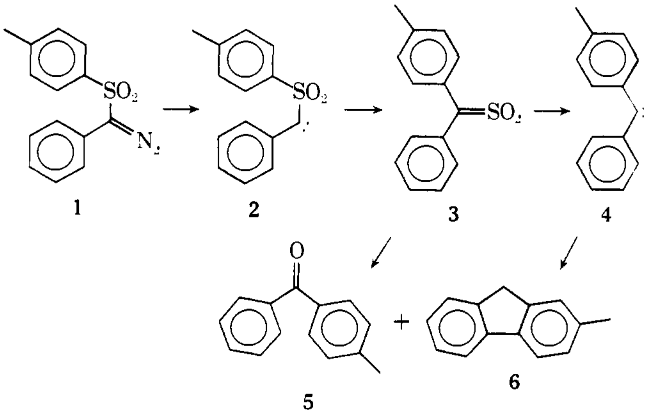
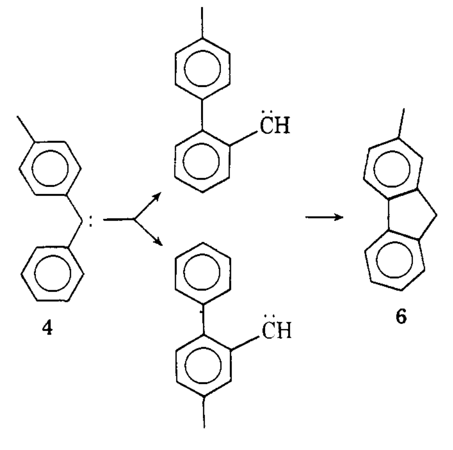
sulfene itself.[4] Our choice for a target intermediate was *p*-tolylphenylcarbene (**4**) (Scheme I) and thus the diazo compound **1** was indicated as the starting material.

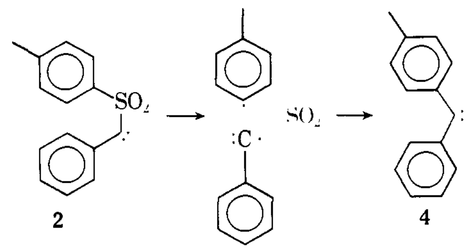
Scheme I



At 350-600° *p*-tolyl phenyl ketone (**5**, 13-15%) and 2-methylfluorene (**6**, 3-5%) appeared as the only two nonvolatile monomeric compounds of the pyrolysis of **1**.[10] Substantial amounts of polymer and a gas (ca. 10%) were recovered as well. Infrared analysis of the gas showed it to consist mainly of sulfur dioxide. These results are quite consistent with loss of nitrogen from **1** to give *p*-tolylsulfonylphenylcarbene **2** followed by rearrangement to the sulfene **3**. Sulfenes are known to lose sulfur monoxide to give the residual carbonyl compound,[3,11] and this appears to be the major observable route followed by **3**. The presence of 2-methylfluorene reveals that *p*-tolylphenylcarbene must have been present as well. Fluorenes are the ultimate products of gas-phase rearrangements of diphenylcarbenes, and the methyl group serves as a further label, ensuring that the "migration" to the 2-position required by the carbene-to-carbene process does take place.[12,13]



An alternative mechanism involves fragmentation of **2** to an aryl radical and a carbyne. Were these two reactive species to recombine, *p*-tolylphenylcarbene would result. However, the gas phase should not be conducive to facile recombination, and we would expect to find other products if such a fragmentation were taking place. We are not certain what to expect of phenylcarbyne, but we are unable to detect the product of dimerization, tolan. The aryl radical should appear as toluene and bitolyl, and we can find neither. We could detect substantially less than 1% of these three compounds. In other gas-phase carbene reactions proceeding through aryl radicals, biaryls are found in 10-20% yield.[14]



Data bearing on the lifetime of the sulfene, possibilities of trapping with external agents, and the effect of substituents on the ease of cleavage of the carbon-to-sulfur double bond await further experiments.

References and Notes

(1) This work was supported by the National Science Foundation through Grants GP-30797X and MPS74-05690. We are very grateful.
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(10) The pyrolysis was conducted by slowly dropping the solid diazo compound onto a hot Pyrex or quartz surface in vacuo, and trapping the resultant pyrosylate on a cold finger at −196°. In the Pyrex apparatus the cold finger was inserted into the reaction vessel and held approximately 80 mm from the hot surface. In the quartz apparatus (for temperatures above 400°) the cold finger was situated at the end of a tube leading from the reaction vessel and was about 240 mm from the site of the pyrolysis. While it is impossible to measure the pressure at the surface where the molecules decompose, the system was pumped down to less than a tenth of a micron before the pyrolysis was begun and then to pressures of about 1 μ after each addition of diazo compound. Temperatures at the glass surface were measured with a thermocouple before the pyrolysis.
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Brian E. Sarver, Maitland Jones, Jr.*
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

A. M. van Leusen
Department of Organic Chemistry, The University
Zernikelaan, Groningen, The Netherlands

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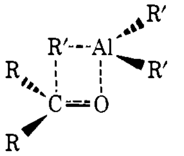
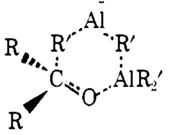
Stereochemistry of Ketone Insertion and Enol Salt Formation at Alkyl Carbon–Aluminum Bonds[1]

Sir:

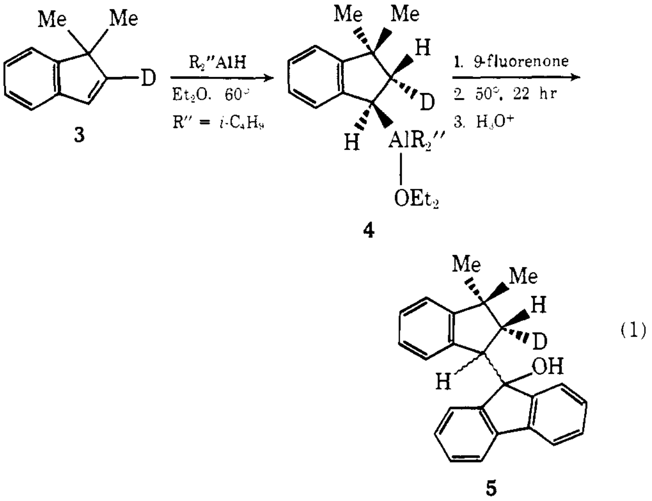
Much attention has been given to the reactions of ketones with aluminum alkyls, with the hope of finding new, selective alkylations and reductions and of unraveling the intricate reaction mechanisms involved. By changing the structure of the reactants or the experimental conditions, varying amounts of alkylation,[2] reduction,[3] enol salt formation,[2b,3b] and free radical-induced conjugate alkylation[4] can be observed. Indeed, even the simple insertion of a ketone into the carbon–aluminum bond has been shown to proceed via two competing pathways, each having a different rate law and a distinctive stereoselectivity.[5-7] In donor solvents or in hydrocarbon media, with a ratio of $R_2CO/R_3'Al \leq 1$, the transfer of R′ to the carbonyl carbon is viewed as ensuing through a four-membered transition state (**1**). On the other hand, the accelerated rate observed in hydrocarbon solvents, with a reactant ratio of $R_2CO/R_3'Al > 1$, is consistent with some type of six-membered cyclic transition state (**2**). Implicit in both views of alkylation, as well as in alternative transition states proposed,[7,8] is the assumption that the transfer of R′ from aluminum to carbonyl carbon occurs in a synchronous process of R′–Al bond rupture and R′–C bond formation. Yet, up to the present, the exact nature of such an alkyl transfer step has remained a subject of speculation, rather than of experimental proof.[5c]


1

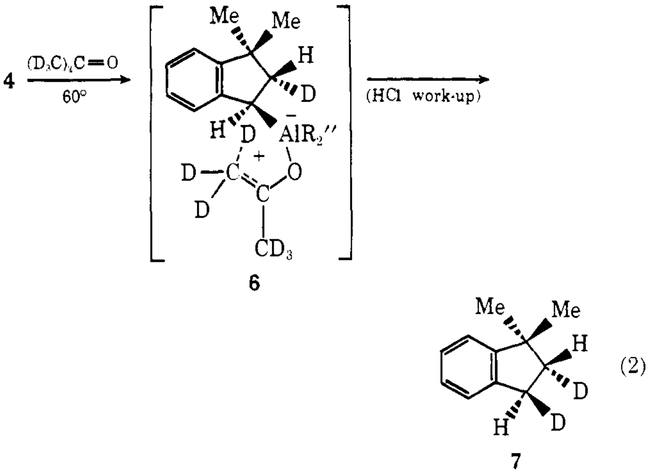

2

Since we had recently prepared, by controlled hydralumination, aluminum alkyls having carbon–aluminum bonds of known configuration,[9] we were in a position to test the above mechanistic assumption of bond-making and bond-breaking in R′ transfer. The concerted transfer, as depicted in **1** and **2**, further implied that a flank attack on R′ would lead to a retention of configuration by R′. Such a retention of configuration has, in fact, been observed for the insertion of phenylacetylene into an alkyl carbon–aluminum bond.[9]

We now wish to report that the reactions of the diisobutyl(2-deuterio-3,3-dimethyl-1-indanyl)aluminum etherate (**4**), with a suitable aromatic ketone and a typical aliphatic ketone, provide insight into the stereochemistry of both the ketone insertion and the enolization reactions. Thus, the reaction of **4** with 9-fluorenone (ratio of $R_2CO/R_3'Al > 1$ or < 1) gave a 90% yield of 9-(2-deuterio-3,3-dimethyl-1-indanyl)-9-fluorenol[10] (**5**) mp 146–147° (MeOH), after column chromatographic separation from 9-fluorenol (eq 1). By its ^2H-decoupled NMR spectrum in $CDCl_3$, compound **5** was shown to have, in equal amounts, its C_2 proton cis and trans with respect to the 9-hydroxy-9-fluorenyl group at C_1. Thus, ketone insertion into the C_1 carbon–aluminum bond had occurred with complete loss of configuration: NMR data (δ, TMS) 1.14 (s, CH_3), 1.19 (d, H_2 cis to fluorenyl group, $J_{trans} = 8.5$ Hz), 1.47 (s, CH_3), 1.91 (d, H_2 trans to fluorenyl group, $J_{cis} = 9.7$ Hz), 3.10 (s, OH), 4.56 (br d, H_3), and 7.0–8.45 (m, aromatic; in which spectrum the area of the trans H at C_2 (1.91) was equal to one-half that of the OH or the H_3 signal). The partly obscured doublet at 1.19 ppm, corresponding to the H_2 cis to the fluorenyl group, was completely visible in a spectrum taken after **5** was admixed with small amounts of europium(III) 2,2,6,6-tetramethylheptanedioneate.

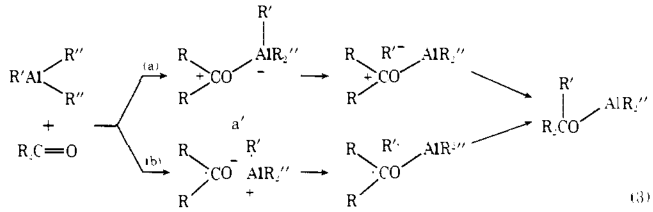


In contrast, when **4** was allowed to react with acetone-d_6, addition to the carbonyl group was insignificant. Instead, enol salt formation resulted, with the stereospecific formation of *trans*-2,3-dideuterio-1,1-dimethylindan[11] (**7**) (eq 2).

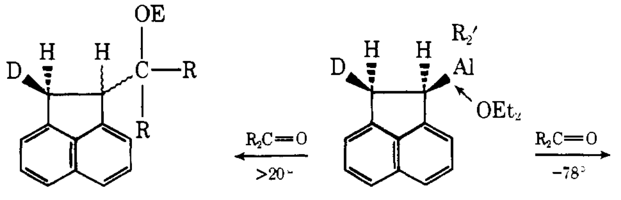


This experiment not only demonstrates that enolization cleaves the carbon–aluminium bond with retention of configuration but that simple complexation of the carbonyl oxygen with the aluminum center[5] does not itself destroy the configuration at the carbon–aluminum bond. This latter point is important, for one might attribute the loss of configuration in eq 1, not to the actual ketone insertion, but to a reversible σ complex between **4** and 9-fluorenone. Such a supposition can be dismissed by the failure to observe any such configurational loss with acetone (eq 2), which should form an even stronger σ complex than 9-fluorenone.

Thus, the loss of configuration for ketone insertion means that such transition states, as **1** and **2**, cannot be valid for all ketone substrates. Therefore, one must consider pathways that permit R′ to undergo rapid configurational inversion, namely, ionic and electron-transfer R′Al bond ruptures (eq 3). Although compound **4** and 9-fluorencone do fulfill the criteria for those systems that tend to react by an electron-transfer mechanism,[12] no side products characteristic of electron-transfer processes, namely, fluorenopinacol or its relatives,[13] could be detected. Not only does the absence of free-radical products seem to weaken the case for pathway b causing the loss of configuration (eq 3) but the behavior of the acenaphthenylaluminum system (**8**) toward these ketones argues for the development of much carbenium ion character, as in pathway a.

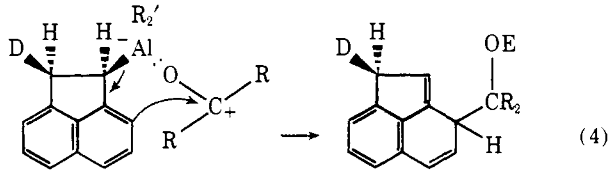


Thus, 2-deuterio-1-acenaphthenyl(diisobutyl)aluminum etherate, whose stereochemistry, as given in **8**, is supported by its mode of formation (cf. preparation of **4** from **3** in eq 1), reacts with 9-fluorenone ($R_2CO/R_3'Al > 1$ or < 1), propiophenone, cyclopentanone, and acetone at −78° to yield the allylic rearrangement products, **10** (eq 4). This tendency of **8** to undergo ortho alkylation, compared with that of **4** to undergo either protolysis (eq 2) or alkylation (eq 1) at C_1, can be attributed to the greater ease with which the naphthalene ring in **8** can be attacked by a ketone complex (**11**) having carbenium ion character (pathway a, eq 3).



9a, E = $R_2'Al$
b, E = H (after H_3O^+)

8



(4)

11

10a, E = $R_2'Al$
b, E = H (after H_3O^+)

Noteworthy is the observation that **8** reacts with these ketones at higher temperature (20-80°) to yield 1-acenaphthenylcarbinols (**9**), the thermodynamically controlled products, but the transformation of the kinetically controlled products, **10a**, into **9a** seems to involve dissociation into $R_2'Al{:}O{=}CR_2^+$ and $C_{12}H_8D^-$, for the configuration at C_1 in **9a** was shown to have been lost.

The foregoing results demonstrate that direct insertion of ketones into certain carbon-aluminum bonds does not involve synchronous breaking of C-Al bonds and making of C-C bonds, as suggested by the transition states depicted in **1** and **2**. Rather, the loss in configuration for such alkylations is more consistent with the formation of acyclic, carbenium ion intermediates (**6** and **11**), which can decompose stereospecifically with proton transfer (**6** in eq 2) or which can collapse nonstereospecifically to the insertion products (**5** and **9**) or to the allylic rearrangement products (**10a**).

Acknowledgment. This research was supported by the Public Health Service and the National Science Foundation through Grants GM-20304 and GP-28209, respectively.

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(1) Part XXXI of the series, "Organometallic Compounds of Group III", devoted to carbometalation and hydrometalation; cf. J. J. Eisch and S.-G. Rhee, *J. Am. Chem. Soc.*, in press, for the previous part.

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(10) New compounds gave elemental analyses and spectra in agreement with the assigned structures.

(11) Compound **7** has previously been characterized; cf. ref 9.

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(14) For example the structure of **9b** (R_2CO = 9-fluorenone), mp 172–174°, was established by its ^2H-decoupled NMR spectrum in benzene-d_6 at 60° (δ, TMS): 1.68 (s, OH), 2.30 (d, H_2 cis to fluorenyl group, J_{trans} = 4.0 Hz, 2.77 (br d, H_2 trans to fluorenyl group, J_{cis} = 8.5 Hz), 4.36 (br d, H_1), and 6.25–7.75 (m, aromatic H). The resonance signals at 2.30 and 2.77 ppm each integrated to an intensity of 0.5 proton.

(15) Structure **10b** (R_2CO = acetone) is based upon its NMR spectrum in CCl_4: 1.3 (s, CH_3), 1.9 (s, CH_3 (diastereotopic groups), 2.72 (s, OH), 3.21 (s, C_1H), 3.50 (s, C_3H), 5.70 (d of d, C_4–H, $J_{4,5}$ = 10.0 Hz, $J_{3,4}$ = 4.3 Hz, 6.15 (d, C_2–H, $J_{1,2}$ = 2.4 Hz), 6.44 (d of d, C_5–H, $J_{4,5}$ = 10.0 Hz, $J_{3,5}$ = 2.0 Hz), 6.75–7.5 (m, aromatic). This compound could be dehydrated, with a prototropic shift, to yield 3-isopropenylacenaphthene: mp 50–50.5°; NMR (CCl_4) 2.23 (s, CH_3), 3.25 (s, CH_2CH_2), 5.13 (br d of d, $=CH_2$), and 7.15–7.5 (m, aromatic).

John J. Eisch,* Kenneth C. Fichter
Department of Chemistry
State University of New York at Binghamton
Binghamton, New York 13901

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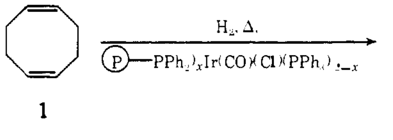
Unusual Rate Effects in the Hydrogenation of 1,5-Cyclooctadiene Catalyzed by Polymer-Anchored $Ir(CO)(Cl)(PPh_3)_2$

Sir:

Increased attention has recently been given to anchoring homogeneous transition metal catalysts to polymers.[1,2] Heterogenized catalysts can have advantages over their homogeneous counterparts such as (1) ease of separation from products,[1-5] (2) enhanced size[3] and positional[6] selectivity, (3) ability to carry out sequential catalytic reactions,[7,8] and (4) the potential isolation of reactive catalytic species which would normally further react.[9] However, the need for reagents to diffuse into cross-linked resins can retard reaction rates.[3,4,10] We now report example catalytic hydrogenations of 1,5-cyclooctadiene (1,5-COD), using resin-anchored $Ir(CO)(Cl)(PPh_3)_2$, which are faster than those catalyzed homogeneously at equivalent P/Ir ratios.[11] Furthermore, the internal mobility of resin-anchored phosphine ligands results in some unusual rate effects on changing temperature and varying the ligand concentration.

1,5-COD, **1**, was selectively hydrogenated over $Ir(CO)(Cl)(PPh_3)_2$ and its styrene-divinylbenzene-anchored analog. Successive isomerization to 1,4-COD, **2**, and 1,3-COD, **3**, occurs followed by hydrogenation to cyclooctene, **4**, and, finally, cyclooctane, **5**.



1

2 3 4 5

A series of diphenylphosphinated resins was prepared,[12] where the per cent P was varied: 1.25% (corresponds to 12% of the rings phosphinated), 1.91 (18), 2.02 (19), 4.02 (38), and 10.28 (96). Each of these resins was treated with $Ir(CO)(Cl)(PPh_3)_2$ to give a series of resin-anchored catalysts where P/Ir ratios of 3, 4, 7, 11, 12, and 22 were achieved. Thus, hydrogenation rates could be studied as a function of the P/Ir ratio over a range of total phosphine levels.

The rates of homogeneously and heterogeneously catalyzed reactions were compared using the same solvent volume and equal amounts of catalyst at equal P/Ir ratios.[13]