of 2-acetylphenanthrene. Thus, k_q for xanthone is probably a lower limit for k_{ET}^{**}. The value of k_q is close to that for diffusion control in acetonitrile which in itself represents the upper limit for k_{ET}^{**}. Thus, as a first approximation we estimate $k_{ET}^{**} \sim 10^{10}$ M^{-1} s^{-1}, which leads to $\tau^{**} \sim 620$ ps for 2-acetylphenanthrene in acetonitrile. A number of other substrates are currently being examined by using the same approach. For 2-acetonaphthone we obtained $k_{ET}^{**}\tau^{**} = 1.8$ M^{-1}, and for dibenzosuberenone preliminary experiments suggest a very short lifetime for τ^{**}, probably ≤ 100 ps;[17] experiments of this type are difficult because the intercept in plots generated according to eq 1 is small. *p*-Terphenyl also yields triplet biphenyl upon two-laser sensitization, but other absorptions (perhaps resulting from charge transfer) are also produced.

In summary, our results demonstrate the occurrence of upper triplet state energy transfer processes in solution at room temperature and lead to estimates of these upper state lifetimes. The lifetimes can be sufficiently long for intermolecular processes to occur not only with just neat solvents but also with added scavengers/quenchers. Further work is currently in progress which is expected to yield $k_{ET}^{**}\tau^{**}$ values which we hope to correlate with photophysical and chemical processes occurring from these upper states as well as with expectations based on Kasha's rule.

(17) The determination of lifetimes as short as 100 ps requires the addition of biphenyl concentrations up to ~1–2 M. Under these conditions the actual value of k_{ET}^{**} may contain contributions due to both dynamic quenching controlled by diffusion and static quenching. While Andre and co-workers[18,19] have developed a quenching theory which takes into account both static and dynamic processes, we feel that such a refinement is not justified at the current preliminary stage of our work.
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A Simple Synthesis of Dienones via Isomerization of Alkynones Effected by Palladium Catalysts

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The isomerization of alkynes to conjugated dienes can represent a useful synthetic approach to these valuable building blocks due to the ready accessibility and elaboration of alkynes. While the acetylenic migration along an alkyl chain in the presence of base has proven of great value,[1] conjugated dienes are not detected.[2–4] On the other hand, allenes form readily by base rearrangement of alkynes.[3,5] The failure to obtain the thermodynamically

preferred conjugated dienes[3] from acetylenes appears to be a kinetic problem.[6–8] Indeed, in the special case of 4-butynoic acid, the isomerization to 2,4-butadienoic acid succeeds since the allene that arises from base treatment, 3,4-butadienoic acid, requires prototropic shift of a proton from an allylic methylene group that is further activated by a carboxylate group.[7,9] Transition-metal catalysts offer a mild approach for hydrogen migrations that are not necessarily dependent upon acidity. In view of the well-known ability of transition metals to effect olefin isomerizations[10,11] and the vast literature on the reactions of alkynes under the influence of transition-metal catalysts,[12] the absence of a synthetically useful isomerization of alkynes to the thermodynamically more stable isomeric conjugated dienes is quite surprising. We wish to report a facile synthesis of the 2,4-alkadien-1-ones by a palladium-catalyzed isomerization of 2-alkyn-1-ones.

Equation 1 represents the overall sequence. By using the Weinreb–Nahm procedure,[13] we generated the alkynones **2** in 61–97% yield by treating the hydroxylamine derivatives **1** with
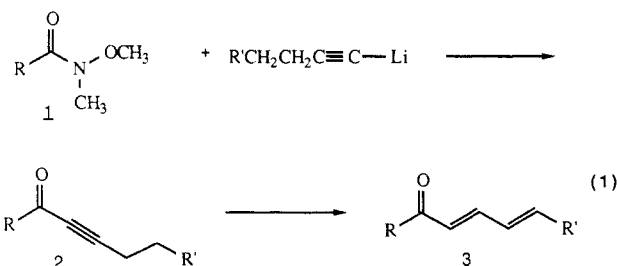
the lithiated terminal acetylene in THF–hexane, initially at –78 °C with subsequent warming to room temperature. The chemoselectivity noted in entry 3 suggests that the hydroxylamine unit specifically activates the carbonyl group toward addition since an amide is normally less reactive than an ester toward nucleophilic addition.

Heating the alkynone **2** with 5 mol% of palladium acetate in the presence of a phosphine in toluene at 100 °C leads to the rearranged dienone in excellent yields as summarized in Table I. The parameters for the isomerization were examined in the case of alkynones **1** and **2**. That the reactions were metal catalyzed was demonstrated by a control experiment in the case of alkynone **2** where, in the absence of the catalyst, only slow decomposition was observed. Addition of DIBAL-H to a reaction identical with entry 5 led only to recovered starting material (84% recovery).

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Table I. A Synthesis of 2,4-Alkadien-1-ones

entry	N-methyl-N-methoxyamide	alkynone	isolated yield (%)	catalyst[a]	time (h)	product	isolated yield (%)
1	(structure)	(structure)	61	Pd(OAc)₂, Ph₃P	22	(structure)	73
2	(structure)	(structure)	96	Pd(OAc)₂, dppb[e]	21[g]	(structure)	73
3	(structure)	(structure)	62	(dba)₃Pd₂·CHCl₃	2	(structure)	78
4	(structure)	(structure) **2**	93	Pd(OAc)₂, dppb[e]	0.75	(structure)	82
	(structure)	(structure) **1**	97			(structure)	
5				Pd(OAc)₂, Ph₃P	4.5		74
6				Pd(OAc)₂, dppb[e]	5		81
7				Pd(OAc)₂, dppf[f]	20		77
8				(dba)₃·Pd₂·CHCl₃, Ph₃P, HOAc[c]	1		53
9				(dba)₃Pd₂·CHCl₃, dppb,[e] HOAc[d]	2.5		82
10	(structure)	(structure) **2**	62	Pd(OAc)₂, Ph₃P	2	(structure)	90[h]
11	(structure)	(structure)	87	(dba)₃Pd₂·CHCl₃, dppb	1.25	(structure)	83

[a] All reactions were run in toluene at 100 °C. For Pd(OAc)₂, 5 mol% was employed; for (dba)₃Pd₂·CHCl₃, 2.5 mol% was employed; for Ph₃P, 35 mol% was utilized; for bidentate phosphines, 17.5 mol% was utilized. [b] 28 mol%. [c] 100 mol%. [d] 55 mol%. [e] 1,4-Bis(diphenylphosphino)butane. [f] 1,1'-bis(diphenylphosphino)ferrocene. [g] Due to the inability to separate product and starting material by GC analysis, the reaction was run for a time that was much longer than necessary. [h] Estimated yield based upon GC analysis. [i] All new compounds have been fully characterized spectroscopically and elemental composition established either by high resolution mass spectroscopy or combustion analysis.

Triisobutylaluminum also was detrimental to this reaction.[14]

Palladium acetate could be replaced with a Pd(0) catalyst, especially in the presence of acetic acid.[15] Comparing entries 5 and 8 or 6 and 9 demonstrates the beneficial effect of this latter catalytic system on rate. Somewhat better yields and, in some cases, better rates were observed with the bidentate ligand dppb in contrast to triphenylphosphine. For example, in entry 11, replacing dppb by triphenylphosphine slowed the reaction by a factor of about 10. Combined with the ease of removal of dppb by a simple filtration through a short plug of silica gel, dppb is the ligand of choice. A ratio of P:Pd of about 7 was employed to maintain an active catalyst and prevent deposition of palladium black. While (dba)₃Pd₂·CHCl₃ plus acetic acid and palladium acetate gave similar results, the greater simplicity in handling palladium acetate normally led to its being preferred.

In entries 3–11, only the (E,E)-dienones were observed. NMR spectroscopy easily establishes the geometry. In entry 2, a small amount of the (Z,E)-dienone was detected in addition to the expected thermodynamically more stable (E,E)-diene. In entry 1, the minor product was not obtained pure and is tentatively assigned the stereochemistry depicted.

The reaction exhibits excellent chemoselectivity as illustrated by the examples in Table I. A very sensitive terminal dienone (entry 2) and a trienone (entry 11) can be generated in excellent yield. The mildness of the reaction is also illustrated by the former example since no noticeable decomposition occurred even though the product was exposed to the reaction conditions for an extended period. No detectable olefin isomerization accompanies acetylene isomerization.[16]

Our results stand in contrast to a recent report on the formation of furans from arylalkynones in the presence of a palladium catalyst.[17] We, therefore, repeated the reaction for alkynone 2 (Table I, entry 4) under similar conditions in which our preferred ligand dppb was substituted for triphenylphosphine (eq 2). The dienone 3 remained the major product (50%), but some furan was detected (14%). The difference in ligand and/or a difference in catalyst preparation[18] may account for the difference in product distribution. On the other hand, use of our preferred catalyst

(14) For a recent discussion of the catalytic species present under such conditions, see: Negishi, E.; Takahashi, T.; Akiyoshi, K. Chem. Commun. 1986, 1338.

(15) Trost, B. M.; Rise, F. J. Am. Chem. Soc. 1987, 109, 3161.

(16) It appears this catalyst system does not effect olefin isomerization because the presumed intermediate hydridopalladium acetate does not add to olefins.

(17) Sheng, H.; Lin, S.; Huang, Y. Tetrahedron Lett. 1986, 27, 4893.

(18) The authors write (dba)₂Pd as their catalyst as it was originally formulated: Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. Chem. Commun. 1970, 1065. We prepared the dba catalyst according to Ukai et al. (Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. J. Organomet. Chem. 1974, 65, 253).

(2)
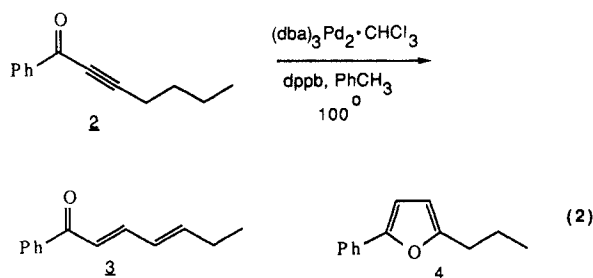
SmplSyn.01

system (Table I, entry 4) gave only the dienone in 82% yield.

The mechanism of this isomerization has not been established, but our qualitative observations suggest a reasonable possibility. Following the reaction by GC does not reveal the buildup of any intermediate. Upon the basis of the efficacy of the reaction when either palladium acetate or $(dba)_3Pd_2$ plus acetic acid is employed and the inefficiency when a Pd(0) species is generated by treating a Pd(2+) salt with an organoaluminum which may serve as an acid scavenger, we propose that the active catalyst is a hydridopalladium acetate.[15] By a series of hydropalladations–dehydropalladations as shown in eq 3, the isomerization proceeds pre-

(3)
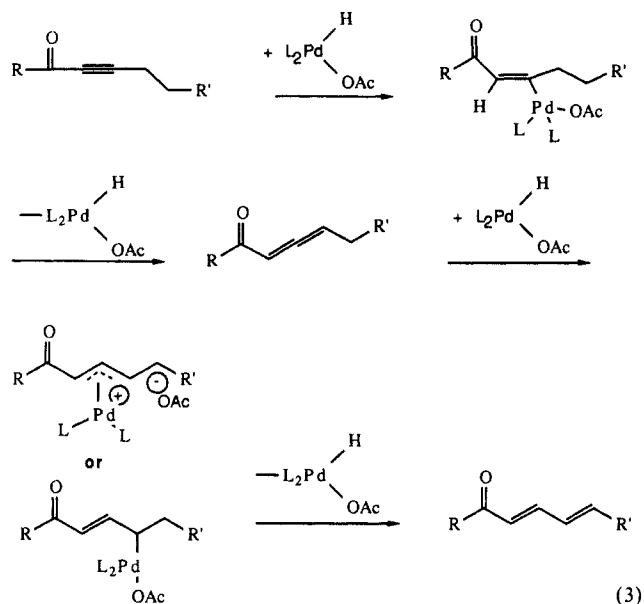
sumably through an allene, either free or still complexed to palladium. Failure to detect the allene may be due to either its more rapid rate of hydropalladation to form the allylpalladium complex compared to the alkyne or because it is not freed from the palladium catalyst. The stability toward β-hydrogen insertion that is normally associated with such vinylpalladium complexes accounts for the previous failures to observe such reactions.[12] Readdition of the palladium hydride generates the allyl complex which may be either the σ-complex or a corresponding π-allyl-complex as depicted. Elimination of the elements of $L_2Pd(H)OAc$ completes the sequence and reforms the catalyst. This last step is analogous to the final stage in the dehydrogenation of enones to dienones utilizing a stoichiometric amount of palladium(2+) salts.[19]

This isomerization suggests that a hydridopalladium acetate, a species not yet detected, may be a useful catalyst for a variety of organic reactions. We previously invoked its participation in a reductive enyne cyclization.[15] In unpublished work brought to

(19) Donati, M.; Conti, F. *Tetrahedron Lett.* **1966**, 4953. Harrison, I. T.; Kimura, E.; Bohme, E.; Fried, J. H. *Tetrahedron Lett.* **1969**, *1589*. Dunne, K.; McQuillin, F. J. *J. Chem. Soc. C* **1970**, 2200. Collins, D. J.; Jackson, W. R.; Timms, R. N. *Tetrahedron Lett.* **1976**, 495. Jackson, W. R.; Strauss, J. V. *Aust. J. Chem.* **1978**, *31*, 1073.

our attention since the latter publication, Binger and Bentz[20] postulated its involvement in the isomerization of methylenecyclopropane. Other applications of this catalyst system are underway in our laboratories. The controlled isomerization of readily available alkynones to dienones should prove to be a simple and practical approach to these useful functional building blocks.

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Trihydrogen Complexes of Iridium

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Recent discoveries by Kubas and co-workers[1] demonstrating that dihydrogen complexes of transition metals are in some cases isolable species has prompted considerable activity in this area.[2] Several cases are now clearly established where metal polyhydride complexes have been shown to contain both dihydrogen and hydride ligands.[3,4] Such polyhydrides undergo facile exchange of hydride and dihydrogen ligands. In the case of the cationic Ir(III) complex $[Ir(bq)(L)_2(H)(H_2)]^+$ (bq = 7,8-benzoquinoline; L = PPh_3) it has been suggested that the H_2/H exchange process may occur via a coordinated H_3 unit.[4] Recent computational studies by Burdett and co-workers have pointed out that coordination of H_3^+ to suitable transition-metal fragments is feasible.[5] We now present evidence for coordination complexes of trihydrogen to Ir moieties of the type $(\eta^5\text{-}C_5H_5)Ir(L)$.

Protonation of $(\eta^5\text{-}C_5H_5)Ir(L)H_2$[6] (L = PMe_3, PPh_3, $AsPh_3$) with $HBF_4\cdot Et_2O$ in Et_2O affords the salts $[(\eta^5\text{-}C_5H_5)Ir(L)H_3]BF_4$ in good yields (eq 1). Complexes 1–3 are colorless, moderately air-stable solids which are air sensitive in solution.[9]

$$(\eta^5\text{-}C_5H_5)Ir(L)H_2 + HBF_4\cdot Et_2O \rightarrow [(\eta^5\text{-}C_5H_5)Ir(L)H_3]BF_4$$
(1)
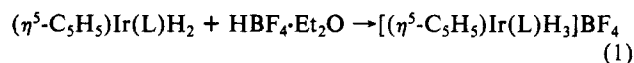
L = PMe₃ (1); PPh₃ (2); AsPh (3)

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