1-Dideuterio-2-(1-naphthyl)-ethane.**—A mixture of 1.08 g. of 1,1-dideuterio-2-(1-naphthyl)-ethyl methanesulfonate, 0.633 g. of sodium bromide and 70 ml. of acetylacetone was stirred and heated at 140–145° for 17 hr. The mixture of black solution and white precipitate was filtered, and the filter cake was washed with acetone. The combined filtrates were evaporated under vacuum, and the brown residue was shaken with a mixture of water and pentane. The organic layer was washed with water, dried and evaporated, and the residue was chromatographed on 61 g. of alumina made up in pentane. Pentane (100 ml.) eluted the desired 1,1-dideuterio-2-(1-naphthyl)-ethyl bromide, 0.964 g. This material was mixed with 0.902 g. of ethyl bromide in 10 ml. of anhydrous ether and added dropwise to 0.360 g. of magnesium turnings and 5 ml. of anhydrous ether in an atmosphere of dry helium. The resulting mixture was heated at reflux for 3 hr., 10 ml. of dry tetrahydrofuran was added, and the mixture was held at reflux for an additional 19 hr. The mixture was cooled, and a cold saturated solution of ammonium chloride was added (ethane was evolved). The mixture was shaken with pentane and water, the pentane-ether was washed with water, dried and evaporated. The residue was submitted to purification by V.P.C. on a column (6 ft. by 0.25 in.) of 10% Carbowax on firebrick (60/80 mesh) at 160° and 5 p.s.i. with helium as carrier gas, retention time 42 min. The product, 1,1-dideuterio-2-(1-naphthyl)-ethane, amounted to 0.112 g. (17% over-all). Deuterium analysis by combustion and falling drop method gave 16.10 atom % excess deuterium, which corresponds to 1.94 atoms of deuterium per molecule.

**1-Ethynaphthalene.**—Reduction of 0.260 g. of 2-(1-naphthyl)-ethyl methanesulfonate directly with 0.110 g. of lithium aluminum hydride in ether by the usual method<sup>15</sup> gave the desired product<sup>16</sup> in 79% yield, b.p. (pot temperature) 140° at 10 mm.

**Reduction of *threo*-2-Phenyl-3-pentyl Methanesulfonate (I) with Potassium in 1,2-Dimethoxyethane.**—To a solution of 0.243 g. of I in 20 ml. of dry pure 1,2-dimethoxyethane stirred in an atmosphere of pure nitrogen was added 0.083 g. of clean potassium metal. The metal disappeared after 9 days of stirring at 25°, after which time 200 ml. of water was added, and the mixture was extracted with four 100-ml. portions of pentane. The combined pentane extracts were washed with 3 50-ml. portions of water, dried, and evaporated through a short column to about 10 ml. The residue was chromatographed over 44 g. of alumina (neutral, activity 1), and the products were eluted with 400 ml. of pentane. The pentane eluate was evaporated to dryness, yielding 0.117 g. (79% yield) of phenylpentanes. Gas chromatographic analysis showed the product to consist of 5.5% 3-phenylpentane and 94.5% 2-phenylpentane.

**Reduction of *threo*-3-Phenyl-2-pentyl Methanesulfonate (III) with Sodium in Liquid Ammonia.**—A solution of 0.259 g. of III in 35 ml. of 1,2-dimethoxyethane was added dropwise to a solution of 0.257 g. of sodium in *ca.* 100 ml. of liquid ammonia. The reaction mixture was stirred at -78° for 1 hr., then allowed to warm to room temperature over a period of 2 hr. Pentane (100 ml.) was added to the colorless solution, and the reaction mixture was cooled in an ice-bath while 150 ml. of a saturated ammonium

(12) G. Stork and J. Tsuji, *J. Am. Chem. Soc.*, **83**, 2783 (1961).

(13) R. H. F. Manske and A. E. Ledingham, *Can. J. Research*, **17B**, 14 (1939).

(14) M. V. Grignard, *Compt. rend.*, **141**, 44 (1905).

(15) J. Strating and H. J. Backer, *Rec. trav. chim.*, **69**, 638 (1950).

(16) G. Lévy, *Compt. rend.*, **193**, 174 (1931).

TABLE I  
 NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA

Compound	Ar-H			O-H			Aliph. C-H		
	$\tau$	Intens. <sup>a</sup>	Mult. <sup>b</sup>	$\tau$	Intens. <sup>a</sup>	Mult. <sup>b</sup>	$\tau$	Intens. <sup>a</sup>	Mult. <sup>b</sup>
$\alpha$ -C <sub>10</sub> H <sub>7</sub> CH <sub>2</sub> CH <sub>3</sub>	1.98-2.81	7.00	m	..	..	..	6.97	2.0 <sup>c</sup>	q
$\alpha$ -C <sub>10</sub> H <sub>7</sub> CH <sub>2</sub> CHD <sub>2</sub>	1.97-2.80	7.00	m	..	..	..	8.67	2.9 <sup>c</sup>	t
$\alpha$ -C <sub>10</sub> H <sub>7</sub> CH <sub>2</sub> CH <sub>2</sub> OH	2.00-2.82	7.00	m	7.42	0.96 <sup>c</sup>	s	6.94	1.93	d
$\alpha$ -C <sub>10</sub> H <sub>7</sub> CH <sub>2</sub> CD <sub>2</sub> OH	2.00-2.83	7.00	m	7.33	1.03	s	8.65	1.01	t
Alc. from acetolysis	1.99-2.82	7.00	m	7.39	0.944	s	6.30	1.8 <sup>c</sup>	q
							6.78	1.8 <sup>c</sup>	q
							6.87	2.00	s
							6.25	0.805	s
							6.84	0.934	s

<sup>a</sup> Intensity measured by setting area under aromatic peaks equal to 7.00 and comparing area under other peaks to this value. <sup>b</sup> s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. <sup>c</sup> Integrator was not working; planimeter was employed.

chloride solution was added cautiously. The aqueous phase was separated and washed with three 100-ml. portions of pentane. The combined pentane extracts were washed with water until neutral, dried, and evaporated to dryness. The yield of hydrocarbons was 69%. Gas chromatographic analysis showed the product to consist of 75% 3-phenylpentane, 3.1% 2-phenylpentane, 17.5% olefin and 4.4% unidentified compound.

**Reduction of *threo*-2-Phenyl-3-methoxypentane (II) with Potassium in 1,2-Dimethoxyethane.**—To a stirred solution of *threo*-2-phenyl-3-methoxypentane (0.175 g.) in 20 ml. of pure dry 1,2-dimethoxyethane under pure, dry nitrogen was added 0.080 g. of clean potassium. When a yellow coating appeared on the surface of the metal, ground glass was added as an abrasive. After 13 days of stirring at 25°, the mixture still contained most of the potassium unreacted, and so the mixture was heated to 85–95° for 5 days, during which time little more potassium had been consumed. After an additional 6 weeks at this temperature, the potassium had been consumed, and product was isolated in the usual manner (see above procedures). Evaporation of the pentane extracts gave 0.101 g. of material, whose VPC analysis indicated it to be 87% starting material II, 6% 2-phenylpentane and 7% 2-phenylpentenes.

An attempt was made to reduce I with sodium in a mixture of 1,2-dimethoxyethane and liquid ammonia. Material isolated from the reaction mixture proved to be 99% starting material and 1% 2-phenylpentane.

**Reduction of 2-(1-Naphthyl)-ethyl Methanesulfonate with Potassium in 1,2-Dimethoxyethane.**—To a solution of 0.145 g. of 2-(1-naphthyl)-ethyl methanesulfonate in 10 ml. of pure dry 1,2-dimethoxyethane stirred in a dry atmosphere of helium was added 0.028 g. of clean potassium. A small amount of ground glass was also added to remove any surface coating that might develop on the surface of the metal. After 6 hr. of stirring at 25°, a brown color began to develop on the surface of the metal. After 10 more hours the potassium had disappeared and the solution was dark green in color. After 4 additional hours, 10 ml. of water was added and the green color was discharged. The milky mixture was shaken with 100 ml. of water and 50 ml. of pentane, and the water was extracted with 3 additional 50-ml. portions of pentane. The combined pentane extracts were washed with three 50-ml. portions of water, dried, filtered and concentrated through a short column to give 0.060 g. of residue; VPC analysis (see later section) of this material demonstrated it to be over 95% 1-ethylnaphthalene. Acenaphthene was demonstrated to be absent.

**Reduction of 1,1-Dideuterio-2-(1-naphthyl)-ethyl Methanesulfonate (IV) with Potassium in 1,2-Dimethoxyethane.**—To a solution of 0.769 g. of the sulfonate ester in 60 ml. of pure, dry 1,2-dimethoxyethane stirred at 0° in an atmosphere of helium was added 0.257 g. of clean potassium. After 20 hr., the potassium had all reacted, and the reaction mixture was poured into 1 l. of water. Three 150-ml. portions of pentane were used for extraction, and the combined pentane extracts were washed, dried and evaporated through a column. The 1-ethylnaphthalene was collected by VPC on a Loenco gas chromatograph using a 10% Carbowax column at 165° and 5 p.s.i. with helium as a carrier gas. The 1-ethylnaphthalene (0.150 g., 31% yield) possessed an n.m.r. spectrum identical with that of 1,1-dideuterio-1-(1-naphthyl)-ethane. Integration indicated that <4% of 1,1-dideuterio-1-(1-naphthyl)-ethane was present.

**Reduction of 1,1-Dideuterio-1-methoxy-2-(1-naphthyl)-ethane (V) with Potassium in 1,2-Dimethoxyethane.**—To a solution of 0.380 g. of V in 40 ml. of pure, dry 1,2-dimethoxyethane stirred at 0° in an atmosphere of dry helium was added 0.173 g. of clean potassium. A green color appeared on the surface of the metal immediately, and after a short time the solution became deep purple. Although all of the potassium had been consumed at the end of 4 hr. at 0°, the reaction mixture was stirred at 25° for an additional 26 hr. The mixture was poured into 600 ml. of

water and extracted with three 100-ml. portions of pentane. The combined pentane extracts were dried and evaporated through a column. VPC analysis (small sample) of the residue demonstrated this material to be approximately 97% 1-ethylnaphthalene, 1% 1,2-dimethoxyethane and 2% lower boiling impurities (see later section). The main portion of the material was submitted to VPC separation on a Loenco gas chromatograph on a 20% silicone gum column at 198° and 5 p.s.i. with helium as carrier gas. The sample of 1-ethylnaphthalene obtained (0.077 g. or 24% yield) possessed infrared and nuclear magnetic resonance spectra identical with those of authentic 1,1-dideuterio-2-(1-naphthyl)-ethane (see later section). It is estimated that as little as 5% 1,1-dideuterio-1-(1-naphthyl)-ethane could have been detected in this mixture.

When a 0.015-g. sample of 1-ethylnaphthalene was subjected to the same VPC conditions used above for obtaining product, 0.0076 g. was recovered. Thus the yield in the reduction of the methyl ether must have been approximately 50%.

**Acetolysis of 1,1-Dideuterio-2-(1-naphthyl)-ethyl *p*-Toluene-sulfonate.**—A solution of 0.352 g. of the above sulfonate ester in 50 ml. of dry glacial acetic acid was heated at 125–130° for 85 hr. The reaction mixture was cooled and shaken with a mixture of pure pentane and water. The water was washed with pentane, and the combined pentane extracts were washed with water, dried and evaporated through a short column. The residue was dissolved in 10 ml. of anhydrous ether and added to 0.276 g. of lithium aluminum hydride in 10 ml. of ether. The resulting mixture was refluxed for 20 hr., cooled and treated with water saturated with ammonium chloride. The aqueous solution was extracted with 1:1 pentane-ether, and the combined organic layers were washed with water, dried and evaporated. The residue was chromatographed on 20 g. of alumina. The column was washed with 200 ml. of pentane, and the product was eluted with 100 ml. of ether. The eluate was evaporated, and the oily product (0.195 g.) crystallized, m.p. 59.5–60.0°. Comparison of the nuclear magnetic resonance spectrum of this material (see later section) with that of 2-(1-naphthyl)-ethanol and 1,1-dideuterio-2-(1-naphthyl)-ethanol indicated that the material was 54% 1,1-dideuterio-2-(1-naphthyl)-ethanol and 46% 1,1-dideuterio-1-(1-naphthyl)-ethanol.

**Reaction of Potassium with Acenaphthene.**—A solution of 0.156 g. of acenaphthene in 20 ml. of anhydrous 1,2-

 TABLE II  
 INFRARED SPECTRAL DATA

Compound	Bands in ( $\mu$ ) and intensity in parentheses <sup>a</sup>
$\alpha$ -C <sub>10</sub> H <sub>7</sub> CH <sub>2</sub> CH <sub>3</sub>	3.30(m); 3.38(s); 3.42(sh); 3.48, 6.25, 6.61, 6.80 6.87, 7.15(all m); 7.25, 7.37, 5.57(all w); 8.55(m) 9.05, 9.43, 9.72, 9.90, 10.31, 10.48, 11.58(all w)
$\alpha$ -C <sub>10</sub> H <sub>7</sub> CH <sub>2</sub> CD <sub>2</sub> H	3.30(m); 3.41(s); 3.48, 4.51(both w); 4.60(vw), 4.71(w); 6.26, 6.62(both m); 6.83(w); 7.16(m); 7.73, 7.92, 8.57, 9.22(all w); 9.79(m); 10.00, 10.30, 10.50, 10.68, 11.62(all w)
Reaction products IV + V	Superimposable on spectrum of $\alpha$ -C <sub>10</sub> H <sub>7</sub> CH <sub>2</sub> CD <sub>2</sub> H
$\alpha$ -C <sub>10</sub> H <sub>7</sub> CH <sub>2</sub> CH <sub>2</sub> OH	2.81(s); 2.92(s and broad); 3.31, 3.40(both s); 3.43(sh); 3.49(s); 3.51(sh); 6.26, 6.62, 7.18, 7.23 (all s); 8.57(m); 9.26(w); 9.60(s); 9.78(sh); 10.05(w)
$\alpha$ -C <sub>10</sub> H <sub>7</sub> CH <sub>2</sub> CD <sub>2</sub> OH	2.81(s); 2.92(s broad); 3.31(s); 3.42(m); 3.50(w); 4.53, 4.77(m); 6.27, 6.62, 7.18, 7.80(all s); 8.21, 8.30, 8.60(all m); 8.93, 9.10(both s); 9.80(m); 10.37, 10.47(both s)
Alc. from acetol.	(Only bands which differ from $\alpha$ -C <sub>10</sub> H <sub>7</sub> CH <sub>2</sub> CD <sub>2</sub> OH) 3.50, 9.80(both stronger); 4.53, 4.77, 7.80, 9.10, 10.37, 10.47(all weaker); 9.52 and 10.00(new)

dimethoxyethane was treated with 0.0937 g. of potassium. A dark green color appeared on the surface of the metal almost immediately. At the end of 3 hr. the solution was almost black and a small piece of potassium remained. The small piece of potassium was still in evidence after an additional 14 hr., when it was removed, wt. 0.012 g. A solution of 0.0612 g. of water in 10 ml. of 1,2-dimethoxyethane was added dropwise. The green color became orange. The reaction mixture was shaken with a mixture of water and pentane. The pentane layer was washed with water, dried, filtered and evaporated to an oil. Gas chromatography on a 20% silicone gum column using a Loenco gas chromatograph preparative column produced two components in approximately equal yields, the first being starting material. The second was demonstrated to be neither 1-ethylnaphthalene nor tetrahydroacenaphthalene by infrared analysis.

**Vapor Phase Chromatographic Analysis.**—Pure samples of 1-ethylnaphthalene (see above), acenaphthene, 2-phenylpentane<sup>17</sup> and 3-phenylpentane<sup>17</sup> were used as standards. The mixture of 2-phenylpentenes and of 3-phenylpentenes obtained by treatment of 2-phenyl-3-pentyl *p*-toluenesulfonate<sup>3</sup> and 3-phenyl-2-pentyl *p*-toluenesulfonate<sup>3</sup> with sodium hydroxide were used as olefin standards.

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For analysis of the products of reduction of methanesulfonates I and III and of ether II, the following techniques were employed.

Analyses were carried out using a Perkin-Elmer model 154 vapor fractometer. Neat liquids (1  $\mu$ l.) were injected onto a 6 ft. by 0.25 in. column of 33% polyethylene glycol on firebrick. At a column temperature of 125° and 15 p.s.i. of helium the retention time of 2-phenylpentane is 12.3 min. and that of 3-phenylpentane is 13.4 min.

For analysis of the products of reduction of ether V, the following techniques were used. The neat liquid (1  $\mu$ l.) was injected onto a 6 ft. by 0.25 in. column of 33% polyethylene glycol on firebrick. At a column temperature of 200° and 25 p.s.i. of helium the retention time of 1-ethylnaphthalene is 5.2 minutes.

**Spectral Analysis.**—The n.m.r. spectra were taken on a Varian Associates Model A60 n.m.r. spectrometer. The absorption bands of the compounds useful in this investigation are reported in Table I.

The infrared spectra of the deuterated and non-deuterated 1-ethylnaphthalenes and naphthylethanols differed somewhat, and were used to corroborate the conclusions derived from the n.m.r. data. The spectra were taken on 10% solutions by weight in methylene dichloride with sodium chloride optics and cells on a Perkin-Elmer model IR-5 infrared spectrophotometer. The data are in Table II.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES, LOS ANGELES 24, CALIF.]

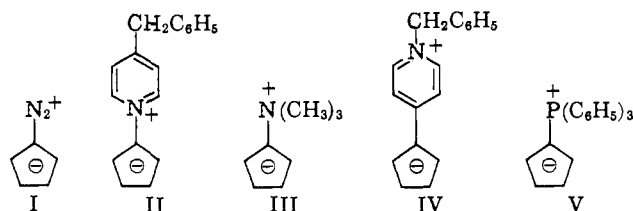
## Electrophilic Substitution and Other Reactions of Diazocyclopentadiene<sup>1</sup>

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Diazocyclopentadiene (I) has been found to undergo five electrophilic substitution reactions without destruction of the ylide  $\pi$ -electron system. Nitration produced two monosubstituted derivatives, the 2- predominating over the 3-isomer by a factor of two. Benzenediazonium tetrafluoroborate gave the 2-substitution product, whereas bromination gave tetrabromodiazocyclopentadiene. Mercuration resulted in formation of a highly unstable 2,5-diiodomercuri derivative, which was readily converted to 2,5-diiododiazocyclopentadiene. Diazocyclopentadiene added 1,2 to tetracyanoethylene to give an unstable acid which readily lost the elements of hydrogen cyanide to produce 2-(tricyanoethylene)-diazocyclopentadiene. No evidence of a Diels-Alder reaction was obtained. The tricyanovinyl group underwent nucleophilic substitution reactions typical of that function without loss of the diazocyclopentadiene nucleus. With dimethyl acetylenedicarboxylate, diazocyclopentadiene underwent a 1,4-dipolar addition reaction to produce a fused 5- to 6-membered ring system (XVII). The acidity of the substance is attributed partially to the presence of 10  $\pi$ -electrons in its conjugate base.

Aside from the molecular sandwich derivatives of which ferrocene is the prototype, five ylides of cyclopentadiene have been prepared; systems I,<sup>2</sup> II,<sup>3</sup> III,<sup>4</sup> IV<sup>5</sup> and V.<sup>6</sup>



The aromatic character of V was demonstrated by its coupling reaction with phenyldiazonium chloride,<sup>7</sup> which occurred in the 2-position.

Reactions of diazocyclopentadiene (I) have been confined to its catalytic reduction to cyclopentanone hydrazone,<sup>2</sup> its coupling reaction with triphenylphosphine to give a phosphazine,<sup>7</sup> its photolysis to give fulvalene,<sup>8</sup> and its reaction with organolithium reagents

to produce salts which in turn gave azoferrocene derivatives when treated with ferrous chloride.<sup>9</sup>

The present investigation is concerned with the electrophilic substitution and cycloaddition reactions of diazocyclopentadiene. From the outset, the work was directed toward answering the following questions. (1) Would the nucleus of I undergo electrophilic substitution without disruption of the diazo linkage? (2) Which position is the most subject to substitution? (3) How reactive is the ring system compared to other aromatic systems? (4) Could the substance be induced to undergo cycloaddition reactions?

**Electrophilic Substitution.**—Diazocyclopentadiene (I) underwent a number of electrophilic substitution reactions, which are discussed in turn in the following sections. In each case, the derivatives themselves serve as focal points for discussion of synthesis, structural assignments, reactions and physical properties.

**Nitration.**—Nitration of I in acetonitrile at 0° with benzoyl nitrate gave a mixture of two mononitrodiazocyclopentadienes, chromatography of which on silica gel gave each component in a pure crystalline state. The dominant isomer (factor of two) preceded the other off the column, and exhibited the lower melting point (32° vs. 90°). These properties suggested the dominant isomer to have structure VI, since this structure should be associated with the less polar of the two isomers VI and VII. This provisional identification was confirmed by both direct chemical evidence and nuclear magnetic resonance (n.m.r.) spectral analysis.

Hydrogenation of the lower melting isomer followed by treatment of the product VIII with 2,4-dinitro-

(1) The authors wish to thank the U. S. Army Research Office (Durham) for a grant used in support of this work.

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