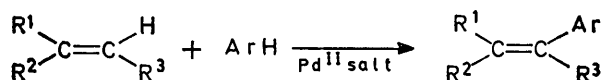


## Aromatic Substitution of Olefins. Part XVIII.<sup>1</sup> Reactions of Cycloalkenes with Benzene

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The reactions of cyclopentene, cyclohexene, cycloheptene, and cyclo-octene with benzene in the presence of palladium(II) acetate have been investigated. The reaction with cyclo-octene, for example, gave the substitution product, 1-phenylcyclo-octene (6%), and the isomerisation products, 3-phenyl- (8%), 4-phenyl- (12%), and 5-phenyl-cyclo-octene (2%). In general the substitution reactions are complicated by isomerisation or disproportionation processes.

We have previously reported that substitution reactions between aromatic compounds and acyclic olefins take place in the presence of palladium(II) salts.<sup>2</sup> Not only benzenoid but also nonbenzenoid aromatic com-



pounds such as ferrocene easily undergo the substitution.<sup>1,3</sup> We have now studied the reaction of cyclic olefins with benzene in the presence of palladium(II) acetate.

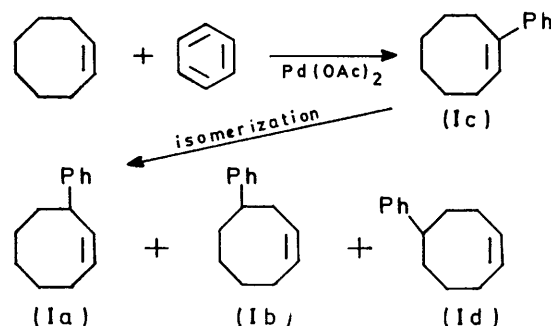
### RESULTS AND DISCUSSION

The reaction of cyclo-octene with benzene under these conditions gave four phenylcyclo-octenes (Ia—d) in addition to a small amount of acetate and reduced metallic palladium. 1-Phenylcyclo-octene (Ic) was identified by comparison of the i.r. spectrum and g.l.c. retention time with those of an authentic sample. Elemental analysis of the mixture of phenylcyclo-octenes gave a satisfactory result and hydrogenation of the mixture over palladium sponge gave phenylcyclo-octane only.

Compounds (Ia) and (Ib) could not be separated by g.l.c., but (Ia) could be identified as 3-phenylcyclo-octene by retention time comparison with an authentic sample. Oxidation of the mixture of (Ia) and (Ib) with permanganate followed by esterification with diazomethane afforded dimethyl 2-phenyloctanedioate and dimethyl 3-phenyloctanedioate. Thus compound (Ib) could be identified as 4-phenylcyclo-octene, and compound (Id) must then be 5-phenylcyclo-octene. The yields of the products were as follows: 1-phenyl- 6%, 3-phenyl- 8%, 4-phenyl- 12%, and 5-phenyl-cyclo-octene 2%.

This reaction is in marked contrast to those with acyclic olefins, in which phenylation takes place selectively on an olefinic carbon atom.<sup>2</sup> However, when 1-phenylcyclo-octene, the expected phenylation product,

was treated under similar reaction conditions, it gave a mixture of compounds (Ia—d); it thus appears that 1-phenylcyclo-octene (Ic) is the initial product, and this isomerizes under the influence of palladium.



The reactions of cycloheptene and cyclopentene also gave mixtures of phenylcycloalkenes. The results are summarized in the Table. In these cases also the expected 1-phenylcycloalkenes isomerized when treated under similar conditions.

In the reaction of cyclohexene, no phenylcyclohexene was obtained, but biphenyl and phenylcyclohexane were formed in 8 and 7% yields, respectively. When 1-phenylcyclohexene, the expected initial product, was treated under similar conditions, biphenyl (64%) and phenylcyclohexane (30%) were obtained. There are two possible routes for biphenyl formation: (i) a coupling reaction of benzene brought about by palladium(II) acetate<sup>4</sup> and (ii) dehydrogenation of initially formed 1-phenylcyclohexene. The former was eliminated by the fact that a similar result was obtained from 1-phenylcyclohexene in the absence of benzene.<sup>†</sup>

Thus cyclohexene reacts with benzene to give phenylcyclohexene, which then rapidly undergoes both hydrogenation and dehydrogenation in the presence of palladium. A similar hydrogenation-dehydrogenation of cyclohexene by palladium, giving benzene and cyclohexane has been reported.<sup>5</sup>

In conclusion, cyclic olefins do undergo the substitution

† Further, it has become apparent that no biphenyl is formed in the aromatic substitution.<sup>2</sup>

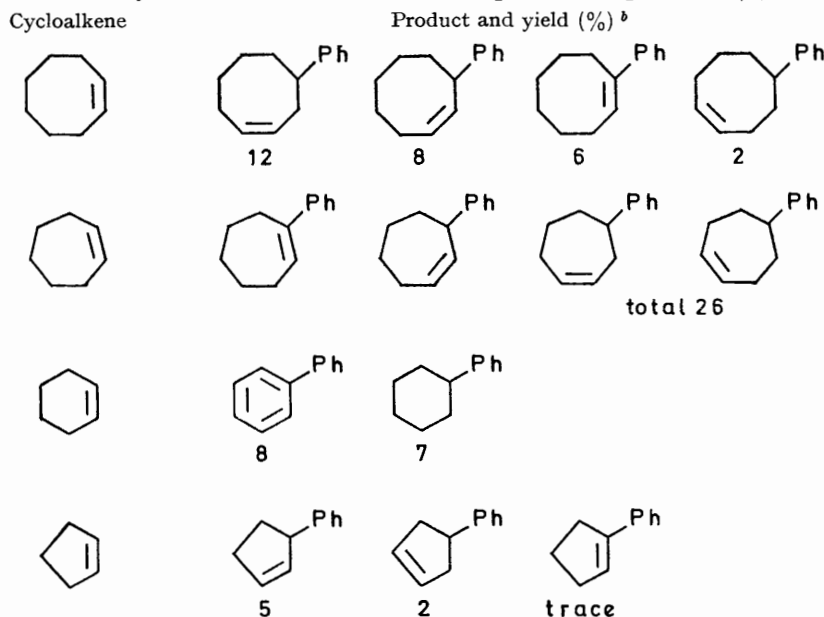
<sup>1</sup> Part XVII, R. Asano, I. Moritani, A. Sonoda, Y. Fujiwara, and S. Teranishi, *J. Chem. Soc. (C)*, 1971, 3691.

<sup>2</sup> Y. Fujiwara, I. Moritani, S. Danno, R. Asano, and S. Teranishi, *J. Amer. Chem. Soc.*, 1969, **91**, 7166.

<sup>3</sup> R. Asano, I. Moritani, Y. Fujiwara, and S. Teranishi, *Chem. Comm.*, 1970, 1293.

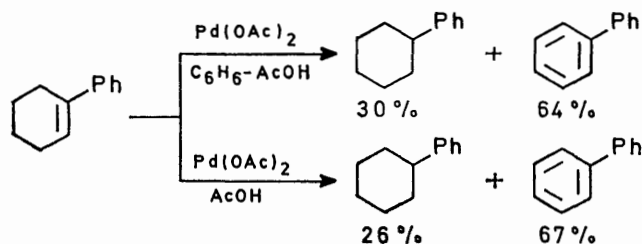
<sup>4</sup> Y. Fujiwara, I. Moritani, K. Ikegami, R. Tanaka, and S. Teranishi, *Bull. Chem. Soc. Japan*, 1970, **43**, 863, and references cited therein.

<sup>5</sup> S. Carra and V. Ragaini, *Tetrahedron Letters*, 1967, 1079.

Reactions of cycloalkenes with benzene in the presence of palladium(II) acetate <sup>a</sup>

<sup>a</sup> Reactions were performed at reflux with stirring for 8 h, with equal amounts (51 mmol) of cycloalkene and palladium acetate, benzene (470 ml), and acetic acid (110 ml). <sup>b</sup> Yields are based on initial amounts of starting materials.

reaction in the presence of palladium(II) acetate, but isomerisation or disproportionation occurs subsequently.



## EXPERIMENTAL

I.r. spectra were recorded on a Hitachi-215 spectrophotometer, and n.m.r. spectra on a JEOL JNR-4H-100 or C-60-HL spectrometer (tetramethylsilane as internal standard). G.l.c. analyses were performed with a Yanagimoto-550-T gas chromatograph. Cyclic olefins were prepared by dehydration of the corresponding cycloalkanols with phosphoric acid.

**Reaction of Cyclo-octene with Benzene.**—A solution of cyclo-octene (5.61 g, 51 mmol) and palladium(II) acetate (11.5 g, 51 mmol) in dry benzene (470 ml) and acetic acid (110 ml) was stirred at reflux for 8 h. After work-up as described previously,<sup>2</sup> the oily material was subjected to g.l.c. (Apiezon L); four components (Ia—d) were detected along with small amounts of acetates. Hydrogenation of the mixture (100 mg) over palladium sponge yielded only phenylcyclo-octane (uptake 14 ml). Elemental analysis agreed with the presence of a mixture of phenylcyclo-octenes (Found: C, 90.4; H, 9.65. Calc. for C<sub>14</sub>H<sub>18</sub>: C, 90.3; H, 9.7%).

3-Phenylcyclo-octene (Ia) was identified by retention

<sup>6</sup> A. C. Cope and R. B. Kinnel, *J. Amer. Chem. Soc.*, 1966, **88**, 752.

<sup>7</sup> A. C. Cope and A. A. D'Addinco, *J. Amer. Chem. Soc.*, 1951, **73**, 3424.

time comparison with authentic material prepared from 3-bromocyclo-octene and phenylmagnesium bromide;<sup>6</sup>  $\nu_{\max}$  (neat) 1600, 745, and 700 cm<sup>-1</sup>;  $\delta$  (CCl<sub>4</sub>) 7.18 (5H, m), 5.60 (2H, m), 3.65 (1H, m), and 2.6—1.2br p.p.m. (10H). 1-Phenylcyclo-octene (Ic) was separated by g.l.c. (Carbowax 20M; 190°) and identified by comparison of the i.r. spectra and retention times with an authentic sample;<sup>7</sup>  $\nu_{\max}$  (neat) 1638, 1600, 757, and 695 cm<sup>-1</sup>;  $\delta$  (CCl<sub>4</sub>) 7.23 (5H, m), 5.91 (1H, t), 2.58br (2H), 2.26br (2H), and 1.55br p.p.m. (8H).

4-Phenylcyclo-octene (Ib) was identified as follows. Permanganate oxidation<sup>6</sup> of the mixture of (Ia) and (Ib) (372 mg) obtained by g.l.c., followed by esterification with diazomethane in ether, gave a mixture of dimethyl 2-phenyl-octanedioate and dimethyl 3-phenyl-octanedioate (2:3). The latter showed  $\nu_{\max}$  (neat) 1720, 1600, 758, and 698 cm<sup>-1</sup>;  $\delta$  (CCl<sub>4</sub>) 7.14 (5H, m), 3.52 (3H, s), 3.48 (3H, s), 3.03 (1H, m), 2.50 (2H, d), 2.15 (2H, t), 1.80—1.35br (4H), and 1.35—1.00br p.p.m. (2H), and was identical with authentic material prepared from the reaction of methyl bromoacetate and methyl 5-benzoylpentanoate followed by hydrogenation over palladium sponge.<sup>8</sup>

**Reaction of Cyclopentene with Benzene.**—The reaction was performed similarly, giving 1-phenyl-, 3-phenyl-, and 4-phenyl-cyclopentene. Hydrogenation of the product mixture over palladium sponge yielded only phenylcyclopentane. The 1-phenyl and 3-phenyl compounds were identified by comparison with authentic samples. 1-Phenylcyclopentene was prepared from the reaction of cyclopentanone and phenylmagnesium bromide, followed by iodine-catalysed dehydration. The product was converted by hydroboration into *trans*-2-phenylcyclopentanol, which was treated with tosyl chloride in pyridine to give the tosylate; treatment with sodium ethoxide then gave 3-phenylcyclopentene;<sup>9</sup>  $\nu_{\max}$  (neat) 1650, 1600, 750, and

<sup>8</sup> C. D. Gutsche, *J. Amer. Chem. Soc.*, 1949, **71**, 3513.

<sup>9</sup> J. H. Brewster and S. F. Osman, *J. Org. Chem.*, 1964, **29**, 121.

698  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CCl}_4$ ) 7.06 (5H, m), 5.75 (2H, m), 3.78br (1H), 2.50—2.00br (2H), and 2.00—1.40br, p.p.m. (2H). The 1-phenyl compound showed  $\nu_{\text{max}}$  (neat) 1630, 1600, 745, and 695  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CCl}_4$ ) 7.13 (5H, m), 5.98 (1H, t), and 2.85—1.50br p.p.m. (6H). The remaining isomer must then be 4-phenylcyclopentene.

*Reaction of Cyclohexene with Benzene.*—The products were biphenyl, m.p. 69—70°, and phenylcyclohexane,<sup>10</sup> identified by comparison with authentic samples. The latter showed  $\nu_{\text{max}}$  (neat) 1605, 755, and 700  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CCl}_4$ ) 7.09 (5H, m), 2.40 (1H, m), and 2.05—1.10 p.p.m. (10H, m).

From the benzene evaporated off, starting cyclo-olefins were recovered in each case.

*Isomerization of 1-Phenylcyclo-octene (Ic).*—A solution of 1-phenylcyclo-octene (1.86 g, 10 mmol) and palladium(II) acetate (2.25 g, 10 mmol) in benzene (94 ml) and acetic acid (22 ml), was stirred at reflux for 8 h. G.l.c. of the

products showed the presence of the phenylcyclo-octenes (Ia) and (Ib) (5%), (Ic) (40%), and (Id) (5%), and diphenylcyclo-octenes (0.2 g). Similarly, isomerization of 1-phenylcyclopentene gave 3-phenylcyclopentene and 4-phenylcyclopentene in a ratio of 5 : 3 (30% conversion).

*Reaction of 1-Phenylcyclohexene in the Presence of Palladium(II) Acetate.*—A mixture of 1-phenylcyclohexene (1.58 g, 10 mmol), palladium(II) acetate (2.25 g, 10 mmol), benzene (94 ml), and acetic acid (22 ml) was heated at reflux for 4 h. The products were biphenyl (64%) and phenylcyclohexane (30%). A similar reaction in the absence of benzene also gave biphenyl (67%) and phenylcyclohexane (26%).

[2/189 Received, 31st January, 1972]

<sup>10</sup> J. Weinstock and F. G. Bordwell, *J. Amer. Chem. Soc.*, 1955, **77**, 6706.