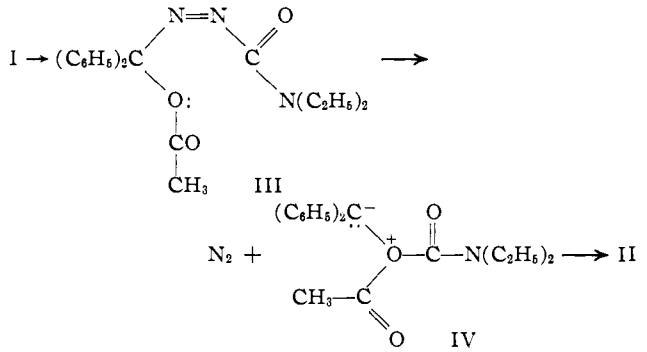
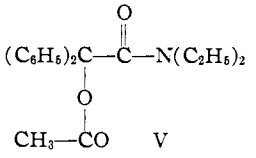
to the procedure employed with ketohydrazones[1] gave a mixture which slowly evolved nitrogen at 0—5°. After 20 hr. at this temperature, II was isolated, m.p. 70–71° (*Anal.* Calcd. for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.15. Found: C, 74.00; H, 7.22; N, 4.15). This compound was characterized as follows: hydrolysis in boiling 20% phosphoric acid gave carbon dioxide and 1-hydroxy-1,1-diphenylpropanone, m.p. 70–71° (*Anal.* Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.23. Found: C, 79.43; H, 6.05). Reported value[3]: m.p. 66–67°. A positive iodoform reaction and the isolation of benzilic acid (m.p. 150°) were achieved with the carbamate and the hydroxy ketone. Strong infrared bands for carbamate and saturated ketone carbonyl groups[4] were found at 1708 and 1720 cm.$^{-1}$, respectively.

The following mechanism is proposed to account for the over-all result



The formation of azoacetate III parallels the reaction of hydrazones with lead tetraacetate[1] and is followed by an intramolecular nucleophilic displacement at the amide carbonyl group.[5] The formation of nitrogen by decomposition of the quasi-five-member ring undoubtedly provides significant driving force for this reaction. By a 1,2-shift analogous to the Stevens rearrangement,[6] IV is converted into II. This appears to be the first proposal of a Stevens-type rearrangement involving an oxonium ion intermediate.

The above formulation leads one to expect an alternate path for the rearrangement of the zwitterion IV, *viz.*, carbanion attack on the amide carbonyl carbon. While the ester V anticipated from this migration has



not been isolated, its presence has been indicated. Concentration of the mother liquor from which II was isolated (0.019 mole) provided an oil which exhibited an acetate infrared band at 1750 cm.$^{-1}$ in addition to bands at 1708 cm.$^{-1}$ and 1720 cm.$^{-1}$. Acid hydrolysis of this oil produced benzilic acid (0.0013 mole) as required for the second rearrangement product as well as the 1-hydroxy-1,1-diphenylpropanone (0.0093 mole) from II. Thus the ratio of the two rearrangement products (II to V) in the original reaction mixture may be approximately 20 to 1.

The following morpholine derivative of benzophenone semicarbazone also reacts with lead tetraacetate at 0 to 5° and produces a carbamate, $(C_6H_5)_2C{=}N{-}NH{-}CO{-}N(CH_2CH_2)_2O$, m.p. 104–105° (*Anal.* Calcd. for $C_{18}H_{19}N_3O_2$: N, 13.58. Found: N, 13.65). After reaction as above, 2-oxo-1,1-diphenylpropyl 4′-morpholine carboxylate was isolated in 52% yield, m.p. 160–161° (*Anal.* Calcd. for $C_{20}H_{21}NO_3$: C, 70.78; H, 6.24; N, 4.13. Found: C, 70.92; H, 6.20; N, 3.96).

A study of the generality of this new rearrangement reaction is in progress as is also the question of whether thiosemicarbazones undergo a similar reaction.

Acknowledgment.—We wish to acknowledge generous support by Public Health Service Research Grant RG 9401 from the National Institutes of Health, Division of General Medical Sciences.

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RECEIVED MAY 17, 1963

(3) C. L. Stevens and A. E. Sherr, *J. Org. Chem.*, **17**, 1228 (1952).

(4) G. H. Beaven, E. A. Johnson, H. A. Willis and R. G. J. Miller, "Molecular Spectroscopy," Macmillan Co., New York, N. Y., 1961, pp. 239, 249.

(5) The possibility that acetic acid also formed in the reaction with lead tetraacetate may catalyze the transformation of III to IV by protonation of the amide carbonyl group is under study.

(6) J. H. Brewster and M. W. Kline, *J. Am. Chem. Soc.*, **74**, 5179 (1952).

On the Mechanism of the Reactions of α-Bromoketones with Triphenylphosphine[1]

Sir:

α-Bromoketones react with tricovalent organophosphorus compounds to give α-keto phosphonium salts[2] or derived α-keto phosphonates[3] or, alternatively, enol phosphonium salts[4] or the derived enol phosphates.

The mechanisms proposed for these reactions include initial attack of phosphorus on oxygen to give enol phosphonium salts directly[4c] or displacement on bromine to give an enolate bromophosphonium ion pair which is then converted to enol phosphonium salts. The formation of α-keto phosphonium salts has been envisaged to occur either by straightforward displacement[5] or by rearrangement of enol phosphonium salts.[6]

We now have found that the formation of α-keto phosphonium salts does not occur by straightforward displacement of bromide ion by tricovalent phosphorus and that enol phosphonium salts are formed irreversibly.

On the basis of our evidence we postulate that tricovalent organophosphorus compounds displace on bromine of α-bromoketones to give enolate bromophosphonium ion pairs which go either to enol phosphonium salts and enol phosphates or α-keto phosphonium salts and α-keto phosphonates.[7]

Reaction of phenacyl bromide with triphenylphosphine, in the presence of methanol, acetic acid, dimedone or diethyl malonate, leads to acetophenone (I) and a decreased yield of phenacyltriphenylphosphonium bromide (II) which is the product formed under anhydrous conditions.[2] The phosphonium bromide (II) has been shown to be stable to refluxing methanol.[4a] The data are summarized in Table I.

Debromination by methanol, acetic acid or dimedone can occur by three pathways: protonation of an enolate ion, or solvolysis of an enol phosphonium salt or a bromophosphonium salt. Diethyl malonate can be effective only as a proton donor and its utilization as a debrominating agent provides evidence for the presence of the enolate bromophosphonium ion pair at some

(1) This research was supported in part by a grant from the Society of the Sigma Xi.

(2) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

(3) F. W. Lichtenthaler, *Chem. Rev.*, **61**, 607 (1961).

(4) (a) I. J. Borowitz and L. I. Grossman, *Tetrahedron Letters*, **No. 11**, 471 (1962); (b) H. Hoffman and H. J. Diehr, *ibid.*, **No. 13**, 583 (1962); (c) S. Trippett, *J. Chem. Soc.*, 2337 (1962).

(5) F. Cramer, *Angew Chem.*, **72**, 239 (1960).

(6) This possibility was suggested by Lord Todd in a discussion session: *Proc. Chem. Soc.*, 106 (1962).

(7) Similar conclusions concerning the Perkow reaction have been reached by: (a) A. J. Speziale and L. R. Smith, *J. Am. Chem. Soc.*, **84**, 1868 (1962); (b) B. Miller, *J. Org. Chem.*, **28**, 345 (1963).

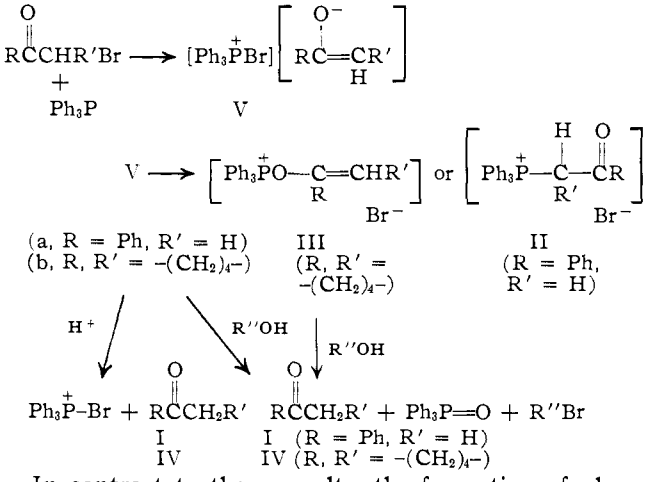
TABLE I
THE REACTION OF PHENACYL BROMIDE WITH TRIPHENYLPHOSPHINE[a]

Reaction conditions[b]	Yields, % II	Acetophenone[c]	Triphenylphosphine oxide
In anhydrous benzene, 1.5 hr.	79	6	19
In anhydrous benzene with excess methanol added	6	64	92
In anhydrous benzene with excess acetic acid	12	73	29
In anhydrous acetonitrile	80	..	20
In anhydrous acetonitrile with 2.5 equiv. of dimedone	40	35[d]	43
In anhydrous diethyl malonate	35	61	62

[a] All products gave satisfactory infrared spectra or melting points and were compared to genuine samples by thin layer chromatography. [b] All reactions were run in refluxing solvents. [c] Yields were based on conversion to the 2,4-dinitrophenylhydrazone. [d] A 6% yield of 5,5-dimethyl-3-bromocyclohexenone was also obtained and was identical with a genuine sample.[4a]

stage of reaction.[8] It also has been found that the reaction of 2-bromocyclohexanone with triphenylphosphine in refluxing acetonitrile to form the enol triphenylphosphonium bromide (III)[4] can be intercepted by the initial presence of diethyl malonate. Under such conditions cyclohexanone (IV) is obtained in 73% yield after 6 hr. while it is obtained in only 15% yield if the malonate is added after the reaction is allowed to proceed for 7.5 hr. Thus, once an enol phosphonium salt is formed it no longer reacts with diethyl malonate, at least to any major extent, although it can still react with an alcohol.[4c] Therefore, an enol phosphonium salt is not in equilibrium with an enolate bromophosphonium ion pair.[9]

The reaction sequence for 2-bromocyclohexanone therefore would appear to be: bromoketone to enolate bromophosphonium ion pair (Va) to III, while for phenacyl bromide the sequence is: bromoketone to enolate bromophosphonium ion pair (Vb) to II.



In contrast to these results, the formation of phenacyltriphenylphosphonium chloride (VI),[10] which occurs in 65% yield from the reaction of phenacyl chloride with 1.02 equivalents of triphenylphosphine in refluxing anhydrous benzene for 24 hr., is not greatly affected by the initial presence of excess methanol since a 56% yield of VI is still obtained. Thus phenacyl chloride reacts with triphenylphosphine primarily *via* straightforward displacement of chloride ion.[11]

Work is now in progress on the related reactions of haloketones with phosphites.

Acknowledgment.—The authors are indebted to Mr. Joseph Pugach of Columbia University for some of the vapor phase chromatography.

(8) As a control a mixture of diethyl malonate and phenacyl bromide, after being refluxed for 22 hr., gave no other compounds as determined by thin layer chromatography. Phenacyl bromide was recovered in 87% yield.

(9) The enol phosphonium salt derived from 2-bromocyclohexanone is also not in equilibrium with starting compounds. Unpublished results by George Gonis, Department of Chemistry, Lehigh University, demonstrated the absence of triphenylphosphine after 1.5 hr. of reaction with 2-bromocyclohexanone in dry 1,2-dimethoxyethane. At this time no alkylation of phosphine with butyl iodide was detected, whereas initially alkylation occurred as the major process in competition with enol phosphonium salt formation.

(10) Identified by conversion, in 66% yield, to the known phosphorane, m.p. 183–185°; genuine phosphorane prepared from II. See ref. 2.

(11) However, the reaction of desyl chloride with triphenylphosphine gives an enolphosphonium salt which then is converted to diphenylacetylene; see ref. 4c. In this case nucleophilic attack on chlorine leading to enolate formation may be enhanced because of the adjacent phenyl ring.

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RECEIVED MAY 17, 1963

A Stereospecific Synthesis of *dl*-Quinic Acid

Sir:

We found it necessary to devise a synthesis of quinic acid, I, utilizing non-symmetrical intermediates, in order that C-14 could be incorporated into specific positions of the molecule. The first total synthesis of quinic acid was reported by Grewe, Lorenzen and Vining[1] in 1954. This route was not applicable to our needs in that their procedure involved the symmetrical molecule hydroquinone in the formation of the ring system of quinic acid.

The synthesis was performed through an initial Diels–Alder reaction of *trans,trans*-1,4-dichlorobuta-1,3-diene,[2] II, with benzyl α-acetoxyacrylate. The latter was prepared from benzyl pyruvate upon refluxing with acetic anhydride in the presence of *p*-toluenesulfonic acid; b.p. 99–101 (0.5 mm.); $n^{22}D$ 1.5075: yield, 32%; *Anal.* Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.68; H, 5.59. Benzyl pyruvate was prepared in 92% yield by refluxing pyruvic acid and benzyl alcohol in anhydrous benzene and removing the water which was formed by azeotropic distillation. The literature values,[3] 103–105° (26 mm.), 103–104° (36 mm.), were inconsistent with our results, 103–105° (2 mm.), $n^{21.5}D$ 1.5100. *Anal.* Calcd. for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.76; H, 5.74.

Benzyl 1α-acetoxy-2α,5α-dichlorocyclohex-3-ene-1β-carboxylate, IV, was converted to the chlorolactone, V, by heating at 150° for 22 hr. The chlorolactone, V, (b.p. 150–152° (0.5 mm.)) was *cis*-hydroxylated using osmium tetroxide to give 1-acetyl-6-chloroquinide, VI, in 46% yield; m.p. 183–185°. *Anal.* Calcd. for $C_9H_{11}ClO_6$: C, 43.13; H, 4.42; Cl, 14.14. Found: C, 43.82; H, 4.20; Cl, 13.80. Hydrogenolysis of the chlorine atom was effected utilizing a freshly prepared W-6 Raney nickel catalyst to yield *dl*-1-acetylquinide, VII, in 87% yield, m.p. 215–216° dec. *Anal.* Calcd. for $C_9H_{12}O_6$: C, 50.00; H, 5.60. Found: C, 49.42; H, 5.45. *dl*-1-Acetylquinide was converted to the triacetyl derivative, VIII, by refluxing in acetic anhydride. The same derivative was prepared from the natural (−)-quinic acid according to the method of Erwig and Koenigs[4] in order to compare the infrared and nuclear magnetic resonance spectra in solution.

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