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ONE STEP FORMATION OF ALKYNES FROM ARYL KETONES

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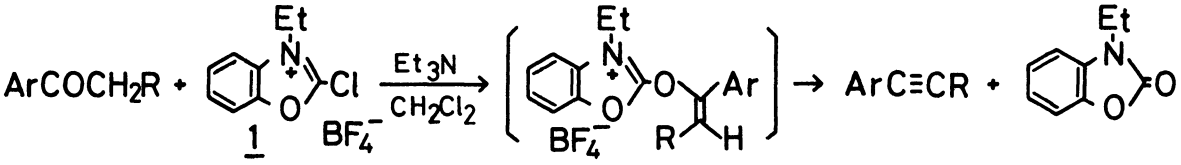
Aryl ketones are converted to the corresponding alkynes by the treatment with 2-chloro-3-ethylbenzoxazolium tetrafluoroborate in the presence of a large excess of triethylamine at room temperature.

The conventional methods for the synthesis of alkynes from ketones involves[1] following two reactions; i) the formation of gem-dichlorides or vinyl chlorides from ketones, ii) the elimination of hydrogen chlorides with alkali amides or alkali hydroxides. These methods are evidently incompatible with compounds having other functional groups which are sensitive to strong acids or bases. Further, several synthetic methods to form alkynes from ketones recently appeared in the literature, but there has been rarely reported an one step formation of alkynes from ketones. Ho et al.[2] reported an one step formation of alkynes from aryl ketones by the treatment with phosphorus pentachloride and pyridine in refluxing benzene. But, in the reaction, alkynes were obtained in a quite low yield along with a large amount of vinyl chlorides.

Recently in the course of our synthetic investigation utilizing the onium salts of azaaromatics, 2-chloro-3-ethylbenzoxazolium tetrafluoroborate 1 has been shown to be a useful reagent for the dehydration.[3] We have now found that aryl ketones were converted to the corresponding alkynes in the presence of a weak base such as triethylamine at room temperature by the treatment with 1 as shown in the following equation.



When 2-naphthylmethylketone 2 (1 mmol) was treated with 1 (1.2 mmol) and triethylamine (17 mmol) in dichloromethane at room temperature 2-naphthylacetylene 3 was obtained in 41% yield and 49% of the ketone 2 was recovered. The yields of the alkyne 3 depended on the amount of triethylamine and better results were obtained in the presence of a large excess of triethylamine as shown in Table I.

A typical procedure is described for the preparation of 2-naphthylacetylene 3. To a suspension of 1 (1.2 mmol) and 2-naphthylmethylketone 2 (1.0 mmol) in dichloromethane (2 ml in Method A, 1 ml in Method B) was added triethylamine (15 mmol in Method A, 7.5 mmol in Method B) slowly at 0°C under an argon atmosphere. The mixture was stirred at room temperature for 44 h to give a clear yellow solution. Then 1 N

Table I. The formation of 2-naphthylacetylene 3.

molar ratio				yield		
1	2	Et_3N	time	3	4[a]	2[b]
1.2	1.0	1.2	157 h	trace	—	c)
1.2	1.0	2.2	36	26%	7%	c)
1.2	1.0	17	44	41 (80%)[d]	4	49%
2.0	1.0	5	48	29 (45)	7	35
2.0	1.0	15	48	43 (61)	4	29

a) Chloro-1-(2-naphthyl)vinyl. b) Recovered. c) Not isolated.
d) Yields in parentheses were based on unrecovered ketones.

HCl was added and the organic layer was extracted with ether. The ether extract was washed with water, dried over anhydrous magnesium sulfate, and evaporated in vacuo. The oily residue was purified by silica gel thin layer chromatography.

In the similar manner, various aryl ketones were converted to the corresponding alkynes in yields as shown in Table II. Alkynes were obtained in higher yields in the case when the reaction was carried out in a high concentration.[4] (Table II, entry 1-4)

It should be noted that the present method is of quite general utility; alkynes are obtained from aryl ketones in one step under mild conditions.

Table II. The formation of alkynes.

entry	ketone	method	time	alkyne	yield	ketone[a]
1	2-Naphthyl-$COCH_3$	A	44 h	2-Naphthyl-C≡CH	41%(80%)[b]	49%
2	2-Naphthyl-$COCH_3$	B	37	2-Naphthyl-C≡CH	47 (63)	25
3	$PhCOC_3H_7$	A	44	$PhC{\equiv}CC_2H_5$	38 (—)	c)
4	$PhCOC_3H_7$	B	20	$PhC{\equiv}CC_2H_5$	50 (68)	26[d]
5	$PhCOCH_2Br$	A	50	PhC≡CBr	40 (40)	0
6	$PhCOCH_2SPh$	A	47	PhC≡CSPh	56 (69)	19
7	$PhCH{=}CHCOCH_3$	B	14	PhCH=CH-C≡CH	47 (—)	c)

a) Recovered. b) Yields in parentheses were based on unrecovered ketone.
c) Not isolated. d) Phenacyltriethylammonium salt was formed.

References and Note

1) T. L. Jacobs, Org. Reactions, 5, 1 (1949).
2) C. M. Wong and T. L. Ho, Synth. Commun. 4, 25 (1974).
3) a) Y. Echigo, Y. Watanabe, and T. Mukaiyama, Chem. Lett., 697 (1977); b) T. Mukaiyama and Y. Echigo, ibid., 49 (1978).
4) When ketones (1 mmol) were added to the solution of 1 (1.2 mmol) and triethylamine (15 mmol) in dichloromethane, no alkynes were obtained. The result indicates that under the condition the reaction between the onium salt 1 and triethylamine takes place prior to the present reaction.

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