Regioselective Ring Opening Reactions of 1-Aminocyclopropenes via Carbenium Ion and Carbene Intermediates

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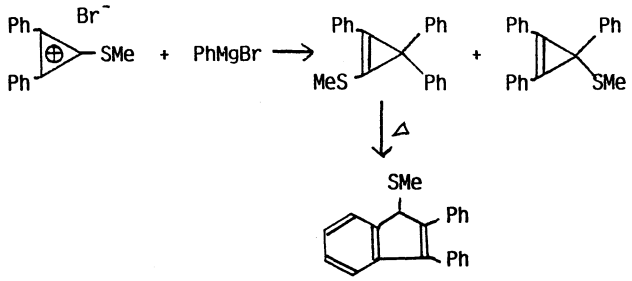
The reaction of 1-(disubstituted amino)-2,3-diphenylcyclopropenium salt with phenyl- and alkylmagnesium halides afforded, regioselectively, 1-aminocyclopropenes in good yields. The reactions of these 1-aminocyclopropenes were studied under acidic and nonacidic conditions to yield regioselective ring-opening products (C_2-C_3 and C_1-C_3 bond fissions of the cyclopropene) associated with the carbenium ions and carbene intermediates, respectively.

The chemistry of cyclopropene derivatives has attracted considerable interest due to 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.[1-3] In a continuation of our studies on the cyclopropenes substituted with heteroatom groups, we have shown, for example, that a facile ring opening of 1-(methylthio)-2,3,3-triphenylcyclopropene via vinylcarbene intermediate at 50 °C, while 3-(methylthio)-1,2,3-triphenylcyclopropene is stable under similar reaction conditions (Scheme 1).[2a]

Here, we report on the preparation and regioselective acid-catalyzed and thermal ring-opening reactions of 1-aminocyclopropenes.

1-Aminocyclopropenium tetrafluoroborates **1a—e** were prepared in moderate-to-good yields by the reaction of diphenylcyclopropenone with triethyloxonium tetrafluoroborate, followed by treatments with secondary amines.[4-6] To a solution of phenylmagnesium bromide **2a** in tetrahydrofuran (THF) at room temperature was added 1-(diphenylamino)-2,3-diphenylcyclopropenium tetrafluoroborate **1a** in one portion; the mixture was stirred, giving a clean solution. After 10 min the resulting solution was poured on ice water and extracted with ether to give 1-(diphenylamino)-2,3,3-triphenylcyclopropene (**3a**) in a 92% yield. The structure **3a** was unambigously evident from its IR (1820 cm^{-1}) and ^{13}C NMR (s at δ=41.3 of sp^3 carbon of



Scheme 1.

Table 1. The Reaction of **1** with **2**

		Reaction Conditions				Products (Yield/%)		
1	**2**	Solvent	Temp/°C	Time/h	Extr. Sol.[a]	**3**	**4**	**5**
1a	**2a**	THF	25	0.1	B, E	**3a**(98)		
	2a	THF	25	0.1	C		**4a**(87)	
	2a	THF	60	1.0	B, E	**3a**(45)		**5a**(30)
	2a	THF	60	7.0	B			**5a**(84)
	2b	THF	25	0.1	B, C, E	**3b**(58)		
	2c	THF	25	0.1	B, C, E	**3c**(82)		
	2d	THF	25	0.1	B, C	**3d**(93)		
1b	**2a**	Ether	25	1.0	E, C		**4e**(19)	
	2a	THF	25	0.1	B, C, E		**4e**(69)	
	2a	THF	25	1.0	B, C, E		**4e**(41)	**5e**(11)
	2a	THF	60	0.1	B, C		**4e**(9)	**5e**(23)
	2a	THF	60	0.1	B, C			**5e**(58)
1c	**2a**	THF	25	0.1	B, C		**4f**(40)	
	2a	THF	60	1.0	B, C			**5f**(25)
1d	**2a**	THF	25	0.1	B, C		**4g**(69)	
	2a	THF	60	1.0	B, C			**5g**(80)
1e	**2a**	THF	25	0.1	B, C		**4h**(58)	
	2a	THF	60	1.0	B, C			**5h**(78)

a) Extraction solvent after the aqueous treatment. B: benzene, C: chloroform, and E: ether.

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C_3) spectra and comparisons of the data with those of the isomer 3-diphenylamino-1,2,3-triphenylcyclopropene (**6a**) prepared from triphenylcyclopropenium perchlorate[5] with diphenylamine (Scheme 3). None of the isomer **6a** was found in the Grignard reaction mixtures, indicating a regioselective nucleophilic attack of Grignard reagent **2a** to **1a**.

The reaction of **1a** with methyl-, ethyl-, and isopropylmagnesium halides **2b—d** yielded cyclopropenes **3b—d** in good yields. In contrast, the reactions of **2a** and the salt **1b—e** yielded two types of products, depending on the reaction conditions employed. Although the reaction of **1b** with **2a** in ether afforded 2-morpholinoindene **4e** in low yield, the use of THF as the reaction medium raised the yield of **4e** up to 41%, together with 1-morpholinoindene **5e**. The reaction at 60 °C afforded **5e**, exclusively, in moderate yield. Similar results were observed for the reaction of **1c—e** with **2a** (Table 1). Attempts to isolate cyclopropenes **3e—h** at low temperature, or direct isolation from the Grignard mixture without aqueous workup, failed, yielding 2-aminoindenes **4e—h** as sole reaction products. These results seem to indicate that the cyclopropenes substituted with relatively basic amino groups undergo a facile ring opening.

The cyclopropenes **3a—d** are relatively stable at room temperature in crystalline form. However, in a chloroform solution at room temperature **3a** afforded **4a** quantitatively, and upon refluxing in benzene for 5 h **5a** in 79% yield. The effect of hydrochloric acid formed from chloroform on the ring opening via the C_2-C_3 bond fission was proven by the conversion of **3a** to **4a** in benzene upon the addition of a small amount of concd HCl, trifluoroacetic acid, or even Lewis acids (Table 2).

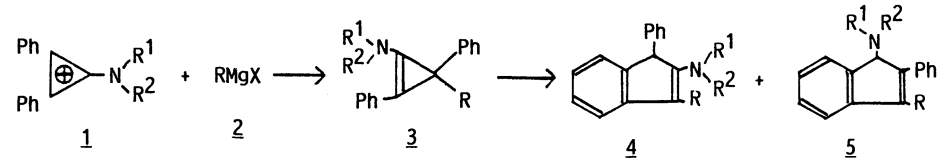
Upon heating at reflux in methanol **3a** gave a mixture of aminal **9** and acetal **10** (failed to separate), both of which were converted to aldehyde **11**.[8] The formations of **9** and **10** are supposed to proceed by an insertion of a vinylcarbene to the OH bond of methanol,[2a] followed by methanolysis to yield **10**. A treatment of **3a** in methanol in the presence of acetic acid yielded only **4a** in a good yield.

The structures of indenes **4a** and **5a** were confirmed on the basis of their spectroscopic data as well as converting to 2-indanone **7** and 1*H*-inden-1-one **8**[7] by

Table 2. Ring Opening of **3a**

Reaction conditions				Product(yield/%)
Solvent	Additive(mol)[a]	Temp/°C	Time/h	
PhH	—	70	5	**5a**(79)
THF	—	60	10	**5a**(85)
$CHCl_3$	—	25	1	**4a**(96)
PhH	AcOH(10)	25	5	**4a**(50)
	CF_3CO_2H(1)	25	0.1	**4a**(90)
	HCl(1)	25	1	**4a**(95)
	$MgBr_2$(1)	25	1	**4a**(90)
	BF_3 · ether(1)	25	0.5	**4a**(96)
MeOH	—	60	140	**9** and **10**(75)[b]
	NaOH(3)	60	140	**9** and **10**(68)[b]
	AcOH(10)	60	24	**4a**(93)

a) A mixture of **3a** (1 mmol), and additive (mmol) in a solvent (10 cm^3) was reacted under respective reaction conditions. b) Yield of **11** obtained by the hydrolysis of the crude reaction mixture of **9** and **10**.

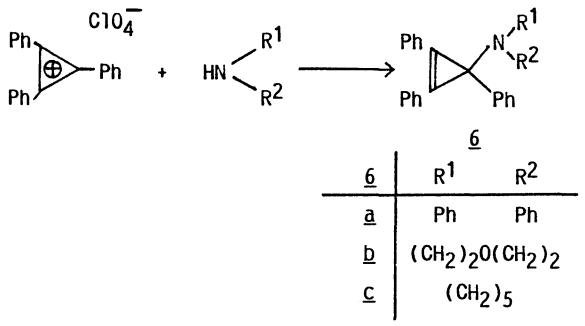


1	R^1	R^2
a	Ph	Ph
b	$(CH_2)_2O(CH_2)_2$	
c	$(CH_2)_5$	
d	Me	Ph
e	$PhCH_2$	Ph

2	R
a	Ph
b	Me
c	Et
d	i-Pr

3,4,5	R^1	R^2	R
a	Ph	Ph	Ph
b	Ph	Ph	Me
c	Ph	Ph	Et
d	Ph	Ph	i-Pr
e	$(CH_2)_2O(CH_2)_2$		Ph
f	$(CH_2)_5$		Ph
g	Me	Ph	Ph
h	$PhCH_2$	Ph	Ph

Scheme 2.



6	R^1	R^2
a	Ph	Ph
b	$(CH_2)_2O(CH_2)_2$	
c	$(CH_2)_5$	

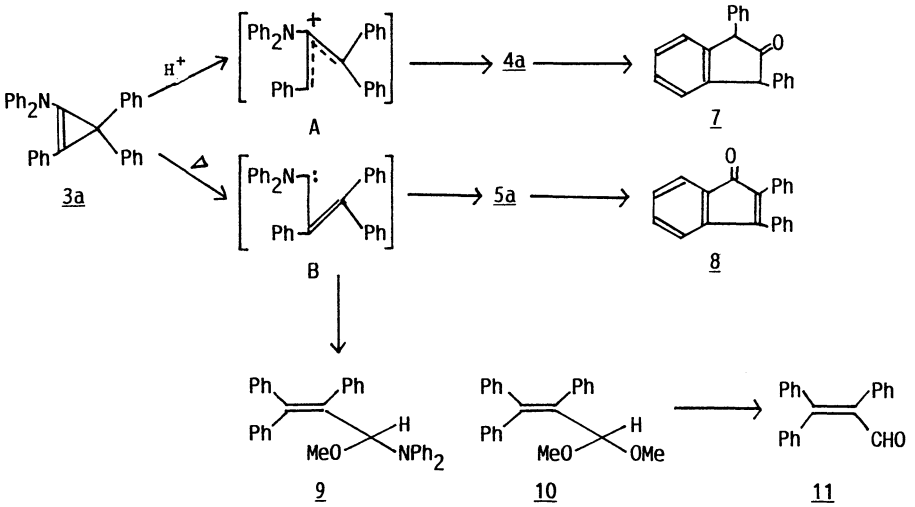
Scheme 3.

hydrolysis or oxidation (Scheme 4). Similar spectra were obtained for all indenes **4** and **5**.

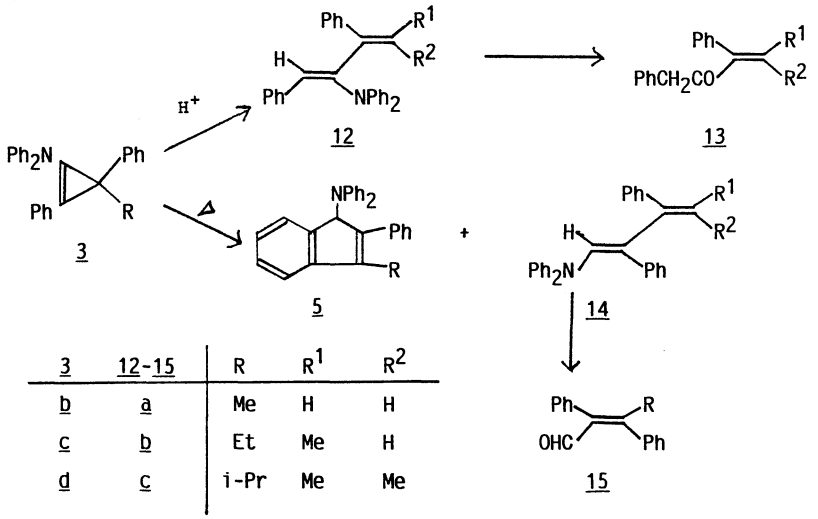
These two types of ring openings were also observed for cyclopropenes **3b—d** substituted with alkyl groups (Scheme 5 and Table 3). Although an addition of trifluoroacetic acid to solutions of **3b** and **3c** in benzene accelerated the ring opening to yield tarry mixtures, treatments of **3b** and **3c** in chloroform at room temperature yielded butadienes **12** in good yields. The isomer **3d** gave a resinous material under similar conditions. In contrast, upon heating in benzene at reflux **3b—d** afforded a mixture of 1-aminoindene **5** and butadiene derivative **14**. Aminobutadienes **12** and **14** were converted to the carbonyl derivatives, **13** and **15**, respectively, by acidic hydrolyses and their structures were confirmed. Ultraviolet irradiation of **15** gave a new set of ^{1}H NMR absorption corresponding to the stereo-

Table 3. Ring Opening Reaction of Alkyl-Substituted Cyclopropenones **3b**, **3c**, and **3d**

	Reaction conditions			Products(Yield/%)
	Solvent	Temp/°C	Time/d	
3b	$CHCl_3$	25	7	**12a**(100)
	PhH	80	4	**5b**(29), **14a**(10)
3c	$CHCl_3$	25	10	**12b**(69)
	PhH	80	5	**5c**(14), **14b**(25)
3d	$CHCl_3$	25	10	Unknown mixture
	PhH	80	7	**14c**(54)



Scheme 4.



3	12-15	R	R^1	R^2
b	a	Me	H	H
c	b	Et	Me	H
d	c	i-Pr	Me	Me

Scheme 5.

isomer of **15**. A shielding effect of the phenyl groups and NOE studies revealed the stereochemistry of **15** to be the *Z*-form.

These results indicate that two routes are possible for the ring opening of 1-amino-substituted cyclopropenes **3**, involving either a carbenium ion or carbene intermediates (Scheme 4). The protonation of **3a** and the fission of the C_2-C_3 bond via a well-known thermally allowed disrotatory ring opening might give a vinylcarbenium ion **A** stabilized by the neighbouring amino group,[9] followed by cyclization[10] to yield **4a**. The higher reactivity of **3e—h** (not isolated), whose amino groups are stronger bases than that of **3a**, seems to furnish intermediate **A**. Another process is the scission of the C_1-C_3 bond of **3a** to give the vinylcarbene intermediate **B**. Stabilization of the carbene by the contiguous amino group might facilitate the ring opening,[11] since tetraphenylcyclopropene rearranges at temperatures over 200 °C,[12] isomer **6** was recovered unchanged upon prolonged heating in refluxing benzene. Thus, the selection of the reaction conditions controls the regioselective ring opening of 1-aminocyclopropenes **3**. The facile ring opening found for phenylcyclopropenes (**3**: R=Ph), rather than alkylcyclopropenes **3b—d**, could be explained in terms of the resonance stabilization of intermediates **A** and **B** by the phenyl group.

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 (1). The salts **1** were prepared by a known method.[4-6]

The Reaction of 1 with Grignard Reagents 2. General Procedure. To a solution of phenylmagnesium bromide **2a** (3 mmol) in THF (20 cm^3) was added **1a** (1 mmol) in one portion; the mixture was stirred at room temperature for 10 min to yield a clear solution. The resulting solution was poured into cold water containing 1% of KH_2PO_4 and extracted with an appropriate solvent. The extract was dried over sodium carbonate, condensed in vacuo, and recrystallization from 2-propanol afforded the cyclopropene **3a** (extraction by ether or benzene) or 2-diphenylaminoindene **4a** (extraction by chloroform). Upon refluxing for 1 h, the Grignard reaction mixture yielded 1-diphenylaminoindene **5a** after a similar treatment as mentioned above. **3a**: mp 145—147 °C; IR (KBr) 1820 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.7—7.5 (m, 25H, 5Ph). ^{13}C NMR ($CDCl_3$) δ=41.7(s), 88.8(s), 120.4(s), 123.8(d), 124.7(d), 125.5(d), 125.9(d), 127.9(d), 128.3(d),128.4(d), 128.5(d), 128.7(d), 129.2(d), 144.2(s), and 145.1(s). Found: C, 90.82; H, 5.62; N, 3.22%; M^+ 435. Calcd for $C_{33}H_{25}N$: C, 91.03; H, 5.75; N, 3.22%; M, 435. **4a**: mp 203—205 °C; IR (KBr) 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.12 (s, 1H, CH) and 6.5—7.6 (m, 24H, Arom). ^{13}C NMR ($CDCl_3$): δ=68.6 (d, CH), 120.9(d), 121.7(d), 121.8(d), 123.6(d), 126.0(d), 126.9(d), 127.6(d), 127.8(d), 128.0(d), 128.6(d), 128.9(d), 129.2(d), 129.5(d), 135.0(s), 135.1(s), 140.2(s), 143.6(s), 144.1(s), and 147.3(s). Found: C, 91.07; H, 5.72; H, 3.10%; M^+ 435. Calcd for $C_{33}H_{25}N$: C, 91.03; H, 5.75; N, 3.22%; M, 435. **5a**: mp 190—191 °C; IR(KBr) 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=5.03 (s, 1H, CH), and 6.5—7.5 (m, 24H, Arom). ^{13}C NMR ($CDCl_3$) δ=55.6(d), 120.6(d), 121.2(d), 122.0(d), 124.0(d), 125.9(d), 126.7(d), 127.0(d), 127.7(d), 127.9(d), 128.1(d), 128.3(d), 128.7(d), 129.0(d), 133.8(s), 140.1(s), 140.7(s), 142.0(s), 145.3(s), and 147.1(s). Found: C, 90.96; H, 5.77; N, 3.02%; M^+, 435. Calcd for $C_{33}H_{25}N$: C, 91.03; H, 5.75; N, 3.22%; M, 435.

Hydrolysis of indene **4a** gave 2-indanone **7** in 70%. A suspension of **4a** in aqueous hydrochloric acid (3 mol dm^{-3}) was srirred at room temperature for 15 h, yielding a clean solution. The chloroform extract gave **7**: mp 150—152 °C; IR (KBr) 1760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.78 (s, 2H, 2CH) and 6.9—7.5 (m, 14H, Arom). ^{13}C NMR ($CDCl_3$) δ=59.0(d), 125.8(d), 127.3(d), 128.3(d), 128.9(d), 138.1(s), 140.9(s), and 212.7(s). Found: C, 88.28; H, 5.73%; M^+, 284. Calcd for $C_{21}H_{16}O$: C, 88.73; H, 5.63%; M, 284.

Indene **5a** was stable to acid hydrolysis. Upon treatment with aqueous hydrogen peroxide in a solution of benzene for one day **5a** gave 1*H*-inden-1-one **8** in 20% yield by crystallization from chloroform-ethanol. **8**: mp 152—153 °C (lit,[7] mp 152—152.5 °C).

The reaction of **1b—e** with Grignard reagents yielded **3—5**, as summarized in Table 1. **3b**: mp 110—111 °C; IR(KBr) 1830 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.85 (s, 3H, Me) and 6.6—7.3 (m, 20H, 4Ph). ^{13}C NMR ($CDCl_3$) δ=22.6(q), 32.2(s), 88.8(s), 123.3(d), 124.5(d), 125.1(d), 125.3(d), 126.4(d), 128.0(d), 128.3(s), 129.3(d), 144.5(s), and 146.8(s). Found: C, 89.46; H, 6.17; N, 3.74%; M^+, 373. Calcd for $C_{28}H_{23}N$: C, 90.08; H, 6.17; N, 3.75%; M, 373. **3c**: mp 120—121 °C; IR (KBr) 1840 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.82 (t, J=7 Hz, 3H, Me), 2.20 (oct, J=7 Hz, 2H, CH_2), and 6.7—7.5 (m, 20H, 4Ph). ^{13}C NMR ($CDCl_3$) δ=11.4(q), 26.4(t), 37.9(s), 85.4(s), 121.5(s), 123.2(d), 124.5(d), 125.4(d), 126.7(d), 128.0(d), 128.3(d), 129.2(d), 129.9(s), 144.5(s), and 146.6(s). Found: C, 89.40; H, 6.57; N, 3.58%; M^+, 387. Calcd for $C_{29}H_{25}N$: C, 89.92; H, 6.46; N, 3.62%; M, 387. **3d**: mp 158—160 °C; IR (KBr) 1830 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.85 (d, J=7Hz, 3H, Me), 1.11 (d, J=7Hz, Me), 2.28 (sept, J=7 Hz, CH), and 6.7—7.5 (m, 20H, 4Ph). ^{13}C NMR ($CDCl_3$) δ=21.9(q), 23.4(q), 31.7(d), 44.4(s), 83.8(s), 123.7(d), 123.9(s), 124.6(d), 124.8(d), 125.4(d), 127.6(d), 127.9(d), 128.2(d), 128.3(d), 128.6(d), 129.2(d), 130.3(s), 144.7(s), and 145.7(s). Found: C, 89.52; H, 6.77; N, 3.40%; M^+, 401. Calcd for $C_{30}H_{27}N$: C, 89.78; H, 6.73; N, 3.49%; M, 401. **4e**: mp 130—132 °C; IR (KBr) 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.3—3.0 (m, 4H, CH_2NCH_2), 3.48 (t, J=5 Hz, 4H, CH_2OCH_2), 4.80 (s, 1H, OH), and 7.0—7.8 (m, 14H, Arom). ^{13}C NMR ($CDCl_3$) δ=49.2(t), 67.6(t), 73.1(d), 120.5(d), 124.6(d), 125.3(d), 126.8(d), 127.4(d), 127.7(d), 128.5(d), 129.3(d), 129.5(d), 135.1(s), 136.0(s), 140.7(s), 142.9(s), 143.1(s), and 144.9(s). Found: C, 85.03; H, 6.56; N, 4.11%; M^+, 353. Calcd for $C_{25}H_{23}NO$: C, 84.93; H, 6.52; N, 3.97%; M, 353. **4f**: mp 94—96 °C; IR (KBr) 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.2—1.6 (m, 6H, $3CH_2$), 2.3—3.0 (m, 4H, CH_2NCH_2), 4.83 (s, 1H, CH), and 7.1—7.7 (m, 14H, Arom). ^{13}C NMR ($CDCl_3$) δ=24.7(t), 26.7(t), 50.1(t), 73.8(d), 120.3(d), 124.5(d), 125.0(d), 126.6(d), 127.2(d), 127.4(d), 127.5(d), 128.0(d), 128.5(d), 129.4(d), 129.6(d), 129.9(d), 135.4(s), 136.3(s), 140.1(s), 143.8(s), 143.9(s), and 144.9(s). Found: C, 88.82; H, 7.06; N, 4.12%; M^+, 351. Calcd for $C_{26}H_{25}N$: C, 88.89; H, 7.12;

N, 3.99%; M, 351. **4g**: mp 153—155 °C IR (KBr) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.30 (s, 3H, Me), 5.93 (s, 1H, CH), and 6.6—7.5 (m, 19H, Arom). ^{13}C NMR ($CDCl_3$) δ=31.9(q), 67.5(d), 113.2(d), 116.9(d), 120.7(d), 123.3(d), 125.8(d), 127.0(d), 127.7(d), 128.0(d), 128.8(d), 129.1(d), 129.3(d), 129.4(d), 134.5(s), 135.2(s), 140.4(s), 143.1(s), 143.4(s), 144.5(s), and 150.4(s). Found: C, 89.99; H, 6.20; N, 3.68%; M^+, 373. Calcd for $C_{28}H_{23}N$: C, 90.08; H, 6.17; N, 3.75%; M, 373. **4h**: mp 158—160 °C; IR (KBr) 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.96 (s, 2H, CH_2), 6.20 (s, 1H, CH), and 6.7—7.6 (m, 19H, Arom). ^{13}C NMR ($CDCl_3$) δ=50.5(t), 68.7(d), 115.1(d), 117.7(d), 120.8(d), 123.6(d), 125.8(d), 126.0(d), 126.7(d), 126.9(d), 127.6(d), 127.9(d), 128.0(d), 128.1(d), 128.3(d), 128.6(d), 129.1(d), 129.3(d), 129.5(d), 134.6(s), 134.8(s), 138.8(s), 140.4(s), 143.5(s), 143.6(s), 144.4(s), and 149.5(s). Found: C, 90.77; H, 6.12; N, 3.13%; M^+, 449. Calcd for $C_{34}H_{27}N$: C, 90.83; H, 6.05; N, 3.11%; M, 449. **5b**: mp 157—160 °C; IR(KBr) 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.11 (d, 3H, J=2Hz, Me), 5.9—6.1 (q, J=2Hz, CH), and 6.5—7.6 (m, 19H, Arom). ^{13}C NMR ($CDCl_3$) δ=11.7(q), 68.4(d), 119.5(d), 121.4(d), 121.6(d), 123.1(d), 125.7(d), 126.7(d), 127.9(d), 128.0(d), 128.8(d), 129.2(d), 135.1(s), 135.6(s), 142.7(s), 143.6(s), 144.7(s), and 147.3(s). Found: C, 89.98; H, 6.21; N, 3.81%; M^+, 373. Calcd for $C_{28}H_{23}N$: C, 90.08; H, 6.17; N, 3.74%; M, 373. **5c**: mp 119—120 °C; IR (KBr) 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.10 (t, J=7Hz, 3H, Me), 2.56 (q, J=7Hz, 2H, CH_2), 5.98 (s, 1H, CH), and 6.5—7.6 (m, 19H, Arom). ^{13}C NMR ($CDCl_3$) δ=13.3(q), 19.1(t), 68.7(d), 119.9(d), 121.4(d), 121.6(d), 123.4(d), 125.6(d), 126.8(d), 127.8(d), 128.0(d), 128.8(d), 129.0(d), 135.7(s), 141.2(s), 142.1(s), 143.5(s), 144.2(s), and 147.3(s). Found: C, 89.97; H, 6.47; N, 3.76%; M^+, 387. Calcd for $C_{29}H_{25}NO_2$: C, 89.77; H, 6.46; N, 3.62%; M, 387. **5e**: mp 170—173 °C; IR (KBr) 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.8—3.2 (m, 4H, CH_2NCH_2), 3.2—3.5 (m, 4H, CH_2OCH_2), 4.70 (s, 1H, CH), and 6.8—7.6 (m, 14H, Arom). ^{13}C NMR ($CDCl_3$) δ=50.1(t), 55,4(d), 66.6(t), 116.4(s), 116.9(d), 122.3(d), 122.9(d), 126.6(d), 126.8(d), 127.8(d), 128.2(d), 128.9(d), 130.0(d), 136.6(s), 140.5(s), 142,1(s), 146.5(s), and 154.0(s). Found: C, 85.08; H, 6.51; N, 3.88%; M^+, 353. Calcd for $C_{25}H_{23}NO$: C, 84.99; H, 6.52; N, 3.97%; M, 353. **5f**: mp 95—97 °C; IR (KBr) 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.9—1.6 (m, 6H, $3CH_2$), 2.8—3.1 (m, 4H, CH_2NCH_2), 4.71 (s, 1H, CH), and 6.8—7.6 (m, 14H, Arom). ^{13}C NMR ($CDCl_3$) 24.1(t), 25.8(t), 51.1(t), 55.6(d), 114.3(s), 116.3(d), 121.6(d), 122.7(d), 126.1(d), 126.5(d), 126.7(d), 127.5(d), 128.0(d), 128.5(d), 128.6(d), 129.4(d), 129.6(d), 129.9(d), 137.3(s), 141.0(s), 142.0(s), 147.0(s), and 155.4(s). Found: C, 88.81; H, 7.14; N, 3.78%; M^+, 351. Calcd for $C_{26}H_{25}N$: C, 88.89; H, 7.12; N, 3.99%; M, 351. **5g**: mp 162—164 °C; IR (KBr) 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.67 (s, 3H, CH_3), 5.05 (s, 1H, CH), and 6.5—7.5 (m, 19H, Arom). ^{13}C NMR ($CDCl_3$) δ=40.0(q), 54.5(d), 117.1(d), 119.0(d), 124.1(d), 124.8(d), 126.6(d), 126.9(d), 127.3(d), 128.2(d), 128.5(d), 128.6(d), 128.7(d), 129.8(s), 134.5(s), 139.1(s), 144.1(s), 144.6(s), 148.2(s), and 153.0(s). Found: C, 89.81; H, 6.20; N, 3.61%; M^+, 373. Calcd for $C_{28}H_{23}N$: C, 90.08; H, 6.17; N, 3.75%; M, 373. **5h**: mp 121—123 °C; IR (KBr) 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.22 and 4.58 (ABq, J=17 Hz, 2H, CH_2), 5.05 (s, 1H, CH), and 6.5—7.5 (m, 19H, Arom). ^{13}C NMR ($CDCl_3$) δ=55.1(q), 57.4(t), 118.6(d), 119.5(d), 120.5(d), 123.7(d), 124.3(d), 126.5(d), 126.7(s), 126.9(s), 127.0(s), 127.1(s), 128.2(s), 128.3(s), 128.6(d), 128.7(d), 129.0(d), 134.7(s), 139.0(s), 139.4(s), 143.8(s), 145.2(s), 147.9(s), and 151.3(s). Found: C, 90.51; H, 5.98; N, 3.08%; M^+, 449. Calcd for $C_{34}H_{27}N$: C, 90.83; H, 6.05; N, 3.11%; M, 449.

Ring-Opening Reactions of 3. Cyclopropene **3a** was treated under various reaction conditions while checking the mixture by TLC at suitable time intervals. The usual treatment of the reaction mixture afforded crystalline products **4a** or **5a**. Reactions in methanol afforded resinous mass. The ^1H NMR spectra of the products indicated the presence of aminal **9** and acetal **10**. Attempts to separate these products by fractional crystallization, TLC, and CC failed. The hydrolysis of the crude mixture by aqueous hydrochloride (3 mol dm^{-3}) yielded 2,3,3-triphenylpropenal **11**: mp 176—178 °C (lit,[8] mp 175 °C); ^1H NMR ($CDCl_3$) 6.8—7.6 (m, 15H, 3Ph) and 9.65 (s, 1H, CHO); MS m/z 284(M^+).

Cyclopropenes **3b, c** were treated as follows.

(i) A solution of **3** (1 mmol) in chloroform (5 cm^3) was allowed to stay at room temperature. After the reaction, the crude product was chromatographed over silica gel or recrystallized. The results are given in Table 3. **12a**: oil; IR (KBr) 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=5.19 (s, 1H, CH), 5.50 (s, 1H, CH), 6.40 (s, 1H, CH), and 6.7—7.5 (m, 20H, Arom). ^{13}C NMR ($CDCl_3$) δ=117.9(t), 120.9(d), 121.1, 121.6, 122.8, 125.2, 127.0, 127.3(d), 127.5(d), 127.8(d), 128.1(d), 128.5(d), 128.8(d), 129.2, 135.1(s), 141.1(s), 143.2(s), 145.3(s), and 148.1(s). Found: C, 90.01; H, 6.13; N, 3.86%; M^+, 373. Calcd for $C_{28}H_{23}N$: C, 90.08; H, 6.17; N, 3.74%; M, 373. **12b**: mp 115—116 °C; IR (KBr) 1570 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.95 (d, J=7 Hz, 3H, Me), 6.11 (s, 1H, =CH), 6.12 (q, J=7 Hz, =CHMe), and 6.6—7.5 (m, 20H, 4Ph). ^{13}C NMR ($CDCl_3$) δ=15.4(q), 16.1(q), 119.4, 121.3(d), 122.1, 123.1, 125.4, 125.6(d), 126.8, 126.9(d), 127.0(d), 127.1(d), 127.4, 127.6(d), 127.8(d), 127.9(d), 128.0(d), 128.1(d), 128.2(d), 128.5(d), 128.7(d), 129.7(d), 131.4, 135.4(s), 136.8, 138.1, 139.0(s), 140.6(s), 141.5, 142.1, 144.7(s), 145.4(s), and 146.6. Found: C, 89.98; H, 6.51; N, 3.51%; M^+, 387. Calcd for $C_{29}H_{25}N$: C, 89.92; H, 6.46; N, 3.62%; M, 387.

Acidic hydrolyses of **12** afforded vinyl ketones **13** in quantitative yields. **13a**: oil; IR(neat) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.95 (s, 2H, CH_2), 5.80 (s, 1H, =CH), 6.05 (s, 1H, =CH), 6.6—8.0 (m, 10H, 2Ph). Found: C, 86.33; H, 6.32%; M^+, 222. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35%; M, 222. **13b**: oil; IR (neat) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.65 (d, J=7 Hz, 3H, Me), 3.80 (s, 2H, CH_2), and 6.7—7.6 (m, 10H, 2Ph). Found: C, 86.36; H, 6.89%; M^+, 236. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82%; M, 236.

(ii) A solution of **3** (1 mmol) in benzene (10 cm^3) was heated at reflux until the disappearance of the absorption at around 1800 cm^{-1} in IR spectrum. Evaporation of the solvent under reduced pressure and trituration with cold ethanol afforded crystalline 1-aminoindene **5** and oily 1-aminobutadiene **14**. The former product was recrystallized from ethanol. The latter oil was hydrolyzed with aqueous hydrochloric acid (3 mol dm^{-3}) at room temperature for one day. The chloroform extract gave crystalline aldehyde **15** from ethanol. The results are collected in Table 3. **14c**: mp 103—105 °C; IR (KBr) 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.75 (s, 3H, Me), 2.08 (s, 3H, Me), 6.40 (s, 1H, CH), and 6.5—7.5 (m, 20H, 4Ph). ^{13}C NMR ($CDCl_3$) δ=22.5(q), 23.1(q), 122.3(d), 122.4(d), 125.7(d), 125.9(d), 127.0(d), 127.6(d), 128.4(d), 128.7(d), 129.6(d), 130.4(s), 132.3(s), 132.4(d), 137.2(s), 138.1(s), 142.4(s), and 145.9(s). Found: C, 89.54; H, 6.75; N, 3.71%; M^+, 401. Calcd for $C_{30}H_{27}N$: C, 89.78; H, 6.73; N, 3.49%; M, 401. **15a**: mp 128—130 °C; IR (KBr) 1660 cm^{-1};

^{1}H NMR ($CDCl_3$) 2.18 (s, 3H, Me), 7.0—7.7 (m, 10H, 2Ph), and 9.61 (s, 1H, CHO). Found: *m/z* 222.1039. Calcd for $C_{16}H_{14}O$: M, 222.1045. **15b**: mp 105—106 °C; IR (KBr) 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.90 (t, *J*=7 Hz, 3H, Me), 2.51 (q, *J*=7Hz, 2H, CH_2), 7.0—7.6 (m, 10H, 2Ph), and 9.58 (1H, s, CHO). ^{13}C NMR ($CDCl_3$) δ=12.7(q), 30.2(t), 127.6(d), 128.3 (d), 128.7(d), 129.2(d), 129.7(d), 135.3(s), 137.8(s), 139.9(s), 165.0(s), and 193.2(s). Found: *m/z* 236.1181. Calcd for $C_{17}H_{16}O$: M, 236.1202.

Irradiation of **15a** in benzene with a high-pressure mercury lamp for 8 h gave an equilibrium mixture of two isomers (6:5). New signals ($CDCl_3$) were 2.57 (s, 3H, Me) and 10.35 (s, 1H, CHO). Similarly **15b** gave 1.18 (t, *J*=7 Hz, 3H, Me), 3.09 (q, *J*=7Hz, 2H, CH_2), and 10.37 (s, 1H, CHO) in 7:5.

Preparation of 3-Amino-1,2,3-triphenylcyclopropenes (6). A mixture of triphenylcyclopropenium perchlorate (2 mmol) and secondary amine (6 mmol) in benzene (30 cm^3) was stirred at room temperature for 2 h. In the reaction of diphenylamine 2 mmol of triethylamine was added. The product was recrystallized from benzene-petroleum ether. **6a** in 15% yield: mp 218—220 °C; IR (Nujol) 1810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.5—8.2 (m, 25H, 5Ph). ^{13}C NMR (C_6D_6) δ=53.0(s), 118.0(s), 121.9(d), 123.5(d), 126.1(d), 128.1(d), 128.3(d), 128.5(s), 129.1(d), and 146.9(s). Found: C, 91.23; H, 5.79; N, 2.97%; M^+, 435. Calcd for $C_{33}H_{25}N$: C, 91.03; H, 5.75; N, 3.22%; M, 435. **6b** in 56% yield: mp 150—151 °C; IR (KBr) 1810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.5—2.8 (m, 4H, CH_2NCH_2), 3.6—3.9 (m, 4H, CH_2OCH_2), and 7.1—7.9 (m, 15H, 3Ph). ^{13}C NMR ($CDCl_3$) δ=50.9(t), 54.4(s), 67.3(t), 119.5(s), 126.0(d), 127.2(d), 128.3(d), 128.9(d), 129.2(s), 129.8(d), and 144.1(s). Found: C, 85.26; H, 6.54; N, 3.99%; M^+, 353. Calcd for $C_{25}H_{23}NO$: C, 84.99; H, 6.52; N, 3.97%; M, 353. **6c**: in 65% yield: mp 128—130 °C; IR (KBr) 1800 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.3—1.9 (m, 6H, $(CH_2)_3$), 2.4—2.7 (m, 4H, CH_2NCH_2), and 7.0—7.8 (m, 15H, 3Ph). ^{13}C NMR ($CDCl_3$) δ=24.7(t), 26.8(t), 51.8(t), 54.9(s), 119.5(s), 125.8(d), 127.2(d), 128.3(d), 128.6(d), 128.9(d), 129.6(s), 129.8(d), and 145.0(s). Found: C, 88.59; H, 7.15; N, 3.82%; M^+, 351. Calcd for $C_{26}H_{25}N$: C, 88.89; H, 7.12; N, 3.99%; M, 351.

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