# *N*-Allylation of Imides Catalyzed by Palladium(0)

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**Synopsis.** Palladium(0)–triphenylphosphine complexes catalyzed the allylic exchange reaction of allylic esters, phenyl ethers, and isoureas with imides such as phthalimide to give *N*-allylic products. Among them, *O*-allylic isoureas were most effective in exchanging the allylic group of more complex structure. *N*-Allylic derivatives were also obtained by the telomerization of butadiene or allene with phthalimide catalyzed by a palladium(0) species.

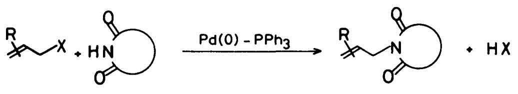
Palladium-catalyzed allylic exchange reaction of esters and ethers with various nucleophiles occurs smoothly usually in the presence of bases. Alcohols, amines, active methylene compounds, and carboxylic acids are typical nucleophiles.1) However there are no reports so far on the use of imides as the nucleophile. If it could be achieved, the product would be *N*-allylic imide. The removal of the dioyl group affords the primary allylic amine. The overall procedure is a modification of the Gabriel synthesis to obtain a primary amine. Primary allylic amine function exists in many natural products and is considerably of preparative importance.2)

On the other hand, the dimerization of 1,3-butadiene or allene by palladium catalysts occurs with incorporation of various nucleophiles to produce functionalyzed allylic derivatives.1) The similar nucleophiles to those employed in the allylic exchange reaction can be used. In this paper we describe the *N*-allylation of imides through allylic exchange reaction or through telomerization of dienes with imides catalyzed by a palladium(0) species.

## Results and Discussion

*Allylic Exchange Reaction.* Allylic esters and phenyl ethers underwent allylic exchange reaction with imides such as phthalimide and succinimide to yield the *N*-allylic imides in the presence of palladium(0)–triphenylphosphine species. Although *N*-allylation of saccharin was achieved by this catalyst system, amides such as benzamide and acetanilide did not participate in the reaction. Results are shown in Table 1. The feature of this reaction is that this proceeds even in the absence of bases. The employment of phthalimide potassium salt affords the product in an increased yield. Allylic acetate needed slightly severe conditions to carry out the reaction compared to allyl phenyl ether.

2-Cyclohexenyl, geranyl, and linaryl acetate did not give the products. The lack of regio- and stereoselectivity shown in the case of crotyl acetate and the dull reactivity mentioned above indicated that the reaction using allylic acetate had limited value.



$X = OAc, OPh, OC(=NC_6H_{11})NHC_6H_{11}$ (1)

To overcome these defects, *O*-allylic isourea **1** was employed as the allylating reagent, which was formed3) by treating the allylic alcohol with dicyclo-

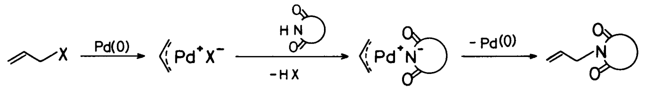
TABLE 1. *N*-ALLYLATION OF IMIDES

| Imide | Allylic compound | Reaction temp/°C | Product$^{a)}$ | Yield % |
|---|---|---|---|---|
| Phthalimide | $CH_2$=$CHCH_2OAc$ | 100 | $CH_2$=$CHCH_2NPth$ | 76$^{b)}$ |
| | | 100 | | 82$^{c)}$ |
| | $CH_2$=$CHCH_2OPh$ | 100 | | 84 |
| | | 60 | | 81 |
| | | r.t. | | 27 |
| | *O*-Allylisourea | r.t. | | 74 |
| | (*E*)-$CH_3CH$=$CHCH_2OAc$ | 120 | $CH_2$=$CHCH(CH_3)NPth$$^{d)}$ | 52 |
| | (*E*)-PhCH=$CHCH_2OAc$ | 120 | (*E*)-PhCH=$CHCH_2NPth$ | 79 |
| | Octadienyl propionate$^{e)}$ | 100 | OctadienylNPth$^{f)}$ | 63 |
| | *O*-Geranylisourea | 60 | GeranylNPth | 65 |
| | *O*-Nerylisourea | 60 | NerylNPth | 71 |
| Succinimide | $CH_2$=$CHCH_2OAc$ | 100 | $CH_2$=$CHCH_2NSuc$ | 60 |
| | $CH_2$=$CHCH_2OPh$ | 60 | | 72 |
| | (*E*)-PhCH=$CHCH_2OAc$ | 100 | (*E*)-PhCH=$CHCH_2NSuc$ | 50 |
| Saccharin | $CH_2$=$CHCH_2OAc$ | 100 | *N*-Allylsaccharin | 51 |

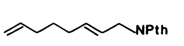
Imide (10 or 5 mmol), allylic compound (1 equiv), $Pd(PPh_3)_3$ (2 mol%), DMF (20 or 10 cm$^3$); 5 h: a) Pth=phthaloyl, Suc=succinyl; all gave satisfactory elemental and spectral data. b) $Pd(dba)_2$ (2 mol%)(dba=dibenzylideneacetone) and $PPh_3$ (4 mol%) were used; 10 h. c) Phthalimide potassium salt (5 mmol) was used in place of phthalimide. d) In addition, (*E*)-and (*Z*)-2-butenyl isomers were formed in 6 and 4% yield, respectively. e) A mixture of (*E*)-2,7-octadienyl propionate (69%) and 1-vinyl-5-hexenyl propionate (30%). f) **2**:**3**=61:39.

hexylcarbodiimide. The reaction of geranyl and neryl derivatives of **1** with phthalimide proceeded smoothly at 60 °C regio- and stereo-selectively with the deposition of *N,N'*-dicyclohexylurea.

This reaction presumably proceeds by oxidative addition to the allylic substrate to palladium(0) to generate a $\pi$-allylpalladium species followed by nucleophilic attack of the imide to give the product.[1] Phthalimide and succinimide are quite acidic and cannot be nucleophiles. So the actual attacking species is the imide anion arised intermediately from the abstraction of the imide hydrogen by the allylic leaving group. The more basic the anion $X^-$ is, the more facile the generation of the imide anion is. The increased reactivity of **1** is ascribed to the high basicity of the dicyclohexylurea anion[4] generated intermediately.



*Telomerization of Dienes with Phthalimide.* The reaction of 1,3-butadiene with phthalimide took place in the presence of $Pd(PPh_3)_3$ yielding *N*-(2,7-octadienyl)phthalimide (**2**) and *N*-(1-vinyl-5-hexenyl)-phthalimide (**3**). The reaction was rather sluggish at 100 °C. Employment of a slightly higher temperature (120 °C) and addition of 10 mol% of phthalimide potassium salt gave reasonable yields of the telomers, **2** and **3**. Longer reaction time (20 h) caused the degradation of the products.[5] Telomerization of isoprene with phthalimide did not occur even under forced conditions. Allene also reacted with phthalimide at 100 °C to give *N*-(3-methy-2-methylene-3-butenyl)phthalimide (**4**) by $Pd(PPh_3)_3$ catalyst in a moderate yield.



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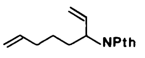

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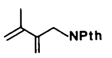

4 Pth=Phthaloyl

Table 2. Telomerization of Butadiene with Phthalimide

| Reaction temp/°C | Reaction time/h | Total yield/%[a] | Composition **2**:**3** |
|---|---|---|---|
| 100 | 5 | 24 | 58:42 |
| 100 | 5 | 39[b] | 58:42 |
| 120 | 5 | 74[b] | 44:56 |
| 100 | 20 | 7 | 78:22 |

Butadiene (14—22 mmol), phthalimide (5 mmol), $Pd(PPh_3)_3$ (0.1 mmol), DMF (10 cm$^3$): a) Based on phthalimide. b) Phthalimide potassium salt (0.5 mmol) was added.

## Experimental

*General Procedure for the Allylic Exchange Reaction of Allylic Ester, Phenyl Ether, and Isourea with Imide.* Imides and allylic compounds were reacted in DMF under nitrogen atmosphere in the presence of Pd(0)–$PPh_3$ catalyst. After the reaction, the DMF was evaporated under reduced pressure. The residue was taken up in benzene (*ca.* 10 cm$^3$) and the mixture was filtered to eliminate the unreacted imide. The pure products were obtained by column chromatography on silica gel.

N-*Geranylphthalimide.* Mp: 58.5—59.2 °C (60—61.5 °C).[6] Anal. ($C_{18}H_{21}NO_2$) C, H, N. IR (KBr) 1760 and 1700 cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$=1.52 (3H, s), 1.58 (3H, s), 1.79 (3H, s), 2.02 (4H, m), 4.02 (2H, d, $J$=7.2 Hz), 4.92—5.42 (2H, m), and 7.68 (4H, m). $^{13}$C NMR ($CDCl_3$) $\delta$=167.68, 140.29, 133.52, 132.35, 131.38, 123.72, 118.07, 39.42, 35.72, 26.31, 25.49, and 17.54.

N-*Nerylphthalimide.* Mp: 57.3—58.1 °C (59—60.5 °C).[6] Anal. ($C_{18}H_{21}NO_2$) C, H, N. IR (KBr) 1765 and 1700 cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$=1.65 (3H, s), 1.68 (3H, s), 1.70 (3H, s), 2.24 (4H, m), 4.27 (2H, d, $J$=7.2 Hz), 4.97—5.50 (2H, m), and 7.72 (4H, m). $^{13}$C NMR ($CDCl_3$) $\delta$=166.09, 140.48, 133.66, 131.91, 131.31, 123.87, 123.04, 118.90, 35.67, 32.06, 26.61, 25.68, 23.29, and 17.69.

*Reaction of Butadiene with Phthalimide.* The reaction was carried out in DMF in the presence of $Pd(PPh_3)_3$ in an autoclave. The products were purified by column chromatography on silica gel (benzene).

N-*[(*E*)-2,7-Octadienyl]phthalimide (2).* Liquid. Anal. ($C_{16}H_{17}NO_2$) C, H, N. IR (neat) 1770, 1700, 1640, 1470, 1420, 990, 960, and 910 cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$=1.2—1.6 (2H, m), 1.7—2.2 (4H, m), 4.1 (2H, d), 4.6—5.05 (2H, m), 5.1—6.0 (3H, m), and 7.65 (4H, m).

N-*(1-Vinyl-5-hexenyl)phthalimide (3).* Liquid. Anal. ($C_{16}H_{17}NO_2$) C, H, N. IR (neat) 1770, 1700, 1640, 1470, 990, and 910 cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$=1.1—1.7 (2H, m), 1.7—2.3 (4H, m), 4.6 (1H, m), 4.85 (1H, d), 4.86 (1H, d), 5.05 (1H, d), 5.15 (1H, d), 5.7 (1H, m), 6.15 (1H, m), and 7.65 (4H, m).

*Reaction of Allene with Phthalimide.* Phthalimide (5.0 mmol), $Pd(PPh_3)_3$ (0.1 mmol), and allene (10.0 mmol) were reacted in DMF (10 cm$^3$) at 100 °C for 5 h in an autoclave. Isolation by column chromatography on silica gel (hexane: ethyl acetate=10:1) gave the product, *N*-(3-methyl-2-methylene-3-butenyl)phthalimide (**4**); yield 0.56 g (49 %). Mp: 108.0—109.0 °C. Anal. ($C_{14}H_{13}NO_2$) C, H, N. IR (KBr) 1770, 1700, 1430, and 880 cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$=1.9 (3H, s), 4.5 (2H, s), 4.95 (2H, m), 5.25 (2H, m),and 7.8 (4H, m).

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