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CHLOROFLUOROCARBENE ADDITION TO ALKYNES: A NOVEL PATH TO CYCLOPROPENONES WITH UNCOMMON SUBSTITUENTS
(Cyclopropenone Chemistry, Part 11[1])

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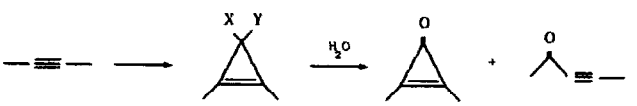
Abstract: Phase transfer catalytically generated chlorofluorocarbene adds to alkynes much more readily than dichlorocarbene. Some sterically shielded or critically substituted compounds that do not give addition with CCl_2 can be reacted with CClF. Chlorofluorocyclopropenes thus formed are hydrolyzed to cyclopropenones in situ. Hitherto unknown α-oxygen functional cyclopropenones were also prepared for the first time. Attempts to isolate α-carbonyl substituted cyclopropenones, however, failed: apparently electron withdrawing groups destabilize the semi-aromatic system.

Reactions between chlorofluorocarbene and alkynes have not found attention hitherto. Having experience with phase transfer catalytic dihalocarbene generations[2] and with dichlorocarbene additions to alkynes in particular[3], we decided to investigate the title reaction using the phase transfer catalysis technique. It was expected that CFCl would give low conversions. This carbene is known to be more stable and more selective than dichlorocarbene, but even with CCl_2 most alkynes give rather low yields of dichlorocyclopropenes. These are hydrolyzed under work-up conditions to cyclopropenones and/or acetylenic ketones:

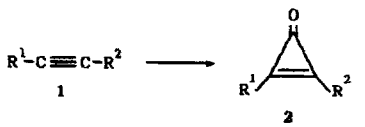


(Scheme 1)

Difluorocyclopropenes are relatively less sensitive towards hydrolysis in contrast. It remained to be seen how CClF adducts would behave.

We can report now that chlorofluorocyclopropenes are being formed and subsequently hydrolyzed to cyclopropenones when dichloromethane solutions of alkynes and dichlorofluoromethane are stirred with 50% aqueous sodium hydroxide in the

presence of a little benzyltriethylammonium chloride (TEBA) as catalyst. To get information about the electronic and steric requirements of such carbene additions, the 16 simple functional acetylenes given in Scheme 2 below were reacted.

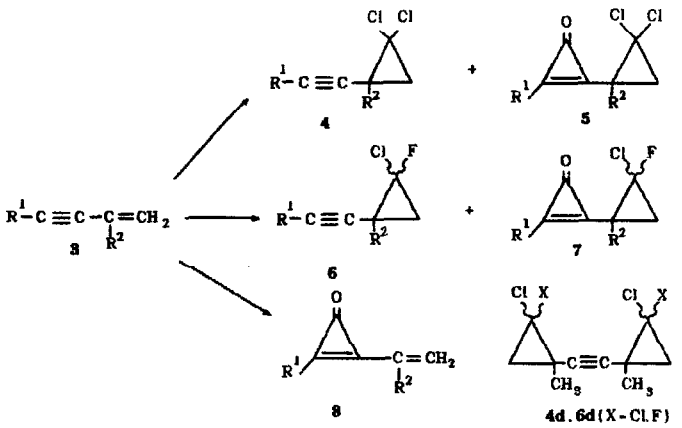


Compound 2	R^1	R^2	Yield (%)
a	1-Adamantyl	1-(1-tert-Butyl)-cyclopropyl	2.1
b	1-Adamantyl	1-(1-tert-Butyl-2,2-dichloro)cyclopropyl	0.5
c	1-Adamantyl	1-(1-tert-Butyl)-2-chloro-2-fluoro)cyclopropyl	0
d	1-Adamantyl	Mesityl	34
e	1-tert-Butyl	1-(1-Methyl)cyclopropyl	9.6
f	Mesityl	Mesityl	8
g	Mesityl	1-(1-tert-Butyl-2,2-dichloro)cyclopropyl	0.4
h	Mesityl	1-(1-tert-Butyl-2-chloro-2-fluoro)cyclopropyl	1.5
i	Mesityl	2-(2-Methoxypropyl)	8.3
j	Mesityl	2-(2-Methoxy-3,3-dimethyl)butyl	0
k	Mesityl	2-(2-Tetrahydropyranyloxy)propyl	18
l	Adamantyl	2-(2-Tetrahydropyranyloxy)propyl	0
m	Mesityl	(1-Tetrahydropyranyloxy)ethyl	55
n	Mesityl	1-(1-Tetrahydropyranyloxy-2,2-dimethyl)propyl	13
o	Mesityl	Diethoxymethyl	18
p	Mesityl	Triethoxymethyl	0

(Scheme 2)

Whereas fair yields are obtained with alkynes like 1d and 1m containing one aromatic and one aliphatic group of moderate steric bulk, severe crowding brings down yields to almost zero or nil (1b, 1c, 1g, 1j, 1l, 1p). It is especially noteworthy how a specific increase in bulk 1m ⟶ 1k ⟶ 1h, 1o ⟶ 1p lowers yields from 55 over 18 to 13 or from 18 to 0%, respectively. A replacement of the aromatic mesityl group by adamantyl (1k ⟶ 1l) brings yields from 18% to 0. Furthermore, a halide substituent in a cyclopropyl group of the alkyne (1a, 1b, 1c) also decreases yields substantially. Quite obviously, aromatic alkynes are much better substrates for the addition than aliphatic ones.

Comparison reactions with dichlorocarbene indicated that the sterically demanding alkynes 1a, 1b, 1d, 1e, 1g, and 1i do not give the respective cyclopropenones under these phase transfer catalysis conditions. Thus, chlorofluorocarbene has distinctively different properties from CCl_2, apparently because of different steric demands and the mentioned greater selectivity.



	R^1	R^2	4 / 5		6 / 7		8
a	Phenyl	Methyl	35	0	42	38	0
b	Mesityl	Methyl	30	4	47	30	0
c	1-Adamantyl	Methyl	43	0	75	3	0
d	Isopropenyl	Methyl	74[a]	0	73[a]	0	0
e	1-Adamantyl	tert-Butyl	20	0	31	0	4.7
f	tert-Butyl	tert-Butyl	25	0	–[b]	0	15
g	Mesityl	tert-Butyl	32	0	31	1.5	0

[a] bis-adducts **4d**, **6d** formed; [b] not isolated in pure form

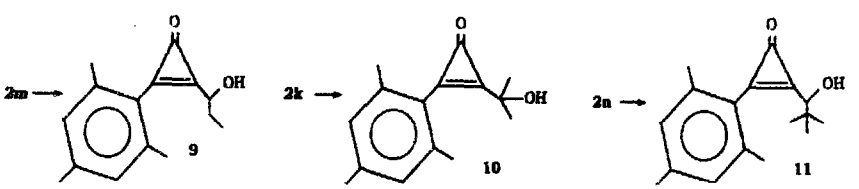
(Scheme 3)

As a second group of acetylenes, various enynes were reacted. It is known that enynes carrying an alkyl group in position 2 add dichlorocarbene first to the double bond. In a second step, a reaction at the triple bound can occur, but this is not a very favoured reaction[4]. Working again with highly substituted compounds, we reacted the enynes of Scheme 3 both with dichloro- and chlorofluorocarbene. The Yields given are from the direct, one-pot conversions. It turns out that CClF behaves similarly to CCl_2, but yields are generally much better with the former. This is a surprising result at first sight. It is known that dichlorofluoromethane is hydrolyzed much faster than chloroform under basic conditions in homogeneous water/dioxane solution[5]. Under phase transfer catalysis, however, the proportion of hydrolysis both of dibromocarbene and dichlorocarbene is repressed strongly by the presence of an alkene as carbene acceptor[6,7]. Furthermore, the relative amount of haloform which is lost by hydrolysis can vary between 4% and 75% depending on the nature of the alkene[6,7]. The present results show that chlorofluorocarbene is well protected from water in the two phase system and that it can be trapped efficiently by suitable carbene acceptors.

The following trends become apparent from the data of Scheme 3 and further

experiments:

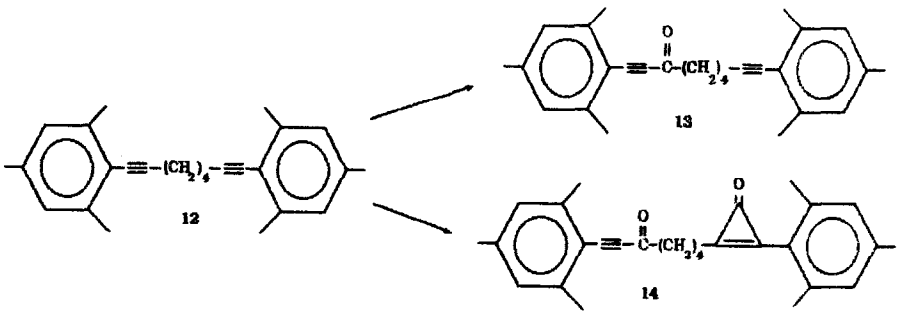
* With dichlorocarbene, almost always only the double bound is cyclopropanated. In some of these cases it is possible, however, to obtain compounds 5 by resubmitting compounds 4 to the reaction conditions.
* With chlorofluorocarbene, combined yields of compounds 6 and 7 are highest if R^1 is aromatic and electron rich. Furthermore, with aromatic R^1 and small R^2 a relatively high proportion of compounds 7 is formed.Severe steric crowding by R^2 = tert-butyl makes addition at the double bond slow or impossible. In these special cases primary reactions at the triple bond may result in the formation of unusual products 8e and 8f, unsaturated cyclopropenones. Desactivation makes a subsequent addition of CClF at the double bond impossible.
* Compounds 5a, 5b, 5c can be made from compounds 4a - 4c and difluorocarbene. The dichlorocarbene addition and subsequent hydrolysis is much less efficient or impossible in these cases.
* Cyclopropenones carrying α-hydroxy, α-carbonyl, or α-carboxyl functions were still unknown classes of compounds, and therefore 2i, 2k, 2m, 2n, and 2o received special attention. Whereas the cleavage of the methyl ether group in 2i needed conditions too severe for a survival of the cyclopropenone, 2m, 2k, and 2n were hydrolyzed to give 9, 10, or 11, respectively. No method was found to cleave the acetal 20 without destroying the cyclopropenone. Similarly, all attempts to oxidize 9 or 11 to the respective ketones using a large arsenal of methods resulted either in no conversion or total destruction. Quite obviously the semi-aromatic cyclopropenone system is destabilized by a neighbouring carbonyl function.



(Scheme 4)

Reaction of 1,8-Dimesityl-1,7-octadiyne (12) with chlorofluorocarbene leads to compounds 13 and 14 in relatively low yields (Scheme 5). In this case ynone-

type ring opening products of the intermediate chlorofluorocyclopropenes were isolated. There are indications that structurally similar compounds were formed in the other cases also, but no attempt was made to isolate these less interesting products in pure form. The direction of ring opening in 13 (and 14) follows from the ^{1}H-NMR which exihibits triplets at δ 2.55 (CH_2 next to the alkyne) and δ 2.75 (CH_2 next to the carbonyl). No bis-cyclopropenone and no formal insertion into the C-C-bound next to the cyclopropenone[8] was found.



(Scheme 5)

CONCLUSIONS

In conclusion then, chlorofluorocarbene (generated by phase transfer catalysis) is more reactive towards alkynes, especially in cases of steric demand, than is dichlorocarbene. The primary products, chlorofluorocyclopropenes are hydrolyzed to give cyclopropenones (and α,ß-acetylenic ketones). α-Hydroxycyclopropenones were made for the first time. α-Carbonyl substituted cyclopropenones are neither available by oxidation of the newly formed α-hydroxy substituted cyclopropenones nor by hydrolysis of respective acetals.

ACKNOWLEDGEMENT

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EXPERIMENTAL

^{1}H-NMR spectra were recorded with the instruments EM 360 (Varian) in CCl_4, WP 80 (Bruker), or AM 300 (Bruker) in $CDCl_3$. ^{13}C-NMR and ^{19}F-NMR: AM 300 in $CDCl_3$. IR spectra were measured with the Beckman Acculab 8 as KBr pellets for solids or as films between NaCl plates. Melting points were determined with the Büchi 510 apparatus. They are uncorrected. Boiling points refer to air bath temperatures of a Kugelrohr distillation. Acetylene starting materials were prepared by conventional

methods and characterized before further reactions with ^{1}H-NMR. Relevant physical data are given in Table 1.

Table 1. Physical Data of New Acetylenic Starting Materials

Comp.	m.p.	b.p./ Torr	^{1}H-NMR (δ)	Mol from	C calc./found	H calc./found
1a[a)]	122°		1.92(m,3H);1.81(m,6H);1.66(m,6H); 0.92(s,9H);0.69(m,2H);0.60(m,2H)	$C_{19}H_{28}$ (256.4)	88.99/88.63	11.01/ 10.99
1d	104°		6.83(s,2H);2.35(s,6H);2.25(s,3H); 1.99-1.74(m, 15H)	$C_{21}H_{26}$ (278.4)	90.59/90.80	9.41/ 9.31
1e[a)]		66°/80	1.22(s,3H);1.17(s,9H);0.78(dd,J= 3.8+6.3,2H);0.51(dd,J=3.8+6.3,2H)			
1f	125°(Lit.[12] 130°C)		6.90(s,4H);2.50(s,12H);2.29(s,6H)			
1i		60°/0.01	6.86(s,2H);3.45(s,3H);2.38(s,6H); 2.26(s,3H);1.57(s,6H)	$C_{15}H_{20}O$ (216.3)	83.29/83.14	9.32/ 9.32
1j		80°/0.01	6.86(s,2H);3.44(s,3H);2.40(s,6H); 2.27(s,3H);1.45(s,3H);1.09(s,9H)			
1k			6.86(s,2H);5.22(m,1H);3.9(m,1H); 3.5(m,1H);2.37(s,6H);2.27(s,3H); 1.6(m,12H)			
1l			5.02(m,1H);3.8(m,1H);3.5(m,1H); 2.0-1.0(m,27H)			
1m			6.85(s,2H);5.1-4.7(m,2H);4.2-3.2 (m,2H);2.38(s,6H);2.26(s,3H);1.8- 1.5(m,9H)			
1n			6.85(s,2H);5.1-3.25(m,4H);2.39(2s,6H); 2.26(s,3H);2.0-1.2(m,6H);1.11+1.07 (2s,9H)			
1o		80°/0.01	6.85(s,2H);5.56(s,1H);3.76(q,4H); 2.40(s,6H);2.27(s,3H);1.27(t,6H)			
1p		80°/0.01	6.86(s,2H);3.80(q,6H);2.41(s,6H); 2.28(s,3H);1.27(t,9H)			
3b		90°/0.2	6.85(s,2H);5.4(m,1H);5.3(m,1H); 2.39(s,6H);2.27(s,3H);2.01(m,3H)	$C_{14}H_{16}$ (184.3)	91.25/91.16	8.75/ 8.97
3c		60°/0.1	5.18(m,1H);5.12(m,1H);1.96(m,3H); 1.86(m,9H);1.68(m,6H)	$C_{15}H_{20}$ (200.3)	89.94/88.72	10.06/ 9.84
3e			5.18(d,J=1.5,1H);5.14(d,J=1.5,1H); 1.96-1.68(m,15H);1.12(s,9H)			
3f		100°/55	5.18(d,1H,J=1.6);5.14(d,1H);1.26 (s,9H);1.12(s,9H)			
3g			6.86(s,2H);5.39(d,1H,J=1.4);5.30 (d,1H);2.42(s,6H);2.27(s,3H);1.22 (s,9H)			
12		78°	6.84(s,4H);2.57(m,4H);2.37(s,12H); 2.26(s,6H);1.84(m,4H)			

[a)] Prepared by Li/t-BuOH reduction of 1b (70% yield) or 1g (42%), respectively.

As an example, the formation of 1a via 3e is described in detail.

1-Adamantylacetylene: 120 g (0.37 mol) 1-Adamantyl-2,2-dibromoethane[9], 4 g tetra-n-octyl-phosphonium chloride (phase transfer catalyst), and 2 g pinacol (cocatalyst to enhance the base concentration in the organic phase), are dissolved in 500 ml toluene and refluxed with 200 g (3.6 mol) powdered KOH for 5 h. The mixture is poured into water, separated, and the aqueous phase is extracted with dichloromethane. The united organic phases are dried over Na_2SO_4 and concentrated by rotatory evaporation. The residue is recrystallized from methanol; m.p. 82°C (Lit.-m.p.[10] 83°C), 42.6 g (72%) yield.

4-(1-Adamantyl)-2-tert-butyl-2-hydroxy-3-butyne: 40 g (0.25 mol) 1-adamantylacetylene in 80 ml ether are added to a Grignard solution from 29.4 g (0.27 mol) ethyl bromide and 6.8 g Mg in 150 ml ether. The mixture is refluxed for 18 h. Thereafter 26 g (0.26 mol) pinacolone in 150 ml ether are added. After boiling for another 40 h, the solution is poured onto ice, acidified, and extracted with ether. The extracts are dried over Na_2SO_4 and concentrated in vacuo. The residue is crystallized from petroleum ether (b.p. 30-60°C). M.p. 150°C, 41 g (63%) yield. – $C_{18}H_{28}O$ (260.4) Calc. C, 83.02; H, 10.84; found C, 82.27; H, 10.97.

1-(1-Adamantyl)-3-tert-butyl-3-buten-1-yne (3e). 31 g (123 mmol) of the precedingly described compound are dissolved in 300 ml ether and stirred with 30 g P_2O_5 for 48 h at room temperature. The mixture is hydrolyzed in water, separated, and the aqueous layer is extracted with dichloromethane. The united organic phases are dried over Na_2SO_4, the solvents are removed, and the residual oil is chromatographed on a silicia gel column with petroleum ether (b.p. 60-80°C) as eluent. Yield 26 g (88%). ^{1}H-NMR: δ 5.18 (d, J = 1.5; 1H), 5.14 (d, 1H); 1.96-1.68 (m, 15H); 1.12 (s, 9H). – MS(CI): m/e 243 (M+1).

1-(1-Adamantylethinyl)-1-tert-butyl-2,2-dichlorocyclopropane (4e). This compound is prepared following the general procedure for dichlorocarbene additions (see below). M.p. 96°C, 20% yield. – ^{1}H-NMR: 1.93 (m, 3H); 1.84 (m, 6H); 1.80 (d, J = 7.4, 1H); 1.67 (m, 6H); 1.53 (d, J = 7.4, 1H); 1.19 (s, 9H). MS (CI): m/e: 325 (M+1 for ^{35}Cl). – $C_{19}H_{26}Cl_2$ (325.3) Calc. C, 70.15; H, 8.06; found C, 69.76; H 8.47.

1-(1-Adamantylethinyl)-1-tert-butylcyclopropane (1a). 6 g (18.5 mmol) 4e are dissolved in 200 ml ether and 4 g tert-butanol. 2.3 g (0.33 mol) Li are added in small lumps over a period of a few hours. From time to time a few drops of water are added to keep the reaction running. After all of the lithium has been used up, the solution is shaken repeatedly with water, separated, dried, and concentrated. The residue is crystallized from ether. M.p. 122°C, 3.6 g (76%) yield. ^{1}H-NMR: δ 1.92 (m, 3H); 1.81 (m, 6H); 1.66 (m, 6H); 0.92 (s, 9H); 0.69 (m, 2H); 0.60 (m, 2H). – $C_{19}H_{28}$ (256.4) Calc. C,88.99; H, 11.01; found C, 88.63; H, 10.99.

General Procedure for Chlorofluorocarbene Additions: A solution of 15 mmol alkyne or enyne, 200 mg benzyltriethylammonium chloride, 1 ml ethanol and 15 ml (200 mmol) dichlorofluoromethane in 50 ml dichloromethane is stirred for 1 day with 40 g 50% NaOH at room temperature using a reflux condenser cooled to -15°C. Then the mixture is diluted with much water, separated, and the organic extract is dried over Na_2SO_4. The solvent is removed, and the residue is chromatographed over a silicia gel column using petroleum ether/ether mixtures. Fractions are purified by distillation or crystallization. ^{19}F-NMR spectroscopy shows that the chlorofluoro-

cyclopropanes are obtained usually as syn/anti mixtures that cannot be separated. Sometimes, with sterically demanding compounds (**2h** = **7g** and **1h** = **6g**, for instance), only one isomer is formed, presumably the one with fluorine and tert-butyl cis.

General Procedure for Dichlorocarbene Additions: 70 mmol alkyne or enyne and 200 mg benzyltriethylammonium chloride are dissolved in 30 ml chloroform and cooled to 0°C. 30 g of an ice-cold 50% NaOH are added gradually, and the mixture is stirred in the beginning at 0°C, then at room temperature for 4 days. After dilution with much water, the phases are separated, and the aqueous layer is reextracted with dichloromethane. The united organic extracts are dried over Na_2SO_4, then concentrated and chromatographed over silicia gel using petroleum ether/ether. Fractions are purified by distillation or crystallization.
Take notice that some compounds **5** cannot be prepared directly from compounds **3** but are obtained rather from compounds **4** by resubmission to the reaction conditions (in most cases with dichlorofluoromethane rather than with chloroform).

1-(1-Adamantyl)-2-(1-tert-butylcyclopropyl)cyclopropenone (**2a**), m.p. 114°C. ^{1}H-NMR: δ 1.9-1.6 (m, 15H); 1.17 (m, 2H); 1.02 (s, 9H); 0.97 (m, 2H). IR: 1840, 1610 cm^{-1}. – $C_{20}H_{28}O$ (284.4) Calc. C, 84.45; H, 9.92; found C, 84.38; H, 10.26.

1-(1-Adamantyl)-2-(1-tert-butyl-2,2-dichlorocyclopropyl)-cyclopropenone (**2b** = **5e**, m.p. 128°C. ^{1}H-NMR: δ 2.08 (m, 5H); 1.94 (m, 6H); 1.74 (m, 6H); 1.22 (s, 9H). IR: 1840, 1635 cm^{-1}. – $C_{20}H_{26}Cl_2O$ (353.3) Calc. C, 67.99; H, 7.42; found C, 68.19; H, 7.44.

1-(1-Adamantyl)-2-mesityl-cyclopropenone (**2d**), m.p. 72°C. ^{1}H-NMR: δ 6.92 (s, 2H); 2.38 (s, 6H); 2.31 (s, 3H); 2.06 (s, 9H); 1.77 (s, 6H). IR: 1835, 1620 cm^{-1}. – $C_{22}H_{26}O$ (306.5) Calc. C, 86.23; H, 8.55; found C, 86.03; H, 8.58.

1-(tert-Butyl)-2-(1-methylcyclopropyl)-cyclopropenone (**2e**). m.p. 54°C. ^{1}H-NMR: δ 1.46 (s, 3H); 1.34 (dd, J = 4.5 + 7.3; 2H); 1.31 (s, 9H); 0.96 (dd, J = 4.5 + 7.3; 2H). $C_{11}H_{16}O$ (164.3) calc. C, 80.44; H, 9.82; found C, 80.21; H, 9.75.

1,2-Dimesitylcyclopropenone (**2f**). m.p. 193°C (Lit.-m.p.[9] 190°C)

1-(1-tert-Butyl-2,2-dichlorocyclopropyl)-2-mesitylcyclopropenone (**2g** = **5g**) only 0.4% from **4g**. ^{1}H-NMR: δ 6.92 (s, 2H); 2.37 (s, 6H); 2.31 (s, 3H); 2.18 (d, 1H); 2.03 (d, 1H), 1.31 (s, 9H). IR: 1840, 1620 cm^{-1}. MS (CI) m/e 337 (M+1 for ^{35}Cl). – $C_{19}H_{22}Cl_2O$ (337.3) Calc. C, 67.66; H, 6.57; found C, 66.41; H, 6.70.

1-(1-tert-Butyl-2-chloro-2-fluorocyclopropyl)-2-mesitylcyclopropenone (**2h** = **7g**), m.p. 85°C. ^{1}H-NMR: δ 6.92 (s, 2H); 2.34 (s, 6H); 2.31 (s, 3H); 2.22 (dd, J = 8.2 + 16.1, 1H); 1.78 (dd, J = 6.5 + 8.2, 1H); 1.24 (s, 9H). ^{19}F-NMR: -142.77 (dd, J = 6.5 + 16.1). IR: 1845, 1630 cm^{-1}. – $C_{19}H_{22}ClFO$ (320.8) Calc. C, 71.13; H, 6.91; found C, 70.84; H, 7.29.

1-Mesityl-2[2-(2-methoxypropyl)]-cyclopropenone (**2i**), m.p. 38°C. ^{1}H-NMR: δ 6.95 (s, 2H); 3.26 (s, 3H); 2.54 (s, 6H); 2.33 (s, 3H); 1.64 (s, 6H). IR: 1830, 1605 cm^{-1}. – $C_{16}H_{20}O_2$ (244.3) Calc. C, 78.65; H, 8.25; found C, 78.37; H, 8.36.

1-Mesityl-2(2-tetrahydropyranyloxypropyl)-cyclopropenone (**2k**), m.p. 69°C. ^{1}H-

NMR: δ 6.93 (s, 2H); 4.7 (m, 1H); 3.8 (m, 1H); 3.4 (m, 1H); 2.54 (s, 3H); 2.50 (s, 3H); 2.32 (s, 3H); 1.8-1..4 (m, 12H). IR: 1850, 1830, 1610 cm^{-1}.

1-Mesityl-2(2-hydroxy)propyl-cyclopropenone (10), from 2k by hydrolysis in ether/10% aqueous HCl at room temperature. m.p. 141°C, 55% yield. ^{1}H-NMR δ 6.93 (s, 2H); 2.52 (s, 6H), 2.32 (s, 3H), 1.68 (s, 6H). IR: 3200 (br.), 1830, 1590 cm^{-1}. – $C_{15}H_{18}O_2$ (230.3) Calc. C, 78.23; H, 7.88; found C, 78.34; H, 7.81.

1-Mesityl-2(1-tetrahydropyranyloxyethyl)-cyclopropenone (2m), mixture of stereoisomers; oil that cannot be distilled without partial destruction. ^{1}H-NMR: δ 6.96 (s, 2H); 5.13 + 4.94 (2q, together 1H); 4.84 + 4.71 (2m, together 1H); 3.86 (m, 1H); 3.50 (m, 1H); 2.57 (s, 2H); 2.55 (s, 4H); 2.33 (s, 3H); 1.9-1.6 (m, 6H);1.58 + 1.55 (2d, together 3H). IR: 1840, 1605 cm^{-1}.

1-(1-Hydroxyethyl)-2-mesitylcyclopropenone (9), from 2m by hydrolysis, 78% yield, m.p. 134°C. ^{1}H-NMR: δ 6.95 (s, 2H); 5.03 (q, 1H); 2.54 (s, 6H); 2.33 (s, 3H); 1.62 (d, 3H). IR: 3360 (br.), 1835, 1600 cm^{-1}. – $C_{14}H_{16}O_2$ (216.3) Calc. C, 77.75; H, 7.46; found C, 77.76; H, 7.49.

1-Mesityl-2-(2,2-dimethyl-1-tetrahydropyranyloxy)-propylcyclopropenone (2n), mixture of stereoisomers; oil, that cannot be distilled without partial destruction. ^{1}H-NMR: δ 6.95 (m, 2H); 4.78-3.52 (m, 4H); 2.58 (s, 3H); 2.55 (s, 3H); 2.33 (s, 3H); 1.86-1.45 (m, 6H); 1.10 and 1.05 (2s, together 9H). IR: 1840, 1825, 1600 cm^{-1}.

1-(2,2-Dimethyl-1-hydroxy)propyl-2-mesitylcyclopropenone (11), by hydrolysis of 2n, 13% yield. m.p. 140°C. ^{1}H-NMR: δ 6.94 (s, 2H); 4.41 (s, 1H); 2.56 (s, 6H); 2.32 (s, 3H); 1.09 (s, 9H). IR: 3360 (br.), 1830, 1590 cm^{-1}. – $C_{17}H_{22}O_2$ (258.4) Calc. C, 79.03; H, 8.58; found C, 78.23; H, 8.58.

1-Diethoxymethyl-2-mesitylcyclopropenone (2o), m.p. 88C. ^{1}H-NMR: δ 6.97 (s, 2H); 5.61 (s, 1H); 3.80 (q, 2H); 3.77 (q, 2H); 2.59 (s, 6H); 2.33 (s, 3H); 1.28 (t, 6H). IR: 1810, 1590 cm^{-1}. – $C_{17}H_{21}O_3$ (273.4) Calc. C, 74.70; H, 7.74; found C, 74.76; H, 7.89.

1,1-Dichloro-2-methyl-2-phenylethinylcyclopropane (4a), b.p. 80°C/0.1 Torr. ^{1}H-NMR: δ 7.30 (m, 5H); 1.84 (d, 1H); 1.66 (s, 3H); 1.54 (d, 1H). ^{13}C-NMR: 131.7 (d), 128.2 (d); 122.8 (s); 89.4 (s); 81.2 (s);65.1 (s); 34.9 (t); 24.8 (s); 21.7 (q). – $C_{12}H_{10}Cl_2$ (225.1) Calc. C, 64.03; H, 4.48; found C, 63.83; H, 4.72.

1,1-Dichloro-2-methyl-2-mesitylethinylcyclopropane (4b), b.p. 75°C/0.1 Torr. ^{1}H-NMR: δ 6.84 (s, 2H); 2.37 (s, 6H); 2.26 (s, 3H); 1.84 (d, 1H); 1.69 (s, 3H); 1.57 (d, 1H). ^{13}C-NMR: δ 140.1 (s); 137.9 (s); 127.4 (d); 119.4 (s); 96.7 (s); 79.2 (s); 65.2 (s); 35.2 (t); 25.3 (s); 22.0 (q); 21.1 (q); 20.8 (q). – $C_{15}H_{16}Cl_2$ (267.2) Calc. C, 67.43; H, 6.04; found C, 67.67; H, 6.16.

1-(1-Adamantyl)ethinyl-2,2-dichloro-1-methylcyclopropane (4c). ^{1}H-NMR: δ 1.93 (m, 3H); 1.84 (m, 6H); 1.67 (m, 6H); 1.63 (d, 1H); 1.52 (s, 3H); 1.40 (d, 1H). ^{13}C-NMR: δ 89.9 (s); 79.0 (s); 65.3 (s); 42.9 (t); 36.4 (t); 34.2 (t); 29.5 (s); 28.0 (d); 24.5 (s); 22.3 (q). – $C_{16}H_{20}Cl_2$ (283.2) Calc. C, 67.85; H, 7.12; found C, 67.70; H, 7.07.

Bis-(2,2-Dichloro-1-methylcyclopropyl)acetylene (**4d**), m.p. 47°C (Lit.-m.p.[11] 47°C).

1-tert-Butyl-2,2-dichloro-1-(3,3-dimethyl-1-butynyl)-cyclopropane (**4f**), b.p. 60°C/0.01 Torr. ^{1}H-NMR: δ 1.80 (d, 1H); 1.52 (d, 1H), 1.20 (s, 9H); 1.19 (s, 9H).

1-tert-Butyl-2,2-dichloro-1-mesitylethinylcyclopropane (**4g** = **1g**). ^{1}H-NMR: δ 6.84 (s, 2H); 2.39 (s, 6H); 2.26 (s, 3H); 1.98 (d, 1H); 1.73 (d, 1H), 1.30 (s, 9H). MS (CI): m/e 309 (M+1 for ^{35}Cl). – $C_{18}H_{22}Cl_2$ (309.3) Calc. C, 69.90; H, 7.17; found C, 69.60; H, 7.43.

1-(2,2-Dichloro-1-methylcyclopropyl)-2-phenylcyclopropenone (**5a**), obtained in the direct CCl_2 addition to **3m** in 4% yield, from isolated **4a** with CClF, however, in 25% yield. m.p. 68°C. ^{1}H-NMR: δ 7.8 (m, 2H); 7.6 (m, 3H); 2.40 (d, 1H); 1.91 (s, 3H); 1.82 (d, 1H). IR: 1845, 1630 cm^{-1}. – $C_{13}H_{10}Cl_2O$ (251.1) Calc. C, 62.18; H, 4.01; found C, 61.50; H, 4.23.

1-(2,2-Dichloro-1-methylcyclopropyl)-2-mesitylcyclopropenone (**5b**) obtained **only** from isolated **4b** with CClF, 20% yield. m.p. 69°C. ^{1}H-NMR: δ 6.97 (s, 2H), 2.55 (s, 3H), 2.34 (s, 3H), 2.23 (d, 1H); 1.79 (d, 1H); 1.70 (s, 3H). IR 1840, 1830, 1600 cm^{-1}. – $C_{16}H_{16}Cl_2O$ (293.2) Calc. C, 65.54; H, 5.50; found C, 65.63; H, 5.80.

1-(1-Adamantyl)-2-(2,2-dichloro-1-methylcyclopropyl)-cyclopropenone (**5c**), obtained **only** from **4c** with CClF, 3% yield. m.p. 111°C. ^{1}H-NMR: δ 2.26 (d, 1H); 2.02 (m, 9H); 1.8 (m, 6H); 1.76 (d, 1H); 1.71 (s, 3H). IR: 1820, 1610 cm^{-1}. – $C_{17}H_{20}Cl_2O$ (309.3) Calc. C, 66.03; H, 6.52; found C, 65.80; H, 6.60.

1-Chloro-1-fluoro-2-methyl-2-phenylethinylcyclopropane (**6a**). ^{1}H-NMR: δ 7.42 (m, 2H); 7.30 (m, 3H); 1.87 + 1.32 (2dd, together 1H); 1.56 (m, 4H). ^{19}F-NMR: δ -134.4 (ddq); -143.8 (ddq) of equal intensity (1:1 isomer mixture). $C_{12}H_{10}ClF$ (208.7) Calc. C, 69.07; H, 4.83; found C, 68.95; H, 5.32.

1-Chloro-1-fluoro-2-methyl-2-mesitylethinylcyclopropane (**6b**). ^{1}H-NMR: δ 6.83 (s, 2H); 2.37 (s, 3H); 2.35 (s, 3H); 2.26 (s, 3H); 1.85 + 1.35 (2dd, together 1H); 1.58 (m, 4H). ^{19}F-NMR: δ -134.2 (m), -143.8 (m) of equal intensity. – $C_{15}H_{16}FCl$ (249.7) Calc. C, 72.14; H, 6.46 found C, 72.06; H, 6.86.

1-(1-Adamantylethinyl)-2-chloro-2-fluoro-1-methyl-cyclopropane (**6c**), δ 1.91 (m, 3H); 1.83 (m, 6H); 1.67 (m, 6H); 1.42 (m, 3H); 1.16 (m, 1H); 0.86 (m, 1H). MS (CI) m/e 267 (M+1 for ^{35}Cl). $C_{16}H_{20}ClF$ (265.8) Calc. C, 72.31; H, 7.58; found C, 72.09; H, 7.64.

Bis-(2-chloro-2-fluoro-1-methylcyclopropyl)acetylene (**6d**). ^{1}H-NMR: δ 1.73 (dd, J = 7.3 + 16.7, 1H); 1.44 (m, 7H); 1.23 + 0.88 (2m, 3:1, 2H). MS: m/e 238 (M$^+$ for ^{35}Cl). – $C_{10}H_{10}Cl_2F_2$ (237.1) Calc. C, 50.66; H, 4.25; found C, 50.38; H, 4.56.

1-(1-Adamantylethinyl)-1-tert-butyl-2-chloro-2-fluorocyclopropane (**6e** = **1c**). b.p. 60°C/0.1. ^{19}F-NMR: -119.7 (m); -143.5 (m) in the ratio of 1:9 (isomer mixture). – $C_{19}H_{26}ClF$ (308.9) Calc. C, 73.89; H, 8.48; found C, 73.83; H, 8.59.

1-tert-Butyl-2-chloro-2-fluoro-1-mesitylethinylcyclopropane (**6g** = **1h**). ^{1}H-NMR: δ 6.84 (s, 2H); 2.39 (s, 6H); 2.26 (s, 3H); 1.99 (dd, J = 7.7 + 17.8, 1H); 1.50 (dd,

J = 7.5 + 7.5, 1H); 1.21 (d, 9H, J = 0.9). ^{19}F-NMR: -142.8 (m). MS (CI): m/e 293 (M + 1 for ^{35}Cl). – $C_{18}H_{22}ClF$ (292.8) Calc. C, 73.83; H, 7.57; found C, 73.79; H, 7.61.

1-(2-Chloro-2-fluoro-1-methylcyclopropyl)-2-phenylcyclopropenone (7a), m.p. 81°C. ^{1}H-NMR: δ 7.82 (m, 2H); 7.55 (m, 3H), 2.21 (dd, 1H), 1.91 (dd, 1H); 1.84 (d, 3H).^{19}F-NMR: δ -132.5 (m); -140.7 (m) in the ratio of 1:9. IR: 1830, 1620 cm^{-1}. – $C_{13}H_{10}ClFO$ (236.7) Calc. C, 65.97; H, 4.26; found C, 65.96; H, 4.47.

1-(2-Chloro-2-fluoro-1-methylcyclopropyl)-2-mesitylcyclopropenone (7b), m.p. 80°C. ^{1}H-NMR: δ 6.97 (s, 2H); 2.52 (s, 6H); 2.34 (s, 3H); 2.26 + 2.04 (2dd, together 1H); 1.82 + 1.59 (2dd, together 1H); 1.63 + 1.59 (2d, together 3H). ^{19}F-NMR: δ-132.4 (m); -142.8 (m); ratio 1:1. – $C_{16}H_{16}ClFO$ (277.8) Calc. C, 69.19; H, 5.81; found C, 68.88; H, 6.13.

1-(Adamantyl)-2-(2-chloro-2-fluoro-1-methylcyclopropyl)-cyclopropenone (7c), m.p. 84°C, ^{1}H-NMR: δ 2.08 (m, 3H), 2.00 (m, 6H); 1.77 (m, 8H), 1.64 (d, 3H). IR: 1825, 1620 cm^{-1}. MS (CI): m/e 295 (M + 1 for ^{35}Cl). – $C_{17}H_{20}ClFO$ (293.8) Calc. C, 69.50; H, 6.86; found C, 68.97; H, 7.02.

1-(1-Adamantyl)-2-(1-tert-butylvinyl)-cyclopropenone (8e), m.p. 66°C. ^{1}H-NMR: δ 5.62 (d, 1H); 5.49 (d, 1H); 2.04 (m, 9H); 1.63 (m, 6H); 1.19 (s, 9H). ^{13}C-NMR: 162.3 (s); 157.7 (s); 153.4 (s); 145.0 (s); 120.0 (t); 39.9 (t); 36.6 (s); 36.2 (t); 35.4 (s); 28.5 (q); 27.7 (d). IR: 1830, 1610 cm^{-1}. – $C_{19}H_{26}O$ (270.4) Calc. C, 84.39; H, 9.69; found C, 83.86; H, 9.98.

1-tert-Butyl-2-(1-tert-butylvinyl)-cyclopropenone (8f). ^{1}H-NMR: δ 5.58 (d, 1H); 5.50 (d, 1H); 1.35 (s, 9H); 1.17 (s, 9H). IR 1820, 1620 cm^{-1}. MS (CI): m/e 164 (M^+-CO).

1,9-Dimesityl-3-oxonona-1,8-diyne (13). ^{1}H-NMR: δ 6.88 (s, 2H); 6.82 (s, 2H); 2.75 (t, 2H); 2.55 (t, 2H); 2.42 (s, 6H); 2.35 (s, 6H); 2.30 (s, 3H); 2.25 (s, 3H); 1.98 (m, 2H); 1.72 (m, 2H). IR: 2180, 1660 cm^{-1}. MS: m/e 370 (M^+).

1-Mesityl-2-(7-mesityl-5-oxo-hept-6-ynyl)-cyclopropenone (14), m.p. 85°C. ^{1}H-NMR: δ 6.94 (s, 2H); 6.83 (s, 2H); 2.87 (t, 2H); 2.59 (t, 2H); 2.57 (s, 6H); 2.50 (s, 3H); 2.35 (s, 6H); 2.33 (s, 3H); 2.0-1.8 (m, 4H). IR: 1820, 1700, 1590 cm^{-1}. MS: m/e 370 (M^+ - CO).

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