Synthesis of Some New Exocyclic Olefins via Phosphonium Ylides

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A series of new 9-alkylidene and 9-arylidene-10-hydroanthracenes has been synthesized by the interaction of a range of nonstabilized and semistabilized phosphonium ylides with 9-anthrones in refluxing benzene. The structure of the products is supported by IR and NMR spectra.

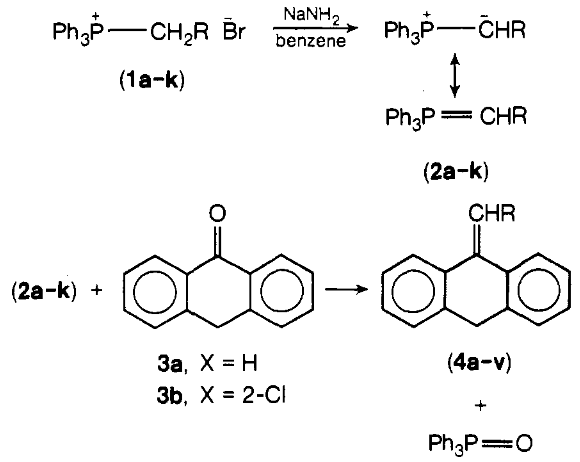
Ylides, particularly phosphonium ylides, have increasingly assumed the status of an important synthetic substrate (*6*) in preparative organic chemistry. Besides their successful participation with aldehydes and ketones in the synthesis of a wide variety of acyclic, cyclic, and heterocyclic unsaturated products (*2, 7, 9*), they possess a remarkable capability to introduce a selective exocyclic carbon–carbon double bond at the combination site, providing a unique procedure for converting an exocyclic carbonyl function into an exocyclic olefinic double bond.

During the course of our investigations (*3–5, 8*) on a program directed toward utilization of the ylides as a reagent in the olefin synthesis, we have studied the reactions of a range of nonstabilized and semistabilized phosphonium ylides with exocyclic ketones, i.e., 9-anthrone and 2-chloro-9-anthrone, to examine their ability to introduce an exocyclic carbon–carbon double bond at C_9 of the anthracene ring.

Results and Discussion

Quaternization of triphenylphosphine with a range of alkyl halides at reflux temperature gave a series of quaternary phosphonium salts (compounds **1a–k**) in good yield. Treatment of these salts with sodamide or sodium hydride in benzene effected proton abstraction affording corresponding phosphonium ylides (compounds **2a–k**). The reactions of ylides (compounds **2a–k**) with 9-anthrone (compound **3a**) and 2-chloro-9-anthrone (compound **3b**) (Scheme I) were carried out at reflux temperature affording the desired exocyclic olefinic products. Thus, the reactions of nonstabilized methylene- and ethylidenetriphenylphosphoranes (compounds **2a** and **2b**) with compounds **3a** and **3b** gave exocyclic olefins (compounds **4a–d**) in 70–80% yields. Similarly the reactions of substituted benzylidenetriphenylphosphoranes (compounds **2c–j**) so called moderated ylides with compounds **3a** and **3b** were carried out successfully at elevated temperatures affording substituted benzylidene-10-hydroanthracenes (compounds **4e–t**) in fair to good yields. Ketones (compounds **3a–b**) also reacted energetically with 2-naphthylmethylenetriphenylphosphorane (compound **2k**) in benzene solution at reflux temperature to give exocyclic olefins (compounds **4u–v**). Our attempts to react stable phosphonium ylides (compound **2**, R = COPh, etc.) with ketones (compounds **3a–b**) were unsuccessful even at elevated temperature probably because of decreased nucleophilicity of the former as a result of delocalization of the carbanionic electron through the carbonyl group.

Scheme I



1,2a, R = H
b, R = CH_3
c, R = C_6H_5
d, R = 4-$OCH_3C_6H_4$
e, R = 4-ClC_6H_4
f, R = 4-BrC_6H_4
g, R = 4-IC_6H_4
h, R = 2-$NO_2C_6H_4$
i, R = 3-$NO_2C_6H_4$
j, R = 4-$NO_2C_6H_4$
k, R = 2-naphthyl

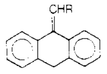
4a, R = H; X = H
b, R = H; X = 2-Cl
c, R = CH_3; X = H
d, R = CH_3; X = 2-Cl
e, R = C_6H_5; X = H
f, R = C_6H_5; X = 2-Cl
g, R = 4-$OCH_3C_6H_4$; X = H
h, R = 4-$OCH_3C_6H_4$; X = 2-Cl
i, R = 4-ClC_6H_4; X = H
j, R = 4-ClC_6H_4; X = 2-Cl
k, R = 4-BrC_6H_4; X = H
l, R = 4-BrC_6H_4; X = 2-Cl
m, R = 4-IC_6H_4; X = H
n, R = 4-IC_6H_4; X = 2-Cl
o, R = 2-$NO_2C_6H_4$; X = H
p, R = 2-$NO_2C_6H_4$; X = 2-Cl
q, R = 3-$NO_2C_6H_4$; X = H
r, R = 3-$NO_2C_6H_4$; X = 2-Cl
s, R = 4-$NO_2C_6H_4$; X = H
t, R = 4-$NO_2C_6H_4$; X = 2-Cl
u, R = 2-naphthyl; X = H
v, R = 2-naphthyl; X = 2-Cl

All the exocyclic olefins synthesized in this study are listed in Table I. The versatile ability of the phosphonium ylides to introduce an exocyclic carbon–carbon double bond at C_9 of the anthracene ring is obvious from the inspection of Table I. All the products, most of which are new, gave correct elemental analysis. Their structures were evidenced by IR (Table I) and NMR spectral results (Table II).

Experimental Section

Melting points were determined on a Gallenkamp apparatus and are uncorrected. IR spectra (KBr) were recorded on a Perkin-Elmer infracord instrument. The nuclear magnetic resonance spectra ($CDCl_3$) were run using a Varian A-60 spectrometer using tetramethylsilane as an internal standard. Analytical samples were purified by column chromatography over neutral alumina. Purity was checked by thin layer chromatography (TLC).

Table I. Exocyclic Olefins (Compounds 4a–v)

					IR data (KBr) (cm^{-1})	
Compound[b]	 R	X	Yield (%)	Mp[a] (°C)	ν(C=C) stretch	Out of plane def of H
4a	H	H	80	156–158	1588	956
4b	H	2-Cl	75	170	1586	956
4c	CH_3	H	75	180	1590	960
4d	CH_3	2-Cl	70	193–194	1594	964
4e	C_6H_5	H	60	226–228	1600	958
4f	C_6H_5	2-Cl	58	185	1596	960
4g	4-$OCH_3C_6H_4$	H	48	210–212	1598	960
4h	4-$OCH_3C_6H_4$	2-Cl	40	190–192	1594	962
4i	4-ClC_6H_4	H	55	155–156	1596	962
4j	4-ClC_6H_4	2-Cl	50	175–177	1598	965
4k	4-BrC_6H_4	H	54	190–192	1595	963
4l	4-BrC_6H_4	2-Cl	50	182–184	1594	960
4m	4-IC_6H_4	H	50	170–172	1596	964
4n	4-IC_6H_4	2-Cl	42	180	1598	968
4o	2-$NO_2C_6H_4$	H	60	252–254	1580	956
4p	2-$NO_2C_6H_4$	2-Cl	58	172–174	1600	965
4q	3-$NO_2C_6H_4$	H	65	122–125	1590	953
4r	3-$NO_2C_6H_4$	2-Cl	62	196–198	1594	960
4s	4-$NO_2C_6H_4$	H	70	205	1590	966
4t	4-$NO_2C_6H_4$	2-Cl	66	180	1594	962
4u	2-Naphthyl	H	45	200	1588	970
4v	2-Naphthyl	2-Cl	40	168–170	1590	968

[a] Satisfactory analytical data (±0.4% for C, H) were reported for all compounds listed in the table. [b] All the products were recrystallized from ethanol or ethanol–water mixture (4:1).

Table II. NMR Spectra ($CDCl_3$) of Exocyclic Olefins[a]

Compound	δ (ppm)	No. of protons	Group
4e	7.35–7.90, m	13H	Aromatic
	7.20, s	1H	Olefinic
	1,30, s	2H	$>CH_2$
4g	7.30–7.88, m	12H	Aromatic
	7.25, s	1H	Olefinic
	3.29, s	3H	OCH_3
	1.40, s	2H	$>CH_2$
4i	7.35–7.85, m	12H	Aromatic
	7.15, s	1H	Olefinic
	1.40, s	2H	$>CH_2$
4k	7.30–7.85, m	12H	Aromatic
	7.21, s	1H	Olefinic
	1.35, s	2H	$>CH_2$
4o	7.50–8.05, m	12H	aromatic
	7.30, s	1H	Olefinic
	1.45, s	2H	$>CH_2$
4p	7.60–8.10, m	11H	Aromatic
	7.35, s	1H	Olefinic
	1.55, s	2H	$>CH_2$
4q	7.42–7.92, m	12H	Aromatic
	7.29, s	1H	Olefinic
	1.25, s	2H	$>CH_2$
4s	7.40–8.00, m	12H	Aromatic
	7.15, s	1H	Olefinic
	1.50, s	2H	$>CH_2$

[a] Key: m = multiplet; s = singlet.

Phosphonium salts (compounds **1a–k**) were prepared by the treatment of α-bromo compounds with triphenylphosphine in benzene at reflux temperature using the procedure given in ref 1. Preparation of 9-alkylidene-10-hydroanthracenes (compounds **4a–d**), (Table I).

A general procedure was used in all the reactions. To a suspension of alkylidenetriphenylphosphorane (compounds **2a–b**), prepared from 0.004 mol of its salt (compounds **1a–b**) and 0.12 g (0.005 mol) of sodium hydride in anhydrous benzene (120 mL), was added under nitrogen 0.004 mol of exocyclic ketone (compounds **3a–b**), and the mixture was stirred at reflux temperature for 6 h. The residue containing triphenylphosphine oxide and unreacted sodium hydride was removed and the filtrate was concentrated on a steam bath under reduced pressure. The resulting product was chromatographed to afford corresponding 9-alkylidene-10-hydroanthracene (compounds **4a–d**), which was further purified by crystallization from ethanol.

Preparation of 9-Arylidene-10-hydroanthracenes (Compounds 4e–v), (Table I). To a stirred solution of 0.004 mol of phosphonium salt (compounds **1c–k**) and 0.19 g (0.005 mol) of sodamide in 100 mL of anhydrous benzene was added a solution of 0.004 mol of exocyclic ketone (compounds **3a–b**) in 20 mL of benzene. The reaction was run at reflux temperature under nitrogen for 6–10 h. The precipitate of triphenylphosphine oxide and unreacted sodamide was separated by filtration and the filtrate was concentrated on a steam bath under reduced pressure. The resulting oily product was extracted with benzene and chromatographed to afford corresponding 9-arylidene-10-hydroanthracene (compounds **4e–v**).

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Literature Cited

(1) Friedrich, K., Henning, H., *Chem. Ber.*, 2756 (1959).
(2) Hudson, R. F., *Chem. Brit.*, **7**, 287 (1971).
(3) Kendurkar, P. S., Tewari, R. S., *Z. Naturforsch. B*, **28**, 475 (1973).
(4) Kendurkar, P. S., Tewari, R. S., *J. Organomet. Chem.*, **60**, 247 (1973).
(5) Kendurkar, P. S., Tewari, R. S., *J. Organomet. Chem.*, **85**, 173 (1975).
(6) Lowe, P. A., *Chem. Ind. (London)*, 1070 (1970).
(7) Maercker, A., *Org. React.*, **14**, 316 (1965).
(8) Tewari, R. S., Kumari, N., Kendurkar, P. S., *J. Chem. Eng. Data*, **21**, 125 (1976).
(9) Witting, G., *Mod. Sviluppi Sint. Org., Corso Estivo Chim.*, **10**, 323 (1968); *Chem. Abstr.*, **74**, 99074 (1971).

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