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SILVER MEDIATED ACETYLENIC OXY COPE REARRANGEMENT

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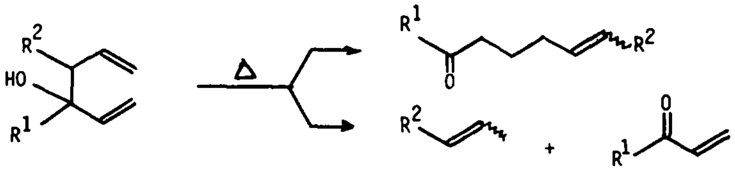
Abstract : Electrophile initiated acetylenic oxy Cope rearrangement of diversely substituted 5-Hexen-1-yn-3-ols leads to the corresponding α,δ-diethylenic aldehydes or ketones in good yields with mainly the E configuration for both double bonds.

Silver nitrate and Silver trifluoromethanesulfonate appear to be the most suitable electrophiles for this purpose and can be used either stoichiometrically (AgTf) or catalytically ($AgNO_3$).

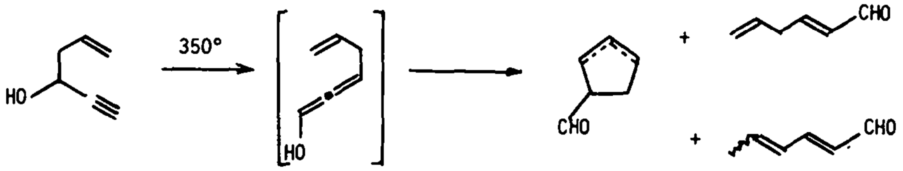
The thermal oxy-Cope rearrangement of 1,5-hexadiene-3-ols to δ-ethylenic ketones is now a long known process (1) but its synthetic utility either for the elongation of open chain compounds or for the four-carbon homologation of cyclic systems is considerably reduced owing to a low stereoselectivity and mainly to a competing cleavage of the molecule due to an ene process involving the hydroxyl group (2).



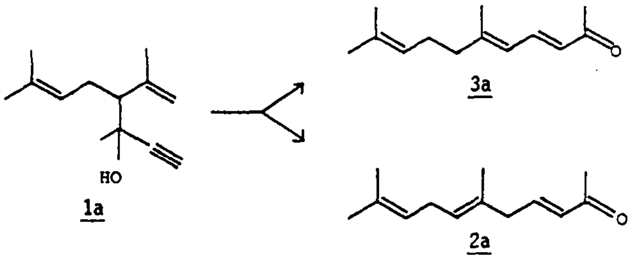
In recent years, the potential of this [3,3] sigmatropic transposition has been highly increased by the development of new conditions that eliminate the cleavage side-reaction and increase markedly its stereoselectivity. Some of them, for example, the siloxy-Cope rearrangement (3), use derivatives of the starting dienol but the more interesting ones are those which start from the alcohol itself and accelerate the oxy-Cope process by aprotic polar solvents (4) or by transforming it to the potassium alcoholate (5).

Since its description by EVANS et al., this low temperature process has been often applied in sequences leading to different natural products (6).

By comparison, only a few examples of the analogous transposition involving triple bonds have been described (7) (8) (9) probably because the synthetic utility of the thermal rearrangement of 5−alken−1−yn−3−ols is limited by the cyclisation of the intermediate allenols to cyclopentenyl compounds and by its transformation to a mixture of the isomeric 2,4− and 2,5−alkadienals (7).



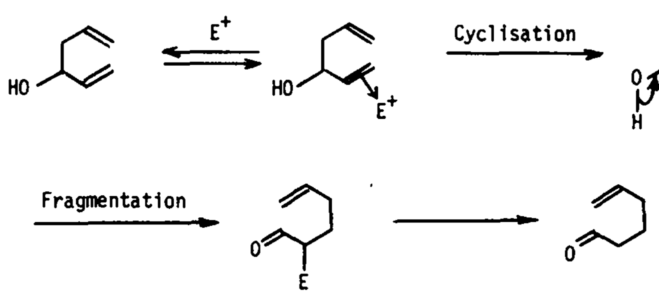
FUJITA *et al* have recently undertaken an interesting study of the rearrangement of the unsaturated alcohol 1a in the purpose of obtaining pseudoionone analogs (9). They have shown that the reported modifications of the oxy−Cope rearrangement were totally inefficient : the siloxy−Cope rearrangement of 1a (165°−4h) followed by hydrolysis gave a mixture of isomeric ketones 2a + 3a in 37% yields only while the Evans procedure (KH, THF, 0°, 3h) afforded trace of pseudoionone and leads only to a retroethynylation reaction.



However, they reported that, by using the solvent assisted rearrangement in liquid phase thermolysis, there was not only a solvent acceleration, but also a facile ketonization of the initial Cope product which prevents any further reactions of the intermediate allenol. Formation of the rearranged ketones then becomes essentially the only functionning process (for instance the use of N−methyl−2−pyrrolidone (NMP) increased the yield of 2a + 3a up to 68%). In addition they described a selective one pot synthesis of pseudoionone 3a from 1a with yield up to 70% via simultaneous oxy−Cope rearrangement and double bond migration using NMP containing a trace of halogen catalyst (10). In spite of its interest, this modification has still too drastic conditions (refluxing NMP : 165°) to be suitable in the case of very sensitive dienones.

Our recent works in the field of the oxy–Cope transposition of 1,5–hexadiene–3–ols were concerned with an electrophilic assistance by metallic salts in order to decrease the required temperature. This methodology, which supposed the cyclisation–fragmentation process depicted in scheme 1, was successfully applied to tertiary dienols which were transformed to δ–ethylenic ketones in fairly good yields at room temperature, by using mercuric trifluoroacetate either in stoichiometric (11) or catalytic (12) amounts or by assisting the transposition by catalytic quantities of bisbenzonitrile palladium dichloride (13).

Scheme 1



Unfortunately 5–alken–1–yn–3–ols such as 1a were transformed invariably to an untractable mixture of products when submitted to these different conditions.

The ability of triple bonds to give π–complexes with silver ions is well documented and, for example, authorizes in soft conditions the isomerisation of propargylic esters to allenic esters via a sigmatropic [3,3] rearrangement (14). This result, which could be explained by a cyclisation–fragmentation process analogous to that of scheme 1, prompted us to try to extend our own approach to the case of acetylenic oxy–Cope using the electrophilic assistance of silver salts.

Results and Discussion.

Our initial attempts were carried out on compound 1a using catalytic amounts (0.1 molar equivalent) of silver nitrate or silver trifluoromethanesulfonate. The best results were obtained when the reaction was performed in acetone at room temperature for twelve hours, leading to 24% of ketone 2a together with 60% of recovered starting material. A major drawback of this reaction seems to be the thermal decomposition of the anticipated vinylic silver (I) organometallic intermediate (15) as evidenced by the slow formation of silver metal in the reaction mixture.

This preliminary results encouraged us to undertake an extensive study of the reactivity of diversely substituted 5-Alken-1-yn-3-ols with stoichiometric amounts of silver salts.

1) Stoichiometric Conditions.

The relative effectiveness of various silver salts : trifluoromethane sulfonate, nitrate, tetrafluroborate, carbonate and fluoride were examined in tetrahydrofurane as solvent at room temperature. Silver triflate and nitrate were by far the most effective, the reaction time being longer with the latter. Silver tetrafluoroborate and carbonate were totally ineffective, while silver fluoride leads only to retroethynylation indicating that the counter ion plays an important role in the reaction.

The effects of solvent and temperature were further investigated. Among the solvents used, a mixture of tetrahydrofurane-water (3:1) was found to be the most efficient; the reaction was complete within 1 to 48 hours depending upon the nature of the starting material and there was not significant decomposition of the dienone product. The use of tetrahydrofurane and acetone increases the rate of the rearrangement but unfortunately the amount of decomposition products is greater than in tetrahydrofurane-water. In most cases, gentle heating of reaction mixture accelerates the transposition without noticeable decomposition.

Consequently, various 5-hexen-1-yn-3-ols were treated with one molar equivalent of silver trifluoroacetate in tetrahydrofurane-water (3:1) as solvent : The results, summarized in table 1, demonstrate the effectiveness of this new method, not only in the case of tertiary alcohols but also (entry 2) in that of alcohol 1b which constitutes the first example of rearrangement of a secondary alcohol using an electrophile mediated reaction. Also, it appears interesting to notice that the reaction successfully proceeds with a compound in which the triple bond is disubstituted (entry 6) although in moderate yield (30%).

The relative instability of the dienones under the purification conditions (see table 1, note c) may explain the moderate yields observed in a few cases. For example, we have shown that the catalytic hydrogenation of the reaction mixture obtained from 1a allows the isolation of the corresponding saturated ketone 4 in 80% yield (scheme 2).

scheme 2

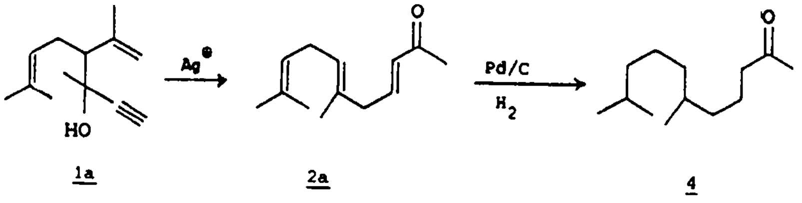
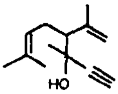
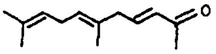
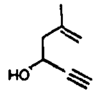
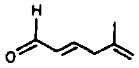
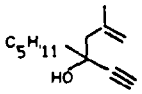
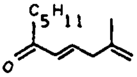
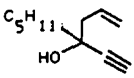
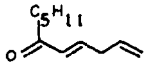
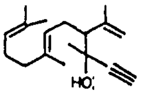
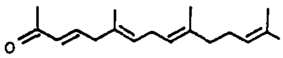
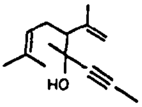
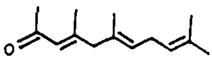
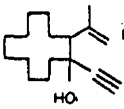
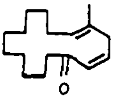
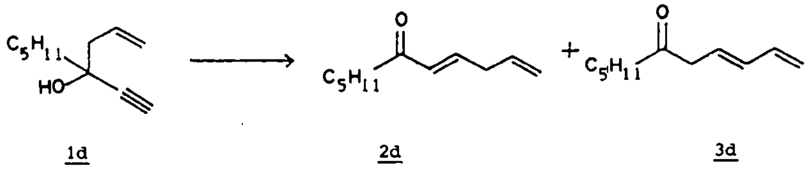


TABLE 1

Entry	Alcohol	Reaction condition[a] (°C)	(h)	Yield[c]	Dienone
1	 1a	40° ;	20	57	 2a
2	 1b	60° ;	1	55	 2b
3	 1c	40° ;	7	73	 2c
4	 1d	60° ;	41	25	 2d + 3d (5%)
5	 1e	20° ;	24	55	 2e
6	 1f	60° ;	21,5	30	 2f
7	 (b) 1g	60° ;	24	40	 2g

a : all reactions were carried out under nitrogen and in the absence of light.
b : the reaction was performed using THF/Water 5/1 as solvent.
c : the yields are calculated on the basis of isolated products after column chromatography on silica gel or neutral alumina

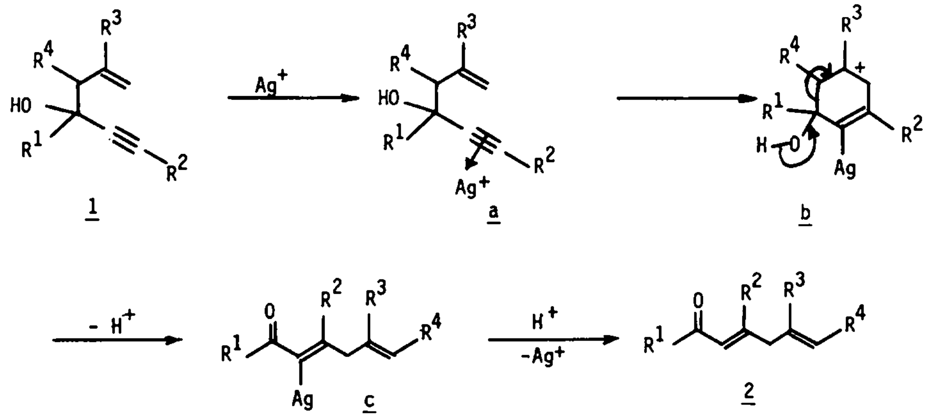
At least, capillary GC and high resolution ^{1}H NMR have shown that in most cases, ketone 2 is the only detectable isomer. The only exception was observed with alcohol 1d which yields 5% of the ketone 3d resulting probably from silver catalyzed slow isomerization of the ketone 2d. This can be due to a longer reaction time due to the less nucleophilic nature of the double bond. The E structure of the δ–disubstituted double bond of ketones 2 was deduced from the coupling constant $^{3}J \sim 16$Hz ; in the case of 2a, the same E configuration was clearly proved by a NOE experiment.



All these results show that this methodology provides a mild way to promote an acetylenic oxy–Cope process, leading to α,δ–dienones in moderate to good yields, with the advantage over the previous variations of being highly stereoselective and also avoiding the isomerization of ketones 2 to more conjugated isomers.

Although we did not investigate exhaustively the mechanism, the pathway we proposed in scheme 1 for dienols seems also plausible in the case of their π–acetylenic homologs : the initial π complexation of the silver cation affords a which is transformed into the carbocationic species b by nucleophilic attack of the double bond. Subsequent Grob–like fragmentation (16) leads to the vinylic silver (I) species c which is protonated giving the rearrangement product 2 (scheme 3).

Scheme 3

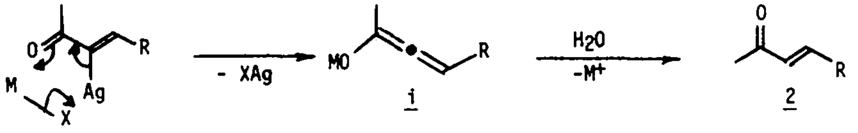


2) Catalytic conditions.

The effectiveness of this stoichiometric electrophilically assisted reaction as well as our earlier report (12) showing that in the case of hexadienones the process can be catalytic referred to the mercuric salt if the reaction is run in the presence of one molar equivalent of lithium trifluoroacetate, intrig us to investigate the effect of various main group metal salts in the silver assisted transposition of acetylenic alcohols 1.

Based on our previous results, we could expect a catalytic process using silver salts together with a main group metal salt through the pathway shown in scheme 4.

Scheme 4



In such a reaction the vinylic α–metallo ketone might be reactive enough to be decomposed, from a "push–pull" effect, to the allenic enolate i which will be further protonated to the ketone 2. The first step regenerates a silver ion while the second one leads to the reformation of the main group metal cation, such as the whole process might be expected to be catalytic in both metallic salts.

In preliminary experiments, this idea was tested with compound 1a by using 0.1 molar equivalent of silver nitrate and one molar equivalent of lithium nitrate. These conditions were totally ineffective, probably because of solvation of lithium cation in the tetrahydrofurane–water mixture. Consequently we used potassium and cesium nitrate whose cations are known to be less solvated than lithium by water molecules.

As shown by the results summarized in table 2 and concerning reactions performed with 0.1 molar equivalent of silver nitrate in refluxing tetrahydrofurane–water (2:1) the addition of these two last salts dramatically changes the course of the reaction, potassium nitrate being the more efficient since it gives fewer side products and a faster reaction time. As expected also, its amount does not noticeably influence the rate and the yield of the transposition which can be realized in the presence of catalytic amounts of both metallic nitrates, but the rate of the reaction drops markedly when the quantity of silver nitrate is decreased to 0.02 molar equivalent.

TABLE 2

Added salt	quantity (in mol.equiv.)	Reaction time(h)	Yield*
$CsNO_3$	1.0	50	48%
KNO_3	1.0	24	55%
KNO_3	0.1	30	47%
KNO_3	3	24	55%

* See Table 1, note C.

At least, it appeared in every case that slow desactivation of this salt occured even under the best defined conditions (0.1 equivalent of $AgNO_3$ + 1 équivalent of KNO_3) and that the reaction did not proceed as far toward completion after almost 60% of starting material 1a was reacted. For this reason, we obtained total engagement of 1a only when the quantity of silver nitrate was divided in two parts and added for one part at the beginning of the process and for the other one after 5–6 hours (see experimental).

These defined conditions were applied to other alcohols 1 which give the results summarized in table 3 when treated with 0.2 molar equivalent of silver nitrate and 1.0 molar equivalent of potassium nitrate in refluxing tetrahydrofurane–water (2:1). In every case the oxy–Cope desired rearrangement was observed giving the expected ketones and aldehyde but with slightly smaller yields than those observed in the stoichiometric conditions. The only difference between the two processes resides in the case of 1a where these new conditions increased the ratio of the isomeric 3a.

TABLE 3

Alcohol	Reaction time	Product (yield)*
1a	15h	2a (64%) + 3a (12%)
1b	6h	2b (50%)
1c	15h	2c (58%)
1e	7.5h	2e (46%)

* See Table 1, note C.

In conclusion, these results show the effectiveness of the electrophile mediated oxy–Cope transposition since 5–alkene–1–yne–3–ols are transformed in mild conditions to α,δ–diethylenic ketones by using silver salts in stoichiometric or catalytic amount. The main feature of this modification is that it can afford regio and stereospecifically the corresponding ketone or aldehyde. That constitutes an advantage over the previous methods and could therefore find useful applications in organic synthesis.

Acknoledgment. *The authors thank Rhone Poulenc Research for financial support and encouragement.*

EXPERIMENTAL

All reactions were carried out with freshly distilled solvents. Unless otherwise noted materials were obtained from commercial suppliers and used without further purification. Infrared (IR) spectra were determined (neat) with a Perkin Elmer Model 297 infrared recording spectrophotometer. NMR were determined using $CDCl_3$ as solvent on the following spectrometer : BRUCKER CW 80 and BRUCKER WH 360 for the ^1H spectra, BRUCKER WM 250 or VARIAN XL 100 for the ^{13}C spectra. Mass spectral analysis were performed on a VARIAN MAT CH5.

Capillary G.C. analysis was done with a GIRDEL 330 using FFAP or OV 101 columns. Preparative liquid chromatography was performed using either MERCK F254 silica–gel or WOELM GRADE III alumina.

5–alken–1–yn–3–ols 1.

The starting acetylenic alcohols were described according to the litterature by several ways.

– reaction of an allylic Grignard reagent with an α–acetylenic ketone or aldehyde referred to (6b) : alcohols 1b, 1c and 1d.

– Reaction of sodium acetylide in liquid ammonia with the corresponding B–ethylenic ketones resulting from the alkylation of mesityl oxide with either prenyl chloride or geranyl chloride as described by FUJITA et al (18) : alcohols 1a and 1e.

– Alcohol 1f was prepared by alkylation of the lithium acetylide of alcohol 1a by methyl iodide following a general process (19). 1f is obtained in 43% yield after column–chromatography over silica–gel.

– Alcohol 1g was obtained in 16% yield (mixture 1–1 of both diastereoisomers) by reaction of lithium acetylide in liquid ammonia with 2–isopropenyl cyclododecanone (20) (33% of the starting ketone are recovered besides other very polar products).

We describe here only the spectral characteristics of the new alcohols which gave satisfactory microanalysis.

3–(2–methyl–1–propen)yl–1–octyn–3–ol 1c

IR : 3450, 3310, 3080, 1645, 900.
^{1}H NMR : 0.92 (t, 3H) ; 1.25–2.75 (M, 8H) ; 1.95 (s, 3H) ; 4.9 (br.s ,1H) ; 5.0 (br.s ,1H) 2.42 and 2.48 (s 3H) (mixture of diastereoisomers).

3–propenyl–1–octyn–3–ol 1d

IR : 3400, 3300, 3070, 1640, 990, 915.
^{1}H NMR : 0.90 (t, 3H) ; 1.18–1.75 (M, 8H) ; 2.32–2.55 (m, 3H) ; 5.0–5.35 (m, 2H) ; 5.75–6.30 (m, 1H).

4,8 dimethyl–4–propenyl–7–nonen–2–yn–4–ol 1f

IR : 3480, 3080, 1640, 1375, 890.
^{1}H NMR : 1,47 (s, 3H) ; 1.65 (s, 3H) ; 1.69 (s, 3H) ; 1.80 (s, 3H) ; 1,82 (s, 3H) ; 2.1–2.5 (M, 3H) ; 4.89 (br. s, 1H) ; 4.95–5.13 (M, 2H)

2–isopropenyl 1–yn cyclododecanol 1g

IR : 3540, 3300, 3300, 3060, 1630, 1465, 1440, 905.
^{1}H NMR : 1.40 (M, 20H) ; 1.88 (br.s, 3H) ; 2.15–2.30 (m, 1H) ; 2.45 (s, 1H) ; 4.95 (br s, 1H) ; 5.1 (br.s, 1H).

Silver–assisted oxy–Cope transposition

Method A. Typical stoichiometric procedure

To a solution of 1 mmole (0.192 g) of 1a in 10 ml of a mixture THF–water (3/1) was added 1 mmole (0.257 g) of silver trifluoromethanesulfonate. The mixture was stirred at 40° for 20 hours under nitrogen in the absence of light. Then, 20 ml of ether were added and the reaction mixture was washed with saturated aqueous K_2CO_3 solution. After the usual work up, the crude material was purified by column chromatography using Woelmn neutral alumina III with Et_2O–ligroin (5/95) as eluent.

Method B. Typical catalytic procedure

To a solution of 1 mmole (0.192 g) of 1a in 10 ml of a mixture THF–water (2/1) was added 0.1 mmole (0.017 g) of silver nitrate and 1 mmole (0.101 g) of potassium nitrate. The mixture was stirred at reflux under nitrogen atmosphere in the absence of light for 6 hours. Then a second portion of 0.1 mmole (0.017 g) of silver catalyst was added and the mixture was stirred for 9 hours. The work–up was the same as in method A.

The aldehyde 2b and the ketones 2a and 2e were previously described (7) (17). We give below the spectral characteristics of all the compounds 2a–g since some of them were missing in previous reports.

6,10-Dimethyl-3,6,9-undecatrien-2-one **2a**.

IR : 3080, 3030, 1670, 1625, 1360, 1250, 980.

^{1}H NMR : 1.57 (s, 6H) ; 1.63 (s, 3H) ; 2.19 (s, 3H) ; 2.64 (t, J=7Hz, 2H) ; 2.80 (d, J=7Hz, 2H) ; 5.02 (t, J=7Hz, 1H) ; 5.12 (t, J=7Hz, 1H) ; 6.00 (d, J=15Hz, 1H) ; 6.70 (dxt, J=15 and 7Hz, 1H).

MS, m/z (relative intensity) 192 ($M^{+\cdot}$, 13) ; 177 (16) ; 152 (36) ; 149 (28) ; 134 (44) ; 124 (69); 119 (61) ; 109 (100).

5-Methyl-2,5-hexadienal **2b**.

IR : 3070, 3020, 2810, 2730, 1690, 1650, 1125, 970, 895.

^{1}H NMR : 1.78 (s, 3H) ; 3.02 (d, J=7Hz, 2H) ; 4.75-4.95 (m, 2H) ; 6.15 (dxd, J=15 and 8Hz, 1H) ; 6.85 (dxt, J=15 and 7Hz, 1H) ; 9.56 (d, J=8Hz, 1H).

MS, m/z (relative intensity) 110($M^{+\cdot}$, 17) ; 95 (100) ; 81 (62) ; 79 (32).

2-Methyl-1,4-undecadien-6-one **2c**.

IR : 3080, 3040, 1680, 1635, 985, 890.

^{1}H NMR : 0.83 (t, J=8Hz, 3H) ; 1.24 (br. s, 4H) ; 1.55 (q, J=11Hz, 2H) ; 1.67 (s, 3H) ; 2.47 (t, J=11Hz, 2H) ; 2.83 (d, J=10Hz, 2H) ; 4.68 (br.s, 1H) ; 4.77 (br. s, 1H) ; 6.08 (d, J=22Hz, 1H); 6.75 (dxt, J=22 and 10Hz, 1H).

^{13}C NMR : 13.8, 22.4, 22.4, 23.9, 31.5, 40.2, 40.7, 112.5, 142.3, 142.3, 143.8, 200.6.

1,4-undecadien-6-one **2d**.

IR : 3080, 3030, 3000, 1675, 1630, 990, 980, 920.

^{1}H NMR : 0.8 (t, J=7Hz, 3H) ; 1.12-1.75 (m, 6H) ; 2.51 (t, J=8Hz, 2H) ; 2.90 (t, J=6Hz, 2H) 4-90-5.12 (m, 1H) ; 5.12-5.25 (br.s, 1H) ; 5.6-6.1 (m, 1H) ; 6.1 (d, J=16Hz, 1H); 6.8 (dxt, J=16 and 6,1H).

6,10,14-Trimethyl-3,6,9,13-pentadecatetraen-2-one **2e**.

IR : 3030, 1680, 1630, 1255, 985.

^{1}H NMR : 1.55-1.72 (m, 12H) ; 1.88-2.12 (m, 4H) ; 2.15 (s, 3H) ; 2.70 (t, J=7Hz, 2H) ; 2.85 (d, J=7Hz, 2H) ; 4.9-5.25 (m, 3H) ; 5.95 (d, J=17Hz, 1H) ; 6.62 (dxt, J=17 and 7Hz, 1H).

4,6,10-trimethyl-3,4,9-undecatrien-2-one **2f**.

IR : 3020, 1690, 1610, 1210.

^{1}H NMR : 1.5-1.75 (m, 12H) ; 2.17 (s, 3H) ; 2.75 (br.s, 4H) ; 5.0-5.4 (m, 2H) ; 6.1 (br. s, 1H).

5-methyl-2,5-cyclodecadienone **2g**.

IR : 1695, 1670, 1623.

^{1}H NMR : 1.22 (br.s, 14H) ; 1.55 (br.s, 2H) ; 1.66 (s, 3H) ; 1.92 (br.s, 2H) ; 2.41 (t, J=7Hz, 2H); 2.87 (dxd, J=6.5 and 1.5Hz, 1H) ; 5.23 (t, J=7Hz, 1H) ; 6.03 (dxt, J=16 and 1.5Hz, 1H) 6.72 (dxt, J=16 and 6.5Hz, 1H).

MS (m/z) : 248 (M^+).

1,3-undecatrien-6-one **3a**.

IR : 3080, 3020, 3000, 1715, 1630, 990, 980, 920.

^{1}H NMR : 0.87 (t, J=7Hz, 3H) ; 1.13-1.75 (m, 6H) ; 2.45 (t, J=7Hz, 2H) ; 3.16 (d, J=6Hz, 2H) ; 4.95-5.13 (m, 2H) ; 5.6-6.13 (m, 2H) ; 6.65-7.05 (m, 1H).

6,10-dimethyl-undecan-2-one **4**.

IR : 2950, 2920, 1715, 1460, 1360, 1160.
^{1}H NMR : 0.88 (d, J=6.5Hz, 9H) ; 1.1–1.8 (m, H12) ; 2.12 (s, 3H) ; 2.4 (t, J=7Hz, 2H).
^{13}C NMR : 19.4 ; 21.4 ; 22.4 ; 22.5 ; 24.6 ; 27.9 ; 29.5 ; 32.6 ; 36.5 ; 37.1 ; 39.3 ; 44.0 ; 208.3.
MS (m/z) (relative intensity) : 198 (m$^{+\cdot}$25) ; 170 (12) 137 (12) ; 110 (12) ; 100 (100) ; 85 (95).

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