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THE REACTION OF TROPONOID WITH YLIDE. V.[1)]

THE REACTION OF TROPYLIUM- AND ALKOXYTROPYLIUM ION WITH STABLE SULFUR YLIDE

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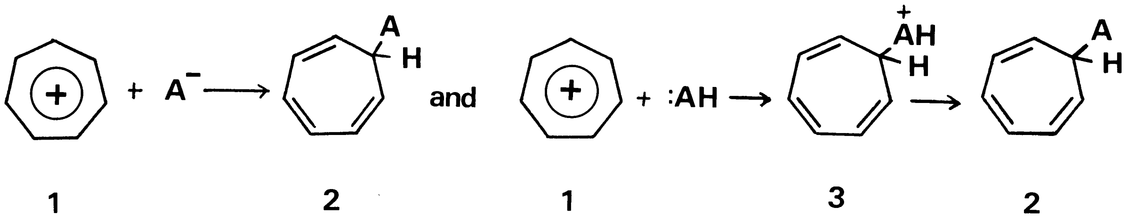
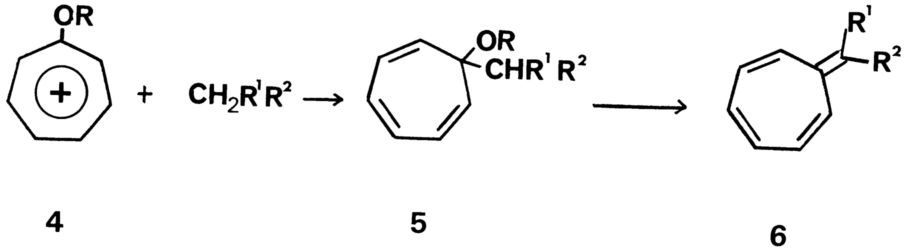
Tropylium ion reacted with stable sulfur ylides accompanying with the rearrangement of the seven membered ring to afford benzal derivatives. Analogous reaction of alkoxytropylium ion afforded o- and p-alkoxybenzylidene derivatives.

Although the tropylium ion (1) is a very stable carbonium ion, it reacts very readily with nucleophilic reagents. The general patterns of these reactions may be formulated by the following schemes:[2)]

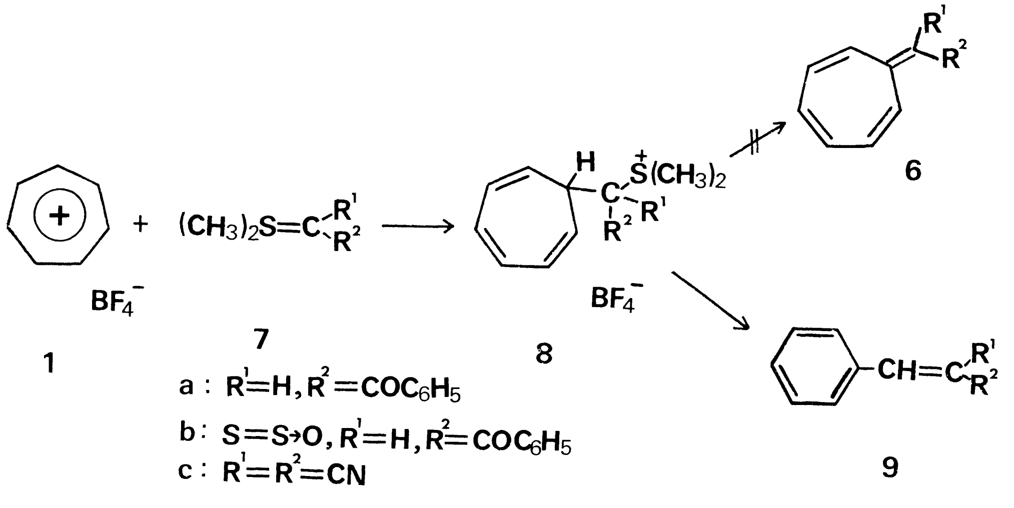


Alkoxytropylium ion (4) which corresponds partly the dipolar structure of tropone, is less stable than the parent tropylium ion and reacts with active methylene compound to give heptafulvene derivatives (6) via an adduct (5)[3,4)].



We already reported some results of the reactions of tropone with S, N, and P ylides. It is anticipated first that in the reaction of tropylium ion with sulfonium ylide (7) an adduct (8) would be formed and that the following elimination of $(CH_3)_2\overset{+}{S}H\ X^-$ from it would yield a heptafulvene (6). In fact, the heptafulvene was not obtained but a benzylidene derivative (9) was isolated.

To a suspension of tropylium fluoroborate (1) in THF was added an equimolar amount of benzoylmethylenedimethylsulfurane (7a) and the mixture was stirred for two hours at 0-25°C. After usual work up chalcone (9a, mp 58°) was obtained in 62% yield. The structure of 9a was identified with a standard sample (mixed melting point and spectrometry). Analogous reactions of benzoylmethylenedimethyloxosulfurane (7b) and dicyanomethylenedimethylsulfurane (7c) with 1 gave correspondingly a chalcone (9a) in 61% yield and benzylidenemalononitril (9b, mp 84°) in 80% yield, respectively.

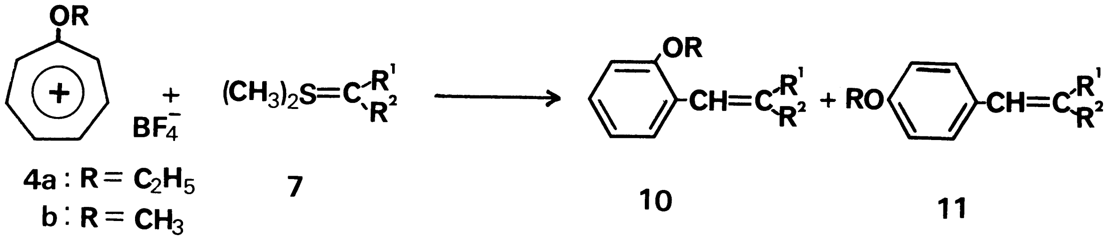


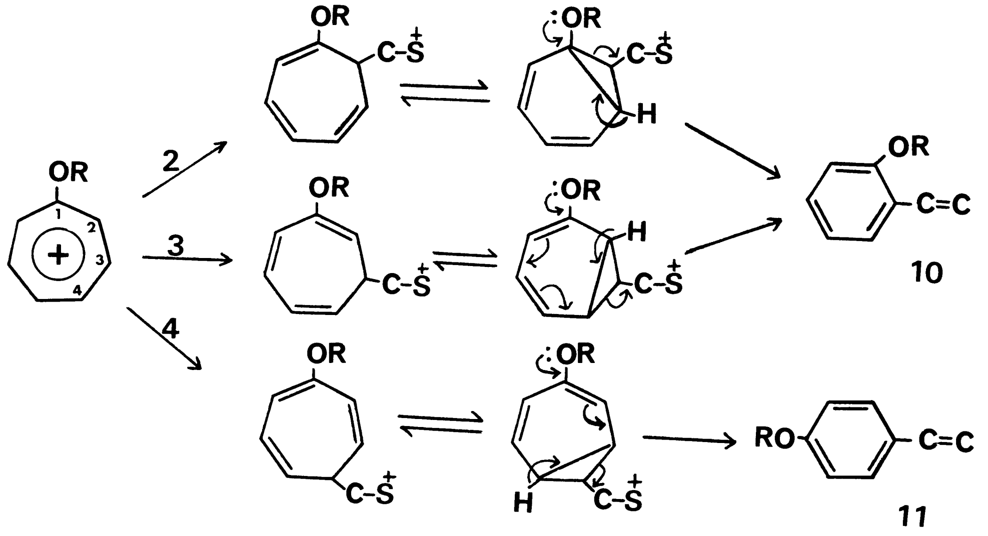
1 7 8 6 9

a : $R^1=H, R^2=COC_6H_5$
b : $S=S\rightarrow O, R^1=H, R^2=COC_6H_5$
c : $R^1=R^2=CN$

9a : $R^1=H$, $R=COC_6H_5$
b : $R^1=R^2=CN$

Alkoxytropylium ion (4) reacted with the stable sulfur ylide (7) analogously. To a suspension of ethoxytropylium fluoroborate (4a), which was prepared from tropone and triethyloxonium fluoroborate$^{3)}$, in methylene chloride was added a solution of an equimolar amount of benzoylmethylenedimethylsulfurane (7a) and the mixture was stirred at room temperature for two hours. After general work up and separation, o-ethoxy- (10a)5) and p-ethoxychalcones (11a)6) (2.6:1) were obtained in 50% total yield. The structure of each 10a and 11a was identified with a proper standard sample which was prepared from the corresponding ethoxybenzaldehydes and acetophenone5,6). The results of the varied modifications of this reaction are summarized in TABLE I. Consideration of reaction mechanism suggested that o-alkoxyderivative (10) should be given by an attack of ylide carbanion at 2 and/or 3 position of alkoxytropylium ion4). While





p-alkoxy derivative (11) should be given only by an attack at 4-position (see the Chart). TABLE I shows that there is no relationship between the product ratio (10 : 11) and nucleophilicity of ylide carbanion. Probably, steric factor would be operative to affect the product ratio, that is, hindered carbanion (such as 7c and 7i) would favorably attack the less hindered position at 4 giving 11. The detailed investigation about the reaction mechanism is in progress using labelled compounds.

TABLE I

Run No.	R	Ylide	S	R^1	R^2	Yield	Product ratio 10 : 11	Melting point
1	C_2H_5	7d	S	H	$COC_6H_4NO_2^p$	45%	2.4 : 1	10b(139^{o}), 11b(157^{o})
2	C_2H_5	7e	S	H	$COC_6H_4Br^p$	47%	4.9 : 1	10c(63^{o}), 11c(134^{o})
3	C_2H_5	7a	S	H	COC_6H_5	50%	2.6 : 1	10a(oil), 11a(44^{o})
4	C_2H_5	7f	S	H	$COC_6H_4CH_3^p$	58%	4.0 : 1	10d(oil), 11d(98^{o})
5	C_2H_5	7g	S	H	$COC_6H_4OCH_3$	48%	3.6 : 1	10e(oil), 11e(106^{o})
6	CH_3	7a	S	H	COC_6H_5	32%	6.5 : 1	10f(oil), 11f(73^{o})
7	CH_3	7d	S	H	$COC_6H_4NO_2^p$	30%	3.9 : 1	10g(152^{o}), 11g(147^{o})
8	CH_3	7a	S	C_6H_5	COC_6H_5	35%	1.4 : 1	10h(140^{o}), 11h(143^{o})
9	C_2H_5	7b	$S\rightarrow O$	H	COC_6H_5	50%	2.5 : 1	10a, 11a
10	CH_3	7b	$S\rightarrow O$	H	COC_6H_5	38%	2.3 : 1	10f, 11f
11	C_2H_5	7c	S	CN	CN	72%	1 : 1.6	10i(79^{o}), 11i(138^{o})
12	CH_3	7c	S	CN	CN	38%	1 : 1.8	10j(72^{o}), 11j(108^{o})
13	CH_3**	7h	S	H	$COOC_2H_5$	60%	3.0 : 1*	10k, 11k mixture not isolated
14	CH_3**	7i	S	$COOC_2H_5$	$COOC_2H_5$	62%	1 : 1.6*	10l, 11l mixture not isolated

* Based on the integration of NMR.

** Prepared by using magic methyl[7)] instead of Meerwein reagent.

Dimethoxytropylium ion (12, mp 136°), which was prepared from methoxytropone and trimethyloxonium fluoroborate, is less reactive than monomethoxy- or parent tropylium ion. Thus it did not react with dicyanomethylenedimethylsulfurane (7c) but did with benzoylmethylenedimethylsulfurane (7a) in methylene chloride to give 2,3-dimethoxychalcone (13a, oil)[8] and 3,4-dimethoxychalcone (14a, 88°)[9] (1 : 2.4) in 51% total yield. Each product was identified with a standard sample, which was prepared from 2,3-dimethoxybenzaldehyde or 3,4-dimethoxybenzaldehyde with acetophenone[8,9]. Analogous results with other ylides are shown in TABLE II.

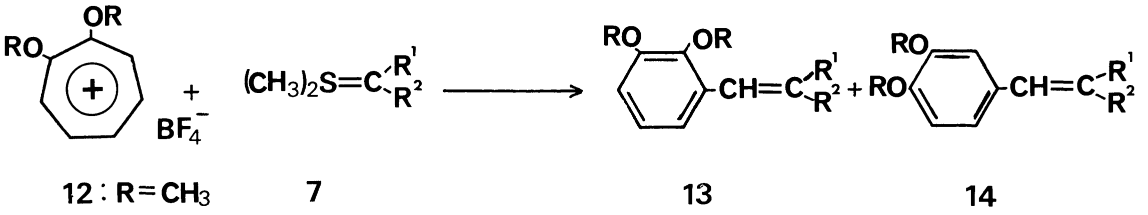


TABLE II

R^1	R^2	Yield	Product ratio 13 : 14	Melting point
H	COC_6H_5	51%	1 : 2.4	13a(oil), 14a(88°)
H	$COC_6H_4NO_2^p$	38%	1 : 2.2	13b(136°), 14b(181°)
H	$COOC_2H_5$	70%	1 : 2.0	13c(oil), 14c(53°)
$COOC_2H_5$	$COOC_2H_5$	70%	1 : 5.0	13d(oil), 14d(oil)

The conversion of tropylium ion to the benzylidene derivatives mentioned above would be useful for the syntheses of some biphenyls and certain particular flavonoids. We are now under investigation on the application of this reaction to such a synthesis.

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