JOC Article

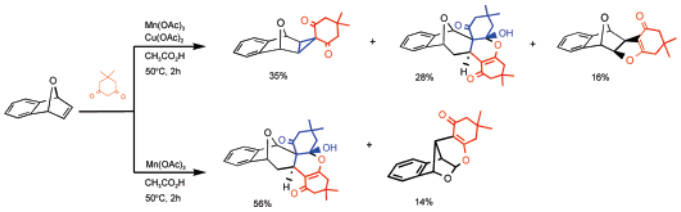
Unusual Manganese(III)-Mediated Oxidative Free Radical Additions of 1,3-Dicarbonyl Compounds to Benzonorbornadiene and 7-Heterobenzonorbornadienes: Mechanistic Studies

Raşit Çalışkan,[†,‡] Mohamed Fadelalla Ali,[†] Ertan Şahin,*[,§] William H. Watson,*[,||] and Metin Balci*[,†]

Departments of Chemistry, Middle East Technical University, 06531 Ankara, Süleyman Demirel University, 32260 Isparta, and Atatürk University, 25240 Erzurum, Turkey, and Texas Christian University, Fort Worth, Texas 76129

mbalci@metu.edu.tr; ertan@atauni.edu.tr; w8watson@hughes.net

Received December 15, 2006

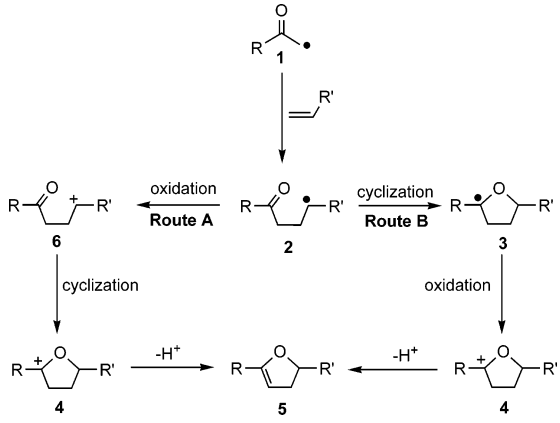


Benzonorbornadiene and heterobenzonorbornadiene were reacted with dimedone/acetylacetone and Mn(OAc)$_3$ in the presence and absence of Cu(OAc)$_2$. The reaction of benzonorbornadiene with dimedone gave mainly the dihydrofuran addition product, whereas the reaction with acetylacetone produced a rearranged product in addition to the dihydrofuran derivative. On the other hand, oxanorbornadiene gave unusual products such as the cycloproponated compound and a product arising from the incorporation of 2 mol of dimedone. The reaction of azanorbornadiene with 1,3-dicarbonyl compounds and Mn(OAc)$_3$ always produced rearranged products. The mechanism of formation of the products is discussed. We generally observe that the cyclization reaction takes place after the oxidation of the initially formed radical.

Introduction

The generation of carbon radicals by the help of transition-metal salts and their addition to carbon−carbon double bonds has become a valuable method for C−C bond formation.[1] Among the metal oxidants, an important place is occupied by Mn(OAc)$_3$. Heiba, Dessau, Bush, and Finkbeiner have demonstrated that Mn(OAc)$_3$ in acetic acid at reflux converts a variety of olefins to γ-lactones (Scheme 1).[2] Generally, an oxidatively

SCHEME 1



or reductively generated radical **1** can add to a double bond, forming a new radical, **2**, which can be reductively or oxidatively terminated. On the other hand, the cyclization[3] of **2** can form

* To whom correspondence should be addressed: (E.Ş.) correspondence concerning X-ray analysis of **34**; (W.H.W.) correspondence concerning X-ray analysis of **21** and **23**; (M.B.) all other correspondence.
[†] Middle East Technical University.
[‡] Süleyman Demirel University.
[§] Atatürk University.
[||] Texas Christian University.

(1) (a) Jasperse, C. P.; Curran, D. P. *Chem. Rev.* **1991**, *91*, 1237. (b) Badanyan, Sh. O.; Melikyan, G. G.; Mkrtchyan, D. A. *Russ. Chem. Rev.* **1989**, *58*, 286. (c) Curran, D. P. *Synthesis* **1988**, 417. (d) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986. (e) de Klein, W. J. In *Organic Synthesis by Oxidation with Metal Compounds*; Mijs, W. J., de Jonge, C. R. H., Eds.; Plenum Press: New York, 1986; p 261.

10.1021/jo0625711 CCC: $37.00
Published on Web 03/27/2007

3. Oxidative termination of **3** followed by loss of a proton can form dihydrofuran **5**.[4,5]

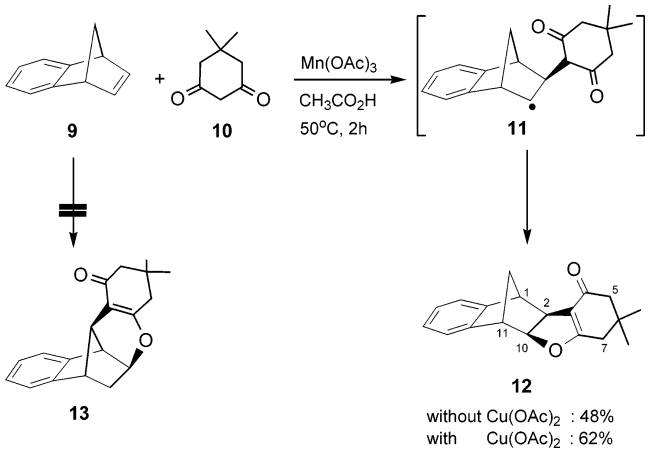
With regard to the cyclization mechanism, some questions have to be answered. For example, what is the fate of the radical **2** formed after additon of an oxyl radical to a C=C double bond? Heiba and Dessau proposed oxidation of the radical **2** to the cation **6** followed by cyclization to the tetrahydrofuran derivative and then loss of a proton to give **5** (route A).[2b,6,7] On the other hand, Fristad et al.[8] have proposed an alternative route B, where the formed radical **2** undergoes first a cyclization reaction followed by oxidation. To address this question, i.e., at which stage the second oxidation takes place, possible intermediates such as **2** and **6**, which undergo cyclization, were incorporated in a bicyclic system (**7** and **8**), benzonorbornadiene (**9**) and its hetero derivatives.

It is well-established that a radical of type **7** does not undergo rapid rearrangement.[9] However, a cation incorporated in a benzonorbornyl system as in **8** gives it great tendency to form rearranged products.[10] Therefore, the structure of the formed products would give us information about the stage at which oxidation takes place. In this paper, we report the reactions of enolizable 1,3-diketones with benzonorbornadiene and 7-heterobenzonorbornadienes in the presence of $Mn(OAc)_3$ and the cooxidant $Cu(OAc)_2$ and without cooxidant.[11]

Results and Discussion

Dimedone (**10**) and acetylacetone were chosen as model compounds to explore the reactions. First, **9**[12] was used as a radical acceptor alkene. Treatment of a mixture of **10** and $Mn(OAc)_3$ in acetic acid with **9** in a ratio of 2:1 (2 h at 50 °C) gave the dihydrofuran adduct **12** in a 48% yield (Scheme 2). Careful examination of the reaction mixture did not reveal the formation of any trace of a rearranged product **13**.

SCHEME 2



The *exo*-configuration of the dihydrofuran ring was confirmed by measuring the coupling constants between H-1 and H-2 and between H-10 and H-11. The absence of any coupling between these protons confirms the *endo*-orientation of the protons H-2 and H-10. In the case of *exo*-orientation of these protons, a high value of $J_{1,2}$ ($J_{10,11}$) (3.5−5.0 Hz) would be expected.[10a,13]

When the reaction was run in the presence of $Mn(OAc)_3$/$Cu(OAc)_2$ in a ratio of 5:1, the product distribution did not change; only the yield of the addition product **12** increased from 48% to 62%. The formation of the product can be explained by the attack of electrophilic dimedone radical to the *exo*-face of the double bond in **9** to form the nucleophilic adduct radical **11** (Scheme 2). This radical **11** may then undergo intramolecular cyclization reaction.

It is well-known that $Mn(OAc)_3$ slowly oxidizes primary and secondary radicals to cations so that hydrogen abstraction from the solvent or other molecules becomes the predominant reaction. Since **11** is a secondary radical, it immediately undergoes a ring closure reaction to give the addition product **12**. The addition of $Cu(OAc)_2$ to the reaction media should facilitate the oxidation of the secondary radical[6] **11**, which would undergo Wagner−Meerwein rearrangement and give **13**. However, this was not found to be the case. Therefore, the formation of **12** can be rationalized by a fast intramolecular capture of the radical **11** by the dimedone unit. On the other hand, a nonclassical carbocation would also form the product **12** (for a detailed discussion see below).

To gain more insight into the formation mechanism of **12**, acetylacetone (**14**) was used instead of dimedone. The reaction of **9** with **14** and $Mn(OAc)_3$ in the absence of $Cu(OAc)_2$ gave only a single product, **15**, in a yield of 6%. The striking difference in the yields of **12** (48%) and **15** (6%) may be attributed to the poor enolizable character of the acetylacetone unit so that the initially formed radical cannot be captured quickly.

On the other hand, the reaction of **9** with $Mn(OAc)_3$ and acetylacetone in the presence of $Cu(OAc)_2$ gave two separable products, the nonrearranged product **15** and the rearranged

(2) (a) Bush, J. B.; Finkbeiner, H. *J. Am. Chem. Soc.* **1968**, *90*, 5903. (b) Heiba, E. I.; Dessau, R. M.; Koehl, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 5905.

(3) For general radical cyclization see: (a) Julia, M. *Acc. Chem. Res.* **1971**, *4*, 386. (b) Breslow R.; Olin, S. S.; Groves, J. T. *Tetrahedron Lett.* **1968**, 1837. (c) Snider, B. B.; O'Neil, S. V. *J. Org. Chem.* **1995**, *47*, 12983.

(4) (a) Corey, E. J.; Kang, M.-C. *J. Am. Chem. Soc.* **l984**, *106*, 5384. (b) Snider, B. B.; Mohan, R. M.; Kates, S. A. *J. Org. Chem.* **1985**, *50*, 3659. (c) Ernst, A. B.; Fristad, W. E. *Tetrahedron Lett.* **1985**, *26*, 3761.

(5) (a) Snider, B. B. *Chem. Rev.* **1996**, *96*, 339. (b) Iqbal, J.; Bhatia, B.; Nayyar, N. K. *Chem. Rev.* **1994**, *94*, 519. (c) Melikyan, G. G. *Synthesis* **1993**, 833.

(6) (a) Heiba, E. I.; Dessau, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 524. (b) Heiba, E. I.; Dessau, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 2888.

(7) Heiba, E. I.; Dessau, R. M. *J. Am. Chem. Soc.* **1974**, *96*, 7977.

(8) (a) Fristad, W. E.; Peterson, J. R.; Ernst, A. B.; Urbi, G. B. *Tetrahedron* **1986**, *42*, 3442. (b) Fristad, W. E.; Peterson, J. R. *J. Org. Chem.* **1985**, *50*, 10.

(9) (a) Whitesides, G. M.; San Flippo, J. Jr. *J. Am. Chem. Soc.* **1970**, *92*, 6611. (b) Davies, D. I.; Cristol, S. J. *Adv. Free-Radical Chem.* **1965**, *1*, 155.

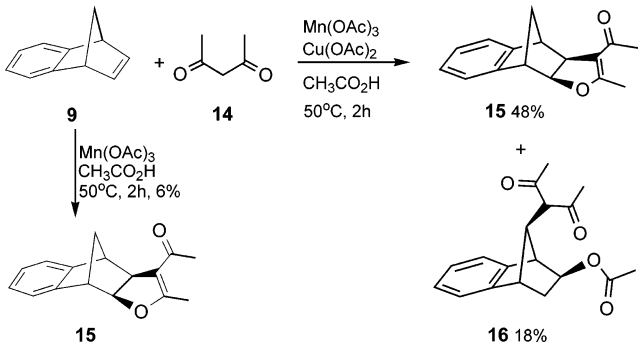
(10) (a) Senocak, E.; Taskesenligil, Y.; Tumer, F. *Turk. J. Chem.* **2002**, *26*, 939. (b) Dastan, A.; Taskesenligil, Y.; Tumer, F.; Balci, M. *Tetrahedron* **1996**, *52*, 14005. (c) Dastan, A.; Demir, U.; Balci, M. *J. Org. Chem.* **1994**, *59*, 6534. (d) Balci. M.; Cakmak, O.; Hokelek, T. *J. Org. Chem.* **1992**, *57*, 6640. (e) Cakmak, O.; Balci, M. *J. Org. Chem.* **1989**, *54*, 181. (f) Wilt, J. W.; Gutman, G.; Ranus, W. J., Jr.; Zigman, A. R. *J. Org. Chem.* **1967**, *32*, 893. (g) Cristol, Stanley, J.; Nachtigall Guenter, W. *J. Org. Chem.* **1967**, *32*, 3727.

(11) For a preliminary communication of this work see: Çalişkan, R.; Pekel, T.; Watson, W. H.; Balci, M. *Tetrahedron Lett.* **2005**, *46*, 6227**.**

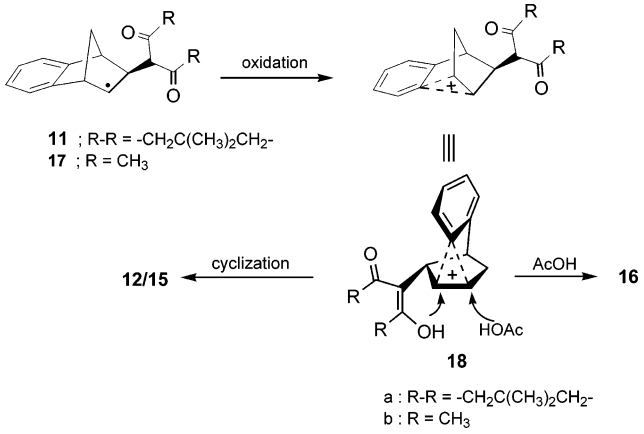
(12) Mich, T. F.; Nienhouse, E. J.; Farina, T. E.; Turariello, J. J. *J. Chem. Educ.* **1968**, *45*, 272.

(13) (a) Kazaz, C.; Daştan, A.; Balci, M. *Magn. Reson. Chem.* **2005**, *43*, 75. (b) Dastan, A. *Turk. J. Chem.* **2004**, *32*, 715. (c) Stanley, J. C.; Nachtigall, G. W. *J. Org. Chem.* **1967**, *32*, 3738.

SCHEME 3



SCHEME 4



product **16** in 48% and 18% yields, respectively (Scheme 3). For the formation of these products the following mechanism is suggested. The radical **17** formed after addition of acetylacetone to the double bond in **9** can be oxidized by $Cu(OAc)_2$ to a nonclassical cation, **18b** (Scheme 4). These cations, **18a** and **18b**, can undergo rapid cyclization with the enol forms of 1,3-dicarbonyl compounds to give **12** and **15** with the *exo*-configuration of the dihydrofuran ring. At this stage it is difficult to distinguish whether the product **12** has been formed by the capture of the radical **11** or by the intramolecular substitution of the formed nonclassical carbocation **18a**. This formed cation **18b** can be attacked by acetate anion to give **16**.[14] Acetylacetone is poorly enolizable compared to dimedone so that there is a competition between acetate anion attack and enol attack in **18b**. The absence of the rearranged product **13** can be ascribed to the complete enolization of **18a** so that the intramolecular cyclization overwhelms the external nucleophilic attack of acetic acid.

However, when the scope of this reaction is expanded to oxabicyclic alkene **19**[15] using the same methodology, the unexpected cyclopropane[16] **20** was isolated as the major product in 35% yield (Scheme 5) when the reaction was run in the presence of $Cu(OAc)_2$. Besides the expected dihydrofuran derivative **22** (16%) yield), the rearranged product **21**, where 2 mol of dimedone is incorporated into the oxanorbornadiene system, was formed in 28% yield. The presence of a three-membered ring was established by measuring the coupling constant ($^1J_{CH}$ = 177 Hz) of the cyclopropyl carbons with attached protons. The structure of compound **21** was determined by X-ray crystallographic analysis (Figure 1).

The completely different behavior of the oxanorbornadiene **19** can be attributed to the presence of the bridging oxygen atom. The addition of dimedone to oxabenzonorbornadiene gives the cyclic radical **24** (Scheme 6). Since dimedone is an easily enolizable compound, the enol functionality may interact with the bridge oxygen atom, resulting in hydrogen bonding. This restricted conformation of the molecule then would be suitable for the formation of a cyclopropane ring. Oxidative termination would result in the formation of the cyclopropane derivative **20**. For the formation of the adduct **21** we assume the primarily formed cyclic radical **24** can be further oxidized to the cation **25**. Fragmentation of **25** will relieve ring strain to give the stable cation **26**. Dimedone, as its enol, will readily add to **26**, which ring closes to give **27**.[17] Finally, intramolecular cyclization of **28** results in the formation of **21**.

In contrast, significantly different products were formed upon reaction of **19** with dimedone and $Mn(OAc)_3$ in the absence of $Cu(OAc)_2$. The rearranged product **21** was formed as the major product. Also, an additional rearranged product, **23**, was isolated in 14% yield. The exact structure of this product was determined by X-ray analysis (Figure 1). We assume that both of these rearranged products, **21** and **23**, are formed from the initially formed classical or nonclassical carbocation **25**. The formation of the rearranged product **23** was actually not expected because oxabenzonorbornadiene (**19**) undergoes mainly ring opening reaction upon reaction with electrophiles.[18] We assume that the initially formed carbocation **25** undergoes a Wagner−Meerwein-type rearrangement, thus forming the new cation **29**, which is stabilized by the lone pair of the oxygen atom. Fast attack by the enol functionality of the dimedone unit results in the formation of the rearranged product **23** (Scheme 7).

It is interesting to notice that the rearranged products **21** and **23** were formed in the absence of $Cu(OAc)_2$. It is well-documented that $Mn(OAc)_3$ oxidizes primary and secondary radicals slowly. Our findings show that the primarily formed secondary radical **24** also undergoes easy oxidation reaction with $Mn(OAc)_3$. We assume that this secondary radical **24** is activated by the oxygen bridge and this oxygen bridge is responsible for the easy oxidation reaction. Furthermore, the stabilization of the formed carbocation **29** after rearrangement with the oxygen lone pair is the driving force for the rearrangement.

Treatment of **19** with acetylacetone in acetic acid and in the presence of $Mn(OAc)_3$ and $Cu(OAc)_2$ gave a 78% yield of the adduct **30** as the single product (Scheme 8). It is interesting to note that no trace of any rearranged products was formed. A rearranged product, **32**, was formed in 8% yield when the reaction was carried out in the absence of $Cu(OAc)_2$. The major product was the reductive termination product **31**. The radical formed after addition of an oxyl radical to the double bond in **19** probably abstracts a hydrogen faster than it is oxidized to form **32**. This may be attributed to the nature of the 1,3-dicarbonyl compound and how easily the dicarbonyl compound can form the enol form.

To see the effect of the bridge heteroatom on the mode of

(14) A similar rearranged product was observed in 1% yield by the reaction of $Mn(OAc)_3$ with norbornene in glacial acetic acid. See ref 8b.

(15) Ziegler, G. R. *J. Am. Chem. Soc.* **1969**, *91*, 446.

(16) For the formation of a three-membered ring during $Mn(OAc)_3$ oxidation see: (a) Snider, B. B.; Che, Q. *Tetrahedron* **2002**, *58*, 7821. (b) Oumar-Mahamat, H.; Moustrou, C.; Surzur, J. M.; Bertrand, M. P. *J. Org. Chem.* **1989**, *54*, 5684.

(17) For a similar addition see: Snider, B. B.; Smith, R. B. *Tetrahedron* **2002**, *58*, 25.

(18) For the bromination of **19** see: Altundas, A.; Dastan, A.; McKee, M. M.; Balci, M. *Tetrahedron* **2000**, *56*, 6115.

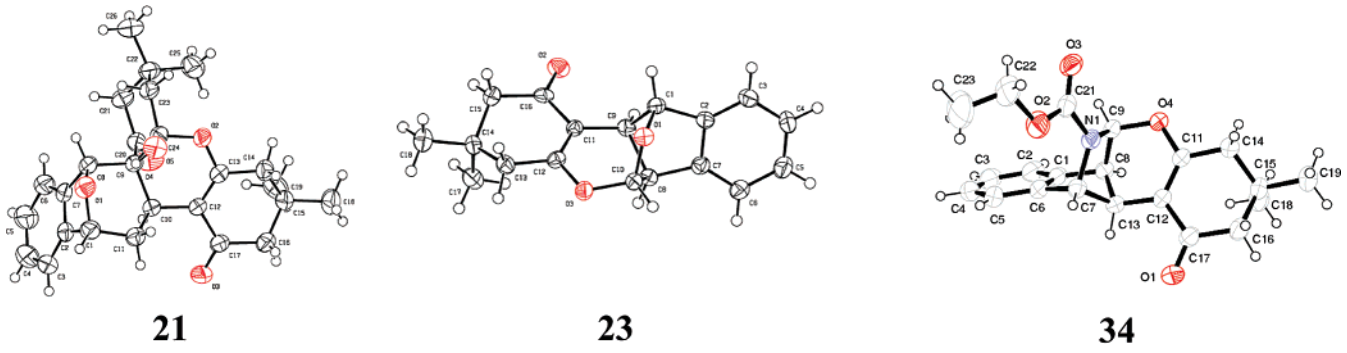
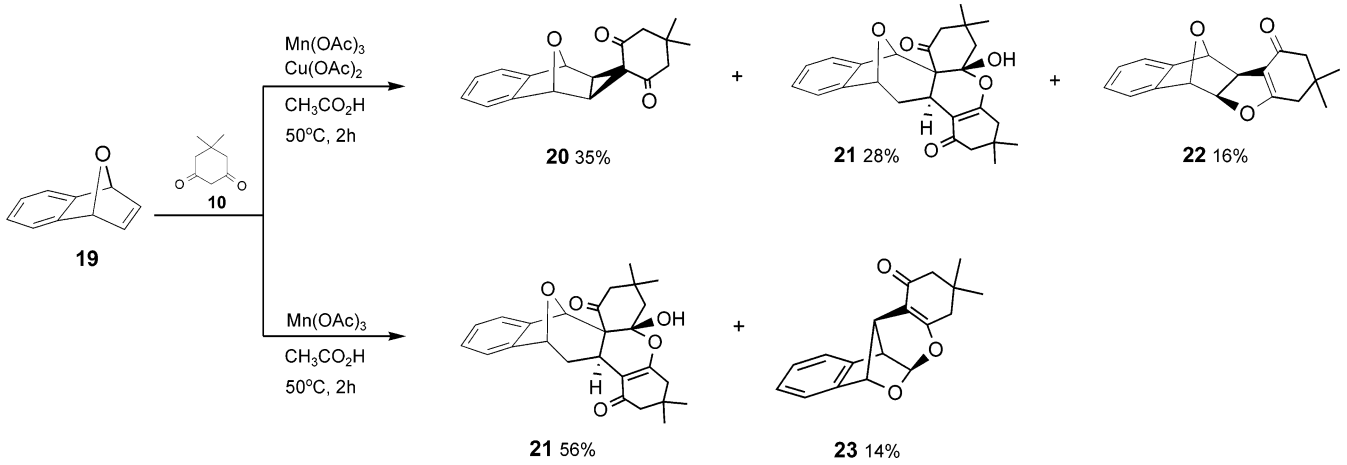
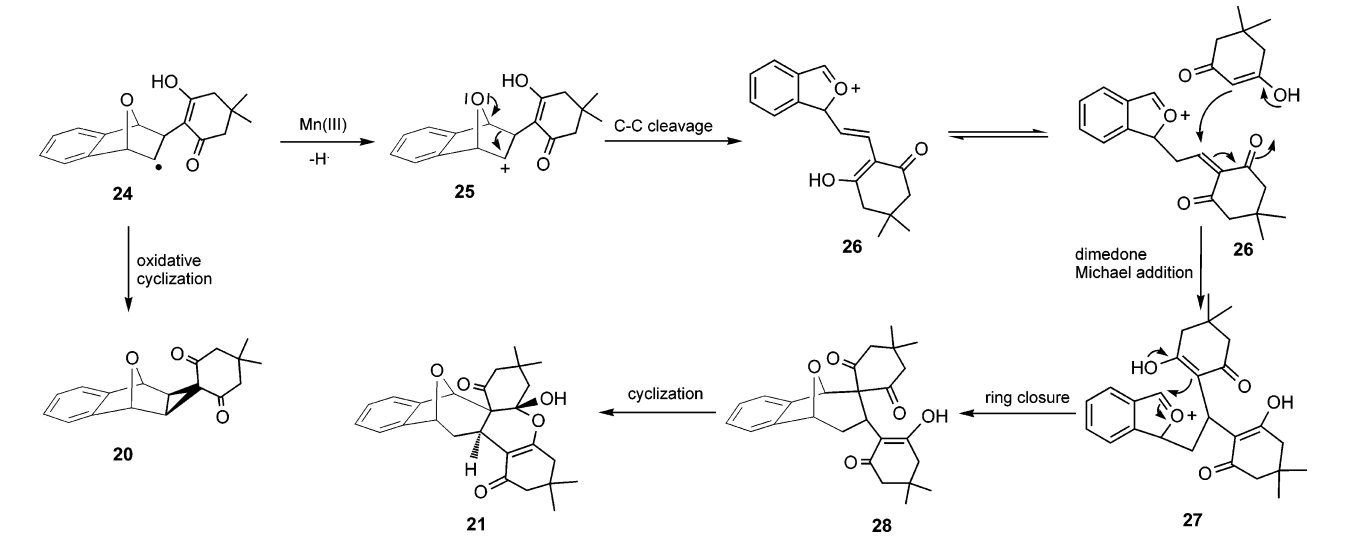


FIGURE 1. Thermal ellipsoid drawing of compounds **21**, **23**, and **34**.

SCHEME 5



SCHEME 6

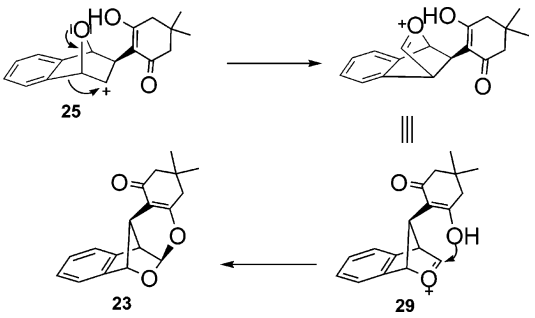


the $Mn(OAc)_3$-mediated oxidation reaction,[19] we turned our attention to the azabenzonorbornadiene derivative **33**.[20] The oxidative reaction of **33** with dimedone was accomplished with $Mn(OAc)_2$, and the rearranged product **34** was isolated as the sole product in 62% yield (Scheme 9). The exact configuration of compound **34** was determined by X-ray crystallographic analysis (Figure 1). The reaction of **33** with dimedone in the absence of $Cu(OAc)_2$ also gave the rearranged product **34** as the sole product in 41% yield. The rearranged product **34** is formed according to the mechanism depicted in Scheme **7**. A dihydrofuran derivative such as **12** or **22** and a cyclopropane derivative having the structure **20** were not formed during this reaction. We assume that the carboethoxyl group is responsible for the product distribution. The *exo*-attack of the dimedone probably causes steric hindrance between the carboethoxyl group and dimedone unit so that the rearrangement releases the strain.

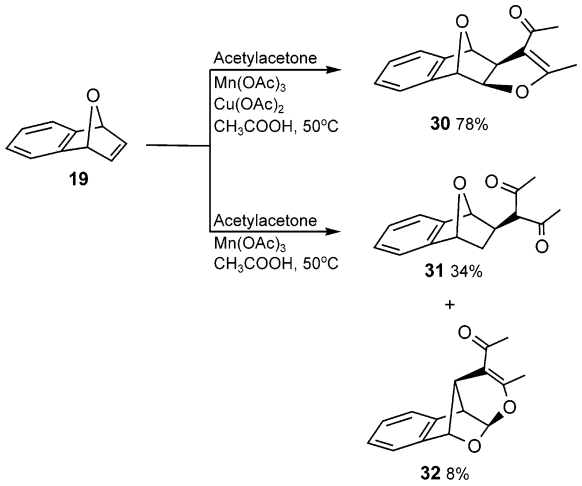
(19) For electrophilic bromination of **33** see: Tutar, A.; Balci, M. *Tetrahedron* **2002**, *58*, 8979.

(20) Anteunis, M. J. O.; Borremans, F. A. M.; Gelan, J.; Marchand, A. P.; Allen, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 4050.

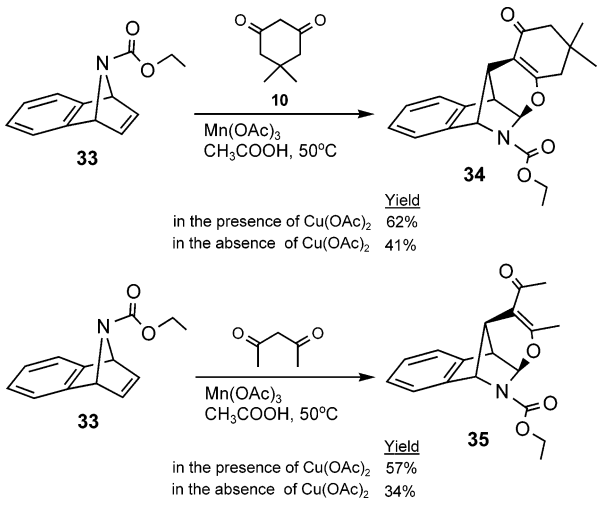
SCHEME 7



SCHEME 8



SCHEME 9



The reaction of **33** with acetylacetone in the absence and presence of $Cu(OAc)_2$ gave results very comparable to those seen with dimedone (Scheme 9).

Conclusions

9 and its hetero derivatives **19** and **33** were reacted with $Mn(OAc)_3$, dimedone, and acetylacetone in the presence of $Cu(OAc)_2$ and in the absence of it. The reaction of benzonorbornadiene with $Mn(OAc)_3$ and dimedone gave mainly a dihydrofuran derivative, **12**. On the other hand, addition of $Cu(OAc)_2$ increases the yield and forms the rearranged product. We assume that $Cu(OAc)_2$ oxidizes the initially formed radical to the cation, which undergoes Wagner−Meerwein-type rearrangement so that the cyclization takes place after oxidation reaction. However, the reaction of **19** with 1,3-dicarbonyl compounds formed mainly the rearranged products. Even in the absence of $Cu(OAc)_2$, the rearranged products were predominantly formed. It is likely that the bridge oxygen atom plays a dominant role in the oxidation reaction of the initially formed radical. The cyclization takes place mainly after the oxidation of the formed radical. Reaction of azabenzonorbornadiene derivative **33** with dimedone and acetylacetone in the presence of $Cu(OAc)_2$ and in its absence gave the rearranged products **34** and **35**, respectively. This strongly supports the oxidation of the initially formed radical to the cation. Here, again, the nitrogen atom is responsible for the easy oxidation. In addition, it is assumed that the strain caused between the carboethoxyl group and the 1,3-dicarbonyl group forces the system to undergo Wagner−Meerwein-type rearrangement. Furthermore, this strain is probably the driving force for the rearrangement and for the nonformation of normal cyclization products. Additionally, it is worth noting that possible hydrogen-bonding between the oxygen bridge in **19** and enol form of the dicarbonyl compounds determines the fate of the reaction.

Experimental Section

General Procedure. A solution of 1,3-diketone (5 mmol) and alkene (5 mmol) in 10 mL of glacial acetic acid in a flame-dried flask was heated to 50 °C under nitrogen. A 10 mmol portion of $Mn(OAc)_3 \cdot 2H_2O$ and 2 mmol of $Cu(OAc)_2$ were then added to the solution. The dark brown solution became lighter as the Mn(III) was reduced. When the reaction was complete, the solution was colorless to light blue-green with variable amounts of white precipitate present. Water was added to the reaction mixture, and the precipitate was dissolved. The solution was extracted with methylene chloride. The combined organic layers were washed several times with saturated $NaHCO_3$ solution and then water and dried ($MgSO_4$). Evaporation of the solvent gave the crude compound, which was purified by crystallization or column chromatography.

Oxidative Addition of Dimedone (10) to Benzonorbornadiene (9) in the Presence of $Mn(OAc)_3$ and $Cu(OAc)_2$. Dimedone (0.70 g, 5 mmol), benzonorbornadiene (0.71 g, 5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (2.7 g, 10 mmol), and $Cu(OAc)_2$ (0.18 g, 1 mmol) in 10 mL of glacial acetic acid were reacted as described above. Evaporation of the solvent after column chromatography on silica gel (hexane/EtOAc, 4:1) gave 6,6-dimethyl-9-oxapentacyclo[9.6.1.$0^{2,10}$.$0^{3,8}$.$0^{12,17}$]-octadeca-3(8),12,14,16-tetraen-4-one (**12**): 0.868 g, 62% yield; mp 151−154 °C from EtOAc/hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 6.9 Hz, 1H), 7.24 (d, J = 6.8 Hz, 1H), 7.10−7.16 (m, 2H), 4.87 (d, J = 7.2 Hz, 1H), 3.61 (br s, 1H), 3.58 (br s, 1H), 3.3 (d, J = 7.2 Hz, 1H), 2.33−2.43 (AB system, J = 18.3 Hz, 2H), 2.23−2.33 (AB system, J = 16.1 Hz, 2H), 1.94−2.00 (AB system, J = 10.0 Hz, 2H), 1.21 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 179.0, 149.1, 142.7, 127.4, 126.4, 122.7, 122.2, 113.4, 91.8, 51.4, 50.5, 48.9, 46.7, 43.1, 38.4, 34.4, 29.7, 28.7; IR (KBr, cm^{-1}) 3051, 2953, 2888, 1633, 1443, 1402, 1140, 962, 746; MS m/z 280 (M^+, 0.2), 178 (0.18), 165 (72.5), 128 (0.4), 116 (100). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.32; H, 7.52.

Oxidative Addition of 10 to 9 in the Absence of $Cu(OAc)_2$. Dimedone (0.70 g, 5 mmol), benzonorbornadiene (0.71 g, 5 mmol), and $Mn(OAc)_3 \cdot 2H_2O$ (2.7 g, 10 mmol) in 10 mL of glacial acetic acid were reacted as described above. The dihydrofuran derivative **12** was formed in 48% yield.

Oxidative Addition of Acetylacetone to 9 in the Presence of $Mn(OAc)_3$ and $Cu(OAc)_2$. Acetylacetone (0.5 g, 5 mmol), **9** (0.71 g 5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (2.7 g, 10 mmol), and $Cu(OAc)_2$ (0.18 g, 1 mmol) were reacted for 6 h as described above. The

chromatography of the residue on silica gel (4:1 hexane/EtOAc) gave 0.576 g of **15** (48%) and 0.27 g of **16** (18%).

Data for 1-(11-methyl-10-oxatetracyclo[6.5.1.0^{2,7}.0^{9,13}]tetradeca-2,4,6,11-tetraen-12-yl)ethan-1-one (15): mp 122−125 °C from EtOAc/hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05−7.3 (t (two overlapped doublets), J = 6.9 Hz, 2H), 7.11 (dt, J = 6.5, 1.3 Hz, 1H), 7.09 (dt, J = 6.9, 1.2, 1H), 4.72 (d, J = 7.7 Hz, 1H), 3.55 (br s, 1H), 3.40 (br s, 1H), 3.30 (d, J = 7.7 Hz, 1H), 2.31 (s, 3H), 2.28 (s, 3H), 1.95 (AB system, J = 10 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 171.5, 148.9, 143.2, 127.3, 126.5, 122.0, 121.8, 114.5, 88,5, 53.0, 50.8, 48.3, 42.8, 29.6, 15.8; IR (KBr, cm^{-1}) 3009, 2955, 2928, 2868, 1731, 1658, 1620, 1398, 1213, 960, 823, 741; MS *m*/*z* 240 (M$^+$, 1), 153 (2), 125 (30), 116 (100), 109 (4). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.52; H, 6.97.

Data for 11-(1-acetyl-2-oxapropyl)tricyclo[6.2.1.0^{2,7}]undeca-2,4,6-trien-9-yl acetate (16): mp 117−119 °C from EtOAc/hexane; ^{1}H NMR (400 MHz, C_6D_6) δ 6.99−7.25 (m, 4H), 4.85 (dd, J = 7.3, 2.6 Hz, 1H), 4.28 (d, A part of the AX system, J = 12.1 Hz, 1H), 3.60 (s, 1H), 2.98 (d, B part of the AX system, J = 12.1 Hz, 1H), 2.94 (br s, 1H), 1.89 (dt, A part of the AB system, J = 13.6, 3.4 Hz, 1H), 1.88 (s, 3H), 1.84 (s, 3H), 1.82 (s, 3H), 1.81 (dd, B part of the AB system, J = 13.6, 7.5 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 202.01, 202.0, 169.72, 148.7, 143.9, 127.2, 126.8, 122.8, 121.3, 76.3, 69.5, 58.3, 51.4, 45.3, 34.3, 28.8, 28.3, 20.9; IR (KBr, cm^{-1}) 3055, 2997, 2968, 2899, 1731, 1697, 1461, 1375, 1035, 758, 509; MS *m*/*z* 300 (M$^+$, 1.6), 240 (16), 225 (8), 197 (30), 158 (60), 148 (55), 116 (100). Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.72; H, 6.99.

Oxidative Addition of Acetylacetone to 9 in the Absence of Cu(OAc)$_2$. The reaction was run under the same reaction conditions as described above. The dihydrofuran derivative **15** was isolated in 6% yield.

Oxidative Addition of 10 to Oxabenzonorbornadiene (19). **10** (0.70 g, 5 mmol), **19** (0.72 g 5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (2.7 g, 10 mmol), and $Cu(OAc)_2$ (0.18 g, 1 mmol) were reacted for 2 h as described above. Evaporation of the solvent after coloum chromatography on silica gel (3:1 hexane/EtOAc) gave 0.493 g of **20** (35%), 0.590 g of **21** (28%), and 0.225 g of **22** (16%).

Data for spiro[12-oxatetracyclo[6.3.1.0^{2,7}.0^{9,11}]dodeca-2,4,6-triene-10,1′-(4′,4′-dimethylcyclohexa-2′,5′-dione)] (20): mp 184−187 °C from EtOAc/hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (AA′ part of the AA′BB′ system, 2H), 7.1 (BB′ part of the AA′BB′ system, 2H), 5.43 (s, 2H), 2.66 (s, 2H), 2.45 (s, 2H), 2.09 (s, 2H), 1.12 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 201.0, 146.6, 126.9, 120.3, 78.6, 59.6, 55.0, 53.7, 37.2, 31.8, 29.7; IR (KBr, cm^{-1}) 3047, 3005, 2955, 2870, 1720, 1689, 1458, 1365, 1217, 186, 991, 766, 548; MS *m*/*z* 282 (M$^+$, 8), 264 (22), 254 (62), 199 (5), 198 (16). 170 (17), 156 (21), 128 (29), 117 (100). Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.83; H, 6.53.

Data for 7-hydroxy-5,5,11,11-tetramethyl-8,24-dioxahexacyclo-[15.6.1.0^{2,7}.0^{2,15}.0^{9,14}.0^{18,23}]tetracosa-9(14),18,20,22-tetraene-3,13-dione (21): mp 145−146 °C from EtOAc/hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06−7.16 (m, 2H), 6.96 (dt, J = 7.4, 2.3 Hz, 1H), 6.66 (d, J = 7.4 Hz, 1H), 6.4 (s, 1H), 5.48 (s, 1H), 5.25 (d, J = 3.3 Hz, 1H), 2.58 (dd, J = 11.0, 6.6 Hz, 1H), 2.35 (d, A part of the AB system, J = 13.5 Hz, 1H), 2.21 (d, A part of the AB system, J = 15.0 Hz, 1H), 2.18 (dd, A part of the AB system, J = 14.0, 6.6 Hz, 1H), 2.09 (d, A part of the AB system, J = 17.2 Hz, 1H), 2.02 (d, B part of the AB system, J = 13.5 Hz, 1H), 2.01 (d, B part of the AB system, J = 15.0 Hz, 1H), 1.87−1.98 (AB system, J = 16.0 Hz, 2H), 1.78 (d, B part of the AB system, J = 17.2 Hz, 1H), 1.69 (ddd, J = 14.0, 11.5, 3.3 Hz, 1H), 0.99 (s, 3H), 0.81 (s, 3H), 0.69 (s, 3H), 0.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 196.5, 163.9, 142.3, 137.9, 129.4, 128.0, 121.4, 120.5, 112.3, 102.9, 81.1, 80.1, 55.3, 52.1, 51.2, 48.1, 42.7, 33.9, 32.9, 32.8, 31.7, 29.8, 28.1, 27.2, 21.2; IR (KBr, cm^{-1}) 3556, 3053, 2957, 2732, 2868, 1716, 1648, 1467, 1380, 1286, 1149, 847, 770, 635, 585; MS *m*/*z* 429 (M$^+$, 1), 414 (0.15), 384 (6.2), 282 (37.5), 267 (18), 254 (50), 239 (7), 222 (9), 198 (20), 181 (8), 164 (40), 141 (22), 128 (28), 108 (100). Anal. Calcd for $C_{26}H_{30}O_5$: C, 73.91; H, 7.16. Found: C, 74.15; H, 7.17.

Data for 18-oxa-6,6-dimethyl-9-oxapentacyclo[9.6.1.0^{2,10}.0^{3,8}.0^{12,17}]octadeca-3(8),1 2,14,16-tetraen-4-one (22): mp 152−153 °C from EtOAc/hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (br d, J = 7.3 Hz, 1H), 7.30 (br d, J = 6.7 Hz, 1H), 7.21 (dt, J = 7.3, 1.3 Hz, 1H), 7.17 (dt, J = 6.7, 1.2 Hz, 1H), 5.40 (s, 1H) 5.33 (s, 1H), 4.90 (d, J = 7.0 Hz, 1H), 3.38 (br d, J = 7.0 Hz, 1H), 2.38 (d, A part of the AB system, J = 17.5 Hz, 1H), 2.30 (dd, B part of the AB system, J = 17.5, 1.8 Hz, 1H), 2.14 (br s, 2H), 1.15 (s, 3H) 1.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 193.7, 178.8, 146.1, 140.4, 128.0, 127.6, 120.7, 120.2, 111.5, 89.3, 83.9, 81.2, 51.0, 48.7, 37.9, 34.2, 28.9, 28.6; MS *m*/*z* 282 (M$^+$, 1), 267 (5), 164 (6), 141 (6.5), 118 (100); IR (KBr, cm^{-1}) 3009, 2955, 2928, 2868, 1731, 1658, 1629, 1398, 1213, 1059, 960, 823, 741, 675. Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.50; H, 6.47.

Oxidative Addition of 10 to 19 in the Absence of Cu(OAc)$_2$. Dimedone (0.72 g, 5 mmol), oxabenzonorbornadiene (0.7 g 5 mmol), and $Mn(OAc)_3 \cdot 2H_2O$ (2.7 g, 10 mmol) were reacted for 5 h as described above. Evaporation of the solvent after coloum chromatography on silica gel (3:1 hexane/EtOAc) gave 0.197 g (14%) of rearrangement product **23** and 1.139 g (56%) of **21**.

Data for 3,3-dimethyl-3,4,6,6a,11,11a-hexahydro-6,11-epoxyindenol[1,2-*c*]chromen-1(2*H*)-one (23): mp 117−118 °C EtOAc/hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.2 Hz, 1H), 7.31 (d, J = 7.0 Hz, 1H), 7.28−7.14 (m, 2H), 5.41 (s, 1H), 5.26 (s, 1H), 3.42 (s, 1H), 3.28 (s, 1H), 2.39 (A part of the AB system, J = 17.6 Hz, 1H), 2.31 (A part of the AB system, J = 16.2 Hz, 1H) 2.26 (B part of the AB system, J = 17.6 Hz, 1H), 2.20 (B part of the AB system, J = 16.2 Hz, 1H), 1.14 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 168.2, 146.8, 142.7, 128.1, 126.9, 123.5, 121.8, 113.9, 98.6, 91.8, 51.7, 50.7, 46.8, 41.3, 32.9, 29.8, 28.0; IR (KBr, cm^{-1}) 3441, 2891, 2961, 1644, 1458, 1390, 1252, 988, 941, 812, 969, 716. Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 75.89; H, 6.28.

Oxidative Addition of Acetylacetone to 19 in the Presence of Mn(OAc)$_3$ and Cu(OAc)$_2$. Acetylacetone (0.5 g, 5 mmol), oxabenzonorbornadiene (0.72 g 5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (2.7 g, 10 mmol), and Cu(OAc) (0.18 g, 1 mmol) were dissolved in 10 mL of glacial acetic acid and reacted for 2 h and 15 min as described below. Crystallization of the residue from hexane/EtOAc (3:1) gave 0.936 g of **30** (78%).

Data for 1-(11-methyl-10,14-dioxatetracyclo[6.5.1.0^{2,7}.0^{9,13}]-tetradeca-2,4,6,11-tetraen-12-yl)ethan-1-one (30): mp 148−150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15−7.35 (m, 4H), 5.54 (s, 1H), 5.35 (s, 1H), 4.7 (d, J = 7.4 Hz, 1H), 3.45 (d, J = 7.4 Hz, 1H), 2.28 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 170.6, 146.0, 140.6, 127.9, 127.1, 120.8, 120.1, 114.1, 85.9, 84.4, 82.4, 52.6, 29.3, 15.8; MS *m*/*z* 242 (M$^+$, 1), 152 (5), 139 (1), 118 (100); IR (KBr, cm^{-1}) 3542, 3410, 2994, 2974, 1625, 1456, 1390, 1203, 1005, 941, 852, 966, 646, 531. Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.81. Found: C, 73.94; H, 5.84.

Oxidative Addition of Acetylacetone to 19 in the Absence of Cu(OAc)$_2$. Acetylacetone (0.5 g, 5 mmol), oxabenzonorbornadiene (0.72 g 5 mmol), and $Mn(OAc)_3 \cdot 2H_2O$ (2.7 g, 10 mmol) were dissolved in 10 mL of glacial acetic acid and reacted for 9 h at 50 °C as described above. Evaporation of the solvent after column chromatography on silica gel eluting with hexane/EtOAc (3:1) gave 0.09 g of **32** (8%) and 0.414 g of **31** (34%).

Data for 1-(3-methyl-1,4a,5,9b-tetrahydro-1,5-epoxyindenol-[1,2-*c*]pyran-4-yl)ethan-1-one (32): pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 7.1 Hz, 1H), 7.23 (d, J = 7.1 Hz, 1H), 7.17−7.08 (m, 2H), 5.33 (s, 1H), 5.08 (s, 1H), 3.36 (s, 1H), 3.01 (s, 1H), 2.22 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 163.0, 146.5 142.8, 128.2, 126.9, 123.7, 121.7, 114.9, 97.3, 91.7, 56.5, 46.4, 29.9, 20.1; IR (KBr, cm^{-1}) 2894, 2812, 1674, 1423, 1370, 1236, 1046, 953, 851, 876, 642, 559. Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.21; H, 6.01.

Data for 3-(1,2,3,4-Tetrahydro-1,4-epoxynaphthalen-2-yl)-pentane-2,4-dione (31): mp 171−174 °C from hexane/EtOAc; ^{1}H NMR (400 MHz, $CDCl_3/CCl_4$) δ 7.14−7.33 (m, 4H), 5.31 (d, J = 4.8 Hz, 1H), 4.87 (s, 1H), 3.78 (d, J = 11.3 Hz, 1H), 2.51 (ddd, J = 11.3, 7.8, 4.11 Hz, 1H), 2.29 (s, 3H), 2.12 (s, 3H), 1.60 (dd, A part of the AB system, J = 11.6, 7.8 Hz, 1H), 1.53 (dt, B part of the AB system, J = 11.6, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 202.2, 145.8, 145, 127.2, 127.2, 119.6, 119.1, 81.8, 79.5, 74.4, 40, 32.7, 30.3, 28.8; IR (KBr, cm^{-1}) 2994, 2851, 1685, 1623, 1390, 1203, 1005, 941, 852, 966, 646, 617. Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.49; H, 6.66.

Oxidative Addition of 10 to Azabenzonorbornadiene 33 in the Presence of $Mn(OAc)_3$ and $Cu(OAc)_2$. Dimedone (0.35 g, 2.5 mmol), azabenzonorbornadiene **34** (0.535 g 2.5 mmol), $Mn(OAc)_3\cdot 2H_2O$ (1.35 g, 5 mmol), and $Cu(OAc)_2$ (0.18 g, 1 mmol) were disolved in 10 mL of glacial acetic acid and reacted for 2 h at 50 °C. Evaporation of the solvent and chromatography on silica gel eluting with hexane/EtOAc (4:1) gave 0.55 g (62%) of **34**: colorless solid; mp 176−178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (isomer A) δ 7.1−7.3 (m, 4H), 5.62 (s, 1H), 5.06 (s, 1H), 4.07 (br q, J = 6.8 Hz, 2H), 3.35 (s, 1H), 3.32 (s, 1H), 2.41 (d, A part of the AB system, J = 17.4 Hz, 1H), 2.34 (d, B part of the AB system, J = 17.4 Hz, 1H), 2.32 (d, A part of the AB system, J = 15.3 Hz, 1H), 2.18 (d, B part of the AB system, J = 15.3 Hz, 1H), 1.22 (t, J = 6.8 Hz, 3H), 1.11 (s, 3H), 1.06 (s, 3H); (isomer B) δ 5.51 (br s, 1H), 5.15 (br s, 1H), 4.01 (br q, 2H), 1.20 (t, 3H), other signals same as for isomer A; ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 168.3, 155.2, 146.5, 141.8, 127.2, 126.6, 123.6, 122.0, 113.6, 86.3, 70.6, 61.6, 51.1, 50.3, 45.7, 41.0, 32.5, 29.7, 27.2, 14.6; IR (KBr, cm^{-1}) 3026, 2967, 2891, 1714, 1646, 1617, 1463, 1394, 1334, 1282, 1192, 1132, 1010, 775, 538. Anal. Calcd for $C_{21}H_{23}NO_4$ C, 71.37; H, 6.56; N, 3.96. Found: C, 71.35; H, 6.53, N, 4.24.

Oxidative Addition of 10 to Azabenzonorbornadiene 33 in the Absence of $Cu(OAc)_2$. The reaction was carried out as described above. The rearranged product **34** was isolated in 41% yield.

Oxidative Addition of Acetylacetone to Azabenzonorbornadiene 33 in the Presence of $Mn(OAc)_3$ and $Cu(OAc)_2$. Acetylacetone (0.25 g, 2.5 mmol), azabenzonorbornadiene (0.535 g 2.5 mmol), $Mn(OAc)_3\cdot 2H_2O$ (1.35 g, 5 mmol), and Cu(OAc) (0.18 g, 1 mmol) were disolved in 10 mL of glacial acetic acid and reacted for 18 h at 50 °C as described above. Evaporation of the solvent and crystallization of the residue from hexane/EtOAc (3:1) gave 0.45 g of **35** (57%): colorless solid; mp 166−168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (isomer A) δ 7.1−7.4 (m, 4H), 5.54 (br s, 1H), 5.10 (s, 1H), 4.08 (br d, J = 7.1 Hz, 2H), 3.37 (s, 1H), 3.15 (s, 1H), 2.31 (s, 3H), 2.29 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H); (isomer B) δ 5.43 (br s, 1H) 5.21 (br s, 1H), 4.04 (br q, 2H), 3.11 (br s, 1H), 1.17 (t, 3H), other signals same as for isomer A; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 163.8, 155.5, 146.2, 141.9, 127.4, 126.6, 123.9, 121.3, 114.5, 85.2, 70.9, 61.7, 55.9, 45.3, 29.7, 20.0, 14.5; IR (KBr, cm^{-1}) 3046, 2980, 2909, 1710, 1670, 1579, 1415, 1379, 1300, 1157, 1008, 949, 760, 679, 513. Anal. Calcd for $C_{18}H_{19}NO_4$: C, 68.99; H, 6.11; N, 4.47. Found: C, 68.96; H, 6.04, N, 4.71.

Oxidative Addition of Acetylacetone to Azabenzonorbornadiene 33 in the Absence of $Cu(OAc)_2$. The reaction was carried out as described above. The rearranged product **35** was isolated in 34% yield.

Acknowledgment. We greatly acknowledge Professor Snider for valuable discussions concerning the mechanism of formation of **21** and providing very useful references. We thank the Scientific & Technological Research Council of Turkey (TUBITAK, Grant No. 106M335), Turkish Academy of Sciences (TUBA), and Department of Chemistry at the Middle East Technical University, where this work was carried out, for financial support of this work. Furthermore, we thank Assoc. Professor H. Kiliç (Atatürk University) for elemental analysis and mass spectral measurements.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra for all new compounds and crystallographic information files (CIFs) for compounds **21**, **23**, and **34**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0625711