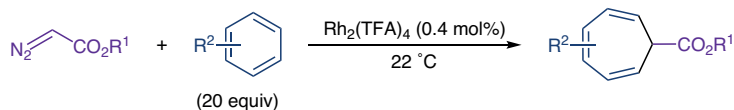


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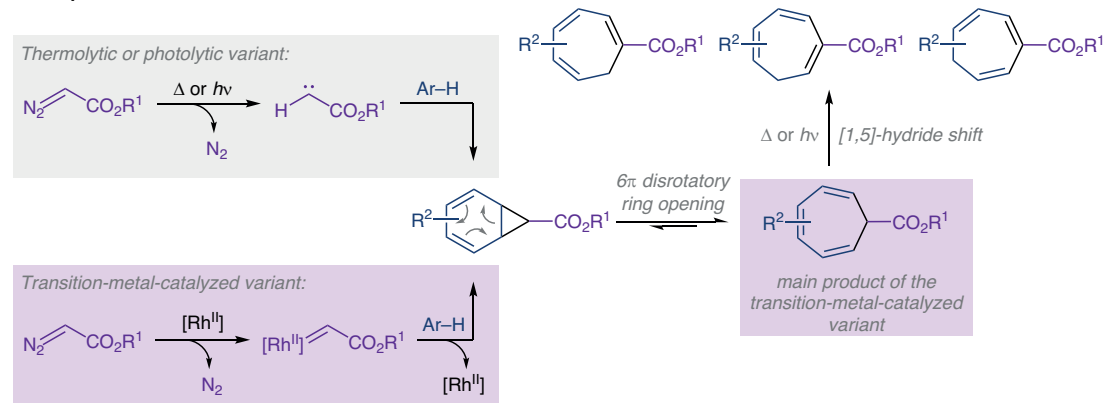
Transition-Metal-Catalyzed Reactions of Diazo Compounds. 2. Addition to Aromatic Molecules: Catalysis of Buchner's Synthesis of Cycloheptatrienes

J. Org. Chem. **1981**, *46*, 873–876, DOI: 10.1021/jo00318a010

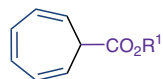
The Transition-Metal-Catalyzed Buchner Reaction: Ring Expansion of Arenes to Cycloheptatrienes



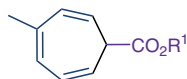
— Proposed mechanism: —



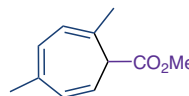
— Selected examples: —



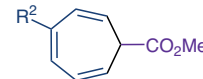
R¹ = Me: >99% yield
R¹ = Et: 98% yield
R¹ = *t*-Bu: 80% yield



R¹ = Me: 95% yield, rr = 56:23:17
R¹ = Et: 89% yield, rr = 70:15:10
R¹ = *t*-Bu: 45% yield, rr = 32:13:0



90% yield
rr = 85:10:5



R² = OMe: 73% yield, rr = 56:8:29
R² = Cl: 72% yield, rr = 80:15:5

Significance: Discovered in 1885, the Buchner reaction transforms arenes into cycloheptatrienes (*Ber. Dtsch. Chem. Ges.* **1885**, *18*, 2377–2379). In the seminal work, a carbene is generated in situ at high temperature or under light irradiation, and then undergoes insertion into an arene to form a norcaradiene. Reversible 6 π disrotatory electrocyclic ring opening and [1,5]-hydride migration then leads to a complex isomeric mixture of ‘Buchner esters’. The transition-metal-catalyzed variant, first reported by Noels, Hubert and co-workers in 1981, allows for much milder reaction conditions to generate a metal carbenoid species and usually yields the kinetic non-conjugated cycloheptatrienyl ester as one main regioisomer.

Comment: While rhodium(II) complexes are typically used, silver(I), copper(II) and iron(III) have also been reported as efficient catalysts for this transformation. Intramolecular variants have proven to be extremely useful and regioselective, and have been applied in several total syntheses.¹ More recently, the scope of carbene source has been extended to alkynes as a less dangerous alternative to diazo compounds and also includes asymmetric variants.²
Reviews: (1) S. E. Reisman, R. R. Nani, S. Levin *Synlett* **2011**, *17*, 2437–2442. (2) G. Ma, K.-F. Wei, M. Song, Y.-L. Dang, Y. Yue, B. Han, H. Su, W.-B. Shen *Org. Biomol. Chem.* **2023**, *21*, 5150–5157.