Diene–Iron Tricarbonyl Complex.—The iron carbonyl complex separated from triene fraction 3 by argentation–c.c.d. was isolated in 47.9% yield (20.7% of original hydrogenated linolenate). T.l.c. ($AgNO_3$–silica gel) showed one component of same retention as diene–$Fe(CO)_3$ from linoleate.[15] Infrared showed bands at 4.88 and 5.05 μ (ϵ 1420 and 2830).

Anal. Calcd. for $C_{22}H_{34}FeO_5$: C, 60.9; H, 7.8; Fe, 12.9; mol. wt., 434. Found: C, 61.0; H, 7.8; Fe, 12.3; mol. wt. 427 (osmometric, benzene).

The n.m.r. spectrum was the same as the n.m.r. spectrum of diene–$Fe(CO)_3$ from linoleate[15] (Figure 3). Decomposition of 0.415 g. of complex with $FeCl_3$[15] gave 0.230 g. of conjugated diene (recovery 82.2%; ϵ_{230} 25,800, $\epsilon_{10.15\mu}$ 315; 100% *trans,trans*-conjugated diene by g.l.c.). Oxidative cleavage analysis is given in Table III.

Triene–Iron Tricarbonyl Complexes (I and II).—The separation of hydrogenated methyl linolenate by c.c.d. between *n*-hexane and acetonitrile gave a fraction (4, transfer 640–820, Figure 2) in 18.6% yield, shown to be pure triene–$Fe(CO)_3$ complex. Argentation–t.l.c. ($AgNO_3$–silica gel) showed three main components with same R_f as that of diene–$Fe(CO)_3$ (from linoleate), methyl elaidate, and methyl oleate, successively. The infrared spectrum showed bands at 4.89 and 5.07 μ (ϵ 1920 and 3220; corresponding bands for diene–$Fe(CO)_3$ of linoleate, ϵ 1970 and 3450) and at 10.4 μ (isolated *trans*, ϵ 42.7).

Anal. Calcd. for $C_{22}H_{32}FeO_5$: C, 61.2; H, 7.4; Fe, 12.9; mol. wt., 432. Found: C, 61.8; H, 7.9; Fe, 11.6; mol. wt., 405.

Decomposition of 0.1075 g. of triene–$Fe(CO)_3$ with $FeCl_3$ gave 0.0582 g. (recovery 80%) of a mixture of *trans,trans*-conjugated diene–triene and conjugated triene (g.l.c., 68% conjugated diene–triene, 32% conjugated triene; infrared, $\epsilon_{10.1\mu}$ 209, $\epsilon_{10.4\mu}$ 45.4; ultraviolet, ϵ_{231} 18,750, ϵ_{267} 9950). On fractionation through a silver-saturated ion-exchange resin column[18] (225 × 2.1 cm.) 0.782 g. of triene–$Fe(CO)_3$ complex yielded four fractions (4a, 0.075; 4b, 0.143; 4c, 0.321; and 4d, 0.144 g.). Analysis by t.l.c. ($AgNO_3$–silica gel) showed one component in fraction 4a with a retention corresponding to diene–$Fe(CO)_3$, two components in both fractions 4b and 4c migrating like methyl elaidate, and one component in fraction 4d migrating like methyl oleate. These fractions were decomposed with $FeCl_3$ and the conjugated products were analyzed by g.l.c., ultraviolet, and infrared (Table IV). Complex fractions 4a and 4d were also analyzed by n.m.r. (CCl_4, Varian A-60) (Figure 3). The following signals given in τ values were obtained: 4.95 and 4.65 in fraction 4a, 5.01 and 4.65 in fraction 4d (olefinic protons), and in both fractions 6.3 (methoxy protons), 7.75 (methylene α to C═O), 8.0 (allylic protons), 8.7 (methylene), and 8.9–9.0 (methyl). The intensity of the olefinic bands corresponded to 4 protons [2 protons due to –CH═CH– and 2 central protons of diene–$Fe(CO)_3$ system] assuming a total of 32 protons. The other bands were too poorly resolved to estimate accurately.

The triene–$Fe(CO)_3$ complex (0.227 g.) was treated in a manometric system under 1 atm. of hydrogen with a reduced palladium catalyst (5% on alumina) in 4 ml. acetic acid, but no hydrogen absorption occurred within 3 hr. at 25°. The recovered product (0.224 g.) showed no change by t.l.c. ($AgNO_3$–silica gel). To reduce the complex with hydrazine it was first saponified by refluxing 0.506 g. with 10 ml. of 95% ethanol and 0.5 ml. of 50% KOH for 45 min. under nitrogen. The product was neutralized, extracted with petroleum ether (b.p. 39–52°), and dried over Na_2SO_4 (0.315 g., $a_{4.87\mu}$ 3.43, $a_{5.09\mu}$ 6.34). The triene–$Fe(CO)_3$ fatty acid was reduced by treating a solution of 0.295 g. in 15 ml. of absolute ethanol with 0.5 ml. of hydrazine (64% in water), bubbling air, and stirring magnetically at ambient temperature. After 22 hr. the solvent was evaporated; the product was neutralized, extracted with diethyl ether, and dried over Na_2SO_4. The reduced complex (0.244 g., $a_{4.87\mu}$ 3.29, $a_{5.05\mu}$ 6.41) gave the same n.m.r. spectrum as a preparation of linoleate–$Fe(CO)_3$ complex subjected to the same saponfication and hydrazine reduction. The relative intensity of the olefinic band at τ 5.0 was equivalent to 1.6 protons compared with 3.7 before reduction. Decomposition of the reduced triene–$Fe(CO)_3$ complex with $FeCl_3$ yielded a mixture containing 70.6% *trans,trans*-conjugated diene, 17.2% unreduced conjugated trienes, and hydrogenated products (stearate 7.2, monoene 3.7, and diene 1.0%) apparently derived from decomposition of the complex ($a_{10.15\mu}$ 0.816, a_{233} 66.0, a_{267} 15.5). The dibasic acids obtained on oxidation with $KMnO_4$–KIO_4 showed a similar distribution to that of the double bonds in the free conjugated dienes (Table III), but the larger levels of C_9 acids are due to impurities.

Acknowledgment.—We are grateful to R. O. Butterfield for simulating kinetic data on an analog computer; C. A. Glass for the n.m.r. analysis; Mrs. Clara E. McGrew and Mrs. Bonita Heaton for elemental analyses; and Drs. J. C. Cowan, H. J. Dutton, and R. B. Bates (University of Arizona) for their helpful discussions.

The Pyrolysis of Alkyl Diphenylphosphinates[1]

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Received February 16, 1965

Examination of the thermal decomposition of a series of alkyl esters of diphenylphosphinic acid indicates the pyrolysis occurs smoothly to give olefins in essentially quantitative conversions. A mechanism for the thermal transformation is postulated to involve a cyclic transition state.

Although the pyrolysis of phosphonium hydroxides, corresponding to the Hofmann degradation of amines, has been known for many years,[3] it has very little synthetic utility and is more useful as a degradative process. Pyrolysis of organophosphorus compounds involving elimination reactions to give olefins[4] in preparative yields has become available only recently,[5-11] and, in most cases, the starting materials are somewhat difficult to obtain.

Results included herein describe a simple process by which alkenes of high purity are obtained in excellent yields from readily accessible phosphinates. A series

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(2) Predoctoral candidate, 1962–1965.

(3) G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929).

(4) For lead references to other types of thermal decompositions of organophosphorus compounds, see (a) K. L. Marsi and G. D. Homer, *J. Org. Chem.*, **29**, 2150 (1964); (b) D. B. Denney and H. A. Kindsgrab, *ibid.*, **28**, 1133 (1963); (c) S. T. D. Gough and S. Trippett, *J. Chem. Soc.*, 543 (1964); (d) W. S. Wadsworth and W. D. Emmons, *J. Org. Chem.*, **29**, 2816 (1964).

(5) W. J. Bailey, W. M. Muir, and F. Marktscheffel, *ibid.*, **27**, 4404 (1962).

(6) D. B. Denney, C. J. Rossi and J. J. Vill, *J. Am. Chem. Soc.*, **83**, 3336 (1961).

(7) H. E. Baumgarten and R. E. Allen, *J. Org. Chem.*, **26**, 1533 (1961).

(8) D. B. Denney, C. J. Rossi, and J. J. Vill, *ibid.*, **29**, 1003 (1964).

(9) W. M. Hanneman and R. S. Porter, *ibid.*, **29**, 2996 (1964).

(10) V. Mark and J. R. VanWazer, *ibid.*, **29**, 1006 (1964).

(11) D. B. Denney and L. C. Smith, *Chem. Ind.* (London), 290 (1961).

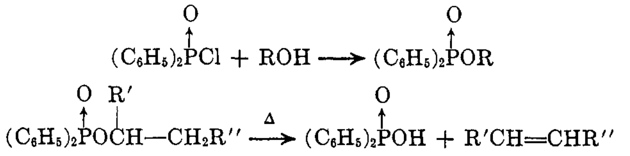
TABLE I

PHOSPHINATE ESTERS, $(C_6H_5)_2P(O)OR$

Compd.	R	Yield, %	M.p., °C. or n_D (deg.)	Infrared, μ		Calcd., %			Found, %		
				P→O	P–O–C	C	H	P	C	H	P
1[a]	C_6H_{11}	78.5	119–120								
2	n-C_8H_{17}	98.7	1.5318 (29)[b]	8.1	10.2	72.72	8.24	9.38	72.38	8.21	9.38
3	2-C_8H_{17}	72.5	1.5302 (28)	8.1	10.2	72.72	8.24	9.38	72.38	8.39	9.48
4	C_8H_9	88.4	65–66	8.1	9.9	74.52	5.94	9.61	74.45	6.20	9.84
5[c]	$C_{27}H_{45}$	80.1	153–154	8.05	9.85	79.82	9.45	5.28	79.50	8.43	5.37

[a] See ref. 12. Thin layer chromatography showed only one spot for each of the esters. [b] Lit.[20] n^{25}_D 1.5330; this ester is reported,[20] but, since its purity was not checked, it was analyzed again. [c] $[\alpha]^{24}_D$ −20.1° ($HCCl_3$).

of alkyl diphenylphosphinates were prepared[12] by reaction of diphenylphosphinic chloride with the corresponding alcohol in the presence of triethylamine (see Table I). Static pyrolysis of the esters was effected under a nitrogen atmosphere at atmospheric pressure.



$$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}Cl + ROH \longrightarrow (C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}OR$$

$$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}O\overset{\overset{R'}{|}}{C}H{-}CH_2R'' \xrightarrow{\Delta} (C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}OH + R'CH{=}CHR''$$

The volatile olefins collected were analyzed by gas-liquid chromatography using a hydrogen flame ionization detector. A thermometer placed directly in the reaction medium permitted the temperature to be observed throughout the pyrolysis. Temperature ranges for the thermal decompositions given in Table II are wide, but the over-all processes were completed within a maximum of 1 hr. In the case of the cyclohexyl diphenylphosphinate, for example, the time elapsed from the first appearance of condensate in the delivery tube until no additional condensate was observed was not more than 15 min. Consequently, the actual decomposition is probably a rapid process although the pyrolysate residue was heated an additional 20 min. for the sake of completeness.

TABLE II

PYROLYSIS DATA OF PHOSPHINATE ESTERS[a]

Ester	Pyrolysis temp., °C.	Olefin isolated, %[b]	Product distribution
1	195–230	Quant.	. . .
2	245–280	82.2	96% 1-octene 4% 2-octene
3	215–235	Quant.	21% 1-octene 21% *cis*-2-octene 58% *trans*-2-octene
4	240–270	Quant.	. . .
5	255–260	96	*c*

[a] A minimum of two pyrolyses was examined with each ester. [b] Per cents shown refer to actual quantities obtained of high purity as shown by g.l.c. [c] Mixture not completely characterized.

In each experiment it was necessary to filter the olefinic distillate, since in all cases a small amount of diphenylphosphinic acid was present in the receiver. Surprisingly, gas chromatography of the filtrate showed the olefinic product to be relatively free from impurities. In some instances no further purification was necessary since the refractive indices of the olefins isolated were essentially the same as those observed with known samples.

The residue from the decompositions showed little discoloration. In one example, namely with the residue from cyclohexyl diphenylphosphinate, the observed melting point of the residual material taken immediately after cooling was 189–192° compared with 193–194° for an authentic sample of diphenylphosphinic acid. Although diphenylphosphinic acid is produced in this reaction, apparently it is not acidic enough to induce isomerization of the simple alkenes. The amount of 2-octene present in the pyrolysate from the decomposition of *n*-octyl diphenylphosphinate never exceeded 5%. Other experiments also seem to support this conclusion. Distillation of 1-octene over diphenylphosphinic acid at atmospheric pressure produced no detectable isomerization. Similarly, no isomerization was observed when *cis*-2-octene was heated at reflux over diphenylphosphinic acid for 2.5 hr.

Other pyrolytic syntheses of olefins from phosphorus compounds reported recently gave rise to large amounts of isomerized materials unless precautions were taken.[6,8] In some cases the isomerization could not be minimized easily.[5,7,9] No skeletal rearrangement in the products was observed in the pyrolyses of the phosphinates, whereas in previously reported work with several classes of phosphorus compounds, such molecular alterations appeared to be important.[5–7] It should also be noted that styrene, formed from the decomposition of β-phenethyl diphenylphosphinate, did not polymerize during the course of the reaction. This suggests that a radical mechanism is probably not operative.

Another advantage of this process is the relatively low temperatures which are required. At higher temperatures (*ca.* above 350°) there is a greater tendency for isomerization and skeletal rearrangements of olefins to occur.[5,7] This reaction bears a formal analogy to the pyrolysis of carboxylic acid esters,[13] and a similar cyclic transition state resulting in abstraction of *cis*-hydrogen is an attractive mechanism for the reaction. However, product distribution varies quite markedly in our examples from that observed in pyrolyses of similar acetates. Unfortunately, no example involving the pyrolysis of 2-octyl acetate was found in the literature, but comparison of the pyrolysis products of 2-octyl diphenylphosphinate with that of 2-butyl acetate[14] was instructive. Although the butenes reported were in essentially statistical amounts, the octenes from the phosphinate decomposition did not resemble statistical proportions but were more closely in accord with what would be anticipated from a thermodynamic equilibration. Product distribution in the pyrolysate

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[12] K. D. Berlin, T. H. Austin, and M. Nagabhushanam, *J. Org. Chem.*, **30**, 1267 (1965).

[13] C. H. Depuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

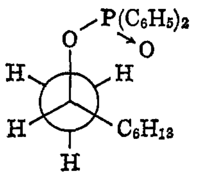
[14] D. H. Froemsdorf, C. H. Collins, G. S. Hammond, and C. H. Depuy, *J. Am. Chem. Soc.*, **81**, 463 (1959).

of 2-heptyl acetate[15] affords the same conclusion. This discrepancy could possibly be a result of the quite marked differences in temperature of the reactions and this, no doubt, has some effect on the increased amounts of 2-octene found in our work. However, a comparison of the pyrolysis of 2-heptyl S-methylxanthate[16] and 2-butyldimethylamine oxide,[17] in which the temperatures of reaction are more closely related to that of the phosphinate pyrolysis, indicated that the amounts of 1-isomer in both examples are far in excess of that found in the pyrolysate of 2-octyl diphenylphosphinate.

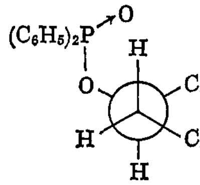
Interestingly, equilibration of isomeric butenes over several catalysts[18,19] at temperatures approximating those used in the decomposition of 2-octyl diphenylphosphinate gives, in one case,[18] 14.5% 1-butene, 33.2% *cis*-2-butene, and 52.3% *trans*-2-butene or 14.5% 1-butene and 85.5% 2-butene. The pyrolysate of 2-octyl diphenylphosphinate contained 21% 1-octene, 21% *cis*-2-octene, and 58% *trans*-2-octene. However, we do not imply that the product distribution from the pyrolysis of 2-octyl diphenylphosphinate results from an equilibration. On the contrary, data obtained from the pyrolysis of 1-octyl diphenylphosphinate which was conducted at even higher temperatures, indicate that equilibration of 1-octene does not occur under these conditions.

The possibility arises that this reaction might occur through a carbonium-ion intermediate.[19] Such an intermediate is not strongly supported by data from the pyrolysis of *n*-octyl diphenylphosphinate[20] which gave high yields of 1-octene and less than 5% of 2-octene. Had a carbonium ion been generated, it would have been expected to rearrange to a more stable ion resulting in increased formation of isomeric octenes which were not detected. The possibility exists that an intimate ion pair could form from heterolytic carbon–phosphorus bond cleavage which is followed by rapid abstraction of a proton by the anion, $R_2P(O)\text{-}O^-$. Reports are unavailable as to the ability of this anion to remove protons from alkyl carbon, and thus such a situation cannot be fully evaluated.

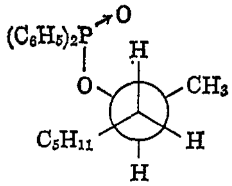
Examination of molecular models indicates that there is little steric compression in the conformations required to produce either 1-octene or *trans*-2-octene from the 2-octyl ester. As expected, a more pronounced effect is evident for the conformation which leads to the formation of *cis*-2-octene. Consideration of Newman projections indicates there is less nonbonding interactions in C than in B. However, on steric grounds alone A would appear to be the preferred conformation. Possible *gauche* interaction between the alkyl groups is offered to explain the predominance of *trans*-2-octene over *cis*-2-octene but does not rationalize the over-all predominance of 2-isomer. From the data available it is postulated that the transition state leading to 2-octene is inherently favored over that leading to 1-octene in the pyrolysis of 2-octyl diphenylphosphinate.



A (gives 1-isomer)



B (gives *trans* isomer)



C (gives *cis* isomer)

The existing data are most consistent with and are reasonably viewed as including a mechanism with a cyclic transition state in the pyrolysis of the phosphinates. The degree of bond breaking and bond formation in the transition states cannot be wholly defined. If a radical mechanism were operative, polymerization of styrene would have been expected in the pyrolysis of 2-phenethyl diphenylphosphinate. The other arguments against fully separated ionic intermediates appear justifiable in view of the isomerization studies with the octenes.

Thermolysis of cholesteryl diphenylphosphinate resulted in a quantitative conversion but gave a mixture which showed two spots when eluted on silica gel by petroleum ether on a thin layer chromatographic plate. Instrumental evidence (infrared, ultraviolet, and n.m.r. spectroscopy) indicates that at least one product and probably both are conjugated dienes. The material possessed an observed positive rotation, but from the absorption maximum in the ultraviolet, one of the products is believed to be 3,5-cholestadiene.[21]

Experimental[22]

Octyl Diphenylphosphinate.—The following is typical of the procedure used to prepare the two octyl esters. The other esters are accessible by the method reported previously.[12] Diphenylphosphinic chloride (94.64 g., 0.40 mole) in 175 ml. of anhydrous ether was added under anhydrous nitrogen over a period of 0.5 hr. to a stirred solution of *n*-octyl alcohol (37.54 g., 0.288 mole) and triethylamine (50.60 g., 0.50 mole) in 500 ml. of anhydrous ether (the temperature rose to 38°). The mixture was held at reflux (39–40°) for 1.5 hr. The reaction mixture was washed thoroughly with excess 10% aqueous sodium bicarbonate solution and then with excess 2 *N* hydrochloric acid. These washings successfully removed all of the acid chloride, the acid, and the amine. The solution was then washed thoroughly with distilled water and, after drying (magnesium sulfate), was concentrated to an oil. The material was then heated *in vacuo* to 100° at 2–4 mm. while passing a stream of anhydrous nitrogen into the rapidly stirred ester for 2.5 hr. to remove the last traces of solvent and any unreacted *n*-octyl alcohol. The yield of *n*-octyl diphenylphosphinate[20] was 98.7% (94.0 g.).

Pyrolysis of Esters.—The following procedure is typical of the method used for thermal decomposition of the phosphinates.

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(15) E. E. Royals, *J. Org. Chem.*, **23**, 1822 (1958).

(16) F. C. Whitmore and C T. Simpson, *J. Am. Chem. Soc.*, **55**, 3809 (1933).

(17) A. C. Cope, N. A. Lebel, H. H. Lee, and W. R. Moore, *ibid.*, **79**, 4720 (1957).

(18) H. H. Voge and N. C. May, *ibid.*, **68**, 550 (1946).

(19) S. W. Benson and A. N. Bose, *ibid.*, **85**, 1385 (1963).

(20) This compound has been reported by C. Stuebe, W. M. LeSuer, and G. R. Norman [*J. Am. Chem. Soc.*, **77**, 3526 (1955)]. Isolation was achieved by distillation, although in poor yield. It is felt that decomposition during distillation may have resulted in this low yield since the compound was prepared here under similar conditions in very high yield.

(21) D. H. Gould, K. H. Schaaf, and W. L. Ruigh, *ibid.*, **73**, 1264 (1951).

(22) All melting points are corrected. All boiling points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. The gas-liquid chromatographic analyses were performed using an Aerograph HyFi 550 from Wilkens Instrument and Research Co., Walnut Creek, Calif.

Cyclohexyl diphenylphosphinate (14.45 g., 0.048 mole) was placed in a flask which was part of a system containing a thermometer and a delivery tube leading to a series of three traps with a drying tube at the exit. The entire system was swept with anhydrous nitrogen and the receivers were then immersed in Dry Ice–acetone traps. With a slow stream of nitrogen passing through the entire system, the material was melted and the temperature was raised quickly to 195° with rapid stirring. Condensate could be observed in the delivery tube. After holding the temperature at 200–205° for approximately 15 min. at which time no additional condensate was observed forming in the delivery tube, the temperature was increased to 230° during a period of 20 min. The distillate was filtered immediately into a capped vial: yield of cyclohexene, 3.56 g. (90.2%). Identification was completed by g.l.c., infrared analysis, and refractive index measurement ($n^{22}\text{D}$ 1.4462, lit.[23] $n^{15.1}\text{D}$ 1.44921). In a similar run on a larger scale (36.7 g., 0.122 mole of ester) the yield was 96.6%. The pyrolysis residue melted at 189–92° and was only slightly discolored. This was taken up in 10% aqueous sodium hydroxide solution and extracted with benzene. Upon acidification of the solution, diphenylphosphinic acid was deposited as a finely divided solid which, after filtering and drying, gave 10.47 g. (99.7%) of the acid, m.p. 192–193.5°. No depression was found on a mixture melting point determination with an authentic sample.

In the case of the cholesteryl ester, no material distilled from the flask. Cold aqueous sodium hydroxide removed diphenylphosphinic acid while ether dissolved the residual material. Concentration of the ether gave an oil which was chromatographed on 200 g. of acid-washed alumina. Elution with petroleum ether (b.p. 30–60°) gave 9.60 g. (96% based on theoretical diene) of an uncrystallizable, viscous material which showed a positive rotation chloroform, $[\alpha]^{24}\text{D}$ +13°. Ultraviolet absorption maxima were visible at 237 mμ (shoulder at 230 mμ) and at 245 mμ (shoulder at 255 mμ) in cyclohexane (3,5-cholestadiene has a maximum at 235 mμ in isopropyl alcohol[21]). Thin layer chromatography on silica using petroleum ether for elution showed two spots. The reported rotation for 3,5-cholestadiene is $[\alpha]^{20}\text{D}$ −129.6° ($HCCl_3$).[24]

G.l.c. Analysis of Pyrolysis Products.—All analyses were obtained using a 6 ft. × 0.125 in. column packed with 5% silicone 30 on 60–80-mesh acid-washed Chromosorb G, DMCS. Several other columns were tested but gave poorer results. Samples were taken from capped vials and injected neat. Areas under peaks were determined from averages of several injections by measurement of peak height times width at half-height.[25] In the analysis of the octenes it was shown that the areas represented by the different isomers were equivalent when equal weights of isomers were injected. From this information, analysis of these olefins consisted of taking the ratio of the area of each peak to total area of all three peaks to obtain per cent distribution.

Attempted Isomerization of 1-Octene.—Diphenylphosphinic acid (0.830 g., 0.0038 mole) and 1-octene (4.98 g., 0.0445 mole) were mixed (heterogenous mixture) and distilled through a small Vigreux column. Four cuts were taken (112–130°), all of which were shown to be identical by g.l.c. and to contain only 1-octene.

Attempted Isomerization of *cis* 2-Octene.—Diphenylphosphinic acid (0.604 g., 0.0027 mole) and *cis*-2-octene (6.036 g., 0.0538 mole) were mixed and the heterogenous mixture was heated at reflux (125°) for 2.5 hr. G.l.c. analysis indicated only one peak for *cis*-2-octene.[26]

Acknowledgment.—The authors wish to thank Dr. E. J. Eisenbraun for helpful discussions and the American Petroleum Institute Research Grant 58A for supplying samples of some of the hydrocarbons needed in this work.

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[23] E. Beckmann and H. Eickelberg, *Ber.*, **29**, 418 (1896).

[24] F. S. Spring and G. Swain, *J. Chem. Soc.*, 83 (1941).

[25] R. P. W. Scott and D. W. Grant, *Analyst*, **89**, 179 (1964). This article gives a thorough review of methods used for measuring chromatograms and indicates that the method used above is preferred.

[26] Two months after this paper was submitted, Dr. Paul Haake informed us he had found the same pyrolytic elimination. Different examples of alkyl diphenylphosphinates were studied but results were similar to ours.

Reduction of Alkylidenecyanoacetates with Sodium Borohydride

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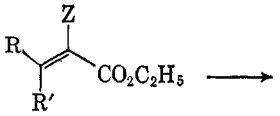
Received March 23, 1965

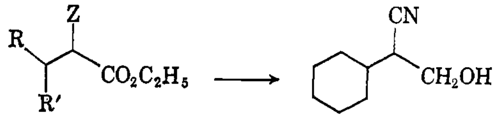
Reduction of diethyl isopropylidenemalonate (**1**), ethyl cyclohexylidenecyanoacetate (**2**), and the decalylidenecyanoacetates **7** and **22** with sodium borohydride proceeds readily with saturation of the carbon–carbon double bond. The ratio of epimers at C-2 in cyanoacetates **8** and **9** depends upon the solvent and nature of the hydride species employed. Reduction of unsaturated cyanoacetate **22** affords the axial dihydro compound **23**. Stereochemical results suggest the reduction is controlled by approach of the reducing agent rather than product stability.

We were confronted in our pursuit of certain synthetic objectives with the problem of selective double-bond reduction in alkylidenemalonic and alkylidenecyanoacetic esters. Our search for a satisfactory solution to this problem prompted us to examine the potential of sodium borohydride as a reducing agent for such carbon–carbon double bonds. We now report initial results to demonstrate the feasibility of this reaction and reveal, for the first time, its stereochemical outcome.

Addition of ethanolic sodium borohydride to a solution of diethyl isopropylidenemalonate (**1**)[1] or ethyl cyclohexylidenecyanoacetate (**2**)[2] resulted in complete reduction of the carbon–carbon double bonds within 4 hr. Reduction of the latter compound was particularly facile and required only 1 hr. at 0° with 1 molar equiv. of sodium borohydride. The respective products, diethyl isopropylmalonate (**3**)[3] and ethyl cyclohexylcyanoacetate (**4**),[4] were obtained in 72 and 85% yield (Table I, entries 1 and 2). Prolonged reaction



1, R = R' = CH_3; Z = $CO_2C_2H_5$
2, R = R' = $(CH_2)_5$; Z = CN



3, R = R' = CH_3; Z = $CO_2C_2H_5$ **5**
4, R = R' = $(CH_2)_5$; Z = CN

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