The Reaction of 1-Amino-2,3-diphenylcyclopropenium Ions with 1,3-Diketones to Afford 2,4-Cyclopentadien-1-ols: The Regioselective Ring-Opening of 1-Amino-cyclopropene Intermediates

Hiroshi YOSHIDA,* Tomoji TAMAI, Tsuyoshi OGATA, and Kiyoshi MATSUMOTO†
Department of Applied Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu 432
†College of Liberal Arts and Sciences, Kyoto University, Kyoto 606
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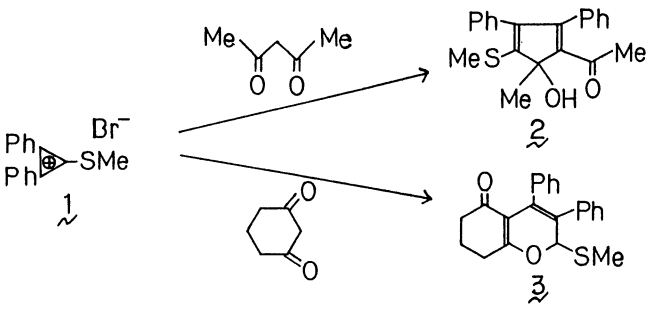
1-Amino-2,3-diphenylcyclopropenium tetrafluoroborates (**4**) reacted with cyclic or acyclic 1,3-dicarbonyl derivatives (**5**) such as 1,3-diketones, β-keto esters, or gem-diesters in the presence of triethylamine to give 2,4-cyclopentadien-1-ols in moderate to good yields. Some isolated cyclopropene intermediates were, upon heating, converted to the corresponding cyclopentadienols. The factors that influence on the reactivities of **4** and **5** (basicities of the amino groups of **4** and bulkiness of the substituents of **4** and **5**) are discussed qualitatively.

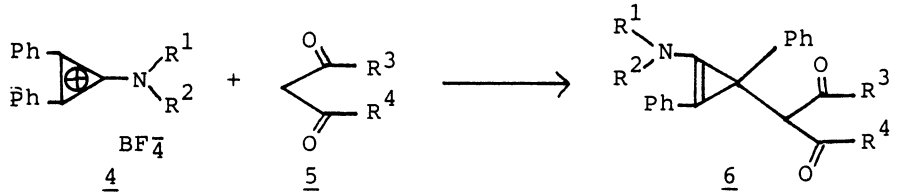
The chemistry of cyclopropene derivatives has attracted considerable interest because of the high strain energy associated with the unsaturated three-membered ring. A number of studies on the photochemical and thermal ring-opening reactions of cyclopropenes have appeared in recent years.[1,2]

We have recently reported the reaction of 1-(methylthio)-2,3-diphenylcyclopropenium ion (**1**) with 2,4-pentanedione and with 1,3-cyclohexanedione to yield cyclopentadienol (**2**)[3] and 2*H*-pyran derivative (**3**),[4] respectively (Scheme 1). In this connection we have been interested in the effect of heteroatom substituents (such as alkoxy, alkylthio, and amino groups) on the attacking position of cyclopropenium ions and ring opening of the resulting cyclopropenes.[2-4] This paper describes the reaction of 1-amino-2,3-diphenylcyclopropenium ions (**4**) with 1,3-dicarbonyl compounds **5** to afford cyclopropenes **6**, followed by regioselective ring opening to give cyclopentadienols **7**.

1-Amino-2,3-diphenylcyclopropenium tetrafluoroborates (**4**) were prepared by a reaction of 2,3-

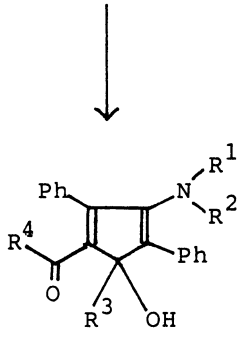


Scheme 1.

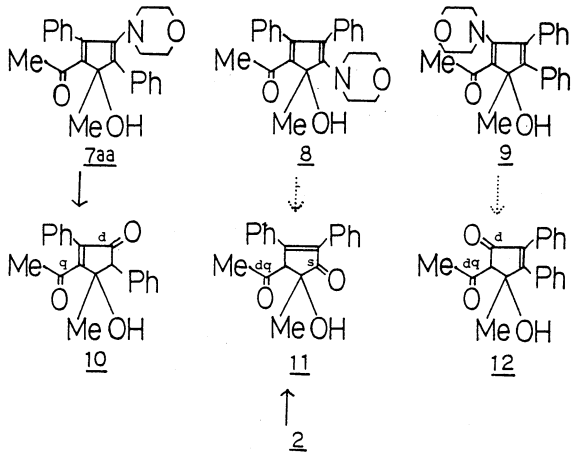


4	R^1	R^2
a	$(CH_2)_2O(CH_2)_2$	
b	$(CH_2)_5$	
c	$(CH_2)_4$	
d	C_2H_5	C_2H_5
e	CH_3	CH_3
f	CH_3	Ph

5	R^3	R^4
a	CH_3	CH_3
b	CH_3	Ph
c	Ph	Ph
d	$(CH_2)_3$	
e	$CH_2C(CH_3)_2CH_2$	
f	$(CH_2)_2$	
g	CH_3	OCH_3
h	CH_3	OC_2H_5
i	CH_3	OBu-t
j	OC_2H_5	OC_2H_5



Scheme 2.

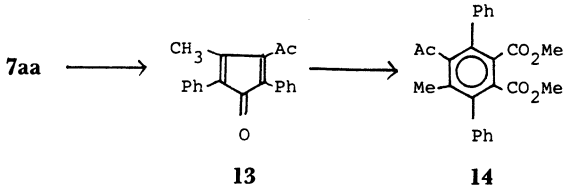


Scheme 3.

diphenylcyclopropenone with triethyloxonium tetrafluoroborate, followed by a treatment with secondary amines.[5-7] A mixture of 1-morpholino-2,3-diphenylcyclopropenium tetrafluoroborate (**4a**), 2,4-pentanedione (**5a**), and triethylamine in a mole ratio of 1 : 1.1 : 2 was stirred in dry benzene at room temperature for 1 h to yield the reaction product **X** as yellow needles. The ^{1}H and ^{13}C NMR, and mass spectra of **X** revealed the structure to be a cyclopentadienol derivative arising from a 1 : 1 adduct of **4a** and **5a**, but did not permit a clear choice among mechanistically possible isomers (**7aa**, **8**, and **9** in Scheme 3).

Upon hydrolysis **7aa**, **8**, and **9** might give cyclopentenones **10**, **11**, and **12** respectively (Scheme 3). Previously we have shown[3] that desulfurization of **2** yields 2-cyclopentenone **11** (mp 184—185 °C), whose ^{13}C NMR spectrum shows two carbonyl carbons at δ=204.9 (dq, $\underline{C}OCH_3$) and 206.8 (s, C_1). Cyclopentenone **12** might yield two carbonyl carbons as a dq ($\underline{C}OCH_3$ due to coupling with $COCH_3$ and $C_5\underline{H}$) and a d (C_1 due to $C_5\underline{H}$). Hydrolysis of **X** under mild conditions (formic acid in benzene) afforded cyclopentenone as a colorless crystalline mass (mp 159—161 °C), whose ^{13}C NMR spectrum showed a d at 203.1 ($^{2}J_{CCH}$=6.8 Hz, C_1) and a q at 204.1 ($^{2}J_{CCH}$=6.0 Hz, $\underline{C}OCH_3$) due to carbonyl carbons, establishing the structure of the cyclopentenone to be **10**. Consequently, **X** was unambigously revealed to be 1-acetyl-2,4-diphenyl-5-hydroxy-5-methyl-3-morpholinocyclopentadiene (**7aa**).

Although stable under basic conditions (NaOH in ethanol) **7aa** upon being treated with trifluoroacetic acid produced complex mixtures. In a mixture of chloroform and ethanol containing a small amount of trifluoroacetic acid, **7aa** yielded the cyclopentadienone **13** in quantitative yield, which underwent a Diels-Alder addition with dimethyl acetylenedicarboxylate (DMAD) to give the hexasubstituted benzene **14** in a 28% yield.



13 **14**

Table 1. The Reaction of **4** with **5** in the Presence of Triethylamine at Room Temperature

Reactant 4	Reactant 5	Reaction time /h	Product (yield/%)
4a	**5a**	1	**7aa** (71)
	5b	1	**7ab** (33)
	5c	24	**6ac** (28)
	5d	1	**7ad** (67)
	5e	1	**7ae** (82)
	5f	1	**7af** (43)
	5g	4	**6ag** (66)
	5h	4	**7ah** (63)
	5i	4	**6ai** (60)
	5j	4	**6aj** (65)
4b	**5a**	1	**7ba** (45)
	5b	1	**7bb** (7)
	5c	1	**7bc** (56)
	5d	1	**7bd** (79)
	5e	1	**7be** (76)
	5f	1	—
	5g	2	**7bg** (43)
	5h	2	**7bh** (51)
4c	**5a**	1	—
	5c	1	—
	5d	1	—
	5f	1	—
4d	**5a**	1	**7da** (74)
	5b	1	**7db** (4)
	5c	1	—
	5d	1	**7dd** (86)
	5g	4	**6dg** (71)
	5h	4	**6dh** (93)
4e	**5a**	1	**7ea** (38)
	5d	1	**7ed** (70)
4f	**5a**	1	—
	5d	1	**7fd** (45)

Table 2. Thermal Ring Opening of Cyclopropenes **6**

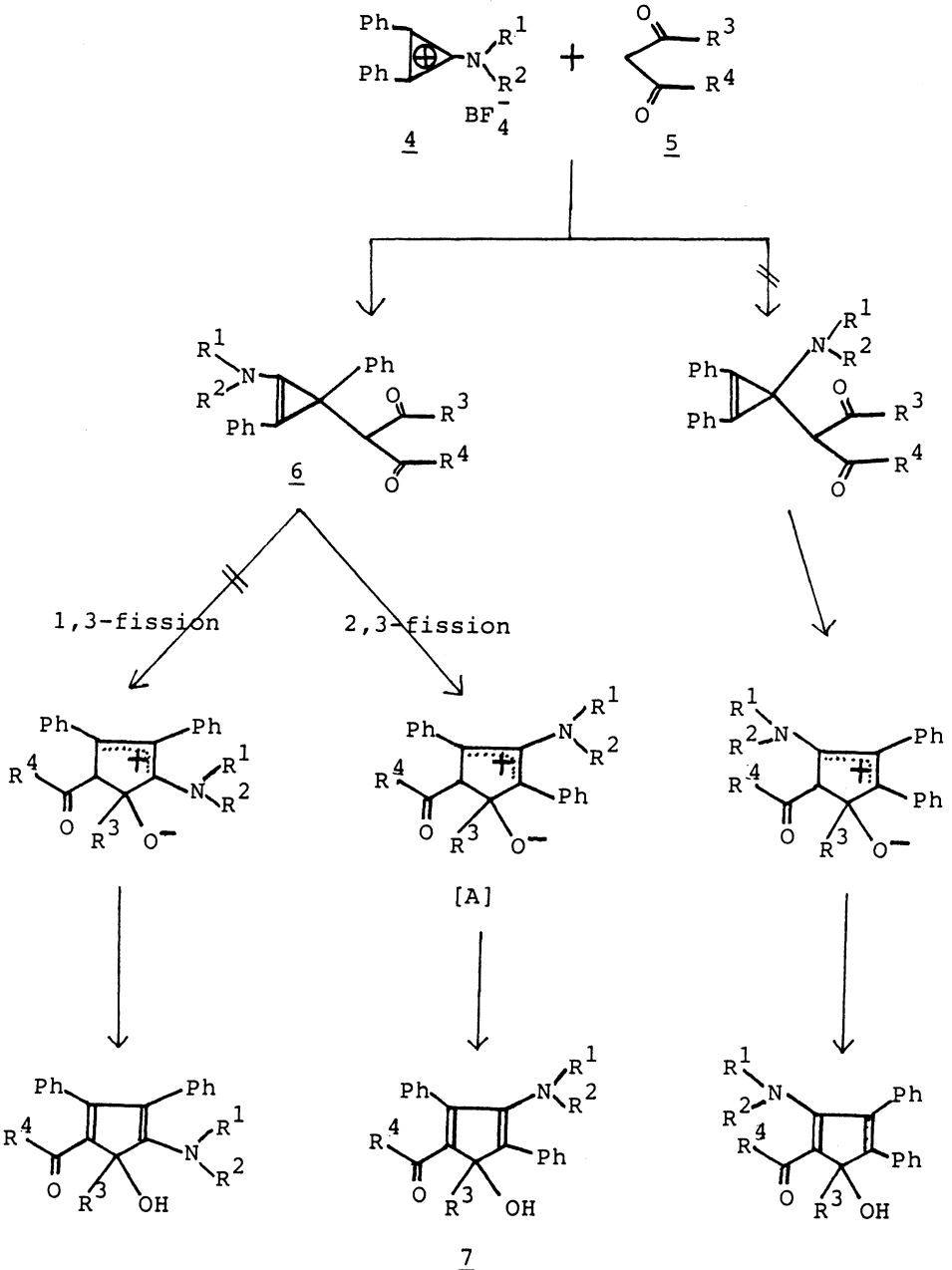
Reactant 6	Reaction condition: Solvent	Temp/°C	Time/h	Product (Yield/%)
6ac	Xylene	120	3	Recovery
6ag	Benzene	50	3	**7ag** (73)
6ai	Benzene	50	3	**7ai** (52)
6aj	Benzene	80	5	Unknown mixture
6dj	Benzene	80	3	**7dj** (84)
6dh	Benzene	80	3	**7dh** (76)

The results of the reaction of cyclopropenium ions possessing amino substituents **4a—4d** with acyclic and cyclic 1,3-diketones, -ketoesters, and diethyl malonates **5a—5j** are collected in Table 1. In certain cases, 1-aminocyclopropenes **6** were isolated, whose structure were elucidated on the basis of their IR (around 1840 cm^{-1}) and ^{13}C NMR (C_3, sp^3 carbon) spectroscopic studies. The cyclopropenes could be isolated when they were derived from either small enolizable[8-10] or bulky

diketones **5**, and/or bulky amines **4** (Table 1). The cyclopropenes **6** were converted to the corresponding cyclopentadienols **7** under the stronger conditions as listed in Table 2.

Six-membered cyclic ketones **5d** and **5e** showed high reactivities toward ions **4** yielding good crystalline products, whereas, a 5-membered ketone **5f** gave unstable mixtures from which no crystalline product could be isolated. The reaction of **4a** and **4b** with sterically hindered ketones **5c** afforded **6ac** and **7bc**, respectively, while **4d** gave no crystalline product with **5c**. Thus, the reactivities of the ions **4** seem to have been influenced by the basicities of the amines and bulkiness of the amino substituents. The pyrrolidinyl substituted **4c** reacted with diketones **5a**, **5c**, and **5d**, but gave unidentifiable tarry mixtures, probably because the enamine-type products would be hydrolyzed under the purification procedure.[11]

Finally, we propose a mechanism for the reaction of **4** with **5**, as illustrated in Scheme 4. The initial step involves a nucleophillic attack of the carbanion generated fron 1,3-diketones **5** on the C_2 or C_3 of **4** to yield 1-aminocyclopropene **6**, since the electron-releasing properties of the amino group would increase the electron density of C_1. Two routes are possible for the ring opening of the cyclopropenes. As we mentioned in an earlier paper,[3] 3-(1,2,3-triphenylcyclopropenyl)-2,4-pentadienone was stable at 100 °C in both the presence and absence of triethylamine. This observation indicates that the electron-attracting nature of the carbonyl



Scheme 4.

groups does not facilitate a ring opening of the cyclopropene. Considering the products obtained (**7**), a process involving a carbenium ion like **A** seems to be most stabilized by the adjacent amino group.

In the reaction of **1**, as shown in Scheme 1, acyclic and cyclic diketones gave two kinds of products, respectively (**2** and **3**). These results can be well-explained in terms of the electron-releasing and -accepting properties of the alkylthio group.[3] The electron-releasing nature of the amino substituent does not permit a formation of 2*H*-pyran derivatives (**3** analogues), yielding only cyclopropentadienol **7**(**2** analogues).

Experimental

General. Melting points were uncorrected. The ^{13}C NMR spectra were recorded either on a JEOL JMN FX-60 spectrometer (15.04 MHz) or JEOL JNM FX-90Q (22.49 MHz) and ^1H NMR spectra on a Hitachi R-24B (60 MHz). The IR spectra were recorded on a JASCO A-3 spectrometer.

Preparation of 1-Amino-2,3-diphenylcyclopropenium Tetrafluoroborates 4. The salts **4** were prepared by a known method.[5-7] Analytical and spectroscopic data for new derivatives are as follows. **4a** in 85% yield: mp 273—275 °C; IR(KBr) 1890 cm^{-1}; ^1H NMR ($CDCl_3$-CF_3CO_2H in 10:1) δ=4.04 (s, 8H, $2N(CH_2)_2O$) and 7.4—8.1 (m, 10H, 2Ph). Found: C, 62.53; H, 4.88; N, 3.69%. Calcd for $C_{19}H_{18}BF_4NO$: C, 62.84; H, 5.00; N, 3.86%. **4b** in 56% yield: mp 252—253 °C; IR(KBr) 1890 cm^{-1}; ^1H NMR ($CDCl_3$-CF_3CO_2H in 10:1) δ=1.88 (bs, 6H, $(CH_2)_3$), 3.8—4.2 (m, 4H, $N(CH_2)_2$), and 7.5—8.1 (m, 10H, 2Ph). Found: C, 66.62; H, 5.53; N, 3.99%. Calcd for $C_{20}H_{20}BF_4N$: C, 66.51; H, 5.58; N, 3.88%. **4c** in 15% yield: mp 275—278 °C; IR(KBr) 1900 cm^{-1}; ^1H NMR ($CDCl_3$-CF_3CO_2H in 10:1) δ=2.3—2.7 (m, 4H, $(CH_2)_2$), 4.0—4.4 (m, 4H, $N(CH_2)_2$), and 7.5—8.2 (m, 10H, 2Ph). Found: C, 65.47; H, 5.06; N, 4.12%. Calcd for $C_{19}H_{18}BF_4N$: C, 65.74; H, 5.23; N, 4.03%.

The Reaction of 4 with 1,3-Diketones 5. A general procedure. A mixture of **4** (1 mmol), **5** (1.1 mmol), and triethylamine (2 mmol) in 15 cm^3 of dry benzene was stirred at room temperature. After the reaction (no change of the precipitate and TLC of the reaction mixture) the solution was poured into cold water, and the organic layer was separated and dried over sodium carbonate. Recrystallization of the product from benzene-petroleum ether afforded faint-yellow crystals. Yields are listed in Table 1.

Thermal Reaction of 6. A solution of **6** (0.2 g) in an appropriate solvent (10 cm^3) was heated at reflux and the reaction was checked by TLC. After the reaction the mixture was condensed and the products which separated were recrystallized from benzene-petroleum ether (Table 2). The physical properties are as follows. **7aa:** mp 143—144 °C; IR(KBr) 3440 and 1620 cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.41 (s, 3H, CH_3), 1.80 (s, 3H, $COCH_3$), 2.3—2.6 (m, 4H, $N(CH_2)_2$), 3.1—3.4 (m, 4H, $O(CH_2)_2$), 3.95 (s, 1H, OH), and 7.2—7.7 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$) δ=25.4(q), 30.2(q), 50.9(t), 66.6(t), 83.4(s), 127.5(d), 128.6(d), 128.9(d), 130.2(d), 134.3(s), 134.4(s), 137.5(s), 144.1(s), 147.3(s), 153.5(s). and 196.1(s). Found: C, 76.57; H, 6.58; N, 3.83%; M^+, 375. Calcd for $C_{24}H_{25}NO_3$: C, 76.76; H, 6.72; N, 3.73%; M, 375. **7ab**: mp 164—165 °C; IR(KBr) 3350 and 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.50 (s, 3H, CH_3), 2.2—2.5 (m, 4H, $N(CH_2)_2$), 3.1—3.4 (m, 4H, $O(CH_2)_2$), 3.57 (s, 1H, OH), and 6.8—7.8 (m, 15H, 3Ph). Found: C, 79.55; H, 6.21; H, 3.19%; M^+, 437. Calcd for $C_{29}H_{27}NO_3$: C, 79.61; H, 6.22; N, 3.20%; M, 437. **6ac**: mp 179—181 °C; IR (KBr) 1840, 1700, and 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.66 (t, J=5Hz, 4H, $N(CH_2)_2$), 3.51 (t, J=5 Hz, 4H, $O(CH_2)_2$), 6.8—8.1 (m, 20H, 4Ph). ^{13}C NMR ($CDCl_3$) δ=51.0(t), 66.4(t), 87.5(s), 92.8(d), 124.7(s), 126.8(d), 127.2(d), 128.0(d), 128.2(d), 128.3(d), 128.6(d), 129.0(d), 129.6(d), 131.5(d), 132.2(d), 133.0(d), 133.9(d), 137.2(s), 139.7(s), 147.1(s), 150.8(s), 185.4(s), and 195.1(s). Found: C, 81.71; H, 5.61; N, 2.73%; M^+, 499. Calcd for $C_{34}H_{29}NO_3$: C, 81.74; H, 5.85; N, 2.80%; M, 499. **7ad**: mp 160—162 °C; IR(KBr) 3400 and 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.5—2.2 (m, 6H, $(CH_2)_3$), 2.2—2.7 (m, 4H, $N(CH_2)_2$), 3.1—3.4 (m, 4H, $O(CH_2)_2$), and 7.0—7.8 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$) δ=18.7(t), 34.6(t), 41.7(t), 50.9(t), 66.4(t), 85.9(s), 127.0(d), 127.3(d), 127.7(d), 128.4(d), 129.5(d), 130.4(d), 132.1(s), 134.9(d), 142.2(s), 145.2(s), 146.8(s), and 197.9(s). Found: C, 77.42; H, 6.60; N, 3.76%; M^+, 387. Calcd for $C_{25}H_{25}NO_3$: C, 77.48; H, 6.52; N, 3.62%; M, 387. **7ae**: mp 131—133 °C; IR (KBr) 3430 and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.82 (s, 3H, CH_3) 1.10 (s, 3H, CH_3), 1.9—2.4 (m, 4H, $(CH_3)_2C(C\underline{H}_2)_2$), 2.4—2.7 (m, 4H, $N(CH_2)_2$), 3.2—3.6 (m, 4H, $O(CH_2)_2$), 5.85 (s, 1H, OH), and 7.2—7.9 (m, 10H, 2Ph). Found: C, 77.73; H, 7.08; N, 3.65%; M^+, 415. Calcd for $C_{27}H_{29}NO_3$: C, 78.03; H, 7.05; N, 3.37%; M, 415. **7af**: mp 136—138 °C; IR (KBr) 3450 and 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.82 (bs, 4H, $(CH_2)_2$), 2.1—2.5 (m, 4H, $N(CH_2)_2$), 2.8—3.3 (m, 4H, $O(CH_2)_2$), 5.65 (s, 1H, OH), and 6.7—7.6 (m, 10H, 2Ph). Found: C, 77.23; H, 6.18; N, 3.39%; M^+, 373. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.18; N, 3.75%; M, 373. **6ag**: oil; IR (KBr) 1850 and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.77 (s, 3H, CH_3), 2.7—2.9 (m, 4H, $(CH_2)_2$), 2.93 (s, 3H, OCH_3), 3.1—3.4 (m, 4H, $O(CH_2)_2$), 4.71 (s, 1H, OH), and 6.9—7.4 (m, 10H, 2Ph). Found: C, 73.53; H, 6.24; N, 3.51%; M^+, 391. Calcd for $C_{24}H_{25}NO_4$: C, 73.63; H, 6.44; N, 3.58%; M, 391. **7ag**: mp 168—170 °C; IR (KBr) 3350 and 1680; cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.46 (s, 3H, CH_3), 2.48 (t, J=5 Hz, 4H, $O(CH_2)_2$), 3.28 (t, J=5 Hz, $O(CH_2)_2$), 3.53 (s, 3H, OMe), and 7.1—7.5 (m, 10H, 2Ph). Found: C, 73.22; H, 6.41; N, 3.46%; M^+, 391. Calcd for $C_{24}H_{25}NO_4$: C, 73.63; H, 6.44; N, 3.58%; M, 391. **7ah**: mp 148—149 °C; IR (KBr) 3500 and 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.99 (t, J=8 Hz, 3H, $C\underline{H}_3CH_2$), 1.45 (s, 3H, CH_3), 2.3—2.7 (m, 4H, $N(CH_2)_2$), 3.1—3.5 (m, 4H, $O(CH_2)_2$), 3.70 (s, 1H, OH), 4.01 (q, 2H, $CH_3C\underline{H}_2$), and 7.1—7.6 (m, 10H, 2Ph). Found: C, 73.78; H, 6.64; N, 3.40%; M^+, 405. Calcd for $C_{25}H_{27}NO_4$: C, 74.04; H, 6.72; N, 3.45%; M, 405. **6ai** oil; IR (KBr) 1850, 1720, and 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (s, 6H, $C(CH_3)_2$), 1.11 (s, 3H, CCH_3), 2.88 (t, J=5Hz, 4H, $N(CH_2)_2$), 3.42 (t, J=5Hz, 4H, $O(CH_2)_2$), 4.73 (s, 1H, OH), and 6.9—7.5 (m, 10H, 2Ph). Found: C, 74.91; H, 7.01; N, 3.33%; M^+, 433. Calcd for $C_{27}H_{31}NO_4$: C, 74.80; H, 7.21; N, 3.23%; M, 433. **7ai**: mp 178—179 °C; IR (KBr) 3520 and 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.21 (s, 9H, *t*-Bu), 1.45 (s, 3H, CH_3), 2.48 (t, J=5Hz, 4H, $N(CH_2)_2$), 3.24 (t, J=5Hz, 4H, $O(CH_2)_2$), 3.82 (s, 1H, OH), and 7.2—7.5 (m, 10H, 2Ph). Found: C, 74.82; H, 7.11; N, 3.20%; M^+, 433. Calcd for $C_{27}H_{31}NO_4$: C, 74.80; H, 7.21; N, 3.23%; M, 433. **6aj** oil; IR (KBr) 1850 and 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.00 (s, J=9Hz, 6H, $2C\underline{H}_3CH_2$), 3.2—4.0 (m, 12H, $2CH_3C\underline{H}_2$ and $O(CH_2CH_2)_2$), and 7.0—8.2 (m, 10H, 2Ph). Found: C, 71.68; H, 6.90; N, 3.61%; M^+, 435. Calcd for $C_{26}H_{29}NO_5$: C, 71.70; H, 6.71; N, 3.22%; M, 435. **7ba**: mp 167—168 °C; IR (KBr)

3430 and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.0—1.3 (m, 6H, $(CH_2)_3$), 1.45 (s, 3H, CH_3), 2.3—2.6 (m, 4H, $N(CH_2)_2$), 4.00 (s, 1H, OH), and 7.2—7.5 (m, 10H, 2Ph). Found: C, 80.38; H, 7.40; N, 3.91%; M^+, 373. Calcd for $C_{25}H_{27}NO_2$: C, 80.38; H, 7.30; N, 3.75%; M, 373. **7bb**: mp 161—163 °C; IR (KBr) 3470 and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.1—1.4 (m, 6H, $(CH_2)_3$), 1.21 (s, 3H, CH_3), 2.4—2.7 (m, 4H, $N(CH_2)_2$), 4.75 (s, 1H, OH), and 6.8—7.6 (m, 10H, 2Ph). Found: C, 80.64; H, 8.79; N, 3.06%; M^+, 445. Calcd for $C_{30}H_{39}NO_2$: C, 80.85; H, 8.82; N, 3.14%; M, 445. **7bc**: mp 189—191 °C; IR (KBr) 3450 and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.7—1.5 (m, 6H, $(CH_2)_3$), 2.7—3.2 (m, 4H, $N(CH_2)_2$), and 6.5—7.9 (m, 20H, 4Ph). ^{13}C NMR ($CDCl_3$) δ=23.7(t), 25.1(t), 51.7(t), 118.6(s), 125.4(d), 126.4(d), 127.4(d), 127.9(d), 128.2(d), 128.5(d), 129.3(d), 129.8(d), 130.4(s), 132.5(s), 137.3(s), 139.0(s), 139.4(s), 140.9(s), 154.2(s), 160.1(s), and 192.8(s). Found: C, 84.21; H, 6.18; N, 2.93%; M^+, 497. Calcd for $C_{35}H_{31}NO_2$: C, 84.47; H, 6.28; N, 2.82%; M, 497. **7bd**: mp 163—165 °C; IR (KBr) 3330 and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.2—1.4 (m, 6H, $(CH_2)_3$), 1.4—2.3 (m, 6H, $CO(CH_2)_3$), 2.3—2.6 (m, 4H, $N(CH_2)_2$), and 7.2—7.6 (m, 10H, 2Ph). Found: C, 80.86; H, 7.12; N, 3.57%; M^+, 385. Calcd for $C_{26}H_{27}NO_2$: C, 81.00; H, 7.07; N, 3.57%; M, 385. **7be**: mp 155—157 °C; IR (KBr) 3340 and 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.00 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 0.8—2.9 (m, 14H, $(CH_2)_5$ and $C(CH_2)_2$), and 7.1—7.8 (m, 10H, 2Ph). Found: C, 81.23; H, 7.62; N, 3.49%; M^+, 413. Calcd for $C_{28}H_{31}NO_2$: C, 81.31; H, 7.57; N, 3.39%; M, 413. **7bg**: mp 169—172 °C; IR (KBr) 3530 and 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.0—1.4 (m, 6H, $(CH_2)_3$), 1.41 (s, 3H, CH_3), 2.3—2.6 (m, 4H, $N(CH_2)_2$), 3.51 (s, 3H, CO_2CH_3), and 7.2—7.6 (m, 10H, 2Ph). Found: C, 77.12; H, 6.98; N, 3.57%; M^+, 389. Calcd for $C_{25}H_{27}NO_3$: C, 77.08; H, 7.00; N, 3.57%; M, 389. **7bh**: mp 150—152 °C; IR (KBr) 3480 and 1670 cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.00 (t, J=8 Hz, 3H, $C\underline{H}_3CH_2$), 1.1—1.4 (m, 6H, $(CH_2)_3$), 1.49 (s, 3H, CH_3), 2.3—2.7 (m, 4H, $N(CH_2)_2$), 4.09 (s, q, J=8Hz, 2H, $CH_3C\underline{H}_2$), and 7.2—7.5 (m, 10H, 2Ph). Found: C, 77.31; H, 7.19; N, 3.45%; M^+, 403. Calcd for $C_{26}H_{29}NO_3$: C, 77.39; H, 7.24; N, 3.47%; M, 403. **7da**: mp 103—105 °C; IR (KBr) 3480 and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.62 (t, J=7 Hz, 6H, $C\underline{H}_3CH_2$), 1.38 (s, 3H, CH_3), 1.69 (s, 3H, $COCH_3$), 2.43 (q, J=7 Hz, 4H, $2CH_3C\underline{H}_2$), 3.95 (s, 1H, OH), and 7.2—7.5 (m, 10H, 2Ph). Found: C, 79.55; H, 7.42; N, 3.59%; M^+, 361. Calcd for $C_{24}H_{27}NO_2$: C, 79.74; H, 7.53; N, 3.88%; M, 361. **7db**: mp 149—150 °C; IR (KBr) 3450 and 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.70 (t, J=5Hz, 6H, $2CH_2C\underline{H}_3$), 1.41 (s, 3H, CH_3), 2.48 (q, J=5 Hz, 4H, $2CH_3C\underline{H}_2$), 4.59 (s, 1H, OH), and 6.7—7.4 (m, 15H, 3Ph). Found: C, 81.96; H, 6.77; N, 3.40%; M^+, 423. Calcd for $C_{29}H_{29}NO_2$: C, 81.96; H, 6.90; N, 3.31%; M, 423. **7dd**: mp 150—151 °C; IR (KBr) 3340 and 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.75 (t, J=6 Hz, 6H, $2CH_3$), 1.5—2.2 (m, 6H, $(CH_2)_3$), 2.45 (q, J=6 Hz, 4H, $2CH_3C\underline{H}_2$), 5.40 (s, 3H, OH), and 6.9—7.5 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$) δ=12.6(q), 18.9(t), 35.3(t), 41.8(t), 44.6(t), 81.6(s), 127.0(d), 127.9(d), 128.0(d), 128.2(d), 129.4(d), 129.8(d), 131.6(s), 133.2(s), 135.6(s), 142.3(s), 146.1(s), 147.2(s), and 198.1(s). Found: C, 80.65; H, 7.31; N, 3.91%; M^+, 373. Calcd for $C_{25}H_{27}NO_2$: C, 80.65; H, 7.30; N, 3.75%; M, 373. **7de**: mp 118—119 °C; IR (KBr) 3440 and 1650 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.80 (t, J=5 Hz, 6H, $2CH_2C\underline{H}_3$), 0.80 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 2.0—2.5 (m, 4H, $(CH_3)_2C(C\underline{H}_2)_2$), 2.65 (q, J=6 Hz, 4H, $2CH_3C\underline{H}_2$), 5.62 (s, 1H, OH), and 7.2—7.7 (m, 10H, 2Ph). Found: C, 80.82; H, 7.91; N, 3.55%; M^+, 401. Calcd for $C_{27}H_{31}NO_2$: C, 80.76; H, 7.22; N, 3.49%; M, 401. **6dg**: mp 103—105 °C; IR (KBr) 1750, 1700, and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.93 (t, J=7 Hz, 6H, $2C\underline{H}_3CH_2$), 1.90 (s, 3H, $COCH_3$), 3.00 (q, J=7 Hz, 4H, $2CH_3C\underline{H}_2$), 3.10 (s, 3H, CH_3), 4.84 (s, 1H, CH), and 7.1—7.5 (m, 10H, 2Ph). ^{13}C NMR (C_6D_6) δ=13.0(q), 28.2(q), 42.2(t), 50.4(d), 50.9(q), 70.8(s), 103.3(s), 126.1(d), 127.2(d), 127.8(d), 128.0(d), 129.1(d), 130.0(d), 136.3(s), 137.6(s), 171.1(s), and 201.5(s). Found: C, 76.38; H, 7.16; N, 3.65%; M^+, 377. Calcd for $C_{24}H_{27}NO_3$: C, 76.35; H, 7.22; N, 3.71%; M, 377. **7dg**: mp 124—125 °C; IR (KBr) 3490 and 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.78 (t, J=7Hz, 6H, $2C\underline{H}_3CH_2$), 1.50 (s, 3H, CH_3), 2.51 (q, J=7 Hz, 4H, $2CH_3C\underline{H}_2$), 3.55 (s, 3H, CO_2CH_3), and 7.2—7.7 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$) δ=13.0(q), 25.1(q), 44.8(t), 50.9(q), 82.8(s), 127.0(d), 127.5(d), 127.7(d), 128.9(d), 129.6(d), 134.4(s), 135.0(s), 135.2(s), 135.3(s), 145.9(s), 154.9(s), and 164.8(s). Found: C, 76.14; H, 7.09; N, 3.88%; M^+, 377. Calcd for $C_{24}H_{27}NO_3$: C, 76.35; H, 7.22; N, 3.71%; M, 377. **7dh**: mp 96—98 °C; IR (KBr) 3500 and 1670 cm^{-1}. ^1H NMR ($CDCl_3$) 0.79 (t, J=7 Hz, 6H, $2C\underline{H}_3CH_2$), 0.98 (t, J=8 Hz, 3H, $C\underline{H}_3CH_2CO_2$), 1.49 (s, 3H, CH_3), 2.51 (q, J=7 Hz, 4H, $2CH_3C\underline{H}_2$), 4.00 (q, J=8Hz, 2H, $CH_3C\underline{H}_2CO_2$), and 7.1—7.6 (m, 10H, 2Ph). Found: C, 76.58; H, 7.44; N, 3.62%; M^+, 391. Calcd for $C_{25}H_{29}NO_3$: C, 76.69; H, 7.47; N, 3.58%; M, 391. **7ea**: mp 121—122 °C; IR (KBr) 3500 and 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.40 (s, 3H, CH_3), 1.75 (s, 3H, $COCH_3$), 2.18 (s, 6H, $N(CH_3)_2$), and 7.1—7.5 (m, 10H, 2Ph). Found: C, 79.09; H, 6.97; N, 4.34%; M^+, 333. Calcd for $C_{22}H_{23}NO_2$: C, 79.24; H, 6.97; N, 4.20%; M, 333. **7ed**: mp 146—148 °C; IR (KBr) 3350 and 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.4—2.7 (m, 6H, $(CH_2)_3$), 2.15 (s, 6H, $2CH_3$), and 6.8—7.4 (m, 10H, 2Ph). Found: C, 79.82; H, 6.64; N, 4.13%; M^+, 345. Calcd for $C_{23}H_{23}NO_2$: C, 79.96; H, 6.72; N, 4.04%; M, 345. **7fd**: mp 118—120 °C; IR (KBr) 3340 and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.7—2.8 (m, 6H, $(CH_2)_3$), 2.40 (s, 3H, CH_3), and 6.8—7.5 (m, 15H, 3Ph). Found: C, 82.66; H, 6.42; N, 3.51%; M^+, 407. Calcd for $C_{28}H_{25}NO_2$: C, 82.52; H, 6.18; N, 3.44%; M, 407.

Hydrolysis of 7aa with Formic Acid in Benzene. A solution of **7aa** (200 mg) and formic acid (0.08 cm^3) in benzene (5 cm^3) was heated at 50 °C for 40 h. Evaporation of the solvent under the reduced pressure and TLC separation over aluminum oxide yielded 3-acetyl-4-hydroxy-4-methyl-2,5-diphenyl-2-cyclopentenone **10** in 27% yield. **10**: mp 159—161 °C; IR (KBr) 3450 and 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.33 (s, 3H, CH_3), 2.13 (s, 3H, $COCH_3$), 3.35 (s, 1H, OH), 4.14 (s, 1H, CH), and 7.0—7.6 (m, 10H 2Ph). ^{13}C NMR ($CDCl_3$) δ=25.9(q), 31.3(q), 66.0(d), 80.0(s), 127.6(d), 128.3(d), 128.5(d), 128.7(d), 129.1(d), 129.5(d), 129.9(d), 134.7(s), 141.8(s), 163.4(s), 203.1(s), and 204.1(s). Found: C, 78.22; H, 5.61%; M^+, 306. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92%; M, 306.

Hydrolysis of 7aa with Trifluoroacetic Acid. Hydrolysis of **7aa** (0.3 g) in chloroform (10 cm^3) and ethanol (1 cm^3) catalyzed by trifluoroacetic acid (0.01 cm^3) was run for 40 h at room temperature. The reaction mixture was washed with water, dried over magnesium sulfate, chromatographed over aluminum oxide to yield a purple resinous mass, 3-acetyl-4-methyl-2,5-diphenyl-2,4-cyclopentadienone **13** in a quantitative yield. **13**: IR (Nujol) 1710 and 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.50 (s, 3H, CH_3), 1.67 (s, 3H, $COCH_3$), and 6.5—7.2 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$) δ=14.3 (q), 30.9(q), 127.7(d), 128.0(d), 128.1(d), 128.3(d), 128.4(d), 128.6(d), 129.2(s), 129.5(s), 130.0(s), 130.5(s), 149.7(s), 154.2(s), 199.7(s), and 201.8(s). Found: C, 83.05; H, 5.66%; M^+, 288. Calcd for

$C_{20}H_{16}O_2$: C, 83.31; H, 5.59%; M, 288.

The Reaction of 13 with DMAD. A mixture of **13** (0.1 g) and DMAD (3 times excess) in benzene (2 cm^3) was allowed to react at room temperature for 20 h. Condensation of the solution yielded colorless prisms of dimethyl 4-acetyl-5-methyl-3,6-diphenylphthalate **14**: mp 200—202 °C; IR (KBr) 1740 and 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.90 (s, 3H, CH_3), 2.20 (s, 3H, $COCH_3$), 3.42 (s, 3H, CO_2CH_3), 3.47 (s, 3H, CO_2CH_3), and 7.1—7.6 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$) δ=17.4(q), 31.9(q), 52.1(q), 127.7(d), 128.1(d), 129.0(d), 129.4(d), 133.9(s), 135.5(s), 136.9(s), 137.7(s), 140.2(s), 167.7(s), 167.8(s), and 205.7(s). Found: C, 74.54; H, 5.64%; M^+, 402. Calcd for $C_{25}H_{22}O_5$: C, 74.61; H, 5.51%; M, 402.

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