II, and the ytterbium complex, I, yield 2:1 complexes with tri-*n*-butylphosphine of composition $M[N(SiMe_3)_2]_2(P\text{-}n\text{-}Bu_3)_2$, where M is Eu[16] or Yb.[17]

Acknowledgment. This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under contract number W-7405-Eng-48. We also thank Dr. F. J. Hollander, staff crystallographer of the U.C. Berkeley X-ray facility (CHEXRAY), for collecting X-ray data.

Registry No. I, 81770-53-8; II, 81802-35-9; $Yb[N(SiMe_3)_2](dmpe)$, 81770-54-9; $Eu[N(SiMe_3)_2]_2(dmpe)_{1.5}$, 81770-55-0; $Eu[N(SiMe_3)_2]_2(P\text{-}n\text{-}Bu_3)_2$, 81770-56-1; $Yb[N(SiMe_3)_2]_2(P\text{-}n\text{-}Bu_3)_2$, 81770-57-2.

Supplementary Material Available: Positional and thermal parameters and structure factors with their estimated standard deviations (10 pages). Ordering information is given on any current masthead page.

(15) Orange prisms from pentane (−10 °C). Anal. Calcd for $C_{21}H_{60}N_2EuP_3Si_4$: C, 36.1; H, 8.67; N, 4.01; P, 13.13. Found: C, 35.4, H, 8.34, N, 3.80; P, 13.0. The ^1H NMR spectrum of a benzene extract of a solution of the complex that had been hydrolyzed with D_2O showed resonances due to $DN(SiMe_3)_2$ and dmpe in area ratio 2:1.5.

(16) Orange crystals from pentane (−70 °C), mp 48–49 °C. Anal. Calcd for $C_{36}H_{90}N_2EuP_2Si_4$: C, 49.3, H, 10.3; N, 3.19; P, 7.06. Found: C, 49.0; H, 10.2; N, 2.79; P, 6.82. The paramagnetic complex, 7.4 μ_B (Evan's method, 30 °C, PhH), was hydrolyzed with water, and the ^1H NMR of an aliquot in benzene gave resonances due to $(Me_3Si)_2NH$ and P-*n*-Bu_3 in a 1:1 area ratio.

(17) Brown-red prisms from pentane (−70 °C), mp 46–48 °C. Anal. Calcd for $C_{36}H_{90}N_2P_2Si_4Yb$: C, 48.1; H, 10.1; N, 3.12; P, 6.89. Found: C, 48.8; H, 10.0; N, 2.87; P, 7.47. ^1H NMR (26 °C, PhH-d_6) δ 0.48 (s, 36 H, $N(SiMe_3)_2$), 1.00 (an apparent t with the separation between the outermost lines being 12 Hz, 18 H, $P(CH_2CH_2CH_2CH_3)_3$), 1.49 (an apparent s, 36 H, $P(CH_2CH_2CH_2CH_3)_3$); $^{13}C\{^1H\}$ NMR (26 °C, PhH-d_6) δ 6.27 (s, $N(SiMe_3)_2$), 14.0 (an apparent s due to the γ-C of P-*n*-Bu_3), three apparent doublets at 24.9 (separation of 10 Hz), 26.9 (separation of 10 Hz), 28.3 (separation of 11 Hz due to the other three carbon atoms); $^{31}P\{^1H\}$ NMR (26 °C, PhH-d_6) δ −29.6. The coordination chemical shift is zero.

Palladium(0)-Catalyzed Allylic Alkylation and Amination of Allylnitroalkanes

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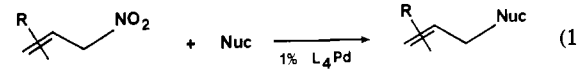
Received March 24, 1982

The chemistry of nitroalkanes has been the subject of considerable recent development. Nitro-stabilized carbanions effected substitution reactions with benzyl halides, tosylates, and nitro compounds, resulting primarily in C-alkylation of the carbanion.[1,2] In a related process, nitroalkyl anions effected the displacement of a nitro group from α-nitro esters, α-nitro ketones, α-nitro nitriles, and α,α-dinitro compounds.[3] α-Halonitroalkanes and *gem*-dinitroalkanes underwent displacement of a halide or nitro group, respectively, when treated with stabilized carbanions[4-6] or thiolate anions.[7] The ease of replacement of a nitro group by hydrogen with use of the sodium salt of methanethiol,[8] trialkyltin hydrides,[9,10] or 1-benzyl-1,4-dihydronicotinamide[11] has significantly increased the synthetic utility of nitroalkanes. All of these reactions are thought to proceed by electron-transfer radical chain processes.

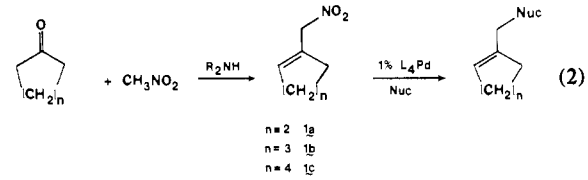
In contrast, the anion of (phenylsulfonyl)nitromethane[12a] and other nitroalkanes[2,12b] cleanly alkylated allylic acetates in the presence of 10–20% of tetrakis(triphenylphosphine)palladium, in a process presumed to be a straightforward nucleophilic attack on a π-allylpalladium complex intermediate.[13-15] In this paper we report the use of allylic nitro compounds as *substrates* for palladium(0)-catalyzed allylic alkylation and amination reactions (eq 1). These results, summarized in Table I, make the extensive



(1)

chemistry of π-allylpalladium complexes[16] accessible to a new class of allylic substrates.

Cyclic allylic nitro compounds were readily available from the reaction of cyclic ketones, nitromethane, and an amine.[17,18] These reacted readily with stabilized carbanions and amines in the presence of 1% L_4Pd to result in allylic alkylation or amination in good yield and without allylic transposition (eq 2). The anion



(2)

of ethyl cyanoacetate underwent substantial dialkylation, as is typical for this carbanion. The cyclohexenyl substrate **1b** was considerably less reactive than either **1a** or **1c** and required prolonged heating in Me_2SO to effect reaction. Under these conditions, some decarboxylation was observed.

Acyclic allylnitro compounds were not available from the condensation of a nitroalkane carbanion with aldehydes or ketones since the vinylnitro compound was the sole product from reactions of this type because of facile isomerization.[19-21] In the hopes that the allylnitro compound would be in equilibrium with the vinylnitro compound under basic conditions, 2-nitro-2-butene (from nitroethane and acetaldehyde) was treated with dimethyl sodiomalonate and the usual palladium(0) catalyst. However, only Michael addition of the enolate to the vinylnitro compound was observed. A solution to this problem was offered by the observation that the anion of **1a** reacted with dimethyl malonate itself (in the presence of a palladium(0) catalyst) to give a 69% yield of this allylic alkylation product. This indicates that the nitro-stabilized anion, although a much weaker base, was in equilibrium with

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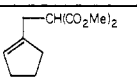
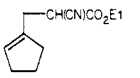
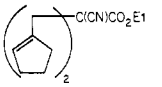
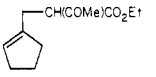
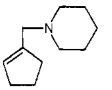
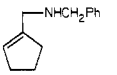
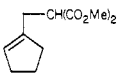
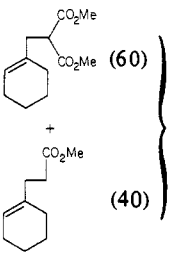
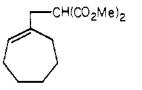
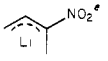
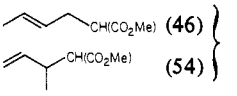
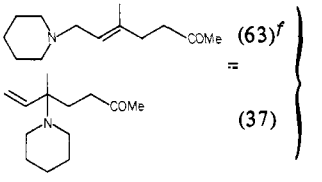
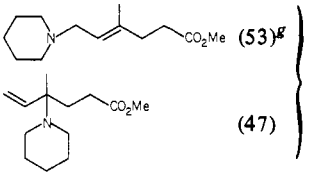
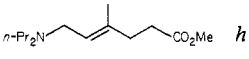
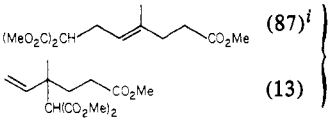
Table I. Palladium(0)-Catalyzed Allylic Alkylation and Amination of Allylnitro Compounds (eq 1)[a]

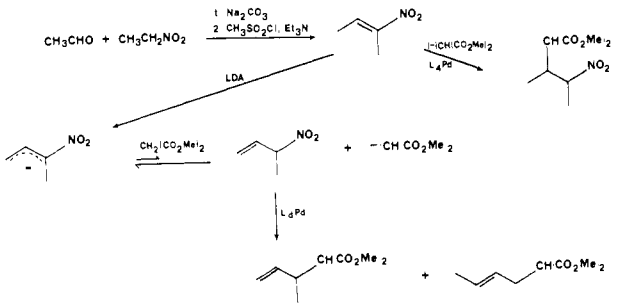
substrate	nucleophile	solvent	time, h/temp, °C	product	product yield, %[b]
1a	$NaCH(CO_2Me)_2$	DMF	3/70		70
1a	$NaCH(CN)CO_2Et$	DMF	4/70		32
					43[c]
1a	$NaCH(COMe)CO_2Et$	DMF	10/70		47
1a		CH_3CN	10/80		85
1a	$PhCH_2NH_2$	CH_3CN	6/80		40[d]
Na-1a	$CH_2(CO_2Me)_2$	DMF	3/70		69
1b	$NaCH(CO_2Me)_2$	Me_2SO	18/115	 (60) + (40)	37
1c	$NaCH(CO_2Me)_2$	DMF	18/70		71
	$CH_2(CO_2Me)_2$	CH_3CN	22/80	 (46) (54)	36
2a		CH_3CN	10/80	 (63)[f] (37)	91
2b		CH_3CN	10/80	 (53)[g] (47)	97
2b	$n\text{-}Pr_2NH$	CH_3CN	19/80	 [h]	50
2b	$NaCH(CO_2Me)_2$	DMF	6/70	 (87)[i] (13)	66

[a] Reactions were carried out under argon with 1% $(Ph_3P)_4Pd$ as catlayst and an additional 2% Ph_3P. [b] Reported yields are for isolated, purified products. Satisfactory infrared, ^1H NMR, and mass spectra and elemental analyses were obtained for all new compounds. [c] Yield based on amount of substrate 1a. [d] The initial yield of this material was considerably higher, but it decomposed during purification. [e] This reaction was run with 5% $(Ph_3P)_4Pd$ and 5% bis(diphenylphosphino)ethane. [f] The E/Z ratio was 87/13, as determined by GLPC. [g] The E/Z ratio was 83/17 as determined by GLPC. [h] The E/Z ratio was 89/11 as determined by GLPC. [i] The E/Z ratio was >95% E by GLPC.

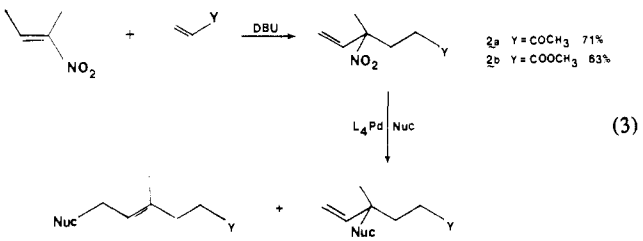
malonate anion to an extent sufficient to permit the allylic alkylation to proceed. Thus, the anion of 2-nitro-2-butene reacted with dimethyl malonate in the presence of palladium(0) catalyst to give a mixture of regioisomers of allylic alkylation products. These results are summarized in Scheme I.

Finally, allylic nitro compounds were also prepared by the base-catalyzed 1,4-addition of β-alkylnitro olefins to conjugated enones. These quaternary allylnitro compounds underwent pal-

Scheme I



ladium-catalyzed allylic alkylation and amination in good yield (eq 3). With dimethyl malonate and piperidine, mixtures of



(3)

regioisomers were obtained, whereas di-*n*-propylamine attacked exclusively at the least substituted position.

Although the mechanism of this palladium-catalyzed allylic alkylation and amination of allylnitro compounds has not yet been studied, it is assumed to proceed in a fashion analogous to the palladium(0)-catalyzed allylic alkylation[14,22] and amination[23] of other allyl substrates such as acetates and ethers—oxidative addition of the allylnitro compound to the palladium(0) complex, followed by nucleophilic attack on the thus-formed allylpalladium(II) species.

The reactions in Table I were carried out in the following manner. The nucleophile (1.2 mmol) in solvent (3 mL) was added to a mixture of substrate (1.0 mmol), $(Ph_3P)_4Pd$ (12 mg, 0.01 mmol), and triphenylphosphine (5 mg, 0.02 mmol) in solvent (1 mL). The resulting yellow mixture was heated for the stated period of time, cooled, and partitioned between ether and water. The ether extracts were washed with saturated brine and dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. Products were purified by evaporative distillation.

The above chemistry significantly expands the scope of palladium-catalyzed allylic alkylation and amination reactions. Allylnitro compounds are generally reactive substrates for this process. Since they are directly available from the condensation of ketones with nitroalkanes or from conjugate additions of β-alkylnitroolefins to α,β-unsaturated carbonyl compounds, the extensive synthetic chemistry of allylpalladium complexes can now be applied directly to these functional groups, which are ubiquitous in organic synthesis. Finally, nitroolefins having γ protons can be made to react as if they were allylnitro compounds. Since nitroolefins are directly available from olefins,[24] ketones, and aldehydes,[25] these classes of compounds are also subject to allylpalladium chemistry. The application of this chemistry to the synthesis of complex organic molecules, including steroid side-chain elaboration, is in progress.

Acknowledgment. Support for this research by the National Science Foundation under Grant CHE-7907832 is gratefully acknowledged.

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Registry No. 1a, 2562-42-7; **1a**·Na, 4404-08-4; **1b**, 5330-61-0; **1c**, 52315-51-2; **2a**, 81769-16-6; **2b**, 81769-17-7; dimethyl propanedioate sodium salt, 18424-76-5; ethyl cyanoacetate sodium salt, 18852-51-2; ethyl 3-oxobutanoate sodium salt, 19232-39-4; piperidine, 110-89-4; benzenemethanamine, 100-46-9; dimethyl propanedioate, 108-59-8; dipropylamine, 142-84-7; dimethyl (1-cyclopentenylmethyl)propanedioate, 81769-18-8; ethyl 2-cyano-3-(1-cyclopentenyl)propanoate, 81769-19-9; ethyl 2-cyano-2,2-bis(1-cyclopentenylmethyl)acetate, 81769-20-2; ethyl 2-acetyl-3-(1-cyclopentenyl)propanoate, 81769-21-3; 1-(1-cyclopentenylmethyl)piperidine, 81769-22-4; *N*-(1-cyclopentenylmethyl)-benzylamine, 81769-23-5; methyl 3-(1-cyclohexenyl)propanoate, 54445-57-7; dimethyl (1-cycloheptenylmethyl)propanedioate, 81769-24-6; dimethyl (2-butenyl)propanedioate, 61979-94-0; dimethyl (1-methyl-2-propenyl)propanedioate, 61979-92-8; (*E*)-7-piperidino-5-methyl-5-hepten-2-one, 81769-25-7; (*Z*)-7-piperidino-5-methyl-5-hepten-2-one, 81769-26-8; 5-piperidino-5-methyl-6-hepten-2-one, 81769-27-9; methyl (*E*)-6-piperidino-4-methyl-4-hexenoate, 81769-28-0; methyl (*Z*)-6-piperidino-4-methyl-4-hexenoate, 81769-29-1; methyl 4-methyl-4-piperidino-5-hexenoate, 81769-30-4; methyl (*E*)-4-methyl-6-(dipropylamino)-4-hexenoate, 81769-31-5; methyl (*Z*)-4-methyl-6-(dipropylamino)-4-hexenoate, 81769-32-6; dimethyl (*E*)-2-(methoxycarbonyl)-5-methyl-4-octenedioate, 64562-42-1; dimethyl (*Z*)-2-(methoxycarbonyl)-5-methyl-4-octenedioate, 81769-33-7; dimethyl 2-(methoxycarbonyl)-3-methyl-3-ethenylhexanedioate, 81769-34-8; dimethyl (1-cyclohexenylmethyl)propanedioate, 60045-25-2; 3-nitro-1-butene lithium salt, 81769-35-9; $(Ph_3P)Pd$, 14221-01-3.

Octalene–[14]Annulene Conversion: 1,8-Dimethyl[14]annulene†

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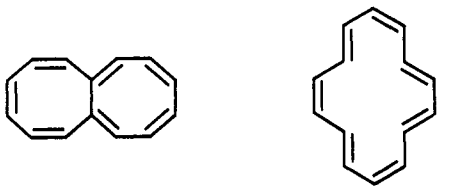
Received February 19, 1982

The theoretically interesting 14 π-system octalene (**1**), whose



(1) (2)

synthesis has recently been achieved,[1] was found by NMR spectroscopic investigations to be a nonplanar olefinic molecule,[2] having the double bonds arranged around the periphery of the two fused eight-membered rings and experiencing a degenerate π-bond shift.[3] In view of its double-bond configuration, octalene can be derived from Sondheimer's [14]annulene (**2**)[4] by connecting carbon atoms 1 and 8, and thus, in a formal sense, it constitutes a perturbed [14]annulene.

That this structural relationship between **1** and **2** actually has chemical significance is shown by the reductive methylation of **1** to give 1,8-dimethyl[14]annulene, reported in this communication.

Conceptually, a conversion of **1** to **2** or derivatives of this annulene by cleavage of the central octalene carbon–carbon bond

† Dedicated to the memory of the late Professor Franz Sondheimer.

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