The organic reagents and solvents (Aldrich Chemical Co., K & K Laboratories, Fisher Scientific, J. T. Baker Chemical Co., and Eastman Chemical Co.) were commercial compounds used without further purification. The KCN was ground and then dried under vacuum at 100° for 24 hr.

General Procedure. The starting solutions were prepared by weighing the reactive substrate directly into a 25-ml volumetric flask and diluting to the mark with a stock solution (known concentration)[15] of 1 in CH_3CN or C_6H_6. The prepared solutions were placed directly over solid, dry KCN (twofold excess of salt per functional group being displaced) and the reaction mixture was stirred vigorously at ambient or reflux temperature. Small aliquots of solution were removed at intervals and the extent of reaction was followed by glc and/or nmr analysis. Work-up involved separating the solid-liquid phases, removing the bulk of the solvent, diluting the remains with distilled water, extracting the product, and distilling the product after drying and removal of the extraction solvent.

1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6,[3a] 1) The crown was synthesized and purified by a previously described procedure.[16]

Preparation of Nitrile Compounds. Preparation of 1,3-Dicyanopropane (Glutaronitrile, 2). A. Into a 50-ml round bottom flask equipped with a magnetic stirring bar and a condenser-drying tube system were placed 11.7 g (0.18 mol) of dry KCN (Fisher Scientific) and 25 ml of an acetonitrile solution containing 5.08 g (0.045 mol) of 1,3-dichloropropane (Aldrich Chemical Co.) and 1.01 g (0.0038 mol) of **1**. The two-phase system was heated to reflux with vigorous stirring and the extent of reaction was followed by glc techniques. After 1.5 hr, the reaction mixture was cooled, filtered, and evaporated to *ca.* one-third volume. Distilled water was then added, and the mixture was extracted with CH_2Cl_2.[17] The CH_2Cl_2 solution was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The residue was distilled under vacuum to give 4.10 g (96.8%) of **2**: bp 78–82° (0.15 mm); ir (neat, NaCl plates) 2950, 2875, 2240, 1450, 1420 cm^{-1}; ^1H nmr (neat, external TMS, $CHCl_3$) 2.65 (t, 4 H), 2.15 ppm ("spiked" q, 2 H); mass spectrum *m/e* 94, 93, 54, 41, 28; these spectra and glc analysis of the synthesized product corresponded to those of commercial 2 (K & K Laboratories).

Preparation of 1,2-Dicyanopropane (3). B. Into a 50-ml round-bottom flask equipped as in A were placed 0.32 g (0.005 mol) of dry KCN, 25 ml of an acetonitrile solution containing 3.03 g (0.045 mol) of methacrylonitrile (Eastman Chemical Co.) and 1.04 g (0.0039 mol) of **1**, and 4.42 g (0.052 mol) of acetone cyanohydrin (J. T. Baker Chemical Co.). The system was brought rapidly to reflux with vigorous stirring and the extent of reaction was monitored by glc and nmr techniques. After 0.6 hr, the system was cooled and the solution was worked up as in A.[17] Distillation of the isolated crude product[18] gave 3.89 g (91.9%) of the colorless, transparent liquid **3**: bp 68–71° (0.15 mm); ir (neat, NaCl plates) 2975, 2940, 2250, 1520, 1425, 1380 cm^{-1}; ^1H nmr (neat, external TMS, $CHCl_3$) 3.05 (m, 1 H), 2.65 (d, with spikes, 2 H), 1.35 ppm (d, 3 H); mass spectrum *m/e* 94, 93, 54, 41, 28.

Registry No.—Cyanide, 57-12-5; 18-crown-6, 17455-13-9; 1-octene, 111-66-0; *cis*-2-octene, 7642-04-8; *trans*-2-octene, 13389-42-9.

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(6) Monocyanated products could be isolated in the runs involving difunctional halides when the reactions were not allowed to proceed to completion.

(7) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 29–31.

(8) The octenes produced in runs 16 and 17, Table I, were not isolated from the reaction mixtures. Low-temperature glc analysis revealed three alkenes to be present in both runs, assigned as 1-octene and *cis*- and *trans*-2-octene. The glc graphs were identical with that given by a known mixture of the three alkenes. Also, nmr splitting and position of the vinyl proton absorptions were overlapping with those of the known mixture.[9]

(9) The known mixture of octenes was supplied by Mr. H. P. Harris, and was isolated from the reaction of 2-bromooctane with "naked" fluoride.[1]

(10) (a) D. J. Mowry, *Chem. Rev.*, **42**, 189 (1948); (b), C. S. Marvel and E. M. McColm, "Organic Syntheses," Collect. Vol. I, 2nd ed, Wiley, New York, N. Y., 1941, p 536; (c) F. H. Allen, *ibid.*, p 156; (d) R. Adams and A. F. Thal, *ibid.*, p 107.

(11) (a) R. A. Smiley and C. Arnold, *J. Org. Chem.*, **25**, 257 (1960); (b) L. Freidman and H. Schechter, *ibid.*, **25**, 877 (1960).

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(13) More recent advances than those listed[10] have shown that addition of catalytic amounts of iodide to the ethanol-water system has a beneficial effect on nucleophilic displacements of alkyl halides: H. O. House, *Org. React.*, **9**, 139 (1957), and references cited therein.

(14) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, Chapter 9, pp 623–628, and references cited therein.

(15) It has been found that the upper limit of concentration of **1** in CH_3CN is approximately 0.2 *M* at room temperature, while concentrations as high as 1.5 *M* have easily been achieved in C_6H_6.[1]

(16) C. L. Liotta, H. P. Harris, F. L. Cook. G. W. Gokel, and D. J. Cram, *J. Org. Chem.*, **39**, 2445 (1974).

(17) Extraction of the nitrile compounds can be accomplished by hand (three to five extractions) or by a CH_2Cl_2 continuous extractor (20–24 hr). As nitriles are soluble in H_2O (especially dinitriles) to various extents, the continuous-extraction method is recommended in cases where small quantities are involved and complete extraction from the water layer is desired. For larger runs, the hand-extraction technique is preferred. Both methods were used with comparable results in preparing this report.

(18) On evaporation of the extraction solvent, the crystalline adduct (complex) of **7** and **1** precipitates spontaneously. However, on heating the distillation flask the complex readily melts, and the liquid **7** is then easily distilled. The characteristics of this and a number of other crystalline complexes of nitrile compounds and **1** have been reported: F. L. Cook, H. P. Harris, and C. L. Liotta, *J. Org. Chem.*, submitted for publication.

Carbanion Mechanism in the Alkylation of Certain Tosylhydrazones. 9,9-Disubstituted Fluorenes from Fluorenone Tosylhydrazone

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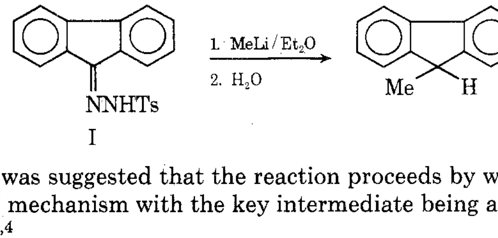
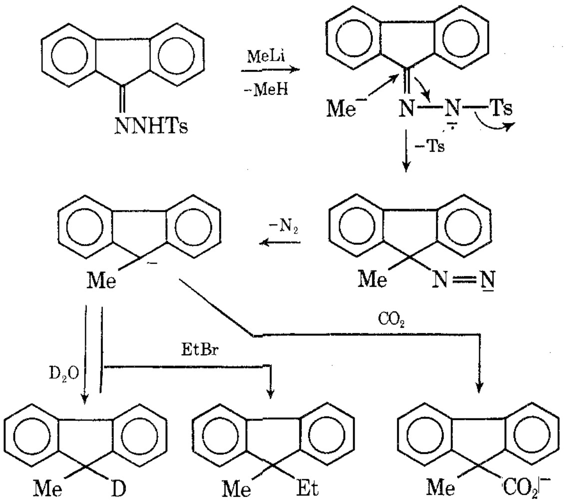
In the first publication of the reaction of tosylhydrazones with alkyllithium reagents it was reported that fluorenone tosylhydrazone (I) undergoes substitution, since elimination is precluded.[1] Herz and his coworkers have more recently shown that substitution of this type occurs with tosylhydrazones capable of undergoing elimination, provided that a very large excess of alkyllithium reagent is used.[2,3]



I

It was suggested that the reaction proceeds by way of an S_N2' mechanism with the key intermediate being a carbanion.[2,4]

We have now trapped the carbanion generated from I with D_2O, CH_3CH_2Br, and CO_2 demonstrating its existence as well as providing a new route to 9,9-disubstituted fluorenes. The probable reaction route is illustrated in the following sequence.



Experimental Section

Fluorenone Tosylhydrazone (I). Fluorenone tosylhydrazone was prepared from fluorenone by the method of Bamford and Stevens.[5] The tosylhydrazone was recrystallized from methanol to give yellow needles, mp 185–186° dec, reported[5] mp 180–182° dec.

9-Methylfluorene. To a solution of fluorenone tosylhydrazone (3.48 g, 0.01 mol) in 50 ml of anhydrous tetrahydrofuran under an atmosphere of nitrogen was added 1.65 *M* methyllithium in ether (Ventron, 18 ml, 0.03 mol) during 5 min. Gas evolved and the solution turned from yellow to deep magenta during the addition. The mixture was stirred at room temperature for 3 hr (gas evolution ceased after ~2 hr) and water was added carefully. The organic phase was washed with saturated sodium chloride solution and dried over calcium chloride. Evaporation of the solvent gave a brown oil which was crystallized from 2-propanol–water as yellow needles, mp 45–46° (reported[6] 45–46°), yield 73%. The mass spectrum showed important peaks at *m/e* 180 ($M\cdot^+$) and 165 ($M - CH_3$).

9-Methylfluorene-*9-d*$_1$. Following the procedure for 9-methylfluorene with the exception of decomposing the reaction mixture with D_2O instead of H_2O, we obtained 9-methylfluorene-*9-d*$_1$. The pmr spectrum of unlabeled 9-methylfluorene contained a three-proton triplet at 1.5 and a one-proton quartet at 3.9 ppm, whereas that of the labeled compound showed a three-proton singlet at 1.5 and no signal at 3.9 ppm. The mass spectrum showed that this compound contained 94% d_1 (reaction yield 71%).

9-Methyl-9-ethylfluorene. Following the same procedure as above but decomposing the reaction mixture with ethyl bromide (2.18 g, 0.02 mol), we obtained an oil which was crystallized from 2-propanol–water as yellow plates, mp 60–61° (reported[7] 61–62°). The yield was 77%. The pmr spectrum showed a three-proton singlet (9-methyl) at 1.4, a two-proton quartet at 2.0, and a three-proton triplet at 0.4 ppm. The mass spectrum showed important peaks at *m/e* 208 ($M\cdot^+$), 193 ($M - CH_3$), and 179 ($M - C_2H_5$).

9-Methyl-9-fluorenecarboxylic Acid. Decomposition of the reaction mixture with dry finely divided solid CO_2 gave 9-methyl-9-fluorenecarboxylate, which was dissolved in aqueous sodium hydroxide. After acidification of the aqueous phase with hydrocholoric acid, the free acid separated as an oil. The oil was dissolved in acetic acid and crystallized by the dropwise addition of H_2O to the boiling solution, followed by cooling. The acid separated as pale yellow needles, mp 163–165° (reported[8] 166–167°) in 79% yield. The mass spectrum showed characteristic peaks at *m/e* 224 ($M\cdot^+$) and 179 ($M - CO_2H$). The 9-methyl group appeared as a singlet in the pmr at 1.8 ppm.

Registry No.—I, 52341-51-2; 9-methylfluorene, 2523-37-7; methyllithium, 917-54-4; 9-methylfluorene-*9-d*$_1$, 15480-50-9; 9-methyl-9-ethylfluorene, 42348-903; ethyl bromide, 74-96-4; 9-methyl-9-fluorenecarboxylic acid, 1989-33-9.

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Oxidation of Phenylhydrazine with Nitrosobenzene

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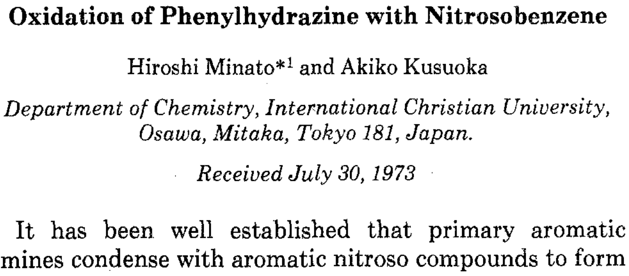
It has been well established that primary aromatic amines condense with aromatic nitroso compounds to form azo compounds. However, the literature about the reaction of phenylhydrazine with nitrosobenzene is conflicting. 1,3-Diphenyltriazene should be the product expected if the reaction is simple condensation between the two with elimination of water. In no case, the formation of 1,3-diphenyltriazene expected was reported. Azobenzene has been reported as the only product when phenylhydrazine is added slowly to a large excess of nitrosobenzene in unheated acetic acid.[2] In another case, *N*-hydroxydiaryltriazenes have been reported to be the major products.[3] In another case, a quantitative gasometric analytical method for *C*-nitroso compounds has been developed according to path c by warming a nitroso compound with an excess of phenylhydrazine in acetic acid.[4] In another case, diarylamine has been reported to be a significant product.[5]



An investigation on this reaction was carried out in our laboratories, and we found that the reaction between nitrosobenzene and phenylhydrazine does not yield 1,3-diphenyltriazene, but the products are azoxybenzene, diphenylamine, benzene, and nitrogen.[6] The mechanism for formation of diphenylamine appeared to be puzzling. A tentative mechanism presented was of ionic nature. Work has been continued, and in this paper we wish to describe the results and propose a modified mechanism involving the phenyl radical.

The products of the reaction between phenylhydrazine and nitrosobenzenes were studied. The samples giving relatively greater yields of diphenylamines are shown in Table I. When a phenylhydrazine solution was added to a nitrosobenzene solution, the yield of diphenylamine was greater; when the order of addition was reversed, the yield was smaller. From the results of the reactions with *p*-nitrosotoluene and *p*-dimethylaminonitrosobenzene, it is clear that one of the two phenyl groups in diphenylamine comes from phenylhydrazine and the other phenyl group comes from nitrosobenzene.

The mechanism of the formation of diphenylamine from the reaction between nitrosobenzene and phenylhydrazine is of interest. Recently Lamson, *et al.*, reported that the reaction of nitrosobenzene with benzylamine did not yield