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Preliminary communication

THE PALLADIUM-CATALYZED CONJUGATE ADDITION TYPE REACTION OF 2-BROMO-ARYLMERCURY COMPOUNDS AND 2-BROMO-ARYL IODIDES WITH α,β-ENONES: A NEW ENTRY TO 1-INDANOLS

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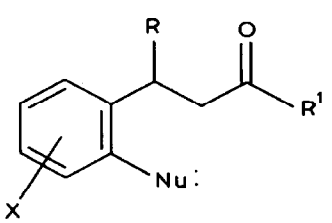
Summary

The palladium-catalyzed reaction of 2-bromoarylmercury compounds or of 2-bromophenyl iodide with α,β-enones gives conjugate addition type products which can be cyclized to 1-indanols in the presence of magnesium.

The palladium-catalyzed reaction of arylmercury compounds containing oxygen and nitrogen nucleophiles in the *ortho* position with α,β-enones has been reported to provide new routes to the chromanol [1] and quinoline [2] skeleton through cyclization of the initially formed conjugate addition type product (I).

It is apparent that open-chain compounds of this kind have potential as convenient reagents for a variety of annulation reactions depending on the nature of the nucleophilic and electrophilic sites. In extension of our studies on palladium-



(I)

(Nu: = HO: , RHN:)

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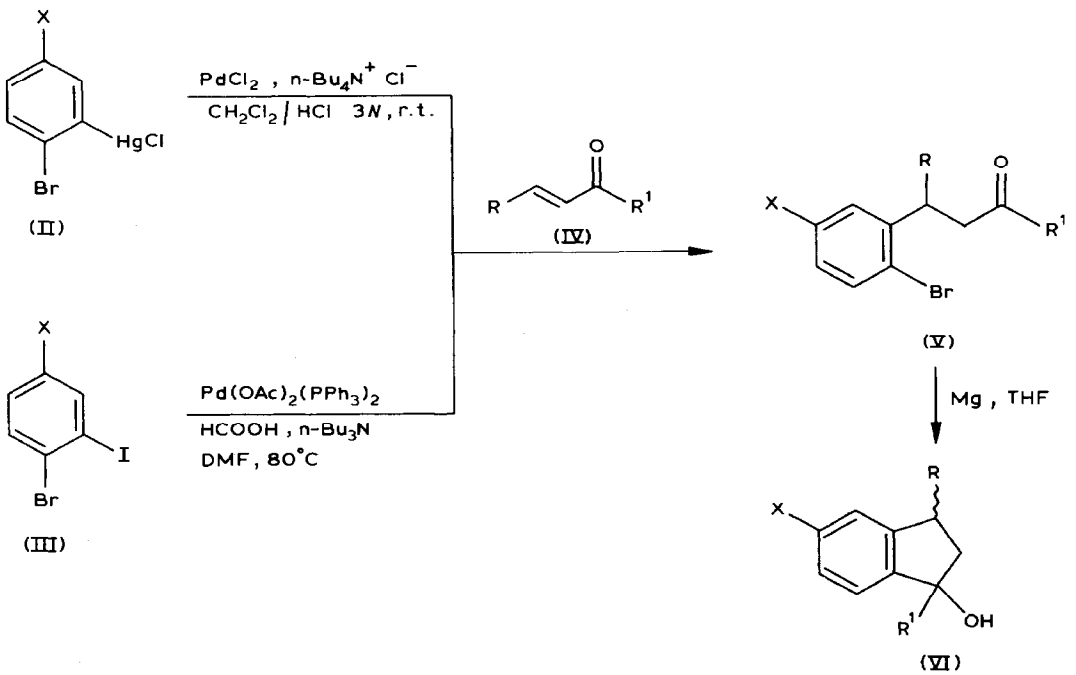
TABLE 1

PALLADIUM-CATALYZED CONJUGATE ADDITION TYPE REACTION OF 2-BROMOARYLMERCURY COMPOUNDS (II) AND 2-BROMOPHENYL IODIDE (III) WITH α,β-ENONES (IV)

Entry	Aryl mercury compound II, X =	Aryl iodide III, X =	α,β-Enone IV R	α,β-Enone IV R^1	Reaction time (h)	Yield of V (%)[a]	M.p. (°C)	IR ν (cm^{-1})	^1H NMR ($CDCl_3$) δ (ppm)
a	MeOCO	—	H	Me	15	87	55—58	1720,1300,1255, 1115,765[b]	7.95—7.40 (m, 3H); 3.90 (s, 3H); 3.15—2.90 (m,2H); 2.90—2.65 (m, 2H); 2.18 (s, 3H)
b	MeOCO	—	Ph	Me	20	83	65—67	1720,1300,1260, 765,705[b]	7.95 (d, *J* 2.0 Hz, 1H); 7.70 (dd, *J* 2.0 Hz, *J* 8.7 Hz, 1H); 7.58 (d, *J* 8.7 Hz, 1H); 7.35—7.10 (m, 5H); 5.08 (t, *J* 7.5 Hz, 1H); 3.83 (s, 3H); 3.19 (d, *J* 7.5 Hz, 2H); 2.08 (s, 3H)
c	HCO	—	H	Me	24	76	56—57	2740,1700,1160, 1030,820,760[b]	9.97 (s, 1H); 7.85—7.50 (m, 3H); 3.20—2.97 (m, 2H); 2.97—2.74 (m, 2H); 2.17 (s, 3H)
d	—	H	H	Et	4	31[d]	oil	1710,1460,1020, 750[c]	7.60—6.90 (m, 4H); 3.13—2.90 (m, 2H); 2.83—2.60 (m, 2H); 2.40 (q, *J* 7.2 Hz, 2H); 1.00 (t, *J* 7.2 Hz, 3H)
e	—	H	Ph	Ph	7	—[e]			

[a] Yields given are for isolated products, and are based on the starting α,β-enone. They refer to single not optimized runs. Reactions were carried out as described in the cited references. [b] Nujol. [c] Liquid film. [d] 1-(2-Bromophenyl)pent-1-en-3-one was also obtained in 42% yield: oil; IR (liquid film) 1670, 1610, 1190, 1120, 1025, 975, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.92 (d, *J* 16.5 Hz, 1H); 7.70—7.07 (m, 4H); 6.63 (d, *J* 16.5 Hz, 1H); 2.71 (q, *J* 7.2 Hz, 2H); 1.15 (t, *J* 7.2 Hz, 3H). [e] Phenyl bromide was obtained in 73% yield, and no addition product was detected in the reaction mixture.

catalyzed addition/cyclization reactions we now report that β-(2-bromoaryl) ketones (V), prepared from 2-bromoarylmercury compounds (II) [2] or 2-bromoaryl iodides (III) [3] and α,β-enones (IV), can be utilized as useful intermediates for the synthesis of 1-indanols (VI).



2-Bromo-5-carbomethoxyphenylmercury chloride (m.p. 192—194°C) and 2-bromo-5-formylphenylmercury chloride (m.p. 183—186°C), obtained from the corresponding arenes [4], and the commercially available 2-bromophenyl iodide were used as the arylpalladium precursors for the synthesis of compounds V (Table 1).

Intramolecular carbon—carbon bond forming reactions were carried out as follows: β-(2-bromo)aryl ketone (V, 2.36 mmol) dissolved in dry tetrahydrofuran (2 ml) is added to magnesium turnings (0.128 g, 5.30 mmol) in a dry flask under nitrogen and the mixture is maintained at gentle reflux. 1,2-Dibromoethane (0.451 g, 2.40 mmol) in dry tetrahydrofuran (2 ml) is added dropwise during 6 h. After 2 h further reflux the mixture is cooled to room temperature, treated with 1 *N* hydrochloric acid to pH 4—5, and extracted with dichloromethane (3 × 50 ml). The organic layer is separated, dried over magnesium sulfate, and concentrated at reduced pressure. The residue is purified by open-column chromatography by eluting with cyclohexane/ethyl acetate mixtures. The purities of compounds VI were checked by HPLC.

Representative results are summarized in Table 2. It can be seen that no significant generalizations can be drawn, but it is evident that, as expected, substituents in the aromatic ring can affect the cyclization step. For example, when cyclization of compound Vc was attempted, a complex reaction mixture of unidentified products was obtained. In addition, preparation of β-(2-bromoaryl) ketones by palladium-catalyzed conjugate addition type of 2-bromoaryl iodides to

TABLE 2

1-INDANOLS (VI) PREPARED

VI			Yield	M.p.	IR	^{1}H NMR ($CDCl_3$)	MS
X	R	R^1	(%)[a]	(°C)	ν (cm^{-1})[b]	δ (ppm)	*m/e*
MeOCO	H	Me	47	oil	3450, 1720, 1275, 1200, 775	7.97—7.25 (m, 3H); 3.87 (s,3H); 3.15—2.65 (m,2H); 2.40 (bs, exchange with D_2O, 1H); 2.33—2.10 (m, 2H); 1.53 (s, 3H)	206,191
MeOCO	Ph	Me	54	oil	3450, 1720, 1295, 1100, 705	8.10—7.10 (m, 8H); 4.23 (bt, *J* 8.6 Hz, 1H); 3.81 (s, 3H); 2.78 (dd, *J* 7.5 Hz, *J* 12.7 Hz, 1H); 2.30 (bs, exchange with D_2O, 1H); 2.26 (dd, *J* 9.7 Hz, *J* 12.7 Hz, 1H); 1.57 (s, 3H)	282,267
H	H	Et	52	oil	3550, 3400, 1170, 1030, 920, 760	7.35—7.05 (m, 4H); 3.05—2.50 (m, 2H); 2.75 (bs, exchange with D_2O, 1H); 2.33—2.87 (m, 2H); 2.87—1.45 (m, 2H); 0.82 (t, *J* 7.2 Hz, 3H)	144,129, 115

[a] Yields given are for isolated products, are based on the amount of starting compound V, and refer to single not optimized runs. [b] Liquid film.

α,β-enones appears to be strongly dependent on the nature of the α,β-unsaturated system. Apparently substituents on the β-carbon slow down the reaction rate (see Table 1, entry e) while the use of β-unsubstituted α,β-unsaturated carbonyl compounds leads to high yields of the vinylic substitution by-products (see Table 1, entry d). Within its limitations, however, this further example of the palladium-catalyzed addition/cyclization methodology in organic synthesis appears to provide a useful route to the indane skeleton. Work is in progress along these lines.

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References

1 S. Cacchi, D. Misiti and G. Palmieri, J. Org. Chem., 47 (1982) 2995.
2 S. Cacchi and G. Palmieri, Tetrahedron, (1983) 3373.
3 S. Cacchi and A. Arcadi, J. Org. Chem., 48 (1983) 4236; S. Cacchi and G. Palmieri, Synthesis, (1984) 575
S. Cacchi, F. La Torre and G. Palmieri, J. Organomet. Chem., 268 (1984) C48.
4 Prepared according to the procedure described for the synthesis of 3-formylphenylmercury chloride (R.F. Heck, J. Am. Chem. Soc., 90 (1968) 5518.).