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CYCLOHEPTATRIENE SYNTHESES THROUGH RHODIUM(II) ACETATE-CATALYZED INTRAMOLECULAR ADDITION REACTIONS OF N-BENZYLDIAZOACETAMIDES

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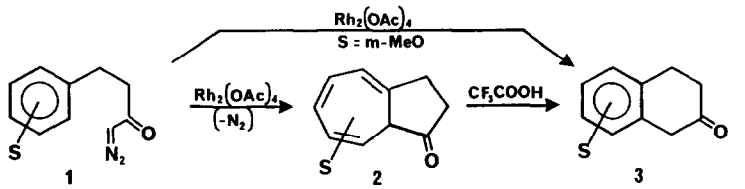
Summary: Rhodium(II) acetate catalyzes high yield intramolecular conversions of N-benzyldiazoacetamides to azabicyclo[5.3.0]decatrienones, and the controlling influences of amide substituents on this transformation have been determined.

Carbene addition reactions with aromatic compounds provide a potentially convenient route to cycloheptatrienes,[1-5] but this approach has rarely been employed as a viable synthetic method because of low yield conversions or multiple products that often characterize reactions with carbenoid intermediates generated thermally, photochemically, or through the use of copper catalysts from diazo compounds. Recently, a major improvement in the technology for this transformation has occurred with the use of rhodium(II) carboxylates for decomposition of ethyl diazoacetate resulting in carbenoid addition to benzene and substituted benzenes possessing electron-donating substituents;[6] cycloheptatriene derivatives were formed in moderate to nearly quantitative yields. Relying upon this discovery, McKervey and coworkers reported that α-diazoketones derived from 3-arylpropionic acids (**1**) underwent efficient intramolecular cyclization to bicyclo[5.3.0]decatrienones **2** and, directly with m-methoxy derivatives or subsequently by treatment of **2** with trifluoroacetic acid under mild conditions, 2-tetralones **3** (eq. 1).[7] The

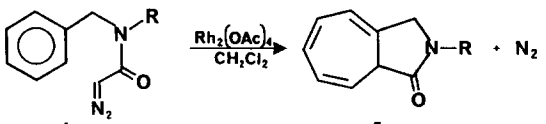


(1)

intermolecular analog leading to benzyl ketones has also been described.[8] However, despite the high yield conversions of **1** to **2** or **3**, similar transformations have not been reported to be nearly so efficient when a heteroatom

is incorporated into the diazo compound, and low yields or multiple products often characterize the limited number of examples that have been reported thus far.[9,10] We have undertaken investigations of intramolecular carbenoid addition reactions that occur upon treatment of N-benzyldiazoacetamides with $Rh_2(OAc)_4$, and we now report the expanded versatility of this catalytic method and the factors that control its selectivity for addition.

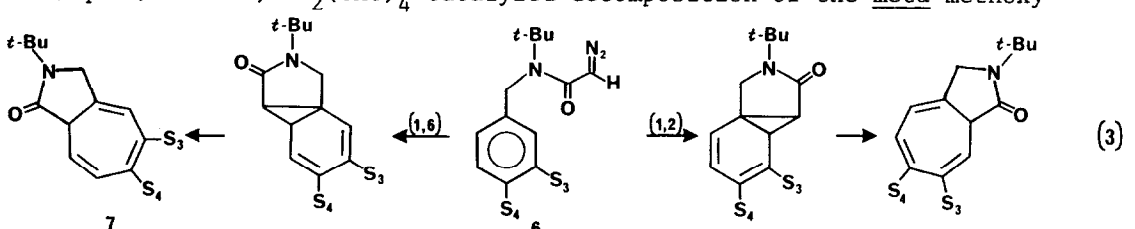
Diazoacetamides were prepared from their corresponding secondary amines by diketene addition,[11] diazo transfer,[12] and deacylation[13] according to established procedures. Treatment of **4a** (R = t-Bu) with $Rh_2(OAc)_4$ (1.0 mol %) at room temperature in anhydrous dichloromethane resulted in the rapid evolution of nitrogen and the formation of azabicyclo[5.3.0]decatrienone **5a**[14] (eq. 2) in quantitative yield. This transformation was remarkably free of



4 5 (2)

competing reactions, and analytically pure samples were conveniently obtained following chromatographic purification. Unlike **2**,[7] however, **5a** was insensitive to either trifluoroacetic acid or boron trifluoride etherate, even in excess, and unrearranged reactant was recovered intact even after prolonged treatment at 25°C. Similarly, **4b** (R = CH_2Ph) produced **5b** in 93% isolated yield without evidence of any other competing process. In contrast, the $Rh_2(OAc)_4$-catalyzed decomposition of the N-methyl derivative **4c** was complex, resulting in **5c** (37%) and at least two other major products, both of which were dimeric but not amide derivatives of fumarate or maleate. Use of rhodium(II) perfluorobutyrate ($Rh_2(pfb)_4$)[15] in place of $Rh_2(OAc)_4$ produced a substantial increase in the yield of **5c** (54%), but with rhodium(II) acetamide ($Rh_2(NHCOCH_3)_4$)[16] the yield of this product was only 21%.

Although para substituents in the benzyl group do not influence the selectivity of carbene addition to the aromatic nucleus,[7] meta substituents do (eq. 3). Thus, $Rh_2(OAc)_4$-catalyzed decomposition of the meta-methoxy

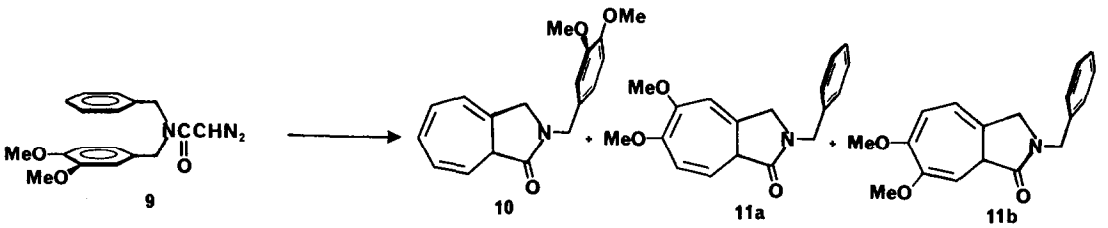


7 6 8 (3)

94%	a S_3 = OMe, S_4 = H	6%
66%	b S_3 = OMe, S_4 = OMe	34%
70%	c S_3 = Br, S_4 = H	30%

derivative **6a** produced two isomers, **7a** and **8a**, in a combined isolated yield of 93%. In this case the predominant isomer (94% relative yield) was **7a**,[17] demonstrating that preferential addition occurred at the 1,6-position of the aromatic nucleus. A similar result has been reported by McKervey and coworkers[7] for the decomposition of **1** (S = m-MeO), although they were unable to intercept **2**. With **6b**, **7b** and **8b** were produced in a 2:1 ratio (94% isolated yield) in contrast to a 4:1 ratio obtained from 3,4-dimethoxy-substituted **1**; in both cases, the methoxy group at the 4-position diminishes the selectivity for addition caused by the electron-donating influence of the m-methoxy substituent. In contrast, a 3-bromo substituent (**6c** → **7c** + **8c**, 89% isolated yield) offers limited selectivity for addition.

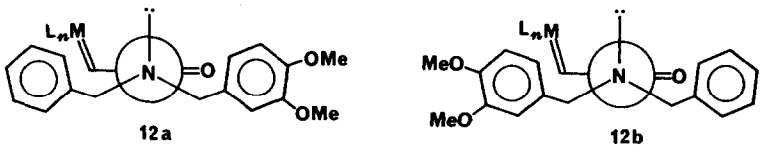
If relative reactivity is a function of the electron-donating ability of substituents, then preferential addition should occur into the activated aromatic nucleus of an unsymmetrically substituted N,N-dibenzyldiazoacetamide. However, rhodium(II) acetate-catalyzed decomposition of N-benzyl-N-(3,4-dimethoxybenzyl)diazoacetamide (**9**) exhibits just the opposite preference (eq. 4)



(4)

$Rh_2(OAc)_4$	61%	26%	13%
$Rh_2(NHCOCH_3)_4$	57%	30%	13%
$Rh_2(pfb)_4$	51%	27%	22%

with addition to the unsubstituted benzyl group occurring in the higher relative yield (91% isolated yield of **10** + **11**). Other rhodium(II) catalysts give results similar to those obtained with the use of $Rh_2(OAc)_4$. These data are consistent with carbenoid addition to the aromatic nucleus from conformations **12a** and **12b** that occurs on a time scale which is more rapid than rotation



around the carbonyl-nitrogen bond. Results that we have obtained demonstrate that the preferred orientation of the intermediate is **12a** rather than **12b**. Additional confirmation is found in results from $Rh_2(OAc)_4$-catalyzed decomposition of N-benzyl-N-(p-chlorobenzyl)diazoacetamide where the expected two addition products are formed in 96% yield with a selectivity of only 58:42 favoring addition to the unsubstituted benzene ring.[18] This interpretation

also explains the yield improvement observed with the use of tert-butyl- as compared with methyl-substituted diazoacetamides since the orientation favored with the N-tert-butyl substituent will be that in which the benzyl group is closest to the metal carbene center. A similar influence by the N-tert-butyl group is evident in results from the trifluoroacetic acid-promoted cyclization of N-benzyldiazoacetamides reported in the accompanying communication by Schwartz and Rishton.

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14. ^{1}H NMR of **5a** ($CDCl_3$, 300 MHz): δ 6.52-6.40 (m, 2H), 6.18-6.19 (m, 2H), 5.27 (d of d, J = 9.6, 3.5 Hz, 1H), 4.29 (s, CH_2N), 3.05 (s, CHCO), and 1.47 (s, t-Bu). IR (neat): 1688 cm^{-1} (C=O). Anal. Calcd. for $C_{13}H_{17}NO$: C, 67.53; H, 7.36. Found: C, 67.52; H. 7.38.
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17. ^{1}H NMR of **7a** ($CDCl_3$, 300 MHz): δ 6.09 (m, J = 9.5, 7.0, 6.8 Hz, 1H), 5.99 (d of d, J = 2.2, 1.1 Hz, 1H), 5.63 (d of d, J = 7.0, 1.0 Hz, 1H), 5.11 (d of d, J = 9.5, 3.4 Hz, 1H), 4.28 (s, CH_2N), 3.13 (br s coupled to absorptions at δ 6.09 and 5.11, CHCO), and 1.46 (s, t-Bu). ^{13}C NMR ($CDCl_3$): δ 174.2 (C=O), 158.8, 132.5, 125.1, 117.3, 116.4, 102.5, 54.6, 49.6, 47.4, and 27.6.
18. Competitive intermolecular addition to benzene and chlorobenzene with methyl diazoacetate favors reaction with benzene by a factor of 10 (see ref. 6a).

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