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GOLD CATALYSED REARRANGEMENTS OF STRAINED SMALL RING HYDROCARBONS[**]

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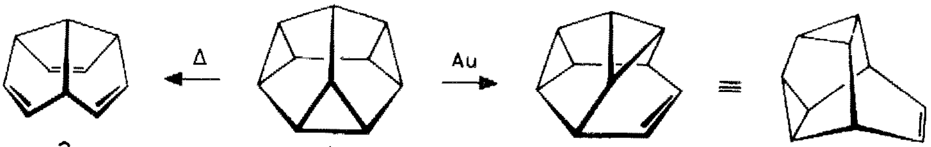
Examples of transition metal catalysis of the rearrangements of strained small ring systems are abundant[1]. Among the literature reports on such observations there is only one on the catalytic effect of gold(III) and gold(I) salts[2]. In fact, gold metal has been found to be the least catalytically active metallic material[3], it has therefore been recommended[3] and used for the construction of flow reactors for gas phase kinetic measurements of hydrocarbon and ester pyrolysis reactions[4,5]. Following the basic principles of published devices[3,5] we have constructed our own thermolysis flow system[6]. We here report on our findings of catalyzed reactions on the metallic gold surface (99.99% purity) of our reactor.

Diademane (1) is known to undergo a facile thermal [2+2+2]-cycloreversion to triquinacene (2)[7], the same rearrangement is catalyzed by silver salts[8]



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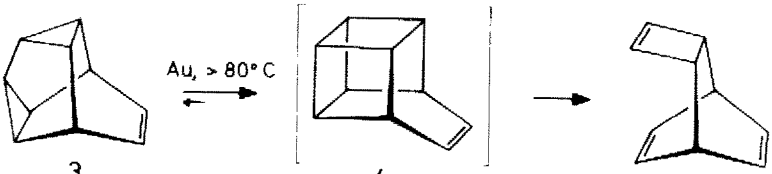


3 4 5

However, when 1 in a stream of helium was run through the gold reactor at $100^{\circ}C$ with a contact time of 20 sec. a 50% conversion to snoutene (3) but less than 5% rearrangement to triquinacene (2) was observed. At higher temperatures and shorter contact times the uncatalyzed thermal rearrangement accounted for a larger fraction of the products, but even at 170° and 3 sec contact time formation of 3 prevailed (see table). Gold(I) complexes like the gold(I)-dicyclopentadiene chloride[9] catalyze the rearrangement of 1 to 3 at room temperature. Apparently gold(I) and silver(I) ions act differently upon 1, but copper(I) clearly catalyzes both rearrangements of 1 to 2 and 3.

Whereas 3 is stable towards silver(I) ions, itself being formed by a silver ion catalysis from basketene (4), at elevated temperatures on the gold surface it rearranges to Nenitzescu's hydrocarbon (5). The most straightforward ex-

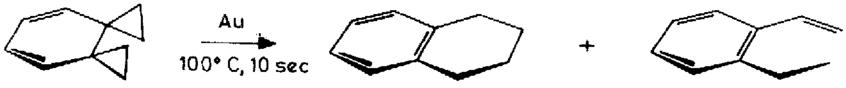
Table: Product distribution in the rearrangements of some polycyclic small ring hydrocarbons catalyzed by gold and related metals or metal salts

Starting material	Conditions	Temp.	Contact time	Products (relative yields)
1	Au-reactor	100°	20 s	1 (50%), 2 (<5%), 3 (>45%)
1	Au-reactor	170°	3 s	1 (30%), 2 (17%), 3 (53%)
1	$Au(C_{10}H_{12})Cl, CHCl_3$	25°	24 h	3 (100%), gold deposition after 10 min
1	$Cu_2(COD)_2Cl_2$, THF	25°	48 h	1 (35%), 2 (60%), 3 (5%)
3	Au-reactor	170°	20 s	3 (89%), 5 (10%), Naphthalin(1%)
3	Au-reactor	270°	20 s	3 (25%), 5 (70%), Naphthalin (5%)
3	Au-wire, 99.99%, C_6H_6	160°	10 d	3 (30%), 5 (70%), Naphthalin (<2%)
3	Au-wire 99.999%, C_6H_6	160°	5 d	3 (60%), 5 (40%)
3	$Au(C_{10}H_{12})Cl, CHCl_3$	25°	24 h	3 (65%), 4 (35%)
3	Ag foil, C_6H_6	160°	10 d	3 (55%), 5 (45%)
3	$Cu_2(COD)_2Cl_2$, THF	25°	24 h	no rearrangement detectable
4	$Au(C_{10}H_{12})Cl, CHCl_3$	25°	24 h	3 (trace, < 1%), 4 (>99%)
4	$AuCl, (C_2H_5)_2O$	25°	24 h	3 (trace, < 1%), 4 (>99%)
6	Au-reactor	100°	10 s	7 (>90%), 8 (<10%)

planation for this result is the assumption that gold catalyzes the rearrangement of 3 to 4, subsequently 4 undergoes the known thermal rearrangement[10] to 5. Indeed, in the presence of gold(I)-dicyclopentadiene chloride at 25° only 4 was formed from 3. The reason for the different effects of silver(I) and gold(I) on 3 and 4 could be a difference in complex formation ability of 3 and 4 with the two ions. We observed, that silver tetrafluoroborate forms a stable complex with 3 (^{1}H-NMR, acetone-d_6 : δ = 6.20 (dd,2H); 2.70 (m,2H); 1.50 (m,2H); 0.95 ppm (m,4H)) and gold(I) chloride forms complexes with both olefins 3 and 4. However, the gold(I) complex of 3 (^{1}H-NMR, $CDCl_3$: δ = 6.45 (dd,2H); 3.50 (m,2H); 2.40 (m,2H) 1.85 ppm (m,4H)) when dissolved in chloroform slowly rearranges to that of 4 (^{1}H-NMR, $CDCl_3$: δ = 6.35 (dd,2H); 3.95 (m,2H); 3.35 (m,2H); 2.90 ppm (m,4H)). It appears that in both cases there is an equilibrium between 3 and 4. In the presence of silver(I) or silver metal 3 prevails in the equilibrium mixture, only at temperatures above 80° C 4 can be removed continually, therefore at elevated temperatures 3 in contact with metallic silver rearranges to 5. Apparently the double bond in 3 and 4 is essential for the gold catalyzed rearrangements to occur. The corresponding saturated pentacyclo[$4.4.0.0^{2,4}.0^{3,8}.0^{5,7}$]decane ("snoutane") did not rearrange to basketane under the same conditions.

The catalytic effect of the metallic gold surface in the flow reactor cannot be due to impurities in the 99.99% gold. A sample of 99.999% gold wire[11] with $<$ 3 ppm silver and 5 ppm platinum and palladium showed the same catalytic activity (see table).

The rather specific catalytic effect of the gold surface is not limited to the examples shown above. Dispiro[2.0.2.4]deca-7,9-diene (6) on the gold sur-



face rearranges to tetrahydronaphthalene (7) predominantly (>90%) whereas the purely thermal rearrangement of 6 yields 87% o-ethylstyrene (8)[12]. The dispiro[cyclopropan-1,2'-bicyclo[2.2.0]hexan-3',1"cyclopropan] under thermal conditions gives 1,1'-divinylbicyclopropyl but tricyclo[6.2.0.0^{1,4}]dec-4-ene on the gold surface[13]. In all the above mentioned cases the catalyzed reactions could be repressed only partially by using short contact times. One should therefore be careful in using flow reactors made from gold for kinetic measurements at least on small ring compounds[14]. We have surpassed this difficulty with a glass reactor, the surface of which was carefully treated to remove all catalytic activity[6].

References and footnotes

[**] Support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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