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SILVER ION INDUCED CYCLIZATION REACTIONS OF 1,1-DIMETHYL-2-TRIMETHYLSILOXYALLYL CHLORIDE WITH 1,3-DIENES

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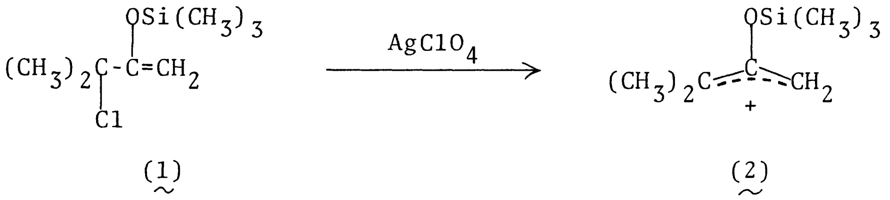
1,1-Dimethyl-2-trimethylsiloxyallyl chloride in the presence of 1,3-dienes gives seven-membered cyclic enones on treatment with silver perchlorate in yields of 85% with furan, 91% with cyclopentadiene, and 64% with isoprene, whereas the reaction with 2-methylfuran yields a mixture of two (5-methyl-2-furyl)butanone derivatives and two bicyclic enones.

2-Trimethylsiloxyallyl chloride, a silyl enol ether of α-chloro ketone, is expected to exhibit interesting chemical reactivities, because two reactive bonds, allylic carbon-Cl and enol oxygen-Si, are involved. Here we communicate that 1,1-dimethyl-2-trimethylsiloxyallyl chloride (1) undergoes a facile 3+4 ⟶ 7 carbocyclic reaction on treatment with silver perchlorate in the presence of 1,3-dienes.

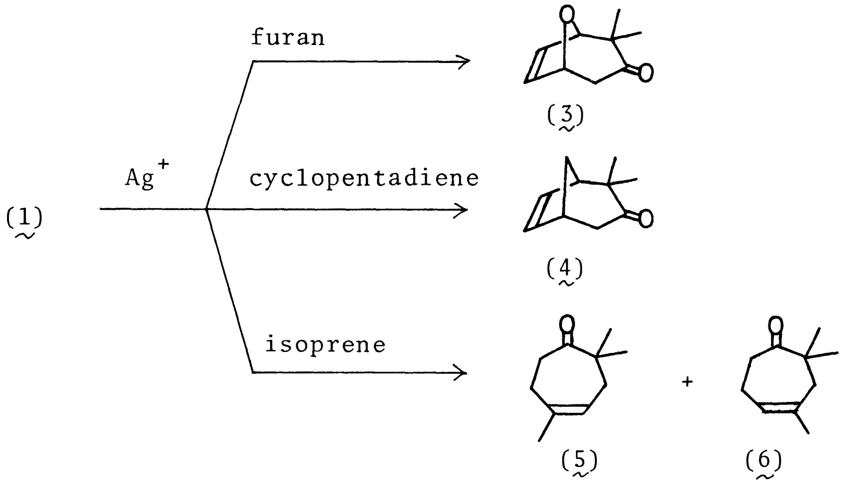
Thus the chloride (1) (1.2 g, 6.2 mmol) in ether (10 ml) was added to a cold stirred solution of silver perchlorate (1.8 g, 7.8 mmol) and furan (5 g) in 15 ml of ether-THF (5:1)[1] suspended with 3 g of calcium carbonate in a period of 15 min at 0° and the resulting mixture was stirred for further 30 min at the same temperature. The mixture was diluted with 50 ml of pentane and a gray solid was removed by filteration. The filtrate was washed first with saturated sodium chloride solution to remove excess silver perchlorate and then with saturated sodium bicarbonate solution. The organic layer was dried over magnesium sulfate and evaporated to leave an oil, which was purified by crystallization from pentane to give 2,2-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (3)[2] (801 mg, 85%) as colorless crystals, mp 46-47°. The reaction was smooth and the formation of silver chloride was almost instantaneous.

A similar reaction with 1.0 g of (1), 1.5 g of silver perchlorate, and 5 g of cyclopentadiene instead of furan afforded 2,2-dimethylbicyclo[3.2.1]oct-6-en-3-one (4)[2], mp 49-50°, in 91% isolated yield. When isoprene (12 times excess moles of the chloride) was used as a dine, there was obtained a mixture of karahanaenone (5)[3] and its isomer (6) in a ratio of 2.5:1 in 64% yield.[4]

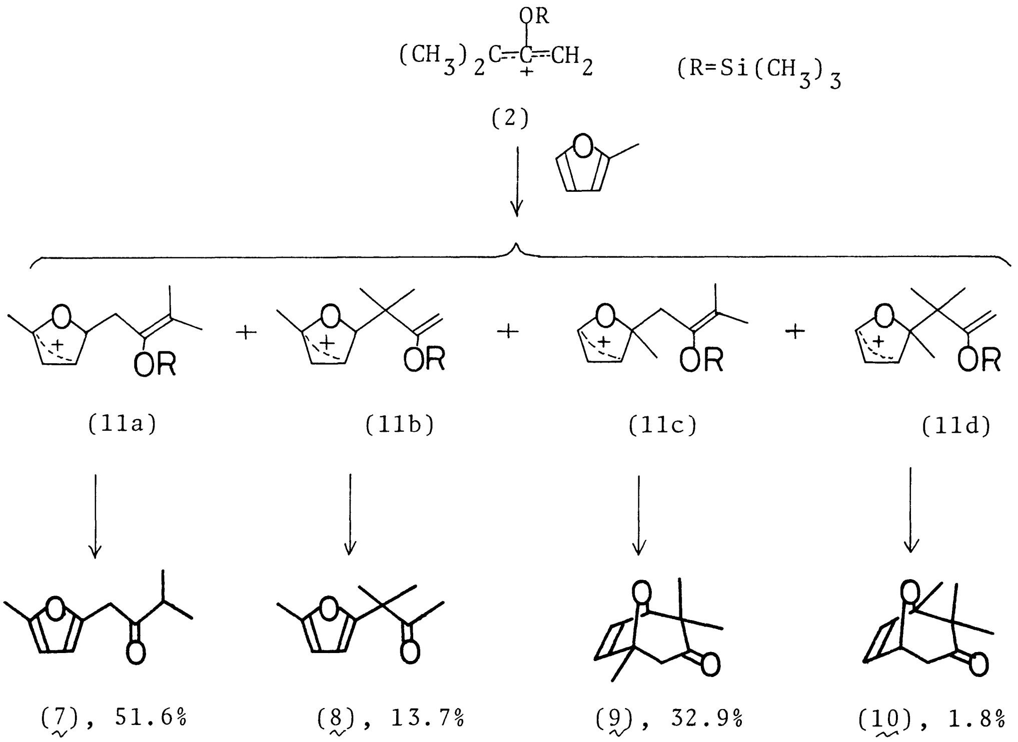
The starting material (1) was prepared in 57% yield by heating 3-chloro-3-methyl-2-butanone[5] with trimethylchlorosilane in DMF at 80° for 10 h using triethylamine as a base,[6,7] bp 55-56° (12 mm): ir (neat) 1630 cm^{-1}; nmr (CCl$_4$) δ 0.23 (s, 9H), 1.68 (s, 6H), 4.05(d, 1H, J=2 Hz), 4.42 (d, 1H, J=2 Hz).



$$(CH_3)_2C(Cl)\text{-}C(OSi(CH_3)_3)\text{=}CH_2 \xrightarrow{AgClO_4} (CH_3)_2C\text{---}\overset{OSi(CH_3)_3}{\underset{+}{C}}\text{---}CH_2$$



Useful information on the mechanism of the present reaction were given by the reaction with 2-methylfuran in which four products, (7) ~ (10), were formed in a ratio of 1.57:0.42:1.0:0.055 in 78% yield.[8] Apparently, the substitution reaction giving (7) and (8) preferentially occurred in this case and this is quite different from the reaction with furan itself. The formation of two types of the substitution products provides a good evidence for 2-trimethylsiloxyallyl cation (2) as a reactive intermediate which can be effectively trapped by 1,3-dienes.[4,9] It should be also noted that the formation of the bicyclic products was highly selective with a preference for (9). It is particularly interesting to compare these findings with the result reported by Turro et al.[2] that the reaction of 2,2-dimethylcyclopropanone



with 2-methylfuran cleanly gives (9) and (10) but with no orientational selectivity. Since this cycloaddition reaction has been considered as a concerted process, a similar poor regioselectivity might be expected in the present system too, if the allyl cation (2) adds to 2-methylfuran in a concerted manner as it has been proposed in the cycloaddition reaction of the related 2-oxyallyl species with 1,3-dienes.[10] The observed high selectivity and the concomitant occurrence of the substitution reaction are reasonably explicable as a stepwise addition of (2) to the diene. The preferential formation of (9) is consistent, since the two processes leading to (10), the formation of (11d) and the cyclization of (11a), should require a combination between two tertiary carbon centers and hence both are sterically very unfavorable. Thus, (11a) loses a proton to give (7) exclusively. Since we found a rather high reactivity ratio (P/T) of the primary to the tertiary carbon of 1,1-dimethyl-2-X (X=Cl, Br)-allyl cation in the electrophilic substitution reaction of furan (P/T ~ 9),[11] a similar ratio might be observed for the present allyl cation (2). If the bicyclic products were formed only from (11a) and (11b), the P/T ratio should be 1.2 (= (7+10)/(8+9)), whereas if (9) was formed exclusively through (11c), then the ratio should be 5.5 (= (7+9)/(8+10)) or 6.3 (= (7+9+10)/(8)). Clearly, the latter case is likely and it seems reasonable to conclude that the addition of (2) to the C-5 of 2-methylfuran preferentially leads to the substitution products, whereas the addition to the C-2 furnishes the bicyclic products, and that the product distribution is largely controlled by the steric factors.

The present reaction of the silyl enol ether of the α-halo ketone can provide a useful method of generating the 2-oxyallyl cation species and further studies on the related 2-trimethylsiloxyallyl cations are in progress.

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References and Notes

1) Silver perchlorate was first dissolved in THF and then the solution was diluted with ether.
2) N. J. Turro, S. S. Edelson, J. R. Williams, T. R. Darling, and W. B. Hammond, J. Am. Chem. Soc., 91, 2283 (1969).
3) Y. Naya and M. Kotake, Tetrahedron Lett., 1645 (1968).
4) A similar mixture of the products has been reported in the cyclocoupling reaction of 3-bromo-1-iodo-3-methylbutan-2-one and isoprene using zinc-copper couple: H. M. R. Hoffmann, Angew. Chem. Int. Ed. Engl., 12, 819 (1973).
5) The chloro ketone was prepared in 61% yield by the literature method (E. M. Kosower, W. J. Cole, G. S. Wu, D. E. Cardy, and G. Meisters, J. Org. Chem., 28, 630 (1963)), but we found that the chlorination using sulfuryl chloride in carbon tetrachloride gave better yields.
6) At more elevated temperatures, triethylamine promoted the elimination reaction of (1) giving 2-methyl-3-trimethylsiloxybuta-1,3-diene.
7) H. O. House, L. J. Czuba, M. Call, and H. D. Olmstead, J. Org. Chem., 34, 2324 (1969).
8) The reaction was carried out taking (1), $AgClO_4$, 2-methylfuran, and $CaCO_3$ (molar ratio 1:1.1:5:4) at 10° for 30 min. The products were analyzed at appropriate time of intervals by GLC (4 mm x 3 m glass column packed with 10% polydiethylene glycol succinate on Chamelite CS at 160°, under which condition (8), (7), (9), and (10) were eluted in order of retention time; 6.0, 10.6, 11.5, and 15.8 min). The product distribution did not change during the reaction and even after 150 min. Prof. R. Noyori kindly informed us their observation that (10) was unstable particularly under acidic conditions. However, careful examinations on the stability of the bicyclic compounds using an isolated mixture of (9) and (10) revealed that both compounds were stable at least under the present reaction conditions.
9) Cycloaddition reactions of 2-oxyallyl species with dienes have been known already: R. Noyori, S. Makino, and H. Takaya, J. Am. Chem. Soc., 93, 1272 (1971); H. M. Hoffmann, K. E. Clemens, and R. H. Smithers, ibid., 94, 3940 (1972); A. E. Hill, G. Greenwood, and H. M. R. Hoffmann, ibid., 95, 1338 (1973); H. Takaya, S. Makino, Y. Hayakawa, and R. Noyori, ibid., 100, 1765 (1978).
10) R. Noyori, F. Shimizu, K. Fukuta, H. Takaya, and Y. Hayakawa, ibid., 99, 5196 (1977).
11) We also found a high P/T ratio in the substitution reaction of anisole with (2).

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