Developmental Photochemistry. The Norrish Type II Reaction

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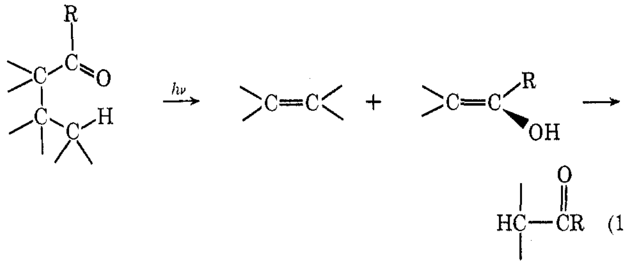
The Norrish type II photochemical reaction results in the splitting of an appropriately substituted ketone into olefinic and enolic fragments (eq 1).[2] The reaction proceeds facilely provided that hydrogens γ to the carbonyl group are available and that the group R (commonly aryl) is devoid of strongly electron withdrawing or donating substituents. The efficacy of this method of carbon–carbon bond cleavage prompted us to devise means of using it as a preparative route to various olefins. Such an effort is practical only if (a) syntheses of starting materials are straightforward involving less work than the preparation of the desired olefinic product by a more classic route, and (b) the olefinic product can be isolated and purified readily. We have found that these conditions can be met uniquely for the preparation of a number of fairly volatile alkenes and dienes.

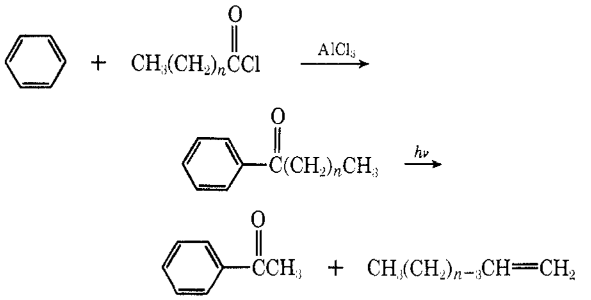


(1)

Results and Discussion

To make the photochemical reaction practical on a synthetic scale, we designed a simple reaction flask attached by means of ground-glass joints to a quartz-jacketed medium-pressure Hanau TQ-81 lamp. A distillation head with condenser was fitted to the flask and the receiver was held in liquid N_2. By means of a manostat any desired vacuum could be maintained in the apparatus which was mounted in a variable temperature bath. The ketone to be irradiated (*ca.* 10 g) was dissolved or suspended in a high-boiling solvent (tetramethylene glycol dimethyl ether). The solution, stirred magnetically, was put under the desired vacuum and warmed to 40–50°. The lamp was then switched on. During irradiation, the alkene fragment, as soon as it formed, was distilled out of solution into the receiving flask cooled in liquid nitrogen. Neither the starting material nor the ketonic fragment (designed to be nonvolatile, *vide infra*) codistils to a serious extent under these conditions. The alkene product may be purified further by normal procedures.

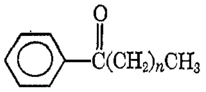
Ketonic precursors to simple linear olefins are obtained easily from the reaction of the appropriate acyl chloride with benzene (eq 2). Irradiation under above described conditions leads to olefin which distils smoothly away from starting material and the other photochemical product, acetophenone. As can be seen from Tables I and II, quite satisfactory yields of simple terminal olefins may be realized.



(2)

Table I

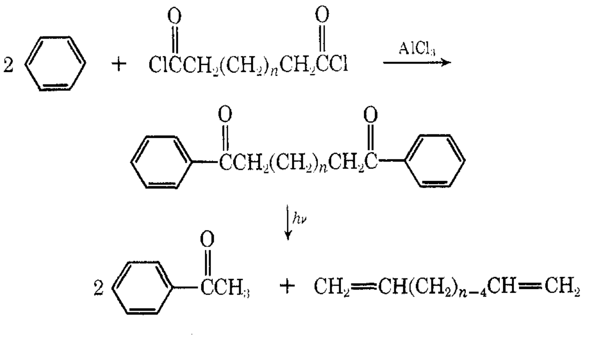
Syntheses of Simple Linear Olefins



Starting material	Registry no.	Irradiation time, hr	Temp, °C	Product (yield, %)[a]
$n = 6$	1674-37-9	9.5	40	Hexene-1 (74)
$n = 7$	6008-36-2	10	40	Heptene-1 (84)
		48	40	Heptene-1 (78)
$n = 8$	6048-82-4	10	42	Octene-1 (75)
$n = 10$	1674-38-0	10	50	Decene-1 (35)

[a] Based on starting ketone.

Both conjugated and nonconjugated terminal dienes are obtainable by the device of a double elimination on a diketone prepared as shown in eq 3. Again, acceptable yields are obtained (Table II) except in the attempted synthesis of allene.



(3)

Combination of routine synthetic methods and the Norrish type II reaction permits the conversion of a

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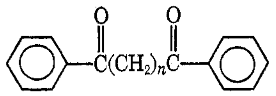
[1] Fellow of the Alfred P. Sloan Foundation, 1971–1973.

[2] For leading references concerning the structural parameters governing Norrish type II reactions, see (a) D. C. Neckers, "Mechanistic Organic Photochemistry," Reinhold, New York, N. Y., 1967; (b) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965; (c) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).

TABLE II

SYNTHESES OF SOME SIMPLE LINEAR DIENES

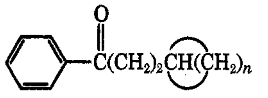


Starting material	Registry no.	Irradiation time, hr	Temp, °C	Product (yield, %)[a]
$n = 6$	6268-58-2	24	40	Butadiene-1,3 (50)
$n = 7$	28861-21-4	20	40	Pentadiene-1,4 (46)
		60	40	Pentadiene-1,4 (51)
$n = 8$	6268-61-7	20	30	Hexadiene-1,5 (53)
$n = 5$	28861-22-5	20	30	Allene (0)[b]

[a] Based on starting ketone. [b] 1-Phenylpenta-4-en-2-one was the only isolated product.

TABLE III

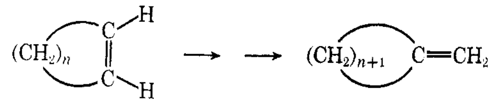
SYNTHESES OF TERMINAL OLEFINS USING NORRISH TYPE II REACTIONS



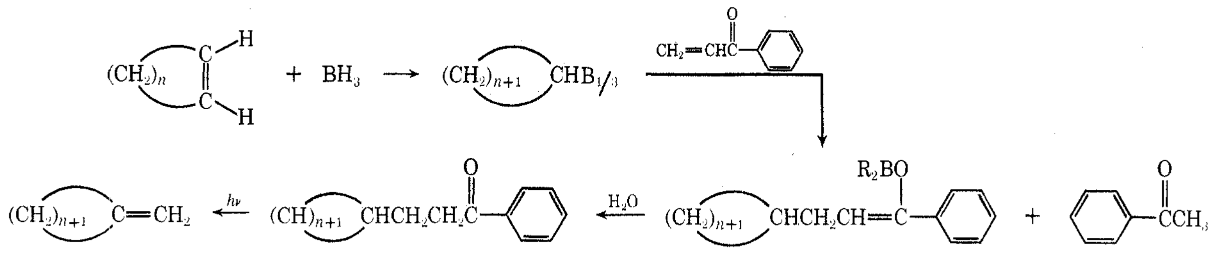
Starting material[a]	Registry no.	Irradiation time, hr	Temp, °C	Product (yield, %)[b]
$n = 7$	28861-23-6	24	40	Methylenecyclooctane (34)
$n = 5$	28861-24-7	24	40	Methylenecyclohexane (54)
$n = 4$	28861-25-8	24	40	Methylenecyclopentane (68)
3-(2-Norbornyl)-1-phenylpropanone	28861-26-9	24	40	2-Methylenenorbornane (30)
3-(3′-Tetrahydropyranyl)-1-phenylpropanone	28861-27-0	24	40	3-Methylenetetrahydropyran (34)

[a] Crude product prepared from alkene as described in the Experimental Section. [b] Based on starting olefin but corrected for loss of two alkene units as borate (eq 5).

readily available cyclic olefin to a homologous exocyclic isomer (eq 4). The requisite ketones for the Norrish type II reaction were obtained as shown in eq 5 and were used without any further purification.[3] As seen from Table III, this approach is remarkably successful and, moreover, considerable variation in the cyclic component is possible as witnessed by the successful syntheses of 2-methylenenorbornane and 3-methylenetetrahydropyran.



(4)



(5)

Several features of the above reactions deserve comment. First, the olefins and dienes obtained are isomerically pure. In the case of 1-octene, for example, no contaminating 2-octene could be detected by glpc. Second, the synthesis of the dienes reported represents a simple entry into compounds of this sort which are often difficult to prepare isomerically pure in other ways. Finally, even though the starting ketone was not always completely soluble in the solvent, the stirring with the flask designed was sufficient so that solid ketone slowly went into solution as the photochemical reaction progressed still leading to acceptable yields. This problem was particularly pronounced with several of the diketones.

The chief limitation of the method derives from volatility considerations. Any olefin whose boiling point under reduced pressure approaches that of acetophenone will be contaminated with the latter. Likewise, olefins not appreciably more volatile than the solvent will necessarily codistil with it. An additional problem is that the photochemical reaction itself fails in certain more esoteric cases as illustrated by the unsuccessful synthesis of allene.[4]

All things considered, however, the Norrish type II reaction can be adopted successfully to the synthesis of volatile olefins on a preparative scale and may, in certain cases, be the method of choice.

Experimental Section

All melting points and boiling points are uncorrected. A Hanau Model TQ-81 medium-pressure mercury arc lamp was used for the irradiations. Nmr spectra were taken in CCl_4 and are reported in δ values downfield from TMS, internal standard.

General Synthesis of Phenyl Ketones.—The procedure of Vogel[5] was followed for the synthesis of all the phenylated ketones.

Phenyl *n*-heptyl ketone: bp 166–168° (14 Torr); mp 22.2–23.2° (lit.[6] mp 22.2–23.2°).

Phenyl *n*-octyl ketone: bp 176–177° (15 Torr) (lit.[7] mp 17°).

Phenyl *n*-nonyl ketone: bp 187° (14 Torr); mp 34–35° (lit.[6] mp 34–35°).

Phenyl *n*-undecyl ketone: mp 41.1–42.1° (lit.[7] mp 41–42).

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(3) Method of A. Suzuki, A. A. H. Matsumoto, M. Itoh, H. C. Brown, M. M. Rogic, and M. W. Rathke, *J. Amer. Chem. Soc.*, **89**, 5708 (1967).

(4) The Norrish type II reaction does not lend itself readily to the synthesis of some strained systems. See, for a recent illustration, R. B. Gagosian, J. C. Dalton, and N. J. Turro, *ibid.*, **92**, 4752 (1970).

(5) A. I. Vogel "Practical Organic Chemistry," Longmans, Green and Co., London, 1962, p 732.

(6) R. Adams and L. H. Ulich, *J. Amer. Chem. Soc.*, **42**, 607 (1920).

(7) F. L. Breusch and M. Oğuzer, *Chem. Ber.*, **87**, 1225 (1954).

1,10-Diphenyl-1,10-dioxodecane: mp 93–94° (lit.[8] mp 92–93°).

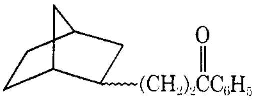
1,9-Diphenyl-1,9-dioxononane: mp 51–53° (lit.[9] mp 55–56°).

1,8-Diphenyl-1,8-dioxooctane: mp 85–87° (lit.[9] mp 91°).

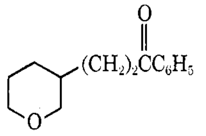
1,7-Diphenyl-1,7-dioxoheptane: mp 65.5–66.5° (lit.[10] mp 65–67°).

Products were identified by comparison of the nmr spectra and ir spectra with those of known samples.

Synthesis of ketonic precursors for terminal olefins was carried out by converting 0.3 mol of the appropriate cycloalkene to the trialkylborane.[3] This borane was partially hydrolyzed with 4.5 g (0.25 mol) of water whereupon 23.7 g (0.18 mol) of phenyl vinyl ketone[11] in 100 ml of THF was added. After 1 hr at 25° the THF was removed and the reaction mixture was held at 60° for 1 hr at 15 mm to remove volatile components. The irradiations were carried out with these crude mixtures. Samples of the respective ketones were isolated as their 2,4-dinitrophenylhydrazones (2,4-DNP): 3-cyclohexyl-1-phenylpropanone-1, mp (2,4-DNP) 179–180°; 3-cyclopentyl-1-phenylpropanone-1, mp (2,4-DNP) 157–159°; 3-cyclooctyl-1-phenylpropanone-1, mp (2,4-DNP) 151–152°; 3-(2-norbornyl)-1-phenylpropanone-1 (a), mp (2,4-DNP) 151–153°; 3-(3′-tetrahydropyranyl)-1-phenylpropanone (b) failed to yield an acceptable derivative; boron hydride is known, however, to add only to the 3 position of 4,5-dihydropyran.[12]



a



b

Methylenecyclohexane,[13] methylenecyclopentane,[13] methylenecyclooctane,[14] and 2-methylenenorbornane[15] had physical properties identical with those of authentic materials. 3-Methylenetetrahydropyran after purification by preparative glpc had $n^{20}{}_D$ 1.4398; nmr (CCl_4) δ 1.70 (multiplet, 2,5 H), 2.28 (t, broadened, 2, J = 6.8 Hz, 4 H), 3.60 (t, 2, J = 5.0 Hz, 6 H), 3.92 (s, 2, 2 H), and 4.68 (s, 2, methylene OH); ir (neat) 3080, 1650, 1070, and 915 cm^{-1}. The mass spectrum had the parent peak at *m/e* 98.

Acknowledgment.—One of the authors (D. C. N.) thanks the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

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[9] L. A. Wiles and E. C. Baughan, *ibid.*, 933 (1953).

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[12] G. Zweifel and J. Plamondon, *J. Org. Chem.*, **35**, 898 (1970).

[13] O. Wallach, *Justus Liebigs Ann. Chem.*, **347**, 316 (1906).

[14] M. Vilkas and N. A. Abraham, *Bull. Soc. Chim. Fr.*, 1197 (1960).

[15] O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **470**, 62 (1929).

Ozonolysis of Unsaturated Phosphorus Compounds[1]

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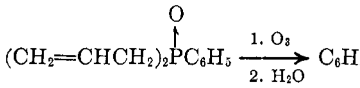
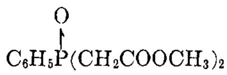
Ozonization has been used only rarely[2] as a synthetic reaction in organophosphorus chemistry except for the oxidation of phosphines to phosphine oxides.[3] Nevertheless, the technique is of general potential use in the high-yield oxidation of olefinic and acetylenic phosphine oxides to the related carboxylic acids.

Oxidation of diallylphenylphosphine oxide by ozone followed by decomposition in the presence of hydrogen peroxide and formic acid gave 2,2′-(phenylphosphinylidene)diacetic acid (**1**) in an 83% yield. Bromination of the methylene positions, formation of the corresponding anhydride, or decarboxylation *via* a Hunsdiecker reaction on **1** did not afford the desired products. The products of these reactions were not fully characterized. Esterification of **1** with methanol in the presence of sulfuric acid, with methanol and thionyl chloride, or with methyl iodide and base failed to yield the desired ester. However, when **1** was allowed to react with diazomethane, dimethyl-2,2′-(phenylphosphinylidene)diacetic acid (**2**) was obtained. The methylene position of **2** was also unreactive toward bromination.



$$(CH_2{=}CHCH_2)_2\overset{O}{\overset{\uparrow}{P}}C_6H_5 \xrightarrow[2.\ H_2O]{1.\ O_3} C_6H_5\overset{O}{\overset{\uparrow}{P}}(CH_2COOH)_2$$

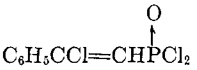
1



$$C_6H_5\overset{O}{\overset{\uparrow}{P}}(CH_2COOCH_3)_2$$

2

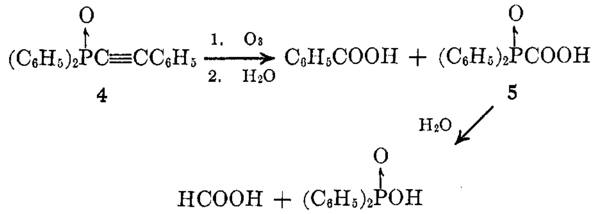
In the course of a related investigation, 2-chloro-2-phenylvinylphosphonic dichloride (**3**) was allowed to react with phenylmagnesium bromide. The product obtained with 3 mol of Grignard reagent was phenylethynyldiphenylphosphine oxide (**4**). Characterization of **4** was based on the absence of a vinylic proton in the nmr spectrum, the distinct presence of the triple bond in the infrared spectrum, a melting point of a mixture of **4** and an authentic sample of **4**, and elemental analysis.



$$C_6H_5CCl{=}CH\overset{O}{\overset{\uparrow}{P}}Cl_2$$

3

Ozonization of phenylethynyldiphenylphosphine oxide (**4**) gave benzoic acid, formic acid, and diphenylphosphinic acid. It has been shown[4] that the probable intermediate, diphenylphosphinylideneformic acid (**5**), is unstable under hydrolysis conditions. In a similar manner, ozonization of 1,2,3,4,5-pentaphenylphosphacyclopentadiene oxide with excess ozone caused complete decomposition of the ring structure to give phenylphosphonic acid and 4 equiv of benzoic acid.



$$(C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}C{\equiv}CC_6H_5 \xrightarrow[2.\ H_2O]{1.\ O_3} C_6H_5COOH + (C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}COOH$$

$$\xrightarrow{H_2O} HCOOH + (C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}OH$$

4 **5**

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[1] This work was supported by a grant, GP-5659, from the National Science Foundation.

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