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THE REACTION OF STABILIZED YLIDES AND RELATED ONIUM SALTS WITH TROPYLIUM ION

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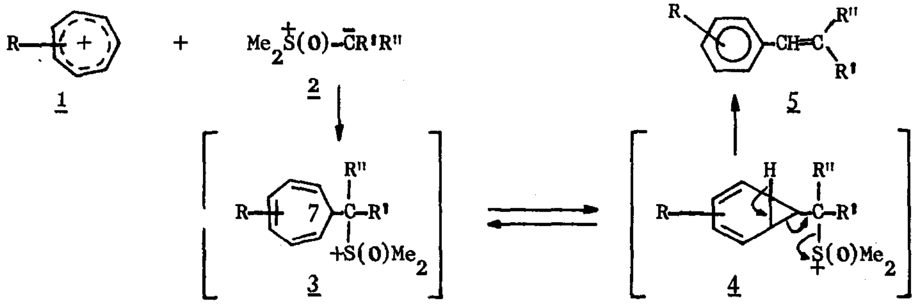
As part of our investigations on the structure and chemistry of ylides and their synthetic applications we have studied in some detail the reaction of a few ylides and the corresponding onium salts with tropylium ion with the aim of obtaining cycloheptatrienyl ("tropenyl") onium salts 9.

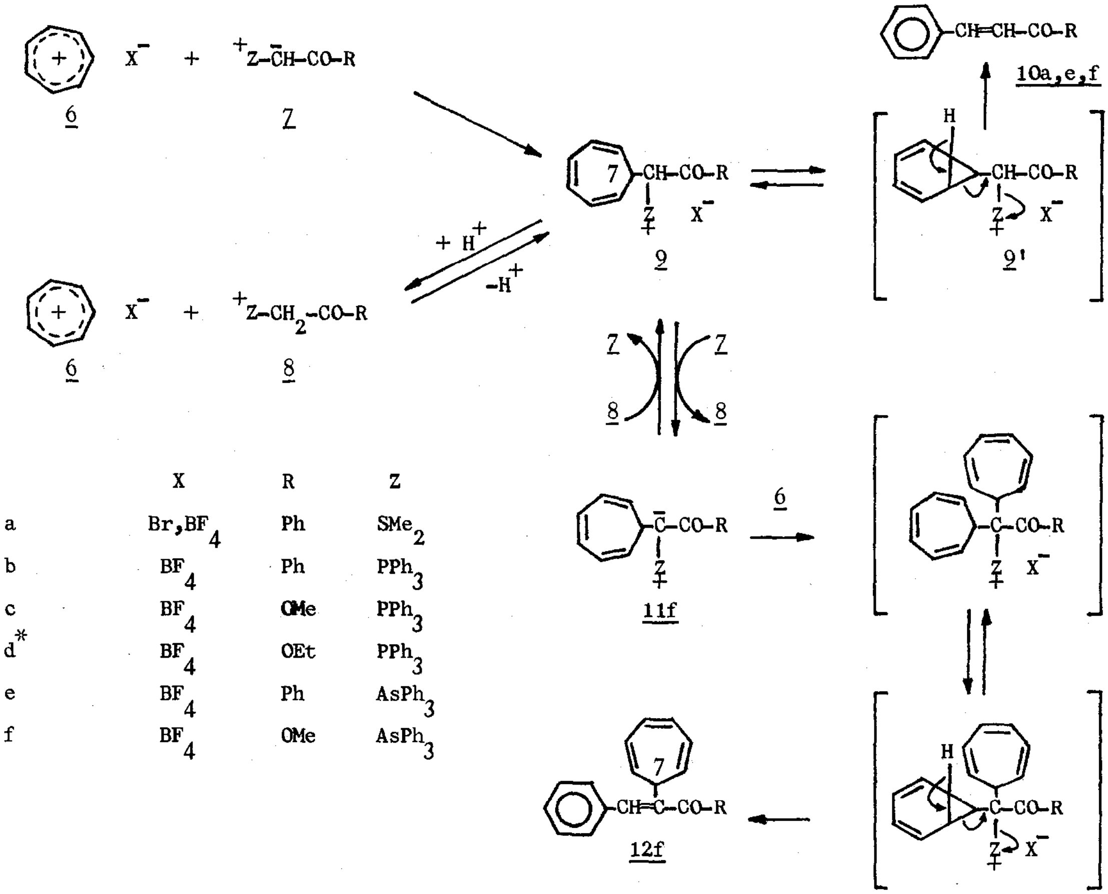
As far as we know only two reports by Y.Sugimura and coworkers[1,2] have been so far recorded on the reaction of tropylium ions 1 with stabilized sulfonium and oxosulfonium ylides 2, whereby styryl derivatives 5 were obtained, most probably through decomposition of the unstable intermediate onium salts 3-4:[3]



This course of the reaction is not surprising since styryl derivatives like 5 are known to be easily formed from 7-substituted cycloheptatrienes, through their norcaradienic valence tautomers when a "good" leaving group is attached α to the ring, as in 3, so that ring contraction can occur through an intermediate carbonium ion[1,2,5].

However we thought it would be possible the isolation of tropenyl onium salts of structure 9, akin to 3, by choosing the proper reaction conditions or leaving groups poorer than DMS or DMSO.

So we first reacted some carbonyl stabilized phosphorous, arsenic and sulfur ylides (7a-f) with trpylium salts 6 in THF at r.t. and found that, while the first step constantly leads to the tropenyl salt 9, the reaction stops and the salt can be isolated (or, at least, spectroscopically detected) when Z is a relatively poor leaving group (PPh_3 and, in a lesser degree, $AsPh_3$). On the contrary, when Z is a good leaving group (SMe_2 and, in a lesser degree, $AsPh_3$), the salt 9 can not be isolated and the rearranged styryl compound 10 is obtained.



	X	R	Z
a	Br,BF_4	Ph	SMe_2
b	BF_4	Ph	PPh_3
c	BF_4	OMe	PPh_3
d*	BF_4	OEt	PPh_3
e	BF_4	Ph	$AsPh_3$
f	BF_4	OMe	$AsPh_3$

So 9b-d were obtained in fair yields by reacting 7b-d with 6 in THF at r.t. Their structures follow from analyses and spectroscopic data : 9b, mp 220° : ν_{max}(nujol) 1670 cm^{-1}(s)(CO); nmr (DMSO-d_6, TMS as int. standard) δ 1.7-2.4 (m, 1H, H_7), 4.6-6.8 (4m at 4.6-5.1, 5.1-5.5, 5.7-6.5, 6.5-6.8, ~6H, HCP?and H_{1-6}?), 7.4-8.2 (m, ~20H, arom.), 8.2-8.5 (m, ~1H, ?). 9c, mp 162°: ν_{max} (nujol) 1735 cm^{-1}(s)(CO); nmr (DMSO-d_6) δ 1.6-2.3 (m, 1H, H_7), 3.68 (s, 3H, Me), 4.6-6.8 (4m at 4.6-5.0, 5.2-5.6, 5.8-6.5, 6.5-6.8, 7H, HCP and H_{1-6}), 7.5-8.3 (m, ~15H, arom.). 9d, mp 151°: ν_{max} (nujol) 1720 cm^{-1}(s)(CO); nmr (DMSO-d_6) δ 1.03 (t, J ~7.5Hz, Me), 1.7-2.3 (m, 1H, H_7), 4.15 (q, J ~7.5Hz, CH_2O), 4.7-6.8 (4m at 4.7-5.1, 5.1-5.6, 5.8-6.4, 6.5-6.8, ~7H, HCP and H_{1-6}), 7.3-8.2 (m, ~15H, arom.).

These salts undergo fragmentation to give 8 when treated with acids, in agreement with the data from the literature for 7-substituted cycloheptatrienes bearing a β-carbonyl group in the side-chain[7]. In fact the nmr spectrum of 9d in $CDCl_3$, typically, on addition of trichloroacetic acid, shows a dramatic lowering of the signals of 9d and a simultaneous rising of a singlet at 9.4 δ ($C_7H_7^+$) and a doublet at ca. 4.5 δ (J = 14 Hz), due to the CH_2-$\overset{+}{P}$ of the newly formed salt 8d.

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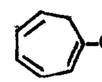
* The reaction between $C_7H_7Mo(CO)_3^+.BF_4^-$ and 7d brings to  -CH_2-COOEt, along with several other products[6].

The reaction between 6 (X = Br or BF_4) and the sulfonium ylide 7a in THF at r.t. brings to trans-chalcone 10a, in agreement with the findings of Y.Sugimuri and coworkers[1,2], in more than 90% yields, presumably through the norcaradienic form 9'of the salt[5a].

Similar behaviour is observed in the reaction between 6 and the arsonium ylide 7e which also brings to trans-chalcone along with $AsPh_3$. Actually in this case we could also detect the formation of the corresponding tropenyl salt 9e through its nmr spectrum which shows a pattern very close to 9b (see below). The salt could not be isolated in pure form from the reaction mixture because of its instability. In fact during the work up it can easily both decompose to chalcone and $AsPh_3$ and suffer fragmentation to 6 and 8e*.

Finally the reaction between the ylide 7f and 6 in THF at r.t. gave similar results. However in this case from the non-ionic portion of the reaction mixture, after separation of $AsPh_3$ by silica gel chromatography (hexane-ether), we obtained a liquid fraction (two partially overlapped spots on tlc) which, on the basis of the mass and nmr spectra was shown to be a ~1:1 mixture of trans-methyl cinnamate 10f and its α-tropenyl derivative 12f. In fact the mass spectrum shows the peaks of methyl cinnamate along with other peaks at 252 (M^+, for 12f), 221 (M^+ - CH_3O), 220 (221 - H), 193 (M^+ - $COOCH_3$), 192 (193 - H), 115, base peak,(192 - C_6H_5) and 91 (C_7H_7) m/e. The nmr spectrum in $CDCl_3$ shows the peaks corresponding to methyl cinnamate toghether with peaks which can be attributed to a cis/trans mixture of the ester 12f : δ 2.6–3.2 (m, 1H, H_7), 3.65 and 3.85 (2s in a 2:1 ratio, 3H, Me), 5.2–7.0 (3m at 5.2–5.7, 6.0–6.5, 6.5–7.0, 6H, H_{1-6}), 7.2–7.7 (m, ~6H, C_6H_5-CH=), 7.9§ (s, ~0.5H, Ph-CH).

Probably the α-tropenyl ester 12f was generated by a double tropenylation of 7f, presumably via the intermediate ylide 11f generated from 9f by transylidation.

Better results in obtaining phosphonium and arsonium salts of structure 9 have been reached by direct tropenylation of the triphenylphosphonium and arsonium salts 8 in aqueous medium. The reaction is related to the tropenylation of doubly activated methylene groups which can normally occur in acidic, neutral and basic medium[8,9]. As an example, when an aqueous solution of 8d was added to an aqueous solution of 6, at r.t., a white precipitate was formed in a few minutes (60% yields) which resulted identical to 9d. Similarly the arsonium salt 9e was obtained in ethanol-water from 8e and tropylium fluoborate 6 in almost pure form.** Its nmr spectrum in CD_3CN shows the three typical multiplets of the vinyl protons of the tropenyl ring, between 4.8 and 7.0 ppm.

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* A certain amount of $Ph_3\overset{+}{As}-CH_2-CO-Ph$ was also isolated from the reaction mixture, presumably because of a transylidation reaction between 9e and 7e.

§ This signal is almost completely overlapped with the downfield peak of the doublet of the methyl cinnamate Ph-CH= (10f).

** Evidently the low solubility in water of 9e prevented its decomposition.

An attempt of obtaining a similar result by reacting 6 with dimethylphenacylsulfonium fluoborate 8a failed: in fact, on mixing aqueous solutions of 8a and 6 at r.t. an oily material separated almost immediately, which resulted to be *trans*-chalcone. Evidently the sulfonium salt 9a is much less stable than the related phosphonium and even arsonium salts.

The chemistry of the cycloheptatrienyl salts 9 and their ylides is currently being investigated.

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