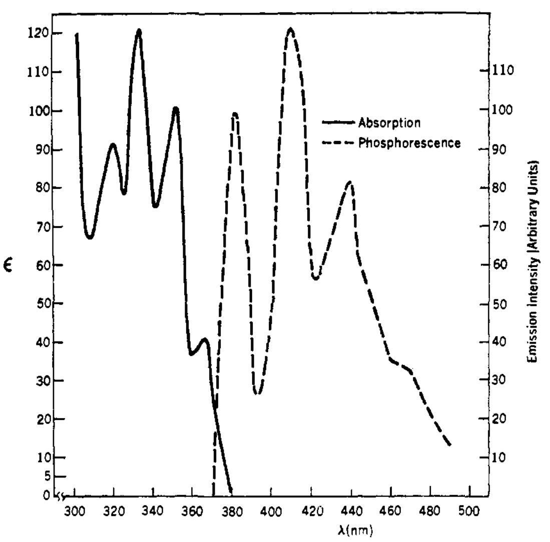

Figure 1. Absorption spectrum (methylcyclohexane) and phosphorescence spectrum (EPA) of 2-phenyl-1-indanone (I).

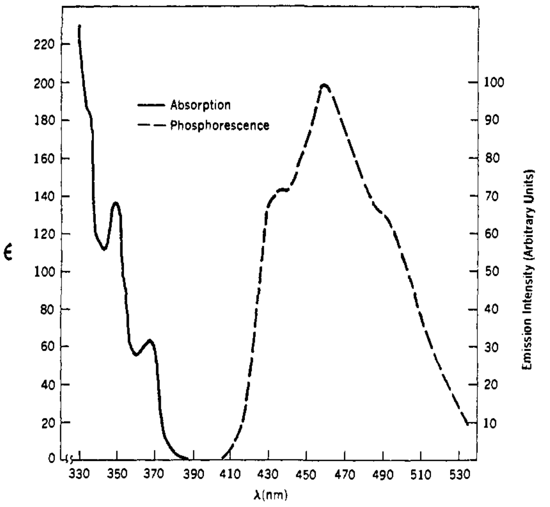

Figure 2. Absorption spectrum (methylcyclohexane) and phosphorescence spectrum (EPA) of 2,6-diphenyl-1-indanone (IV).

trans → cis isomerization of stilbene (using 3660 Å light and 0.01 *M* stilbene) showed that intersystem crossing in this ketone occurs with unit efficiency.

Irradiation of a 0.014 *M* benzene solution of IV through a uranium–glass filter for 9 hr resulted in formation of only trace amounts (<5%) of aldehydic material as shown by nmr analysis. Moreover, silica gel chromatography of the crude photolysate afforded 91% recovery of unchanged starting material.

The reactivity of I and the lack of it in IV can be rationalized in terms of localization (or delocalization) of electronic excitation energy. The phosphorescence spectrum of I (Figure 1) clearly shows that (n,π^*) triplet excitation is mainly associated with the carbonyl portion of the molecule. The probability that energy will be concentrated in the vibrational mode leading to CO–CHPh bond dissociation is expected to be large on a purely statistical basis. In IV the lowest lying triplet is π,π^*, and electronic excitation is associated with the entire π system. Indeed, the phosphorescence is more biphenyl like than phenone like.[12a] Concentration of the energy in the appropriate CO–CHPh vibration should be less likely, and reaction is not observed. Alternatively, the reactivity differences can be discussed in the qualitative molecular orbital terms originally presented by Zimmerman.[13] Thus, n,π^* excitation weakens the CO–CHPh σ bond due to increased overlap of the latter with the electron-deficient n orbital of oxygen. When the excited state configuration is π,π^*, no such overlap is possible and reaction does not occur.

The above results suggest that a necessary condition for facile α cleavage of electronically excited ketones is that the lowest energy excited state configuration be n,π^*.[13a] A similar conclusion has been reached regarding the ability of excited ketones to dehydrogenate suitable hydrogen atom donors.[12b] On the other hand, possession of a lowest energy n,π^* triplet is not a *sufficient* condition for cleavage to unsaturated aldehydes in the indanone series. Thus, both 1-indanone and 2-methyl-1-indanone are photostable in benzene solution even though the lowest triplets are n,π^*.[14] Clearly, other factors such as relative values of the excitation energies and bond dissociation energies and excited state geometry play a role in determining reactivity.[15] A complete investigation of the factors influencing reactivity in the cyclic phenyl ketones is currently in progess.

Acknowledgment. A helpful discussion with Professor N. C. Yang is gratefully acknowledged.

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(13a) NOTE ADDED IN PROOF. After this work was submitted for publication, Lewis reported results which also support this conclusion: F. D. Lewis and J. G. Magyar, *J. Org. Chem.*, **37**, 2102 (1972).

(14) N. Y. C. Chu and D. R. Kearns, *J. Amer. Chem. Soc.*, **94**, 2619 (1972), and references therein.

(15) The CO–CHPh bond dissociation energy in I and IV is estimated to be ~64 kcal mol^{-1}.[16] Thus, the energy content of triplet IV is sufficient to allow for α cleavage.

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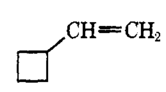
The Cyclodimerization of Ethylene and 1,3-Butadiene to Vinylcyclobutane. Homogeneous Titanium Catalysts

Sir:

The catalyzed cyclodimerization of ethylene and 1,3-butadiene to vinylcyclobutane is here reported for the first time. This is also the first reported instance in

$$CH_2{=}CH_2 + CH_2{=}CHCH{=}CH_2 \xrightarrow[\text{catalyst}]{\text{titanium}}$$



(1)

which ethylene has been involved in a catalyzed reaction giving a four-membered ring.[1] Homogeneous titanium catalysts facilitate vinylcyclobutane production in competition with 1,4-hexadiene, the usual product of

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(1) The cyclotrimerization of butadiene with ethylene to 1,5-cyclodecadiene is known with nickel(0) catalysts; P. Heimbach, P. W. Jolly, and G. Wilke, *Advan. Organometal. Chem.*, **8**, 29 (1970).

Table I. Comparison of Catalysts for Ethylene–1,3-Butadiene Codimerization[a]

Catalyst (molar ratio of components)	% C_4 ring compounds in catalyzed codimers[b,c]	Isomerization of vinylcyclobutane, %[c]	Comparative initial activity[d]
$C_5H_5Ti(CH_2Ph)_3$	54	66	2
$C_5H_5Ti(CH_2Ph)_3$–Et_3Al (1:2)	45	50	1
$C_5H_5TiCl_3$–Et_3Al in THF (1:7.5)	74	58	2
$Ti(CH_2Ph)_4$	44	1	5
$Ti(CH_2Ph)_4$–bipy (1:1)	74	1	6
$(acac)_2TiO$–Et_3Al in THF (1:7.5)	61	1	7
$TiCl_4$–Et_3Al–phen in THF (1:7.5:1)	75	1	*e*
$(n\text{-}C_4H_9O)_4Ti$–Et_3Al (1:2.5)			
alone	33	5	3
in THF	42	2	4
with phen (1:2.5:1)	44	3	6

[a] Typical reaction conditions: 135–150° for 30 min; mmol of Ti–C_2H_4–C_4H_6 = 1.0:480:140; 1200 psi; conversion of C_2H_4, 20%, and of C_4H_6, 60–100%; toluene solvent. [b] For catalyzed codimers only, cyclohexene excluded. [c] Some vinylcyclobutane isomerized to ethylidenecyclobutane. [d] Most active noted as 1. [e] Accompanied by extensive polymerization.

codimerization. By contrast, catalysts of group VIII metals are well known for codimerizing ethylene and butadiene to give 1,4-hexadiene, but in no case has vinylcyclobutane been reported.[2] The simple thermal dimerization of ethylene and butadiene gives only 0.02% vinylcyclobutane with cyclohexene being dominant.[3]

Tetrabenzyltitanium[4] and π-$C_5H_5Ti(CH_2Ph)_3$[5] serve as examples of single component titanium catalysts while two-component catalysts of the Ziegler type can be prepared *in situ* from a number of hydrocarbon-soluble titanium compounds and various reducing agents. Examples of the latter are $(n\text{-}C_4H_9O)_4Ti$ together with Et_2Al, $LiAlH_4$ or $n\text{-}C_4H_9Li$ as reducing agents and also $C_5H_5TiCl_3$, $(acac)_2TiO$, or $(C_8H_8)_2Ti$ in combination with Et_3Al. Although yields of vinylcyclobutane vary greatly, it appears that this is a quite general catalytic property of reduced organotitanium species possessing open coordination sites.

Products formed in competition with vinylcyclobutane include: *cis*-1,4-hexadiene, 1-butene from ethylene, polybutadiene, 4-vinyl-1-cyclohexene (partially thermal), open-chain octatrienes, cyclohexene (thermal dimer at 170°), and C=C isomerization products such as ethylidenecyclobutane and 2,4-hexadiene. Tetrabutyl titanate–Et_3Al is known to convert ethylene to 1-butene and butadiene to 1,2-polybutadiene when either reactant is present alone (reaction temperature of 30–60°);[6] however, when present together, butadiene suppresses ethylene dimerization, and codimerization can then take place at a higher temperature, 135–155°.

The importance of the various competing reactions depended upon the particular catalyst system which, fortunately, could be modified by addition of donor ligands. 2,2′-Bipyridyl (bipy) and 1,10-phenanthroline (phen) were the most effective ligands for improving vinylcyclobutane yields at the expense of all catalyzed side reactions including C=C isomerization. These bidentate amines improved catalyst selectivity for vinylcyclobutane but resulted in less active catalysts. To compensate for this, the reaction temperature could be raised to 170° since these ligands also improved catalyst stability. As an example, a toluene solution of butadiene, ethylene, $(n\text{-}C_4H_9O)_4Ti$, Et_3Al, and 1,10-phenanthroline (respectively, 4.3, 13.2, 0.045, 0.122, and 0.045 mol) was heated in an autoclave at 170–175° for 1.67 hr (1300 psi maximum pressure). A combination of gas chromatography and distillation showed that 96% butadiene and 22% ethylene had reacted to give a product comprised by weight of 1.6% butenes, 60.1% C_6, 18.6% 4-vinylcyclohexene, 14.9% other C_8 + C_{10} oligomers, and 4.8% polymer. The C_6 olefins contained 37.7% vinylcyclobutane, 1.2% ethylidenecyclobutane, 46.6% *cis*-1,4-hexadiene, 2.9% other hexadienes, 1.4% hexenes from ethylene, and 10.2% cyclohexene. The yields of vinylcyclobutane on the basis of converted ethylene and butadiene were 47 and 21%, respectively. Vinylcyclobutane,[3,7] *cis*-1,4-hexadiene and ethylidenecyclobutane were isolated and identified by use of mass spectra and both ^1H and ^{13}C nmr.

Table I highlights the competition between the cyclodimerization of ethylene and butadiene to vinylcyclobutane (and its isomerization product ethylidenecyclobutane) as against codimerization to open-chain hexadienes for a number of catalysts. Initial activity and C=C isomerization are also compared. The cyclobutanes in the codimer ranged from 34 to 73% with catalysts containing the bipyridyl and phenanthroline being the best. Pyridine, phosphines, or *N,N,N′,N′*-tetramethylethylenediamine were less effective for increasing vinylcyclobutane yields. Ethers, such as tetrahydrofuran and 1,2-dimethoxyethane when used as solvent, were also effective in stabilizing the catalyst and improving selectivity for vinylcyclobutane. Thus, "hard" bases[8] proved best for increasing vinylcyclobutane yields.

The opportunity to utilize this new catalytic reaction for organic synthesis was explored with C_5H_5Ti-

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[2] (a) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 6785 (1970); (b) R. G. Miller, T. J. Kealy, and A. L. Barney, *ibid.*, **89**, 3756 (1967); (c) T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *ibid.*, **87**, 5638 (1965); (d) G. Hata, *ibid.*, **86**, 3903 (1964); (e) R. Cramer, *Accounts Chem. Res.*, **1**, 186 (1968); (f) M. Iwamoto and S. Yuguchi, *Chem. Commun.*, 28 (1968); *Bull. Chem. Soc. Jap.*, **41**, 150 (1968); **39**, 2001 (1966); (g) G. Hata and A. Miyake, *ibid.*, **41**, 2443 (1968); (h) Y. Tajima and E. Kunioka, *Chem. Commun.*, 603 (1968); (i) G. Henrici-Olivé and S. Olivé, *J. Organometal. Chem.*, **35**, 381 (1972).

[3] P. D. Bartlett and K. W. Schueller, *J. Amer. Chem. Soc.*, **90**, 6071 (1968); R. K. Lyon, *J. Org. Chem.*, **34**, 3202 (1969).

[4] U. Giannini and U. Zucchini, *Chem. Commun.*, 940 (1968); (b) U. Zucchini, E. Albizzati, and U. Giannini, *J. Organometal. Chem.*, **26**, 357 (1971).

[5] Prepared from $C_5H_5TiCl_3$ and $PhCH_2MgCl$.

[6] (a) G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **2**, 105 (1963); (b) H. Martin, *Angew. Chem.*, **68**, 306 (1956); (c) H. Hirai, K. Hiraki, I. Noguchi, and S. Makishima, *J. Polym. Sci., Part A-1*, **8**, 147 (1970).

[7] C. G. Overberger, H. Kaye, and G. Walsh, *ibid.*, *Part A*, **2**, 755 (1964).

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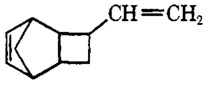
$(CH_2Ph)_3$. Piperylene–ethylene codimers were 64% cyclics, *cis*- and *trans*-1-methyl-2-vinylcyclobutane (52%) and *n*-propenylcyclobutane (12%), accompanied by 3-methyl-*cis*-1,4-hexadiene as the other principal product. However, isoprene–ethylene gave only 2-methyl-*n*-hexadienes (96%) and 3-methyl-*n*-hexadienes (4%) as codimers. Propylene did not codimerize with butadiene. But the strained olefins, norbornadiene and norbornene, reacted with butadiene to give I and II, respectively, in high yields (~90% of the codimer). The same butadiene–norbornadiene codimer I has recently been reported with Fe and Mn catalysts.[9]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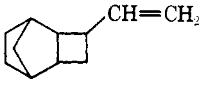
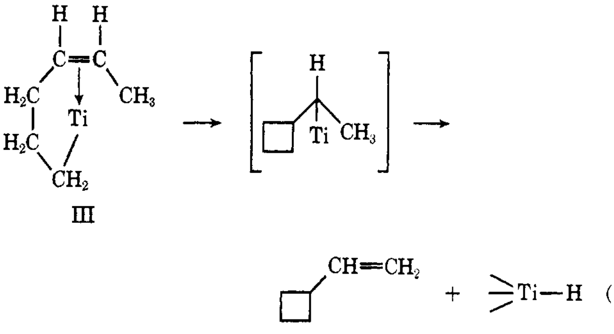

II

Two mechanistic schemes appear possible for ethylene–butadiene cyclodimerization, one wherein the cyclic and open-chain codimers (vinylcyclobutane and hexadienes) have a common intermediate or an alternative wherein they do not. Metal hydride mechanisms have been proposed for the codimerization of ethylene and butadiene to hexadienes by group VIII metals[2a, 2i] and for ethylene dimerization by homogeneous titanium catalysts.[10] Addition of butadiene to a titanium hydride species followed by ethylene would lead to III, a common intermediate, which could give *cis*-1,4-hexadiene by β elimination or vinylcyclobutane by an intramolecular addition–elimination with regeneration of titanium hydride (eq 2). Alternatively, a [2 + 2] cycloaddition mechanism could be proposed for vinylcyclobutane with no common intermediate or movement of hydrogens. The present data do not allow a clear choice between these or other mechanisms. But it does appear easier to account for the observed ethylene codimers with isoprene or piperylene by intermediates analogous to III than by a [2 + 2] cycloaddition.


III

(2)

Acknowledgments. Special acknowledgments are given to Dr. W. Keim and Dr. J. E. Mahler for helpful discussions and to Mr. S. D. Siegel for technical assistance.

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Detection of Steady-State Free-Radical Concentrations by Photoionization

Sir:

The observation of free radicals in ordinary gas-phase reactions is difficult as their steady-state concentrations are very low.[1,2] Only in a few especially favorable reactions have these radical concentrations been measured directly.[3,4] Ionization potentials of free radicals are usually lower than those of the parent molecule, and thus, in principle, radicals can be preferentially ionized. Conventional electron-impact ionization is not well suited to radical detection because of low cross sections near the threshold, interference by fragmentation of larger molecules, and cracking on the hot filament.[5] The use of monochromatic light sources makes photoionization extremely selective. If the energy of the photoionizing quantum is only slightly greater than the ionization potential of a particular intermediate, then no subsequent fragmentation occurs.[6,7]

A photoionization mass spectrometer has been constructed by combining a quadrupole mass filter with argon, krypton, and xenon vacuum-ultraviolet resonance lamps.[8] Reactants from a conventional flow system were sampled through a pinhole inlet into the mass spectrometer where ions were produced by photoionization.[9] Free radicals have been detected during the oxidation of several simple hydrocarbons. Each free radical was uniquely assigned from its mass to charge ratio, with both normal and deuterated fuel, and from limits on its ionization potential obtained by alternating between the several lamps. Oxygen atoms were produced, in the absence of molecular oxygen, by titrating nitrogen atoms with nitric oxide. Scans of the reactants individually showed no detectable fragmentation and no interfering impurities. Concentrations and reaction times were selected to ensure that the oxygen atom and fuel concentrations were close to their initial values (within 15%) for all experiments.

The addition of oxygen atoms to methane produced signals at mass 30, identified as CH_2O, mass 29 (CHO), and mass 15 (CH_3). The time dependence of these products is shown in Figure 1. (CD_4 was used when investigating the formaldehyde peak in order to avoid interference from traces of NO at mass 30.) The $[CD_2O]$ increased linearly with reaction time, as expected for a stable product. The reaction of oxygen atoms with formaldehyde is too slow to be significant except possibly at the longest contact times.[10] The constant signals at mass 29 and 15 indicate that concentrations of these radicals had attained their steady-state values, $[CHO]_{ss}$ and $[CH_3]_{ss}$, respectively. The $[CH_3]_{ss}$ suggests that the rate of methyl radical formation, in the generally accepted first step,[11] reaction 1,

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(2) J. T. Herron, *Advan. Mass Spectrom.*, **5**, 453 (1971).

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