

was filtered and washed with hot benzene. Water (ca. 1 l.) was added to the dimethyl sulfoxide-water filtrate and the resulting aqueous solution was extracted with benzene. The combined organic extracts were washed with saturated sodium chloride, dried (MgSO<sub>4</sub>), and concentrated *in vacuo*. Addition of ethyl ether and petroleum ether to the semisolid and concentration of the mixture gave 9,9'-dinitro-9,9'-bifluorenyl (28), yield 5.45 g, mp 181–182°, no depression by authentic 28. Concentration, cooling, and filtration of the benzene-ethyl ether-petroleum ether filtrate gave fluorenone (27), yield 2.38 g (33%), mp 82–83°, no depression by authentic 27. Reaction of the final filtrate with hydroxylamine hydrochloride resulted in formation of fluorenone oxime, yield 0.23 g (3%), mp 194–195° (from chloroform-petroleum ether), no depression by an authentic sample.

**Reaction of Sodium 1-Propanenitronate with Silver Nitrate.**—The results of the following experiment are typical of those of a series for silver 1-propanenitronate in dimethyl sulfoxide-water, acetonitrile-water, and water.

A solution of sodium hydroxide (11.9 g, 0.209 mol), water (45 ml), and 1-nitropropane (20, 26.7 g, 0.3 mol) was added to silver nitrate (51 g, 0.3 mol) in dimethyl sulfoxide (375 ml)-methanol (45 ml)<sup>25</sup> at 0–5°. After 5 hr the silver was filtered. Water (ca. 1.6 l.), ethyl ether, and hydrochloric acid were added to the filtrate (pH ca. 1.5) at ca. 10° and the mixture was separated. The ether extract was washed with water, dried, and concentrated to give distillate A and residue B. The aqueous extract and washings were acidified.

Residue B was distilled to give (1) highly volatile products; (2) 20,<sup>26</sup> yield 4.7 g (19%); (3) 1,1-dinitropropane<sup>26</sup> (37), yield

(25) The methanol was added to lower the freezing point of the dimethyl sulfoxide.

(26) Identified by comparison with authentic samples.

5.7 g (17%), bp 58–60° (4–4.5 mm), *n*<sub>D</sub><sup>20</sup> 1.4360, ir 6.3 μ [(NO<sub>2</sub>)<sub>2</sub>]; (4) 4-nitro-3-hexanol<sup>26</sup> containing a small amount of 3-nitro-3-hexene, yield 2.6 g (14%), bp 85–88° (4–4.5 mm), *n*<sub>D</sub><sup>20</sup> 1.4458; and (5) 3,4-dinitrohexanes<sup>26</sup> (16), yield 4.0 g (18%), bp ca. 106° (4–4.5 mm), *n*<sub>D</sub><sup>20</sup> 1.4510. The volatile products were combined with distillate A and analyzed for propionaldehyde (17) as its 2,4-dinitrophenylhydrazone. The 1-nitropropane converted into 17 amounted to 10%.

**Registry No.**—Sodium phenylcyanomethanenitronate, 12385-04-5; sodium phenylmethanenitronate, 12321-46-9; ammonium persulfate, 7727-54-0; sodium 1-propanenitronate, 12384-98-4; sodium persulfate, 7775-27-1; sodium 1-butanenitronate, 12385-00-1; sodium 2-methyl-1-propanenitronate 12385-01-2; 2,5-dimethyl-4-nitro-3-hexanol, 22482-65-1; 4-acetoxy-2,5-dimethyl-3-nitrohexane, 22482-66-2; 2,5-dimethyl-3-nitro-3-hexene, 22482-67-3; potassium persulfate, 7727-21-1; sodium 2-propanenitronate, 12384-99-5; silver nitrate, 7761-88-8; potassium cyclohexanenitronate 12385-03-4; 2,3-dinitro-2,3-diphenylbutane, 22479-37-4; *meso*-2,3-dinitro-2,3-diphenylbutane, 22486-14-2; 4, 622-42-4; 16, 22482-64-0; 21, 22485-93-4; 22, 22485-94-5; 23, 12385-05-6; 24, 12385-06-7; 26, 12385-07-8; 33, 12385-02-3.

**Acknowledgment.**—We are pleased to acknowledge support of this research by the Office of Naval Research.

## Arylation by Aromatic Nitro Compounds at High Temperatures.

### VIII. Reactions of Nitrobenzene and Nitrobenzene-*d*<sub>5</sub> with Cyclohexane at 600°

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Nitrobenzene and cyclohexane at 600° give benzene, biphenyl, phenol, ethylene, propylene, and butadiene as major products. Minor products are ethylbenzene, styrene, β-methylstyrene, allylbenzene, indene, and naphthalene; these are formed by reaction of olefins derived from cyclohexane with phenyl radicals derived from nitrobenzene. Only a small amount of benzene comes from cyclohexane; dehydrogenation is mainly to cyclohexene. Phenyl radical prefers to abstract hydrogen from cyclohexane rather than add to the aromatic ring of benzene by a ratio of 16:1. The products from cycloheptane and cyclooctane are similar to those from cyclohexane; cyclopentane differs mainly in giving almost no products derived from a C<sub>4</sub> fragment.

Nitrobenzene decomposes above 400° to phenyl radical and NO<sub>2</sub>.<sup>2</sup> In the presence of aromatic compounds, even of such a completely substituted benzene derivative as hexafluorobenzene, phenyl radical adds to the aromatic system to give biphenyls as the major products.<sup>3</sup> Hydrogen abstraction is a minor process; nitrobenzene with toluene gives mainly methylbiphenyl isomers, rather than benzene and biphenyl.<sup>4</sup>

It was of interest, therefore, to study the behavior of nitrobenzene with compounds that contain only abstractable hydrogens and no carbon-carbon double bonds. This article describes the reactions of nitrobenzene and nitrobenzene-*d*<sub>5</sub> with cyclohexane, and of

nitrobenzene with cyclopentane, cycloheptane, and cyclooctane.

#### Experimental Section

Reactions were run in a Vycor tube filled with Vycor chips in an electric furnace maintained at 600 ± 1° under pure, dry nitrogen with contact times of 14–22 sec. The vapors were condensed in a flask at 0°; the uncondensed effluent gases were passed through a series of three traps containing bromine in chloroform at 0°. The condensates were distilled to recover unreacted material, and the residues were analyzed by gas chromatography, mass spectrometry, and directly coupled gas chromatography-mass spectrometry.<sup>5</sup> The brominated products were analyzed by gas chromatography.

Gas chromatographic-mass spectral analysis was used not only to identify chromatographically separated components of product mixtures but also to determine the isotopic composition of such components from reactions with nitrobenzene-*d*<sub>5</sub>. For the latter purpose, variation of the isotopic distribution over the

(1) (a) Amoco Chemicals Corp.; (b) American Oil Co.

(2) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **89**, 724 (1967).

(3) E. K. Fields and S. Meyerson, *ibid.*, **89**, 3224 (1967); *J. Org. Chem.*, **32**, 3114 (1967).

(4) E. K. Fields and S. Meyerson, *ibid.*, **33**, 2315 (1968).

(5) E. K. Fields and S. Meyerson, *ibid.*, **33**, 4487 (1968).

time span of a chromatographic peak requires repetitive scanning of the molecular-ion region at a preselected reduced ionizing voltage.<sup>6</sup> Intensity corresponding to each isotopic species is then plotted vs. time, and the integrated areas under these curves are taken as measures of the concentrations of the various species.<sup>6</sup>

In a typical experiment, a solution of 10.3 ml (0.1 mol) of nitrobenzene in 43.2 ml (0.4 mol) of cyclohexane was passed through a Vycor tube at 600° under a nitrogen flow of 15 ml/min, with a contact time of 20.1 sec. The vapors were condensed in a flask at 0°. The condensate was distilled to give 21.3 g of distillate and 4.7 g of residue. Analysis of the distillate by gas chromatography on a column of 5% Bentone 34 and 5% DC550 on Chromosorb W showed 15.6 g of cyclohexane, 1.2 g of cyclohexene, and 3.9 g of benzene. Analysis of the residue on a column of 10% OV17 on Chromosorb W gave the results shown in Table I. The bromine solutions were reduced with sodium thiosulfate and extracted with chloroform to give 17.5 g of a mixture which was analyzed on a column of 5% SE-30 on Chromosorb W. This analysis provided the data on the olefins shown in Table I.

TABLE I  
PRODUCTS FROM NITROBENZENE AND CYCLOHEXANE<sup>a</sup>

| Product <sup>b</sup>   | Yield, mol % <sup>c</sup> |
|------------------------|---------------------------|
| Ethylene               | 25.5                      |
| Propylene              | 20.4                      |
| Butenes                | 2.5                       |
| Butadiene              | 13.7                      |
| Benzene                | 54.4                      |
| Cyclohexene            | 15.5                      |
| Phenol                 | 1.7                       |
| Biphenyl               | 0.7                       |
| Ethylbenzene           | 1.0                       |
| Styrene                | 2.0                       |
| $\beta$ -Methylstyrene | 1.0                       |
| Allylbenzene           | 0.2                       |
| Indene                 | 0.7                       |
| Naphthalene            | 1.2                       |

<sup>a</sup> Reaction conditions: 600°, contact time 20.1 sec, 0.1 mol of nitrobenzene, 0.4 mol of cyclohexane. <sup>b</sup> The gaseous olefins were analyzed as bromine addition products. Other gases were methane, ethane, propane, and hydrogen. <sup>c</sup> The yields were determined by gas chromatography and are based on a 94.2% conversion of nitrobenzene.

The reagents and standards for gas chromatography were reagent grade and were used as received.

## Results and Discussion

**Nitrobenzene with Cyclohexane.**—The major products from the reaction of nitrobenzene with cyclohexane are shown in Table I. The alkylaromatic products apparently result from the fragmentation of cyclohexane to C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub> hydrocarbons, which then react with the phenyl radical derived from nitrobenzene. Nitrobenzene alone at 600° gives phenol, biphenyl, and dibenzofuran as major products.<sup>3</sup> The formation of ethylene, propylene, and butadiene from the pyrolysis of cyclohexane is well known.<sup>7</sup> However,

(6) L. P. Lindeman and J. L. Annis, *Anal. Chem.*, **32**, 1742 (1960); W. E. Falcooner and R. J. Cvetanovic, *ibid.*, **34**, 1064 (1962); R. Bentley, N. C. Saha, and C. C. Sweeley, *ibid.*, **37**, 118 (1965); C. C. Sweeley, W. H. Elliott, I. Fries, and R. Ryhage, *ibid.*, **38**, 1549 (1966); J. A. McCloskey, A. M. Lawson, and F. A. J. M. Leemans, *Chem. Commun.*, 285 (1967); F. A. J. M. Leemans and J. A. McCloskey, *J. Amer. Oil Chem. Soc.*, **44**, 11 (1967).

(7) N. D. Zelinskii, B. M. Mikhaizov, and Y. A. Arbutov, *J. Gen. Chem. USSR*, **4**, 856 (1934); L. Kuchler, *Trans. Faraday Soc.*, **35**, 874 (1939); V. Haensel and V. N. Ipatiev, *Ind. Eng. Chem.*, **35**, 632 (1943); L. Berg, G. L. Summer, C. W. Montgomery and J. Coull, *ibid.*, **37**, 852 (1945); Imperial Chemical Industries Ltd., British Patents 567,913 (1945) and 568,536 (1945); J. H. Haslam, U. S. Patent 2,418,879 (1947); H. A. Gollman, U. S. Patent 2,575,341 (1951); W. O. Keelig, British Patent 595,879

SCHEME I

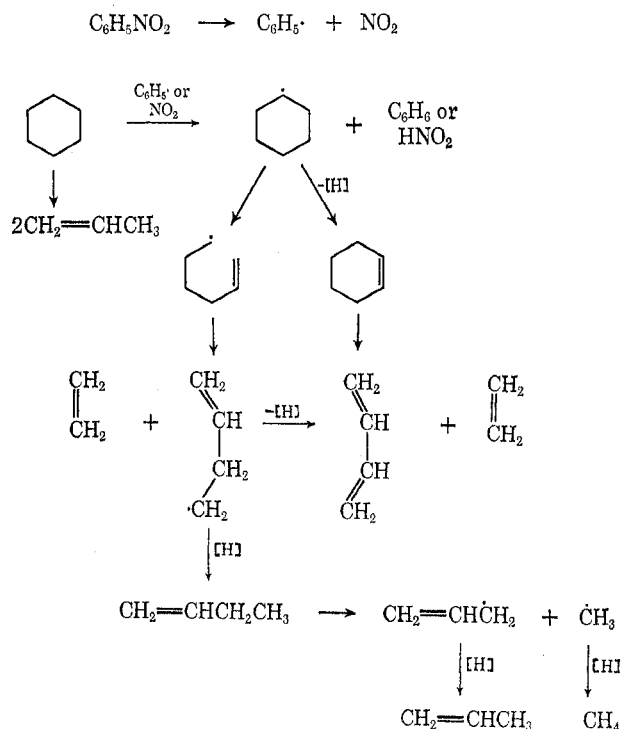


TABLE II  
PRODUCTS FROM CYCLOHEXANE<sup>a</sup>

| Product   | Yield, mol % <sup>b</sup> |
|-----------|---------------------------|
| Ethylene  | 0.07                      |
| Propylene | 0.30                      |
| Butenes   | 0.04                      |
| Butadiene | 0.23                      |

<sup>a</sup> Reaction conditions: 600°, contact time 21.2 sec, 0.4 mol of cyclohexane. <sup>b</sup> The yields were determined by gas chromatography and are based on a 10% conversion of cyclohexane. The material unaccounted for, which was lost with the nitrogen stream, presumably consisted of additional unreacted cyclohexane, low-boiling saturates, and hydrogen.

as shown in Table II, under the reaction conditions employed in this work, cyclohexane alone underwent but little thermal decomposition. The major product from the pyrolysis of nitrobenzene with cyclohexane is benzene, which can arise either by the dehydrogenation of cyclohexane or by hydrogen abstraction by the phenyl radical derived from nitrobenzene, or by both routes. The dehydrogenation of cyclohexane, as evidenced by the formation of cyclohexene, can also be effected by hydrogen abstraction by nitrogen dioxide.<sup>8</sup> Cyclohexene can then undergo a retro Diels-Alder reaction to give ethylene and butadiene.<sup>7,9</sup> However, this is not the only path by which cyclohexane breaks down. Substantial quantities of propylene also formed. The mechanisms underlying the formation of these olefins from cyclohexane in the presence of added free radicals presumably differ from those of the corresponding re-

(1948); S. D. Mekhtiev, Y. G. Kambanov, and A. F. Aliev, *Dokl. Akad. Nauk Azerb. SSR*, **15**, 125 (1959); S. D. Mekhtiev, A. F. Aliev, Y. G. Kambanov, and V. V. Sharov, *Azerb. Khim. Zh.*, **3**, 3 (1959); K. Setivek and V. Bazant, *Collect. Czech. Chem. Commun.*, **26**, 442 (1961); D. L. Fanter, M. A. Grayson, and C. J. Wolf, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, No. B60; Y. M. Paushkin, A. G. Liakumovich, S. V. Adelfson, P. A. Nekeforov, and O. V. Lysykh, *Khim. Prom.*, **44**, 811 (1968).

(8) W. L. Fierce, U. S. Patent 3,413,368 (1968).

(9) H. Kwart and K. King, *Chem. Rev.*, **68**, 415 (1968).

TABLE III  
 REACTION OF NITROBENZENE- $d_5$  WITH CYCLOHEXANE<sup>a</sup>

| Deuterium atoms | Isotopic distributions <sup>b</sup> of products, % |         |         |              |                        |              |        |             |          |        |
|-----------------|--|---------|---------|--------------|------------------------|--------------|--------|-------------|----------|--------|
|                 | Recovered nitrobenzene                             | Benzene | Styrene | Ethylbenzene | $\beta$ -Methylstyrene | Allylbenzene | Indene | Naphthalene | Biphenyl | Phenol |
| 0               |  | 4       | 2       | 13           | 6                      |              | 12     |             |          | 1      |
| 1               |  |         |         |              |                        |              | 1      |             |          |        |
| 2               | 1  |         |         | 3            |                        | 12           |        |             |          | 1      |
| 3               | 1  |         |         |              |                        |              | 8      | 5           |          | 4      |
| 4               | 5  | 7       | 11      | 9            | 17                     | 12           | 47     | 58          | 1        | 23     |
| 5               | 93   | 89      | 85      | 74           | 75                     | 75           | 14     | 27          | 9        | 68     |
| 6               |  |         | 2       | 1            | 2                      |              | 7      | 3           |          | 3      |
| 7               |  |         |         |              |                        |              | 8      | 2           | 2        |        |
| 8               |  |         |         |              |                        |              | 3      | 5           | 8        |        |
| 9               |  |         |         |              |                        |              |        |             | 53       |        |
| 10              |  |         |         |              |                        |              |        |             | 27       |        |

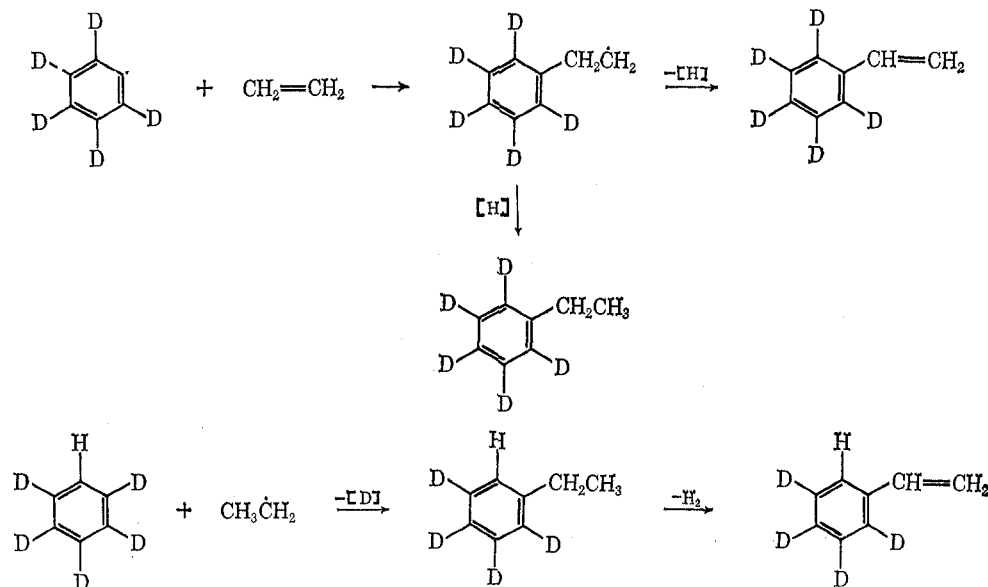
<sup>a</sup> Reaction conditions: 600°, contact time 14.4 sec, 0.04 mol of nitrobenzene- $d_5$ , 0.16 mol of cyclohexane. The isotopic composition of nitrobenzene was 0.1%  $d_3$ , 3.3%  $d_4$ , and 96.6%  $d_5$ . <sup>b</sup> Determined with a directly coupled gas chromatograph-mass spectrometer by repetitive scanning over the parent-mass region at reduced ionizing voltage, followed by integration of the spectral intensities over the duration of the chromatographic peak. <sup>c</sup>  $\alpha$ -Methylstyrene was identified by mass spectrometry; however, it was present at a concentration too low for isotopic analysis.

action carried out in their absence, as evidenced by the difference in product distribution of the gases shown in Tables I and II. Possible reaction paths for the radical-induced decomposition of cyclohexane involve  $\beta$  scission of the cyclohexyl radical, ring scission to propylene, and formation of cyclohexene as an intermediate. Propylene and methane also result from 1-butene by homolytic cleavage and hydrogen abstraction.<sup>10</sup> These routes are outlined in Scheme I.

The low yield of phenol suggests that the phenyl radical derived from the decomposition of nitrobenzene prefers to abstract hydrogen rather than react with

fragments derived from cyclohexane, we treated nitrobenzene- $d_5$  with cyclohexane at 600°. The isotopic distribution of the products is shown in Table III. The scrambling of protium and deuterium, as evidenced by the deuterium distribution of the recovered nitrobenzene, was low enough to allow us to draw valid conclusions.

The isotopic distribution of benzene showed that it was formed mainly by hydrogen abstraction by the phenyl- $d_5$  radical, with only 4% arising by dehydrogenation of cyclohexane. Styrene and ethylbenzene consisted largely of  $d_4$  and  $d_5$  species, with the latter



nitrogen dioxide to form phenol *via* the nitro-nitrite rearrangement.<sup>8</sup> The substantial quantities of unreacted olefins and the low yield of arylation products are additional evidence for predominance of hydrogen abstraction.

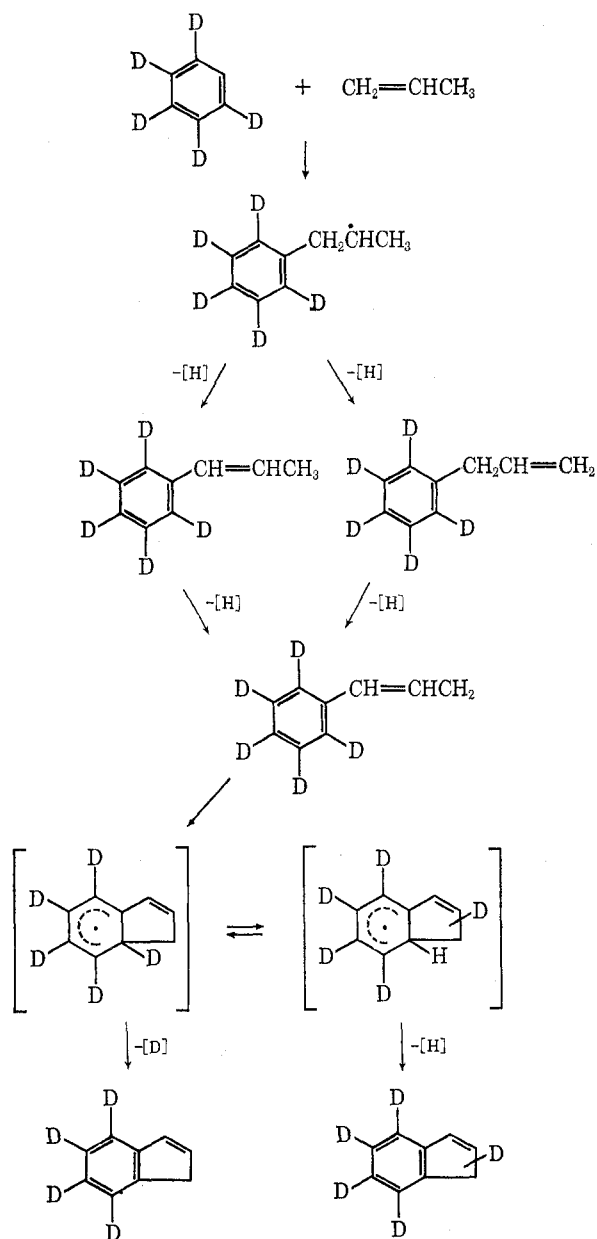
**Nitrobenzene- $d_5$  with Cyclohexane.**—To gain a better understanding of the dehydrogenation of cyclohexane and the interaction of the phenyl radical with the

predominating in both instances, from phenylation of ethylene by the phenyl- $d_5$  radical. The concentrations of the  $d_4$  species relative to benzene- $d_4$  were somewhat high to have arisen solely from arylation by the phenyl- $d_4$  radical, and may have formed in part by alkylation of benzene- $d_6$ .

The isotopic composition of  $\beta$ -methylstyrene and allylbenzene shows the arylation of propylene by the phenyl- $d_5$  radical with subsequent loss of hydrogen. The relatively high concentrations of the  $d_4$  components of these isomers, paralleling those of styrene and

(10) M. Szwarc and A. H. Sehon, *J. Chem. Phys.*, **18**, 237 (1950), and references cited therein; J. A. Kerr, R. Spencer, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 6652 (1965), and references cited therein.

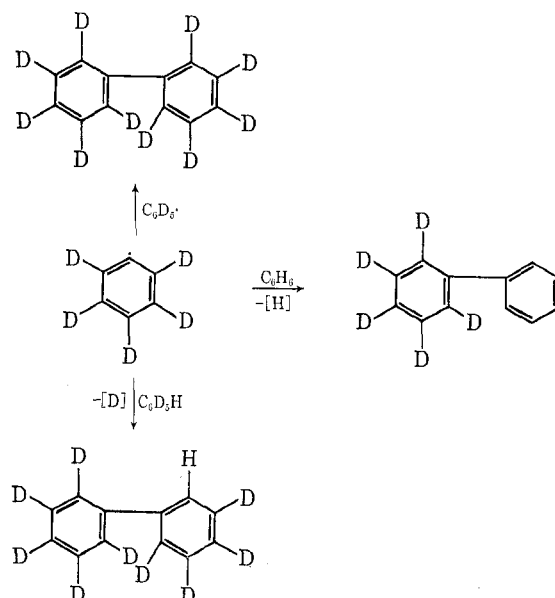
ethylene, indicate the alkylation of benzene- $d_5$  by the allyl radical or, alternatively, propyl-radical alkylation followed by dehydrogenation. Abstraction of an allylic hydrogen from  $\beta$ -methylstyrene- $d_5$  and allylbenzene- $d_5$  gives the same allylic radical, which then cyclizes to form indene- $d_4$ . Indene- $d_5$  arises from protium-deuterium exchange in the intermediate cyclohexadienyl radical. Alkylation of benzene- $d_4$  by the propenyl radical followed by loss of hydrogen and cyclization contributes to indene- $d_4$  and also accounts for the observed indene- $d_3$ . The relatively large amount of unlabeled ethylbenzene and indene must arise solely from cyclohexane. Gas chromatographic-mass spectral analysis of mixtures from reactions with unlabeled nitrobenzene furnished evidence for ethylcyclohexene and propenyl- or allylcyclohexane, and these are likely precursors of such cyclohexane-derived products.



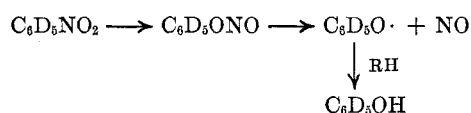
The isotopic distribution of naphthalene is similar to that of indene in that the  $d_4$  and  $d_5$  species predominate. A similar reaction sequence can be invoked in which arylation of butadiene by the phenyl- $d_5$  radical is followed by cyclization and loss of hydrogen. Again,

protium-deuterium exchange in the cyclohexadienyl radical intermediate accounts for naphthalene- $d_5$ .

Biphenyl consisted chiefly of the  $d_9$  and  $d_{10}$  species, with a secondary maximum in the isotopic distribution at  $d_8$ . Arylation by the phenyl- $d_5$  radical of undeuterated benzene derived from cyclohexane accounts for the formation of biphenyl- $d_6$ . The more abundant biphenyl species arise by arylation of benzene- $d_5$  by the phenyl- $d_5$  radical to give biphenyl- $d_9$  and a little biphenyl- $d_{10}$ , and by dimerization of the phenyl- $d_5$  radical to give biphenyl- $d_{10}$ .



Most of the phenol forms *via* a nitro-nitrite rearrangement of nitrobenzene- $d_5$ . Phenol- $d_4$  forms in two ways:



reaction of phenyl- $d_4$  with  $\text{NO}_2$  followed by nitro-nitrite rearrangement, and protium-deuterium exchange of ring deuteriums from phenol- $d_5$ .

Arylation by the phenyl radical is the preferred reaction when nitrobenzene reacts with benzene at  $600^\circ$ ,<sup>3</sup> whereas hydrogen abstraction predominates with cyclohexane. To measure the preference of phenyl radical, we allowed nitrobenzene- $d_5$  to react with an equimolar mixture of cyclohexane and benzene at  $600^\circ$ . The isotopic distributions and yields of benzene and biphenyl are shown in Table IV. The other products from this reaction exhibited a distribution similar to that shown in Table I. The combined yield of benzene- $d_4$  and - $d_5$  (56%) corresponds closely to the yield of benzene (54%) derived from the reaction of nitrobenzene with cyclohexane alone. The yield of biphenyl- $d_4$  and - $d_5$ , resulting from the arylation of benzene by the phenyl- $d_5$  radical, is greater than the yield of biphenyl in the absence of added benzene, probably because a fivefold excess of benzene was employed in this reaction. The higher yield of benzene- $d_5$  over biphenyl- $d_5$ , 16:1, shows the strong preference of the phenyl radical to abstract hydrogen rather than to add to the aromatic system.

To determine whether the reactions of other cycloalkanes parallel those of cyclohexane, we treated cyclo-

TABLE IV  
REACTION OF NITROBENZENE- $d_5$  WITH  
CYCLOHEXANE AND BENZENE<sup>a</sup>

| Product  | Isotopic distribution, % <sup>b</sup> | Yield, mol % <sup>c</sup> |
|----------|---------------------------------------|---------------------------|
| Benzene  | $d_0$ , 89.0                          |                           |
|          | $d_1$ , 1.5                           |                           |
|          | $d_4$ , 0.7                           | 4.2                       |
|          | $d_5$ , 8.6                           | 51.8                      |
|          | $d_6$ , 0.2                           |                           |
| Biphenyl | $d_0$ , 9.0                           |                           |
|          | $d_1$ , 2.3                           |                           |
|          | $d_2$ , 0.9                           |                           |
|          | $d_3$ , 1.4                           |                           |
|          | $d_4$ , 6.8                           | 0.3                       |
|          | $d_5$ , 64.6                          | 3.3                       |
|          | $d_6$ , 2.3                           |                           |
|          | $d_7$ , 2.7                           |                           |
|          | $d_8$ , 1.8                           |                           |
|          | $d_9$ , 5.0                           |                           |
|          | $d_{10}$ , 3.2                        |                           |

<sup>a</sup> Reaction conditions: 600°, contact time 17.1 sec, 0.04 mol of nitrobenzene- $d_5$ , 0.2 mol of cyclohexane, 0.2 mol of benzene. The isotopic composition of nitrobenzene was 2.2%  $d_4$  and 97.8%  $d_5$ . <sup>b</sup> Calculated from low-voltage (7.5 ionizing eV, uncorrected) mass spectrum. <sup>c</sup> Based on an 82% conversion of nitrobenzene- $d_5$ .

pentane, cycloheptane, and cyclooctane with nitrobenzene under similar conditions. The major products boiling over 140°, together with those from cyclohexane and from nitrobenzene alone for comparison, are listed in Table V. All of the cycloalkanes alone, under the same conditions, were recovered 90% or more unchanged.

Among the products from all four cycloalkanes, the yields of those attributed to the reaction of phenyl radical with  $C_2$  and  $C_3$  fragments, styrene and indene, are roughly the same. Naphthalene, from phenyl radical with a  $C_4$  fragment, is formed in almost identical amounts from cyclohexane, -heptane, and -octane, but much less from cyclopentane. This would be expected because fragmentation of cyclopentane, its radical, or cyclopentene into  $C_4$  and  $C_1$  species would not appear energetically likely. The relative yields of phenol, biphenyl, dibenzofuran, and diphenyl ether from the re-

TABLE V  
PRODUCTS FROM NITROBENZENE<sup>a,b</sup> AND CYCLOALKANES

| Product        | Cycloalkane            |       |       |       |       |
|----------------|------------------------|-------|-------|-------|-------|
|                | None                   | $C_5$ | $C_6$ | $C_7$ | $C_8$ |
|                | Relative concentration |       |       |       |       |
| Phenol         | 100                    | 100   | 100   | 100   | 100   |
| Styrene        | ...                    | 87    | 101   | 77    | 87    |
| Indene         | ...                    | 26    | 22    | 15    | 30    |
| Naphthalene    | 7                      | 31    | 122   | 114   | 118   |
| Biphenyl       | 73                     | 115   | 59    | 24    | 30    |
| Dibenzofuran   | 80                     | 55    | 9     | 7     | 15    |
| Diphenyl Ether | 35                     | 15    | 7     | 5     | 6     |

<sup>a</sup> Reaction conditions: 0.1 mol of nitrobenzene, 0.4 mol of cycloalkane, 600°,  $N_2$  flow 20 ml/min, contact time 7-14 sec.

<sup>b</sup> The products listed here represent a small part of the reaction mixtures, the bulk of which was distilled off below 140°. This table is intended only to compare product distributions from the various reactants. <sup>c</sup> Relative intensities in the low-voltage (7.5 ionizing eV, uncorrected) mass spectrum normalized to phenol = 100. Sensitivity, *i.e.*, the proportionality factor between parent-peak intensity and concentration, differs from one compound to another. However, closely related compounds have roughly equal sensitivities at the ionizing voltage employed in our work.<sup>4</sup> In any case, the use of relative intensities is perfectly valid for intercomparison of concentration ratios of identical components in separate samples, within the limits of reproducibility of the low-voltage data. See S. Meyerson and E. K. Fields, *Chem. Commun.*, 275 (1966); E. K. Fields and S. Meyerson, *Advan. Phys. Org. Chem.*, 6, 1 (1968).

action of nitrobenzene with cyclopentane more nearly resemble those from nitrobenzene alone than do those with the other cycloalkanes. This pattern, again, probably reflects the important role of  $C_4$  intermediates in these systems. Because of its failure to produce such intermediates, cyclopentane contributes substantially less than the larger cycloalkanes to reaction products with nitrobenzene and thus acts, in effect, as a relatively inert diluent. We are presently studying the reactions of nitrobenzene and nitrobenzene- $d_5$  with cyclic olefins and polyolefins.

**Registry No.**—Nitrobenzene, 98-95-3; nitrobenzene- $d_5$ , 13657-09-5; cyclohexane, 110-82-7; cyclopentane, 287-92-3; cycloheptane, 291-64-5; cyclooctane, 292-64-8.