

New Cyclization Reaction of Conjugated Dienes with Isocyanate Catalysed by Palladium Complexes

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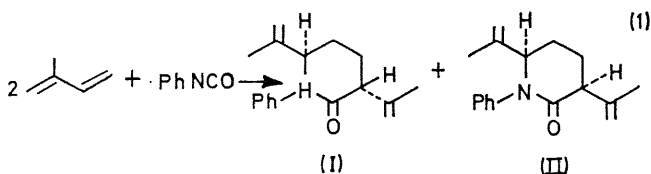
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Summary Novel 2:1 co-cyclization reactions of conjugated dienes with isocyanate to give divinylpiperidones are reported: the reactions are catalysed by palladium-triphenylphosphine complexes.

WE have found that aldehydes react with butadiene to give 1-substituted 2-vinylhepta-4,6-dien-1-ols and 2-substituted 3,6-divinyltetrahydropyrans.¹ In a similar type of reaction we have found that conjugated dienes react with isocyanate to form divinylpiperidones in high yields and selectivity in the presence of catalytic amounts of palladium-triphenylphosphine complexes.²

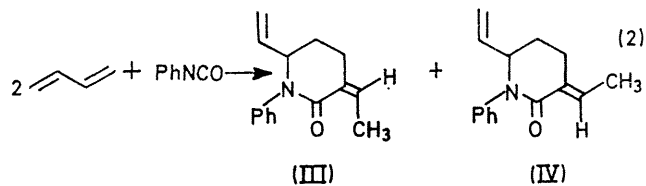
Typically, a benzene solution of phenyl isocyanate (12 g) and isoprene (19 g) (reaction 1) was allowed to react at 100° for 20 h in the presence of bis(triphenylphosphine)(maleic anhydride)palladium (300 mg). The product was collected by distillation (164—167°/2 mm, 21 g). G.l.c. showed the

presence of two compounds (I and II, 1:1). One of them crystallised on treatment with a small amount of hexane and ether. This compound was assigned structure (I),



trans-3,6-di-isopropenyl-1-phenyl-2-piperidone, (m.p. 82°) based on correct analysis and molecular weight (255) for $C_{17}H_{21}NO$, the i.r. spectrum, 1655 (amide), 895 (isopropenyl), 755, 690 cm^{-1} (monosubstituted benzene), and the n.m.r. spectrum, τ 8.35, 8.20 (s, 3H each, CH_3), 7.78—8.15 (m, 4H, $-CH_2CH_2-$), 6.79 (t, 1H, $CH-C=O$), 5.60 (t, 1H, $CH-N$),

5.16 (m, 4H, $CH_2=$), 2.78 (5H, aromatic). The oily product was purified by column chromatography and assigned structure (II), *cis*-3,6-di-isopropenyl-1-phenyl-2-piperidone, based on correct analysis, the i.r. spectrum, 1657 (amide), and the n.m.r. spectrum, τ 8.43, 8.22 (s, 3H each, CH_3), 8.0—8.2 (m, 4H, $-CH_2CH_2-$), 6.97 (m, 1H, $CH-C=O$),



5.74 (t, 1H, $CH-N$), 5.13 (4H, $CH_2=$), 2.88 (5H, aromatic).

Similarly, an oily product from butadiene and phenyl isocyanate (reaction 2) collected at 153—158°/3 mm (75% yield based on phenyl isocyanate) was separated into equal amounts of (*Z*)-3-ethylidene-1-phenyl-6-vinyl-2-piperidone-(III) and corresponding (*E*)-isomer (IV) by column chromatography. In the reaction with butadiene, one of the double bonds migrated. The configuration of the ethylidene moiety was determined by the fact that the olefinic hydrogens of the ethylidene group of (IV) are observed at lower field (3.09) than those of (III) (4.14) as a result of the magnetic anisotropic effect of the carbonyl group.

(Received, November 9th, 1970; Com. 1933.)

¹ K. Ohno, T. Mitsuyasu, and J. Tsuji, submitted for publication in *Tetrahedron Letters*.

² K. Ohno, T. Mitsuyasu, and J. Tsuji, Abstracts of Symposium on Organometallic Chemistry, Kiryu, Japan, 1970, p. 196.