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Synthesis of 2-Indanones by Intramolecular Insertion of α-Diazoketones

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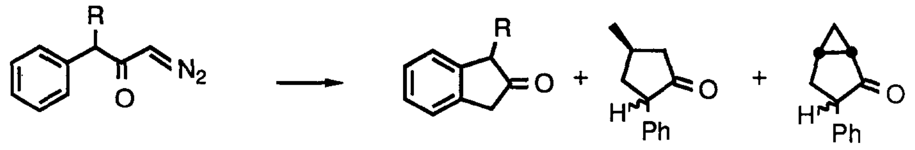
Summary: The reaction of α-diazoketones from phenylacetic acid derivatives affords 2-indanones in good yield. Insertion into the aromatic C-H bond was found to be favored over insertion into an aliphatic one.

In connection with a particular synthetic problem, a simple method was sought for the transformation of phenylacetic acid derivative 1 to the corresponding 2-indanone 3. It is now shown that the goal can be reached via the insertion reaction of a carbenoid species into an aromatic C-H bond.

1 X=OH
2 X=CHN_2
3

The $Rh_2(OAc)_4$–catalyzed decomposition of α–diazoketone and of α–diazo-β–ketoesters has been extensively studied and employed in the synthesis of complex molecules.1) In 1983, Taylor reported that a $Rh_2(OAc)_4$–catalyzed reaction of 5,5-diaryl derivatives of ethyl 2-diazo-3-oxopent-4-enoates afforded naphthoate derivatives.2) It appears, however, that the transformation of simple α-diazoketones from arylacetic acids to afford 2-indanone derivatives has not been developed as a synthetic method.3) It is now shown that the $Rh_2(OAc)_4$–catalyzed intramolecular aromatic C-H bond insertion reaction of α–diazoketones is an efficient reaction.

To a CH_2Cl_2 solution (0.01M) of diazoketone 2, derived from acid 1 by treatment with oxalyl chloride in benzene at room temperature for 4 hours, followed by freshly distilled CH_2N_2 in ether (83% yield), 5 mol% of $Rh_2(OAc)_4$ was added. After gas evolution ceased, the usual work up afforded 2-indanone derivative 3 in 98% yield. No trace of the possible bicyclo[3,2,1]-octanone derivative could be seen in the ^{1}H-NMR spectrum of the crude product. In the case of the α–diazoketone 6 (entry 2,table), however, both the aromatic and aliphatic C-H bond insertion products (7 and 8) were observed in 65% and 13% yields, respectively. The partition between C-H bond insertion and intramolecular cyclopropanation[4] was also examined (entry 3). In this case, the C-H insertion product 10 was obtained as a minor product in 26% yield. The cyclopropanation reaction was preferred over C-H insertion by a factor of 5.



1	4 (R=H)	5 42%	--------	--------	
2	6 (R=n-Pr)	7 65%	8* 18%	--------	5:1**
3	9 (R=allyl)	10 26%	--------	11* 63%	1:4.8*

* a mixture of stereoisomers

** statistically corrected ratio of two products

References and notes:

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1. a) D.E.Cane and P.J.Thomas, *J.Am.Chem.Soc.*,106,5295(1984).b) D.F.Taber and J.L.Schuchardt, *ibid.*,107,5289(1985). c) V.B.Rao and C.F.George and W.C.Agosta, *ibid.*,107,5732(1985). d) M.P.Doyle, *Chem.Rev.*,86,919(1986).
2. E.C.Taylor and H.M.L.Davis, *Tetrahedron Lett.*,24,5453(1983). McKervey has also reported the synthesis of 2-Tetralones via $Rh_2(OAc)_4$-catalyzed cyclization of α-diazoketones derived from 3-arylpropionic acids. M.A.McKervey, S.M.Tuladhar and M.F.Twohig, *J.Chem.Soc.,Chem.Commun.*,129(1984). In both cases the reaction seems to involve addition to the aromatic nucleus. For an early study of copper-catalyzed reaction of diazoketones which led to some aromatic substitution, see H.Ledon,G.Linstrumelle and S.Julia, *Tetrahedron*, 29,3609(1973).
3. In a private communication to G.Stork, D.F.Taber indicated that he had recently observed the $Rh_2(OAc)_4$-catalysed intramolecular aromatic C-H insertion of α-diazo-β-ketoesters, leading to carbalkoxy indanones. The formation of a small yield of indanone as a byproduct of an insertion reaction into a pyrrole has been reported. C.W.Jefford and A.Zaslona, *Tetrahedron Lett.*,26, 6035(1985).
4. For a review of this reaction, first reported by Stork (G.Stork and J.Ficini, *J.Am.Chem.Soc.*, 83,4678(1961).), see S.D.Burke and P.A.Grieco, *Organic Reactions*,26,361(1979).

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