6.15 (s, 1 H, vinylic), and 7.45–7.90 (m, 5 H, aromatic); exact mass calcd for $C_{11}H_{14}SO_3$ (M^+) 226.1226, found 226.1231.

Acknowledgment. This investigation was supported by National Science Foundation Grant CHE 8019750.

Registry No. 1, 73476-18-3; 2, 111976-51-3; 3 (R'p = CH_2=$CHCH_2$), 84363-58-6; 3 (R'p = C_2H_5), 84363-54-2; 3 (R'p = $CH_3(CH_2)_3$), 84363-55-3; 3 (R'p = $CH_3(CH_2)_7$), 73476-19-4; 3 (R'p = $(CH_3)_3C(CH_2)_2$), 84363-57-5; 3 (R'p = $C_6H_5CH_2$), 84363-59-7; 3 (R'p = TMS), 111976-52-4; 5 (R'p = R^2p = $CH_3(CH_2)_3$), 111976-53-5; 5 (R'p = $(CH_3)_3C(CH_2)$ R^2p = CH_2=$CHCH_2$), 111976-54-6; 5 (R'p = C_2H_5, R^2p = $C_6H_5CH_2$), 111976-56-8; 8 (R'p = R^2p = $CH_3(CH_2)_3$), 6795-79-5; 8 (R'p = $(CH_3)_3C(CH_2)_2$, R^2p = CH_2=$CHCH_2$, 111976-55-7; 8 (R'p = C_2H_5, R^2p = $C_6H_5CH_2$), 3968-89-6; 15, 111976-57-9; 16, 111976-58-0; *E*-18 (R' = H, R^2 = C_6H_5), 40595-34-4; *Z*-18 (R' = C_6H_5, R^2 = H), 40595-35-5; 18 (R' = R^2 = CH_3), 18293-99-7; 18 (R' = R^2 = C_6H_5), 83438-57-7; 18 (R', R^2 = -$(CH_2)_4$), 83438-58-8; *E*-18 (R' = H, R^2 = $(CH_3)_2C$=CH), 83438-69-1; *Z*-18 (R' = H, R^2 = $(CH_3)_2C$=CH), 83438-60-2; 18 (R' = R^2 = C_2H_5), 63922-77-0; 18 (R', R^2 = -$(CH_2)_3$), 83438-59-9; 18 (R', R^2 = -$(CH_2)_5$), 63922-76-9; 23, 111976-61-5; 24, 111976-59-1; 25, 111976-60-4; 26, 111976-62-6; 28, 111976-63-7; 29, 111976-64-8; 34 (R' = CH_3), 84363-73-5; 34 (R' = $(CH_3)_2CH$), 111976-65-9; 34 (R' = $CH_3(CH_2)_2$), 111976-66-0; 34 (R' = $(CH_3)_2CHCH_2$), 111976-67-1; 34 (R' = c-C_6H_{11}), 111976-68-2; 34 (R' = C_6H_5), 111976-69-3; 35 (R' = CH_3), 13506-88-2; 35 (R' = $(CH_3)_2CH$), 17869-46-4; 35 (R' = $CH_3(CH_2)_2$), 15047-42-4; 35 (R' = $(CH_3)_2CHCH_2$), 13506-98-4; 38a, 111976-70-6; 38b, 111976-72-8; 39a, 111976-71-7; 39b, 111976-73-9; 42 (from ethylene oxide), 111976-74-0; 42 (from 1-butylethylene oxide), 111976-75-1; 42 (from cyclohexene oxide), 111976-76-2; 42 (from methylenecyclohexane oxide), 111976-77-3; 42 (from propylene oxide), 111976-78-4; 42 (from styrene oxide), 111976-79-5; 42 (from cyclopentene oxide), 111976-80-8; 43, 111976-81-9; 46a, 111976-82-0; 46b, 111976-79-5; 47a, 22628-88-2; 47b, 29817-09-2; 48 (R'p = C_2H_5), 84363-60-0; 48 (R'p = $CH_3(CH_2)_3$), 84363-61-1; 48 (R'p = $CH_3(CH_2)_5$), 84363-62-2; 48 (R'p = $(CH_3)_3C(CH_2)_2$), 84363-66-6; 48 (R'p = CH_2=$CHCH_2$), 84363-67-7; 48 (R'p = $C_6H_5CH_2$), 84363-68-8; 49 (R'p = C_2H_5), 84363-63-3; 49 (R'p = $CH_3(CH_2)_3$), 84363-64-4; 49 (R'p = $CH_3(CH_2)_5$), 84363-65-5; 49 (R'p = $(CH_3)_3C(CH_2)_2$), 84363-69-9; 49 (R'p = CH_2=$CHCH_2$), 84363-70-2; 49 (R'p = $C_6H_5CH_2$), 84363-71-3; 50, 84363-74-6; 51, 84363-75-7; 52, 111976-83-1; 53, 84363-73-5; 54, 111976-84-2; 55, 64489-06-1; 56 (R' = $CH_3(CH_2)_2$), 111976-85-3; 56 (R' = $(CH_3)_2CH$), 111976-86-4; 56 (R' = $(CH_3)_2CHCH_2$), 111976-87-5; 56 (R' = C_6H_5), 111976-88-6; 59 (R' = H, R^2 = $CH_3(CH_2)_2$), 84363-76-8; 59 (R' = H, R^2 = $(CH_3)_2CH$), 84391-09-3; 59 (R' = H, R^2 = c-C_6H_{11}), 84391-10-6; 59 (R' = H, R^2 = CH_2=CH), 84363-78-0; 59 (R' = H, R^2 = C_6H_5), 84363-77-9; 59 (R' = R^2 = CH_3), 111976-89-7; 59 (R' = CH_3, R^2 = C_2H_5), 111976-90-0; 59 (R', R^2 = -$(CH_2)_5$), 111976-91-1; 59 (R', R^2 = -$(CH_2)_3$), 111976-92-2; 60 (R' = H, R^2 = $CH_3(CH_2)_2$), 84363-80-4; 60 (R' = H, R^2 = $(CH_3)_2CH$), 84363-79-1; 60 (R' = H, R^2 = c-C_6H_{11}), 84363-81-5; 60 (R' = H, R^2 = CH_2=CH), 84363-83-7; 60 (R' = H, R^2 = C_6H_5), 84363-82-6; 60 (R' = R^2 = CH_3), 111976-93-3; CH_3CH_2Br, 74-96-4; $CH_3(CH_2)_3Br$, 109-65-9; $CH_3(CH_2)_5I$, 638-45-9; $(CH_3)_3C(CH_2)_2Br$, 1647-23-0; CH_2=$CHCH_2Br$, 106-95-6; $C_6H_5CH_2Br$, 100-39-0; $ClSi(CH_3)_3$, 75-77-4; CH_2=$CH(CH_2)_5CH_3$, 111-66-0; CH_2=$CH(CH_2)_2C(CH_3)_3$, 7116-86-1; CH_2=$CHCH_2C_6H_5$, 300-57-2; C_6H_5CHO, 100-52-7; $CH_3C(O)CH_3$, 67-64-1; $C_6H_5C(O)C_6H_5$, 119-61-9; c-C_5H_8(=O), 108-94-1; $(CH_3)_2C$=CHCHO, 107-86-8; $C_2H_5C(O)C_2H_5$, 96-22-0; c-C_4H_6(=O), 1191-95-3; c-C_6H_{10}(=O), 108-94-1; HCHO, 50-00-0; $(CH_3)_2NH$, 124-40-3; CH_3CHO, 75-07-0; $(CH_3)_2CHCHO$, 78-84-2; $CH_3(CH_2)_2CHO$, 123-72-8; $(CH_3)_2CHCH_2CHO$, 590-86-3; c-$C_6H_{11}CHO$, 2043-61-0; CH_3OCH_2Cl, 107-30-2; CH_2=CHCHO, 107-02-8; $CH_3C(O)C_2H_5$, 78-93-3; 1,1-diphenylethylene oxide, 882-59-7; ethylene oxide, 75-21-8; 1-butylethylene oxide, 1436-34-6; cyclohexene oxide, 286-20-4; methylenecyclohexane oxide, 185-70-6; propylene oxide, 75-56-9; styrene oxide, 96-09-3; cyclopentene oxide, 285-67-6; 2-(phenylsulfonyl)-3-methoxy-1-propene, 84363-84-8; 1-octene oxide, 2984-50-1.

Rhodium(II) Acetate Catalyzed Reactions of 2-Diazo-1,3-indandione and 2-Diazo-1-indanone with Various Substrates

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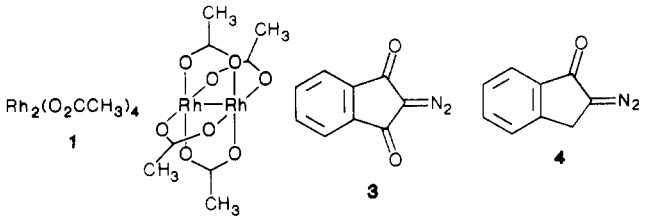
Decomposition of 2-diazo-1,3-indandione (3) by rhodium(II) acetate (1) in cyclohexane and in benzene results in overall carbon–hydrogen insertion to give 2-substituted 1,3-indandiones. Anisole, 1, and 3 yield 2-(4-methoxyphenyl)-1,3-indandione (74%); benzenes substituted by single methyl or halogen groups yield the corresponding ortho- and para-substitution products. Spirocyclopropanes are obtained by rhodium(II)-catalyzed additions of 3 to olefins; electron-deficient olefins do not give adducts. Substituted 4*H*-indeno[1,2-*b*]furan-4-ones and 2,3-disubstituted spiro[cyclopropene-1,2'-[2*H*]indene]-1',3'-diones are formed from rhodium(II)-catalyzed reactions of 3 with acetylenes. Reactions of 1 and 3 with cyclohexane, olefins, acetylenes, and arenes involve selective electrophilic carbenic or ylidic processes. 2-Diazo-1-indanone (4) is converted by 1 to 2,2'-bis[indan-1-one] (48). Thiophenol reacts with 4 and 1 to yield 2-(phenylthio)-1-indanone (49). Cyclopropanations of cyclohexene and styrene by 4 as catalyzed by 1 result in spiro[bicyclo[4.1.0]heptane-7,2'-[2*H*]indan]-1-one (50) and 2-phenylspiro[cyclopropane-1,2'-[2*H*]inden]-1'(3'*H*)-one (51), respectively.

Rhodium(II) acetate (1) is a dimer of $Rh(O_2CCH_3)_2$ containing a rhodium–rhodium single bond and four acetate ligands symmetrically attached to the two rhodium atoms as in 2.[1] Diazo compounds frequently react advantageously in the presence of 1 and related rhodium catalysts.[2] The behavior of 2-diazo-1,3-indandione (3) and 2-diazo-1-indanone (4) with 1 in varied substrates is now reported.

(1) (a) Christoph, G. G.; Yoh, Y.-B. *J. Am. Chem. Soc.* **1979**, *101*, 1422. (b) Adducts are formed from 1 with electron-donating basic ligands such as methanol, water, and tetrahydrofuran but not with olefins. These adducts are stable, crystalline compounds that decompose to 1 upon heating.[1c] (c) Johnson, S. A.; Hunt, H. R.; Neumann, H. M. *Inorg. Chem.* **1963**, *2*, 690.

(2) For summaries of the literature of the utility of 1 in synthesis, see: (a) Maas, G. *Top. Current Chem.* **1987**, *137*, 75. (b) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919. (c) Wulfman, D. S.; Linstrumelle, G.; Cooper, C. F. In *The Chemistry of the Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley: New York, 1978; Part 2, Chapter 18. (d) References in 2a–c.

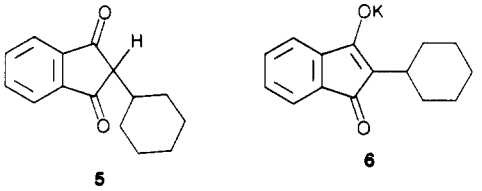
0022-3263/88/1953-2699$01.50/0



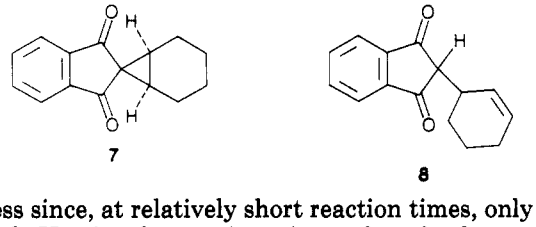
Results and Discussion

Diazo ketone **3** is a readily prepared and handleable solid[3] that is stable to ordinary light and loses nitrogen at ~170 °C. The stability of **3** is revealed upon determining that it does not decompose in or react thermally with refluxing benzene, cyclohexane, cyclohexene, phenylacetylene, styrene/toluene, or *p*-nitrostyrene/toluene or with methyl vinyl ketone, phenyl vinyl sulfone, maleic anhydride, or *p*-benzoquinone under various conditions. Further, little reaction of **3** occurs with benzene (78 °C, 5.5 h) or phenylacetylene (65 °C, >10 h) in the presence of copper(II) acetylacetonate or palladium(II) acetate.[4] Some type of effective catalysis is clearly necessary for **3** to function thermally as a carbenoid or a carbenic reagent.

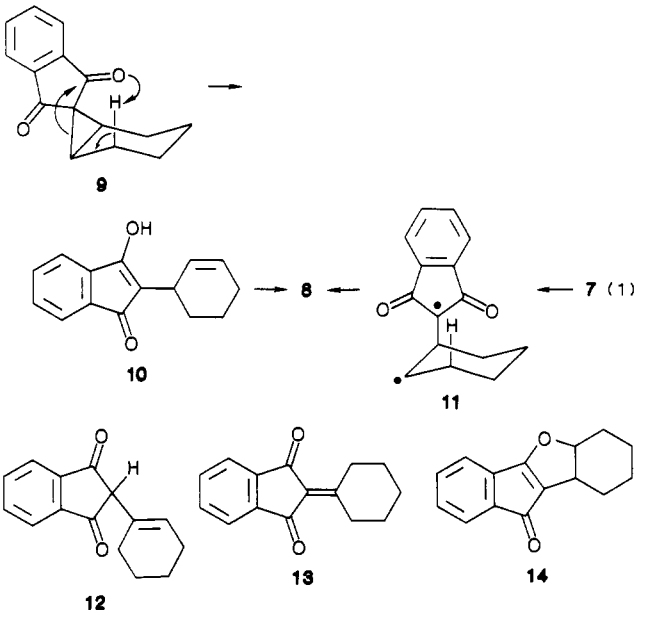
Reaction of **3** occurs with **1** in catalytic quantity in refluxing cyclohexane (78 °C, 17 h) to give 2-cyclohexyl-1,3-indandione (**5**, >53%). The significant results are that the reaction is accelerated further by additional **1** and an intermediate is generated that inserts into secondary carbon–hydrogen (C–H) bonds. The structure of **5** is established from its analysis, its MS, IR, and NMR spectra, and its conversion to **6** by aqueous potassium hydroxide.



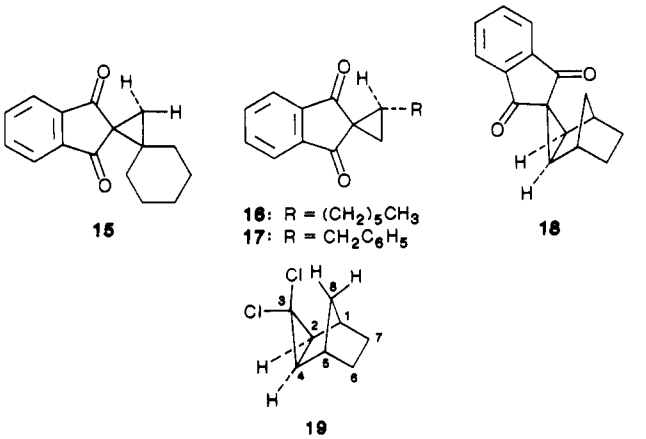
Study has been made of reactions of **3** and **1** with varied olefins. Decomposition of **3** by **1** in refluxing cyclohexene yields spiro[bicyclo[4.1.0]heptane-7,2′-[2*H*]indene]-1′,3′-dione (**7**, 41%) and 2-(3-cyclohexenyl)-1,3-indandione (**8**, 25%). Cyclopropanation to **7** is by far the dominant



process since, at relatively short reaction times, only **7** is formed. Heating the reaction mixture for a few hours then leads to detection of **8**. Confirmation that **7** is the initial product which then isomerizes to **8** is obtained upon determining that **7** converts to **8** (100%) in 3 days in warm cyclohexene. Products **7** and **8** are assignable from their elemental, MS, and NMR analyses. Pathways for isomerization of **7** to **8** (eq 1) include (1) rearrangement as **9** to enol **10** and then **8** and/or (2) homolytic (or heterolytic) ring opening of **7** to diradical **11** (or its zwitterion), which isomerizes by a five-membered path to **8**. The possible isomers 2-(1-cyclohexenyl)-1,3-indandione (**12**), 2-cyclohexylidene-1,3-indandione (**13**) and dihydrofuranoindene **14** are not detectable.



Decomposition of **3** by **1** at 70–80 °C in methylenecyclohexane, 1-octene, allylbenzene, and norbornene, respectively, yields the following cyclopropanated derivatives: 2,2-pentamethylenespiro[cyclopropane-1,2′-[2*H*]indene]-1′,3′-dione (**15**, 46%), 2-*n*-hexylspiro[cyclopropane-1,2′-[2*H*]indene-1′,3′-dione (**16**, 72%), 2-benzylspiro[cyclopropane-1,2′-[2*H*]indene]-1′,3′-dione (**17**, 46%) and (1′α,2′β,4′β,5′α)-spiro[2*H*-indene-2,3′-tricyclo[3.2.1.0^{2,4}]octane]-1,3-dione (**18**, 16%). Products from dipolar addition, thermal ring opening, or oxyvinylcyclopropane rearrangement are not formed. In **18**, the anti and syn protons on the bridging methylene exhibit NMR ($CDCl_3$) absorptions at δ 0.79 and 2.84, respectively, with a coupling constant of J = 10.5 Hz. The exo stereochemistry of **18** is presumed on the basis of steric factors during addition and the NMR spectrum of the product is compatible with that of 3,3-dichloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane (**19**).[5] The anti and syn protons at C-8 in **19** resonate at δ 0.76 and 2.14, respectively, with a coupling constant of J = 10.9 Hz. Thus the bridging methylene group in **18** shows similar environmental differences as that in **19**.



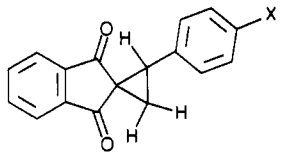
Research then involved rhodium(II) acetate catalyzed reactions of **3** with styrene and various para-substituted

(3) Regitz, M.; Schwall, H.; Heck, G.; Eistert, B.; Bock, G. *Justus Liebigs Ann. Chem.* **1965**, *690*, 125.

(4) Essentially all (>82–95%) of **3** is recovered in these experiments. Copper(II) acetylacetonate, 1-octene, and **3** at 110 °C for 27 h give **16** (27%) and recovered **3** (53%). Palladium(II) acetate, 1-octene, and **3** result in 84% recovery of **8** and an 8% yield of **16**.

(5) DeSelms, R. C.; Combs, C. M. *J. Org. Chem.* **1963**, *28*, 2206.

styrenes. Many experiments were conducted with **3** and **1** in styrene to find conditions for preparing 2-phenylspiro[cyclopropane-1,2′-[2*H*]indene]-1′,3′-dione (**20**) efficiently. Decomposition of **3** by **1** in styrene/toluene at 80 °C gives **20** (72%). Upon heating of **3** and **1** in styrene/toluene at 100 °C, the major process is aromatic substitution (44%) of toluene, as will be discussed later. When reaction of **3**, **1**, and styrene is effected in tetrahydrofuran to increase the catalyst's solubility, conversion to **20** decreases to 24%. Yields of **20** from **3**, **1**, and styrene range from 25% to 72% with only minor changes in experimental conditions. The 72% yield of **20** is a repeatable preparative result for an experimentalist with experience in rhodium(II) acetate catalyzed cyclopropanations of styrene with **3**. Efficiencies to **20** of 46% are obtained from **3** and "recovered" **1** in styrene/toluene at 80 °C (6.5 h) and thus **1** functions as a true catalyst.

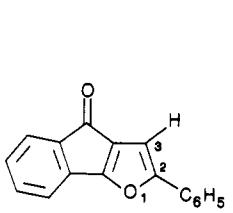


20: X = H, 63–72%
21: X = OCH_3, 0%
22: X = CH_3, 54–59%
23: X = Cl, 80–82%
24: X = Br, 52–53%
25: X = NO_2, 46–48%

Study has also been made of reactions of **3** and varied para-substituted styrenes ($H_2C{=}CHC_6H_4$-*Zp*; *Zp* = OCH_3, CH_3, Cl, Br, and NO_2) in 1:10 mole ratio with **1** at 80 °C in toluene. Intractable products are formed in the experiments with *p*-methoxystyrene. With the other para-substituted styrenes, spirocyclopropanes **22–25** are produced as sharp melting solids identifiable spectrally and by elemental analyses. The structures of **22–25** are clearly assignable from their ^1H NMR, all of which reveal two sets of multiplet absorptions in aromatic regions as well as triplet absorptions for methine hydrogens and multiplet absorptions for the methylene groups of the cyclopropanes.[6]

The relative rhodium(II) acetate catalyzed reactivities of **3** with certain olefin pairs have been determined. Decomposition of **3** with **1** in mixtures of 1-octene (10 equiv) and styrene (10 equiv) at 80 °C gives **16** and **20** in 13.5% and 62.9% yields, respectively. The ratio of **20** to **16**, and thus the relative reactivity of styrene to 1-octene, is 4.67. In a second competitive system, **3** (1 equiv) and **1** in 1-octene (10 equiv) and *p*-nitrostyrene (10 equiv) at 80 °C yield **16** (18.9%) and **25** (48.0%). The ratio of cyclopropanated *p*-nitrostyrene (**25**) to cyclopropanated 1-octene (**16**) is 2.55. The relative rate experiments thus reveal that (1) the reactivities of the olefins studied are styrene > *p*-nitrostyrene > 1-octene and (2) the catalyzed decomposition reactions of **3** by **1** involve attack on carbon–carbon double bonds by an electron-deficient reagent.

Decomposition of **3** by **1** in phenylacetylene at 50–60 °C results in 2-phenyl-4*H*-indeno[1,2-*b*]furan-4-one (**26**, 91%). Cycloadduct **26** is assigned from its elemental analysis, its IR carbonyl absorption at 1718 cm^{-1}, its NMR absorptions at δ 7.77–7.03 (m, 9 H, phenyl and indanyl *H*) and 6.67 (s, H, 3-furanyl *H*), and the similarity of its β-furanyl hydrogen resonance (δ 6.67) with that (δ 6.99) in phenylfuranoacenaphthene **27**.[7] 1,3-Dipolar addition to phenylacetylene is thus regiospecific in that the product obtained (**26**) has its furanyl hydrogen in the 3-position. The orientation in cycloaddition is that expected for attack of an electron-deficient ketocarbenoid intermediate on phenylacetylene and is identical with that for copper-catalyzed[8] and for photolytic reactions[9] of α-diazocarbonyl compounds with monoalkyl- and monoarylacetylenes.



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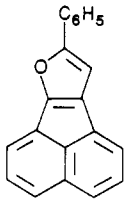

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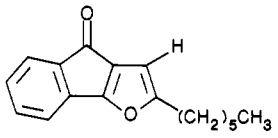
Rhodium(II) acetate catalysis of **3** in 1-octyne results in both possible regioisomers from net 1,3-dipolar cycloaddition: 2-*n*-hexyl-4*H*-indeno[1,2-*b*]furan-4-one (**28**, 28%) and 3-*n*-hexyl-4*H*-indeno[1,2-*b*]furan-4-one (**29**, 15%).



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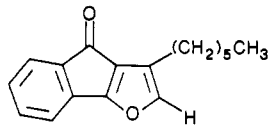

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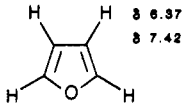
Isomers **28** and **29** are separable and assignable from their IR and MS properties. The NMR ($CDCl_3$) absorptions for **28** integrate properly as a multiplet at δ 7.40–6.87 for indenyl aromatic ring hydrogens, a singlet at δ 6.00 for the 3-furanyl proton, a triplet at δ 2.60 due to the furanylic methylene, a multiplet for tetramethylene and a triplet at δ 0.89 for the methyl group of the side chain. The NMR ($CDCl_3$) absorptions for **29** are basically the same as for **28** except that in **29** the indeno aromatic protons resonate at δ 8.02–7.70 as a multiplet and the 2-furanyl proton at δ 7.37. The assignments are confirmed by the NMR absorptions at δ 7.42 and 6.37, respectively, for the α- and β-protons in furan (**30**)[13] and for the deshielded singlet at δ 6.71 for the β-protons in 2,5-diphenylfuran (**31**).[10] The resonance for an α-proton in a furan is expected to be shifted downfield by an electron-donor substituent at an adjacent β-position.[10]



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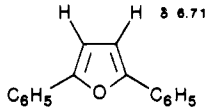

31

1,1- rather than 1,3- cycloaddition occurs in reaction of **3**, **1**, and 3-hexyne to give 2,3-diethylspiro[cyclopropene-1,2′-[2*H*]indene]-1′,3′-dione (**32**, 66%). The proton NMR spectrum ($CDCl_3$) of **32** shows absorptions at δ 8.00–7.72

(6) (a) Spirocyclopropanes **7** and **15–17** exhibit single IR carbonyl absorptions in the 1690–1705-cm^{-1} region whereas **5** and **33** display doublet carbonyl absorptions in the 1693–1702- and the 1739–1749-cm^{-1} regions. The absorptions in the 1740-cm^{-1} regions correspond to the diketo β-dicarbonyl tautomers while that at ~1695 cm^{-1} arise from the enolized β-dicarbonyl isomers. (b) Scheinmann, F. *An Introduction to Spectroscopic Methods for the Identification of Organic Compounds*, 1st ed.; Pergamon: Elmsford, New York, 1970; p 179.

(7) Chang, S.-J. Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1981, p 56.

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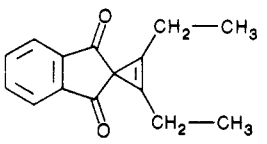
(9) Chang, S.-J.; Ravi Shankar, B. K.; Shechter, H. *J. Org. Chem.* **1982**, *47*, 4226.

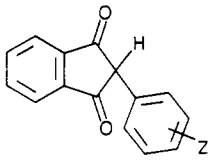
(10) Rosenfeld, M. J. M.S. Thesis, The Ohio State University, Columbus, Ohio, 1983.



32

(m, 4 H, indanyl aromatic *H*) and in particular at δ 2.48 (q, H, J = 16.5 Hz, furanylic $-CH_2-$) and 1.13 (*t*, 6 H, J = 17.25 Hz, CH_3) for two identical ethyl groups. Addition of **3** to a disubstituted acetylene in the presence of **1** to give a cyclopropene is consistent with similar reactions of α-diazocarbonyl compounds as catalyzed by copper reagents.[11] Reasons for the different behavior of **3** and **1** with mono- and disubstituted acetylenes are not clear.

The thermal behavior of **3** and **1** with benzene and certain monosubstituted benzenes was then investigated. Reaction of **3** and **1** in refluxing benzene for 5 h or at 50 °C for 50 h gives 2-phenyl-1,3-indandione (**33**) in 91% and 95% yields, respectively. There is no evidence for addition to or expansion of benzene in the reaction system. Substitution product **33** is identified from its melting point,[12] its NMR spectrum, and its enolization behavior.

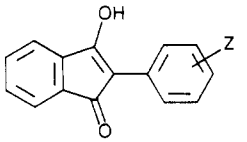


33: Z = H
34: Z = 4-OCH_3
35: Z = 2-CH_3
36: Z = 4-CH_3
37: Z = 4-Cl
38: Z = 2-Cl

Anisole, **3** and **1** at 100 °C (2 h) yield the para-substituted isomer, 2-(4-methoxyphenyl)-1,3-indandione (**34**, 73%) selectively. Determination of the positional substitution of anisole comes from the strong para IR absorption in **34** at 808 cm^{-1}, the NMR ($CDCl_3$) absorptions at δ 7.98 (m, 4 H, indanyl aromatic *H*), 6.97 (q, 4 H, *p*-methoxyphenyl aryl *H*), 4.17 (s, 1 H, 2-methine *H*), and 3.74 (s, 3 H, OCH_3), and comparison with literature properties.[13] IR and NMR analyses of the reaction product reveal the absence of significant quantities of the ortho and meta derivatives, 2-(2- and 3-methoxyphenyl)-1,3-indandiones, and the enol tautomer of **34**. Efficient formation of para-substitution product **34** suggests that anisole undergoes selective aromatic substitution by some type of electrophilic carbenoid or carbenic reactant.

With toluene as substrate for **3** and **1** at 96–100 °C, ortho- and para-substitution products, 2-(2-methylphenyl)-1,3-indandione (**35**) and 2-(4-methylphenyl)-1,3-indandione (**36**), are formed in 20–30/70–80 ratio in 86% yield. The mixture is identifiable from its NMR spectra ($CDCl_3$): a multiplet at δ 8.12–7.73 for four indanyl aromatic protons, a complex multiplet at δ 7.18–6.75 for the four aromatic protons of the tolyl groups, a singlet at δ 4.18 for one methine hydrogen, and a singlet at δ 2.30 for the three methyl protons of the tolyl groups. The isomer assignments come from IR absorptions at 756 cm^{-1} for ortho isomer **35** and at 799 cm^{-1} for para isomer **36** and by comparison with literature data.[14]

Reactions of chlorobenzene with **3** and **1** at 100 °C result in a violet mixture of 2-(2-chlorophenyl)-1,3-indandione (**37**) and 2-(4-chlorophenyl)-1,3-indandione (**38**) in ~75/25 ratio and their enol tautomers **39** and **40** in 62% yield.



39: Z = 2-Cl
40: Z = 4-Cl

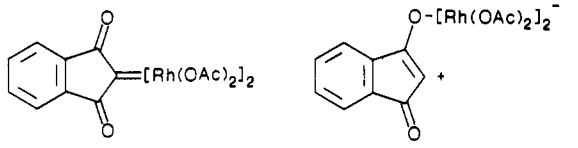
Para isomer **38** is confirmed by strong IR absorption at 829 cm^{-1}.[16b] Assignments of ortho isomer **37** and enols **39** and **40** come from IR bands at 762 cm^{-1} (fairly strong) and 3437 cm^{-1} (weak), respectively.[13b] There is no spectral evidence for the presence of the meta-substitution product, 2-(3-chlorophenyl)-1,3-indandione. Further, the NMR ($CDCl_3$) spectra of **39** and **40** are consistent with the structural assignments: δ 8.08–7.80 (m, 4 H, indanyl *H*), 7.21 (m, 4 H, chlorophenyl *H*), and 4.23 (s, 1 H, $-CH-$). Chlorine in chlorobenzene thus behaves as a traditional ortho,para-directing substituent in aromatic substitution by the reactant derived thermally from **3** and **1**.

Extension of rhodium(II)-catalyzed reactions of **3** to other electronegatively substituted benzenes was much less successful. Bromobenzene undergoes ortho and para substitution at 80 °C in only 21% yield.[15] Separation and assignment of the product proportions is made difficult because of the enolization of the aromatic substitution products. Of greater significance is that nitrobenzene reacts poorly with **3** and **1** under various conditions. Products of aromatic substitution are not found, and the complex materials that are isolable do not contain nitro groups. It is thus clear that substitution of benzenes by **3** and **1** is significantly facilitated by benzenic substituents that are electron-donating rather than electron-withdrawing.

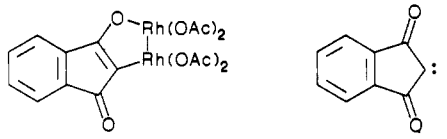
The present research thus reveals that the principal reactions of **3** upon decomposition by **1** with loss of nitrogen are insertion into carbon–hydrogen bonds of cycloalkanes, addition to carbon–carbon double and triple bonds, and directed aromatic substitution by some type of electrophilic species. The mechanisms of rhodium(II)-catalyzed reactions of **3** as follow then become interesting questions.

Among the electrophilic carbenoids, organometallics, or carbenes derivable by displacement of nitrogen from **3** by **1** are **41**–**44**. Collapse of cycloadduct **43** with loss of **1** and reactions of **41** or **42** as an electrophilic ylide with electron-rich olefins and ejection of **1** could thus yield cyclopropanes **46** as in eq 2 or 3. Extensions of such behavior

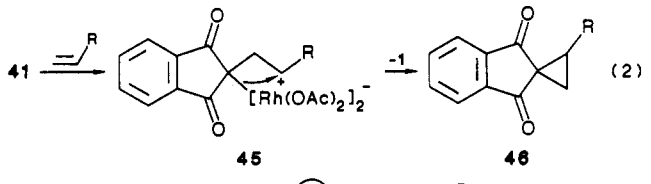
(11) Komendantov, M. I.; Smirnova, T. S.; Dyakonov, I. A. *Zh. Org. Khim.* **1967**, *3*, 1903 and references therein.
(12) Hantzch, A. *Justus Liebigs Ann. Chem.* **1963**, *28*, 2206.
(13) (a) Sperber, N. U.S. Patent 2 899 358, Aug 11, 1959. (b) Horton, R. L.; Murdock, K. C. *J. Org. Chem.* **1960**, *25*, 938.
(14) (a) Molko, D. Fr. Patent 1 085 097, Jan 27, 1955. (b) Goldberg, P. *Ber.* **1900**, *33*, 2818.
(15) Bromobenzene, **3**, and **1** at 80 °C yield (21%) a mixture of 2-(2-bromophenyl)-1,3-indandione and 2-(4-bromophenyl)-1,3-indandione along with their enol tautomers; mp 129–131 °C. The product is identified by its analysis and assigned as a mixture of ortho- and para-substitution products from its IR absorptions at 810, 767, and 749 cm^{-1}. The NMR spectra ($CDCl_3$) of the mixture (a multiplet at δ 8.08–7.70 for indanyl aromatic protons, a multiplet at δ 7.32 for bromophenyl hydrogen, and a singlet at δ 4.20) are also consistent with the assignments; MS, *m/e* calcd for $C_{15}H_9BrO_2$ 299.9786, obsd 299.9786. Anal. Calcd for $C_{15}H_{19}BrO_2$: C, 59.80; H, 3.01; Found: C, 60.08; H, 2.93. Efforts to increase the yields in substitution of bromobenzene by **3** and **1** failed.
(16) (a) Banerjee, P. K.; Mukhopadhyay, D.; Chaudhury, D. N. *J. Indian Chem. Soc.* **1965**, *42*(2), 115. (b) Whether **48** is of *E* or *Z* stereochemistry is not yet known.[16a]

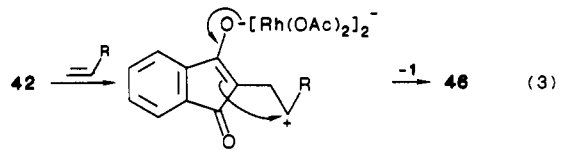


41 42



43 44





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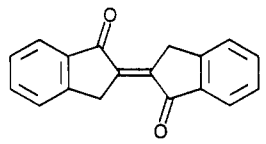
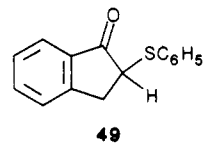
of **41** or **42** to acetylenes, benzenoid derivatives, and even sp^3–s carbon–hydrogen bonds rationalize the presently observed reactions of **3** and **1**. A further mechanistic possibility is that singlet 1,3-dioxo-2-indanylidene (**44**), as produced by decomposition of **41**–**43** or some other metalloid intermediate from **3** and **1**, is the actual reactive intermediate in the present reaction systems.

Reaction of **1** occurs much more rapidly with **4** than with **3**. Thus **4** is decomposed completely in 3 h in benzene at 20–25 °C by **1** in trace quantities. 2,2′-Bis[indan-1-one] (**48**) is produced (>46%)[16] and no substitution or ring-expansion product of benzene is observed. Further, **4** reacts smoothly with **1** in the presence of thiophenol in benzene at 48 °C to yield 2-(phenylthio)-1-indanone (**49**, 54%) along with **48**.[17]

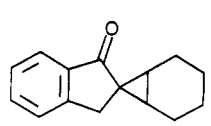


48



49

The behavior of **4** and **1** with olefins has received initial study. Spiro[bicyclo[4.1.0]heptane-7,2′-[2*H*]inden]-1′-one (**50**) of unestablished stereochemistry is formed rapidly but inefficiently (~16%) from **4** (1 equiv) and **1** in cyclohexene (75 equiv) at 20–25 °C. The principal product from **4** and **1** in cyclohexene is **48**; isomerization of **50** as for **7** is not observed.



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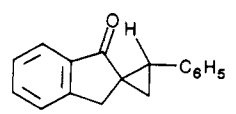

51

Much more reactive olefins than cyclohexene are cyclopropanated effectively however by **4** and **1**. Thus styrene (10 equiv) is converted to 2-phenylspiro[cyclopropane-1,2′-[2*H*]inden]-1′(3′*H*)-one (**51**, 59%, stereochemistry unknown) by **4** (1 equiv) and **1** (catalytic quantity) in toluene at room temperature.

(17) Reaction of **4**, **1**, and thiophenol to give **51** is an extension of the method of McKervey and Ratananuckul [McKervey, M. S.; Ratananuckul, P. *Tetrahedron Lett.* **1982**, *23*, 2509] of ref 5. Of note is that **3** does not react with **1** and thiophenol under the above conditions.

Experimental Section

Rhodium(II) Acetate (1). Rhodium(II) acetate dimer (**1**) was prepared from rhodium(III) chloride trihydrate in 71% yield.[18]

2-Diazo-1,3-indandione (3). 2-Diazo-1,3-indandione (**3**) (mp 146–147 °C, lit.[19] mp 149 °C) was obtained from 1,3-indandione, *p*-toluenesulfonyl azide, and triethylamine in 54–80% yields.

2-Diazo-1-indanone (4). Diazoindanone (**4**) (mp 86.5–88.5 °C, lit.[20a] mp 86–88 °C) was synthesized (60%) from 2-oximino-1-indanone by modification of Forster chloramine/ketone methodology.[20b]

2-Cyclohexyl-1,3-indandione (5). A mixture of **3** (0.1503 g, 0.874 mmol), **1** (0.0100 g, 0.022 mmol), and cyclohexane (25 mL) was refluxed (17.2 h, under N_2), cooled, filtered, concentrated, and then dissolved in hot hexane. After cooling, the solution precipitated gray-green flakes of **5** (0.1049 g, 53%; mp 89–92 °C); IR (KBr, cm^{-1}) 2923, 2852 (C–H, s), 1739, 1693 (enolizable, β-dicarbonyl doublet, s), 754 (ortho-substituted benzene, s); NMR ($CDCl_3$, δ) 7.93–7.57 (m, 4 H, indanyl aromatic *H*), 2.73 (d, 1 H, *J* = 6.0 Hz, indanyl –C*H*–), 1.74–0.92 (m, 11 H, cyclohexyl *H*); MS, *m/e* calcd for $C_{15}H_{16}O_2$ 228.1151, obsd 228.1170, diff 0.0019. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.87; H, 6.97.

Spiro[bicyclo[4.1.0]heptane-7,2′-[2*H*]indene]-1′,3′-dione (7) and 2-(3-Cyclohexenyl)-1,3-indandione (8). A suspension of **3** (0.2500 g, 1.45 mmol), **1** (0.0100 g, 0.022 mmol), and cyclohexene (30 mL) was refluxed (8.75 h, under N_2), concentrated, and column chromatographed (silica gel). Elution with 3:2 benzene–hexane gave **7** (0.1357 g, 41%, mp 162.0–162.5 °C (95% ethanol)); white needles; NMR ($CDCl_3$, δ) 8.00–7.67 (m, 4 H, indanyl *H*), 2.59–2.37 (m, 2 H, cyclopropane *H*), 2.07–1.24 (m, 8 H, –(CH_2)$_4$–); MS, *m/e* calcd for $C_{15}H_{14}O_2$ 226.0994, obsd 226.0975, diff –0.0019. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.65; H, 6.19. Found: C, 79.13; H, 5.86.

The second product was eluted with 5% chloroform in benzene and identified as **8** (81 mg, 25%); a yellow-orange oil; NMR ($CDCl_3$, δ) 8.00–7.67 (m, 4 H, indanyl *H*), 5.83–5.70 (m, 1 H, olefinic *H*), 5.50–5.37 (m, 1 H, olefinic *H*), 3.09–2.94 (m, 1 H, β-dicarbonyl *H*), 2.10–1.88 (m, 3 H, allylic H), 1.74–1.13 (m, 4 H, nonallylic –(CH_2)$_2$–); MS, *m/e* calcd for $C_{15}H_{14}O_2$ 226.0994, obsd 226.0935 diff –0.0059. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.65; H, 6.19. Found: C, 79.25; H, 5.99.

Thermal Isomerization of 7 to 8. A solution of **7** (0.0155 g, 0.069 mmol) in benzene (7.5 mL) was refluxed under nitrogen for 3 days. TLC (hexane–ethyl acetate 3:1) and product isolation revealed that **7** isomerized completely to **8** (0.0153 g).

2,2-Pentamethylenespiro[cyclopropane-1,2′-[2*H*]-indene]-1′,3′-dione (15). Chromatography (silica gel, benzene–chloroform 5:1) of the residue from refluxing methylenecyclohexane (5 g, 52 mmol), **3** (0.2500 g, 1.45 mmol), and **1** (0.0102 g, 0.022 mmol) under nitrogen (1.5 h) yielded **15** (0.1608 g, 46%; mp 124.5–126.5 °C (hexane)); colorless plates; IR (KBr, cm^{-1}) 2920, 2853 (C—H, s), 1690 (C=O, s), 743 (ortho-substituted benzene, s); NMR ($CDCl_3$, δ) 7.98–7.62 (m, 4 H, indanyl aromatic *H*), 1.93 (s, 2 H, cyclopropane –CH_2–), 1.83–1.02 (m, 10 H, –(CH_2)$_5$–); MS, *m/e* calcd for $C_{16}H_{16}O_2$ 240.1151, obsd 240.1131, diff –0.0020. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.02; H, 6.60.

2-*n*-Hexylspiro[cyclopropane-1,2′-[2*H*]indene]-1′,3′-dione (16). A suspension of **3** (0.2501 g, 1.45 mmol) and **1** (0.0099 g, 0.022 mmol) in 1-octene (30 mL) was heated at 100 °C (7 h, under N_2), concentrated, and chromatographed on silica gel (hexane–benzene 1:1) to give **16** (0.2677 g, 72%); a bright yellow oil; IR (neat, cm^{-1}) 2964–2736, 2864 (C—H asym and sym stretch, s), 1705 (C=O, s), 738 (ortho-substituted benzene, s); NMR ($CDCl_3$, δ) 8.00–7.70 (m, 4 H, indanyl *H*), 2.32–1.91 (m, 2 H, cyclopropane

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(19) Regitz, M.; Schwall, H.; Heck, G.; Eistert, B.; Bock, G. *Justus Liebigs Ann. Chem.* **1965**, *690*, 125.

(20) (a) Cava, M. P.; Little, R. L.; Napier, D. R. *J. Am. Chem. Soc.* **1958**, *80*, 2257. (b) Forster, M. O. *J. Chem. Soc.* **1915**, *107*, 260.

$-CH_2-$), 1.91–1.69 (m, 3 H, $-CH_2-$ and cyclopropane $-CH-$), 1.33–1.07 (m, 8 H, $-(CH_2)_4-$), 0.97–0.76 (t, 3 H, $-CH_3$); MS *m/e* calcd for $C_{17}H_{20}O_2$ 256.1503, obsd 256.1464, diff 0.0039. Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 78.90; H, 7.88.

2-Benzylspiro[cyclopropane-1,2′-[2*H*]indene]-1′,3′-dione (17). Vacuum distillation, column chromatography (silica gel, benzene–hexane 3:2), and crystallization (hexane–benzene 3:1) of the product from **3** (0.2506 g, 1.457 mmol), **1** (0.0104 g, 0.022 mmol), and allylbenzene (30 mL) at 90–105 °C (under N_2, 3.5 h) gave a colorless oil, which converted to pale yellow crystals of **17** (0.1758 g, 46%, mp 92–94 °C); IR (neat, cm^{-1}) 1705 (C=O, s), 744 (ortho-substituted benzene, s), 699 (monosubstituted benzene, w); NMR ($CDCl_3$), δ) 8.00–7.67 (m, 4 H, indanyl *H*), 7.16 (s, 5 H, benzyl aryl *H*), 3.13–3.05 (dd, 2 H, benzyl $-CH_2-$), 2.48 (quintet, 1 H, cyclopropane $-CH-$), 2.10–1.81 (m, 2 H, cyclopropane $-CH_2-$); MS, *m/e* calcd for $C_{18}H_{14}O_2$ 262.0994, obsd 262.1024 diff 0.0030. Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.25; H, 5.29.

(1′α,2′β,4′β,5′α)-Spiro[2*H*-indene-2,3′-tricyclo[3.2.1.0^{2,4}]octane]-1,3-dione (18). A mixture of **3** (0.2500 g, 1.45 mmol), norbornene (28 mL), **1** (0.0110 g, 0.025 mmol), and hexane (2 mL) was heated at 70–80 °C (2 h, under N_2). After the mixture was cooled, more hexane was added (10 mL) and the norbornene was codistilled at atmospheric pressure with hexane. Column chromatography of the residue on silica gel (benzene) led to **18** (0.0545 g, 16%, mp 153.5–155.0 °C (95% ethanol)); white needles; IR (KBr, cm^{-1}) 2970 (c—H, s), 1702 (C=O, s), 768 (ortho-substituted benzene, s); NMR ($CDCl_3$, δ) 7.73 (m, 4 H, indanyl *H*), 2.84 (m, 1 H, *J* = 10.5 Hz, syn C-*H*), 2.61 (s, 2 H, bridgehead C-*H*), 2.07 (s, 2 H, cyclopropane C-*H*), 1.54 and 1.30 (2 d, 4 H, *J* = 9.6 Hz, $-(CH_2)_2-$), 0.79 (m, 1 H, *J* = 10.5 Hz, anti C-*H*); MS, *m/e* calcd for $C_{16}H_{14}O_2$ 238.0994, obsd 238.0972, diff −0.0022. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.50; H, 5.87.

2-Phenylspiro[cyclopropane-1,2′-[2*H*]indene]-1′,3′-dione (20). A mixture of **3** (0.2500 g, 1.45 mmol), styrene (1.51 g, 14.5 mmol), **1** (0.0100 g, 0.022 mmol), and toluene (30 mL) was heated at 80 °C for 10 h (under N_2). The progress of reaction was monitored by TLC (hexane–ethyl acetate 3:1). The mixture was cooled, filtered, concentrated, and chromatographed on silica gel (benzene) to **20** (0.2572 g, 72%, mp 133–134 °C (hexane–benzene 3:1)); colorless needles; IR (KBr, cm^{-1}) 1704 (C=O, s), 772, 709 (monosubstituted benzene, s), 749 (ortho-substituted benzene, s); NMR ($CDCl_3$, δ) 8.03–7.71 (m, 4 H, indanyl aromatic *H*), 7.30 (m, 5 H, phenyl *H*), 3.47 (t, 1 H, cyclopropane $-CH-$), 2.55–2.33 (m, 2 H, cyclopropane $-CH_2-$); MS, *m/e* calcd for $C_{17}H_{12}O$ 248.0838, obsd 248.0861, diff 0.0023. Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.26; H, 4.84. Found: C, 81.86; H, 4.85.

2-(4-Methylphenyl)spiro[cyclopropane-1,2′-[2*H*]-indene]-1′,3′-dione (22). Cyclopropane **22** was prepared from **3**, **1**, and *p*-methoxystyrene in 54–59% yield;[21] mp 126–128 °C (hexane–benzene 2:1); IR (KBr, cm^{-1}) 1704 (C=O, s), 865 (para-substituted benzene, s), 749 (ortho-substituted benzene, s); NMR ($CDCl_3$, δ) 7.98–7.67 (m, 4 H, indanyl *H*), 7.31–7.03 (m, 4 H, *p*-tolyl aryl *H*), 3.39 (t, 1 H, cyclopropane C*H*), 2.50–2.17 (m, 2 H, cyclopropane CH_2), 2.30 (s, 3 H, CH_3); MS, *m/e* calcd for $C_{18}H_{14}O_2$ 262.0994, obsd 262.0950, diff 0.0044. Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.40; H, 5.44.

2-(4-Chlorophenyl)spiro[cyclopropane-1,2′-[2*H*]-indene]-1′,3′-dione (23). Synthesis of **23** (80–82%) was effected from **3**, **1**, and *p*-chlorostyrene:[21] mp 164.0–166.5 °C (hexane–benzene 3:1); IR (KBr, cm^{-1}) 1690 (C=O, s), 840 (para-substituted benzene, m), 744 (ortho-substituted benzene, s); NMR ($CDCl_3$, δ) 7.91–7.63 (m, 4 H, indanyl *H*), 7.39–7.02 (m, 4 H, *p*-chlorophenyl *H*), 3.43 (t, 1 H, cyclopropyl C*H*), 2.43–2.17 (m, 2 H, cyclopropyl CH_2); MS, *m/e* calcd for $C_{17}H_{11}O_2Cl$ (for ^{35}Cl) 282.0448, obsd 282.0431, diff −0.0017. Anal. Calcd for $C_{17}H_{11}O_2Cl$: C, 72.20; H, 3.92. Found: C, 72.12; H, 4.01.

2-(4-Bromophenyl)spiro[cyclopropane-1,2′-[2*H*]-indene]-1′,3′-dione (24). Reaction of **3**, **1**, and *p*-bromostyrene resulted in **24** (52–53%):[21] mp 182.5–184.0 °C (hexane–benzene 2:1); IR (KBr, cm^{-1}) 1695 (C=O, s), 846 (para-substituted benzene, m), 760 (ortho-substituted benzene, s); NMR ($CDCl_3$, δ) 7.97–7.62 (m, 4 H, indanyl *H*), 7.44–7.03 (m, 4 H, *p*-bromophenyl *H*), 3.33 (t, 1 H, cyclopropyl C*H*), 2.46–2.17 (m, 2 H, cyclopropyl CH_2); MS, *m/e* calcd for $C_{17}H_{11}O_2Br$ (for ^{79}Br) 325.0042, obsd 325.9988, diff 0.0046. Anal. Calcd for $C_{17}H_{11}O_2Br$: C, 62.39; H, 3.36. Found: C, 62.35; H, 3.25.

2-(4-Nitrophenyl)spiro[cyclopropane-1,2′-[2*H*]indene]-1′,3′-dione (25). *p*-Nitrostyrene, **3**, and **1** gave **25** (46–48%):[21] mp 163.5–165.5 °C (hexane–benzene 2:1); IR (KBr, cm^{-1}) 1704 (C=O, s), 1519 (NO_2, s), 861 (para-substituted benzene, s), 753 (ortho-substituted benzene, s); NMR ($CDCl_3$, δ) 8.21–7.42 (m, 4 H, *p*-nitrophenyl *H*), 7.82 (m, 4 H, indanyl *H*), 3.45 (5, 1 H, cyclopropyl C*H*), 2.55–2.26 (m, 2 H, cyclopropyl CH_2); MS, *m/e* calcd for $C_{17}H_{11}NO_4$ 293.0678, obsd 293.0670, diff −0.0008. Anal. Calcd for $C_{17}H_{11}NO_4$: C, 69.62; H, 3.87. Found: C, 69.12; H, 3.75.

Relative Rates of Cyclopropanation of 1-Octene and Styrene by 3 and 1. A mixture of **3** (0.2500 g, 1.45 mmol), 1-octene (1.63 g, 14.5 mmol), styrene (1.51 g, 14.5 mmol), and **1** (0.0100 g, 0.022 mmol) was heated at 80 °C (13.5 h, under N_2). The reaction progress was monitored by TLC (hexane–ethyl acetate 3:1), and after the disappearance of 1, the mixture was cooled and placed on silica gel. Chromatography resulted in separation of (1) **16** (0.0500 g, 13.5%) as a yellow oil upon elution with benzene–hexane (2:1) and (2) **20** (0.2260 g, 62.9%) as colorless crystals after elution with benzene–hexane (3:1). Compounds **16** and **20** are identical with that obtained previously and are formed in a 4.67:1 ratio.

Relative Rates of Cyclopropanation of 1-Octene and *p*-Nitrostyrene by 3 and 1. A suspension of **3** (0.2500 g, 1.45 mmol), 1-octene (1.63 g, 14.5 mmol), *p*-nitrostyrene (2.16 g, 14.5 mmol), and **1** (0.0103 g, 0.023 mmol) was heated (80 °C, 13.5 h, under N_2) and worked up as in the previous experiments to give (1) **16** (0.0700 g, 19%, a yellow oil, elution with 2:1 benzene–hexane) and (2) **25** (0.2040 g, 48%, colorless crystals, elution with 5:1 benzene–chloroform). Adducts **16** and **25** are pure and formed in a ratio of 2.55:1.

2-Phenyl-4*H*-indeno[1,2-*b*]furan-4-one (26). Filtration, vacuum concentration, and chromatography (silica gel, hexane–benzene 1:1) of the product from **3** (0.2500 g, 1.45 mmol) and **1** (0.0100 g, 0.022 mmol) suspended in phenylacetylene (15 mL) at 50–60 °C (8.3 h) yielded **26** (91%); red crystals; IR (KBr, cm^{-1}) 1718 (C=O, s), 873 (3-furanyl C—H, m), 759 (ortho-substituted benzene, m); NMR ($CDCl_3$, δ) 7.77–7.03 (m, 9 H, phenyl and indenyl aromatic *H*), 6.67 (s, 1 H, 3-furanyl *H*); MS, *m/e* calcd for $C_{17}H_{10}O_2$ 246.0681, obsd 246.0656, diff −0.0025. Anal. Calcd for $C_{17}H_{10}O_2$: C, 82.90; H, 4.07. Found: C, 82.42; H, 4.21.

2- and 3-*n*-Hexyl-4*H*-indeno[1,2-*b*]furan-4-ones (28 and 29). Reaction of **3** (0.2503 g, 1.45 mmol) and **1** (0.0100 g, 0.022 mmol) with 1-octyne (20 mL) at 80 °C (24 h, under N_2) and chromatography on silica gel gave (1) **28** (0.1030 g, 28%); orange-red oil; IR (neat, cm^{-1}) 3040 (aromatic C—H, w), 2930 (aliphatic C—H, s), 1716 (C=O, s), 873 (3-furanyl C—H, s), 755 (ortho-substituted benzene, s); MS, *m/e* calcd for $C_{17}H_{18}O_2$ 254.1307, obsd 254.1355, diff 0.0048 and (2) **29** (0.0553 g, 15%); dark red oil; IR (neat, cm^{-1}) 2934 (aliphatic C—H, s), 1715 (C=O, s), 773 (ortho-substituted benzene, s); NMR ($CDCl_3$, δ) 8.02–7.70 (m, 4 H, indenyl aromatic *H*), 7.37 (s, 1 H, 2-furanyl $-CH-$), 2.43 (t, 2 H, furanylic $-CH_2-$), 1.69–1.17 (m, 8 H, $-(CH_2)_4-$), 0.89 (t, 3 H, CH_3); MS, *m/e* calcd for $C_{17}H_{18}O_2$ 254.1307, obsd 254.1341, diff 0.0034.

2,3-Diethylspiro[cyclopropene-1,2′-[2*H*]indene]-1′,3′-dione (32). Column chromatography (silica gel, chloroform) of the residue from **3** (0.2500 g, 1.45 mmol), **1** (0.0100 g, 0.022 mmol), and 3-hexyne (20 mL) after reflux (15 h, under N_2) and concentration yielded **32** (0.2169 g, 66%); amber oil; IR (neat, cm^{-1}) 3020 (aromatic C—H, w), 2982 (aliphatic C—H, s), 1713 (C=O, s), 753 (ortho-substituted benzene, s); NMR, see text; MS, *m/e* calcd for $C_{15}H_{14}O_2$ 226.0994, obsd 226.1007, diff 0.0013.

2-Phenyl-1,3-indandione (33). Decomposition of **3** (0.1505 g, 0.875 mmol) by **1** (0.0103 g, 0.023 mmol) in benzene (30 mL) at 50 °C for 49 h, filtration, concentration, and column chromatography (silica gel, benzene–chloroform 9:1) afforded **33** (0.1835 g, 95%, mp 148–149 °C (95% ethanol); lit.[22] mp 150–151 °C); white shiny flakes; IR (KBr, cm^{-1}) 1745, 1702 (enolizable β-dicarbonyl doublet, both s), 705 (monosubstituted benzene, s),

(21) The experiment was conducted as that for synthesis of **25**.

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735 (ortho-substituted benzene, s); NMR ($CDCl_3$, δ), 8.15–7.77 (m, 4 H, indanyl *H*), 7.33–7.17 (m, 5 H, 2-phenyl *H*), 4.21 (s, 1 H, –C*H*–); MS, *m/e* calcd for $C_{15}H_{10}O_2$ 222.068 08, obsd 222.068 72, diff 0.000 64. Performing the reaction in refluxing benzene for 5 h resulted in **33** in 91% yield.

2-(4-Methoxyphenyl)-1,3-indandione (34). Anisole (30 mL), **3** (0.2513 g, 1.46 mmol), and **1** (0.0100 g, 0.022 mmol) upon heating at 100 °C for 2 h, cooling, filtration, and vacuum removal of the anisole gave an orange-red residue, which recrystallized from ethanol to **34** (0.2683 g, 73%, mp 147–149 °C, lit.[12] mp 149 °C); beige needles; IR (KBr, cm^{-1}) 1740, 1705 (enolizable, β-dicarbonyl doublet, both vs), 1251 (aryl OCH_3, vs), 808 (para-substituted phenyl, s), 750 (ortho-substituted indanyl, s); NMR, see text; MS, *m/e* calcd for $C_{16}H_{12}O_3$ 252.0787, obsd 252.0768, diff –0.0019. Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found: C, 75.97; H, 4.77.

2-(2-Methylphenyl)-1,3-indandione (35) and 2-(4-Methylphenyl)-1,3-indandione (36). Toluene (30 mL), **3** (02.500 g, 1.45 mmol), and **1** (0.0098 g, 0.022 mmol) after heating at 96–100 °C (50 h, under N_2), concentration, and chromatography (silica gel, benzene) gave a mixture of **35** and **36** (0.295 g, 86%, mp 125–128 °C (hexane–benzene 3:1), lit.[14] mp (**41**) 143.5 °C); beige powder; IR (KBr, cm^{-1}) 1744, 1702 (enolizable β-dicarbonyl doublet, both s), 799 (para-substituted tolyl, s), 768, 756 (ortho-substituted indanyl and tolyl rings); NMR, see text; MS, *m/e* calcd for $C_{16}H_{12}O_2$ 236.0838, obsd 236.0842, diff 0.0004. Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.07; H, 4.98.

Attempts to separate **35** and **36** by high-performance liquid chromatography, preparative TLC, and column chromatography using various eluent mixtures of ethyl acetate–hexane and benzene–chloroform were unsuccessful. Infrared analysis revealed **35** and **36** to be present in ~70/30 ratio.

2-(2-Chlorophenyl)-1,3-indandione (38) and 2-(4-Chlorophenyl)-1,3-indandione (37). *o*- and *p*-chlorophenyl isomers (**38** and **37**, respectively) along with their enol tautomers **39** and **40** were obtained as dark violet crystals (0.2310 g, 62%, mp 134–139 °C (95% ethanol), lit.[16b] mp (**37**) 143 °C) from **3** (0.2506 g, 1.46 mmol), **1** (0.0103 g, 0.023 mmol), and chlorobenzene (30 mL) at 100 °C (2.25 h, under N_2), filtration, vacuum concentration, and chromatography (silica gel, benzene): IR (KBr, cm^{-1}) 3437 (OH, vw), 1745, 1705 (enolizable β-dicarbonyl doublet, both s); NMR, see text; MS, *m/e* calcd for $C_{15}H_9ClO_2$ (^{35}Cl) 256.0292, obsd 256.0262, diff –0.0030. The proportions of **38** to **37** in the product mixture as determined by IR methods were ~25:75. Anal. Calcd for $C_{15}H_9ClO_2$: C, 70.17; H, 3.54. Found: C, 70.12; H, 3.42.

Conversion of 2-Diazo-1-indanone (4) by 1 in Benzene to 2,2′-Bis[indan-1-one] (48). A solution of **4** (0.2002 g, 1.27 mmol) and **1** (0.0105 g, 0.022 mmol) in dry benzene (20 mL) was stirred under nitrogen at room temperature. After 3 h, nitrogen evolution was complete and no **4** remained. The deep purple reaction mixture contained a suspended precipitate, which was filtered. No product was found when the concentrated filtrate was column chromatographed. Recrystallization of the gray precipitate from glacial acetic acid afforded **48** (0.0758 g, 46%, mp 239–241 °C dec, lit.[19] mp 236 °C dec, green-yellow needles).

2-(Phenylthio)-1-indanone (49). To stirred thiophenol (0.305 g, 2.77 mmol), **1** (0.0060 g, 0.018 mmol), and dry benzene (20 mL) under nitrogen at room temperature was added **4** (0.3950 g, 2.5 mmol) in benzene (5.5 mL) over 14 h. The mixture was then heated for 9 h at 48 °C and cooled and its precipitate (**48**, 5.3 mg, 2%, mp 235–236 °C, lit.[19] mp 236 °C) was filtered.

The filtrate was washed with aqueous sodium hydroxide (5%, 25 mL) and water and then dried. Filtration, concentration, and column chromatography (silica gel, benzene) of the red, oily residue afforded **49** (0.3320 g, 54%, mp 63–64 °C, lit.[17] mp 66–67 °C); beige crystals; NMR ($CDCl_3$, δ) 7.89–7.22 (m, 9 H, indanyl and phenyl *H*), 4.17–4.04 (dd, J = 3.2 Hz, 1 H, α-keto *H*), and 3.82–3.02 (m, 2 H, $-CH_2-$).

Spiro[bicyclo[4.1.0]heptane-7,2′-[2*H*]inden]-1′-one (50). A mixture of **4** (0.2500 g, 1.58 mmol) and cyclohexene (30 mL) was added dropwise (6.75 h) at room temperature to **1** (0.0203 g, 0.044 mmol) in cyclohexene (10 mL) under nitrogen. TLC analysis revealed that no **4** remained. The mixture was filtered from the **48** (0.0429 g, 21%, mp 240 °C, lit.[19] mp 236 °C, golden-yellow crystals) formed, concentrated, and column chromatographed (silica gel, benzene–chloroform 3:1) to yield **50** (0.0549 g, 16%, mp 87.5–88.5 °C (methanol)); white crystals; IR (KBr, cm^{-1}) 1700 (C=O, s); NMR ($CDCl_3$, δ) 7.76–7.36 (m, 4 H, indanyl aromatic *H*), 3.03 (s, 2 H, indanyl $-CH_2-$), 2.15–1.25 (m, 10 H, spirocyclohexyl *H*); MS, *m/e* calcd for $C_{15}H_{16}O$ 212.1202, obsd 212.1179, diff –0.0023. Anal. Calcd for $C_{15}H_{16}O$: C, 84.90; 7.55. Found: C, 84.89; 7.45.

2-Phenylspiro[cyclopropane-1,2′-[2*H*]inden]-1′(3′*H*)-one (51). A toluene (20 mL) solution of **4** (0.2500 g, 1.58 mmol) was added in 2 h at 20–25 °C to a suspension of **1** (0.0100 g, 0.022 mmol) in styrene (1.65 g, 15.8 mmol)/toluene (10 mL). Filtration, concentration, and column chromatography (silica gel, benzene–chloroform 3:1) of the reaction product gave **51** (0.2182 g, 59%, mp 98–99 °C (95% ethanol)); white crystals; NMR ($CDCl_3$, δ) 7.80–6.89 (m, 9 H, indanyl aromatic and phenyl *H*), 3.00–2.72 (m, 3 H, indanyl C*H*$_2$ and cyclopropane C*H*), 2.20–1.54 (m, 2 H, cyclopropane C*H*$_2$); MS, *m/e* calcd for $C_{17}H_{14}O$ 234.1045, obsd 234.1012, diff –0.0033. Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 86.87; H, 5.77.

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Registry No. **1**, 15956-28-2; **3**, 1807-49-4; **4**, 1775-23-1; **5**, 114158-17-7; **7**, 114158-18-8; **8**, 114158-19-9; **15**, 114158-20-2; **16**, 114158-21-3; **17**, 61124-68-3; **18**, 114158-22-4; **20**, 105678-94-2; **22**, 114158-23-5; **23**, 114158-24-6; **24**, 114158-25-7; **25**, 114158-26-8; **26**, 114158-27-9; **28**, 114158-28-0; **29**, 114158-29-1; **32**, 114158-30-4; **33**, 83-12-5; **34**, 117-37-3; **35**, 15432-97-0; **36**, 7561-48-0; **37**, 1146-99-2; **38**, 1470-42-4; **48**, 1579-28-8; **49**, 78196-99-3; **50**, 114158-31-5; **51**, 114183-89-0; 1,3-indandione, 606-23-5; *p*-toluenesulfonyl azide, 941-55-9; 2-oximino-1-indanone, 15028-10-1; cyclohexane, 110-82-7; cyclohexene, 110-83-8; methylenecyclohexane, 1192-37-6; 1-octene, 111-66-0; allylbenzene, 300-57-2; norbornene, 498-66-8; styrene, 100-42-5; *p*-methoxystyrene, 637-69-4; *p*-chlorostyrene, 1073-67-2; *p*-bromostyrene, 2039-82-9; *p*-nitrostyrene, 100-13-0; phenylacetylene, 536-74-3; 1-octyne, 629-05-0; 3-hexyne, 928-49-4; benzene, 71-43-2; anisole, 100-66-3; toluene, 108-88-3; chlorobenzene, 108-90-7; thiophenol, 108-98-5; copper (II) acetylacetonate, 13395-16-9; palladium (II) acetate, 3375-31-3; bromobenzene, 108-86-1; 2-(2-bromophenyl)-1,3-indandione, 1470-41-3; 2-(4-bromophenyl)-1,3-indandione, 1146-98-1.