constant of 5.0 c.p.s.) was observed at 5.84 τ and the α-proton (doublet with a coupling constant of 5.0 c.p.s.) at 6.27 τ. The corresponding protons in the *trans*-epoxide have coupling constants of 1.8 c.p.s.[28]

Kinetic Measurements.—Reagent grade solvents (benzene, chloroform, and methanol) were purified by the methods of Vogel[29] and stored over Fisher 4A molecular sieve. Benzene was stored over sodium.[30]

The rates of reaction of the ylids with aldehydes were determined by two methods, each of which gave the same results. In one case, aliquots from the reaction mixture were quenched in cold methanol (0°) and the ylid immediately titrated potentiometrically with aqueous HCl. The other method consisted of quenching aliquots from the reaction mixture in excess acid and back titration of the excess acid with aqueous sodium hydroxide. Both methods were thoroughly standardized with solutions containing known amounts of ylid and reaction products.

In a typical experiment, a solution of the ylid in the appropriate solvent was equilibrated at the desired temperature for at least 2 hr., and a known amount of aldehyde added at time zero. Aliquots of the reaction mixture were periodically withdrawn and treated as described above. Rate constants were calculated from the slopes of $1/C$ or log (A_0B/B_0A) vs. time plots. The kinetics of the reaction of carbethoxymethylenetributylphosphorane with p-methoxybenzaldehyde were performed in a nitrogen atmosphere.

The rate of olefin formation in the reaction of carbomethoxymethylenetriphenylphosphorane with p-methoxybenzaldehyde in benzene was determined as follows: Aliquots of the reaction mixture were removed and extracted twice with a volume of aqueous hydrochloric acid sufficient to remove all of the ylid. (Both the ylid and phosphonium salt react quantitatively with bromine.) The organic phase was then added to a volume of standard $Br_3{}^\ominus$ in methanol[31] containing 1.5–2.0 times as much Br_2 as would be required by the olefin. The mixture was allowed to stand in the dark for 1 hr. (a longer period did not affect results) and the excess bromine titrated with a standard solution of anethole in methanol.[32]

Competition Experiments.—The competition experiments were performed in two ways. In one case a solution of the ylid in

(29) A. J. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1956.

(30) It was found that the values of rate constants obtained in benzene depended upon the method of purification of the benzene. When the benzene was washed with concentrated sulfuric acid prior to distillation from sodium, the rate constants were consistently slightly higher than when the A.R. grade benzene was simply distilled from sodium.

(31) J. Mitchell, I. R. Kolthoff, E. S. Proskauer, and A. Weissberger, "Organic Analysis," Vol. III, Interscience Publishers, Inc., New York, N. Y., p. 239.

(32) L. N. Petrova, *Zh. Priklad. Khim.*, **22**, 122 (1949).

chloroform was added slowly to a solution of a threefold excess of both benzaldehyde and p-nitrobenzaldehyde (m-chlorobenzaldehyde). In each case the product isolated was exclusively that arising from reaction of the ylid with the substituted aldehyde. Product ratios were determined by gas chromatographic analysis of the chloroform solution and by isolation of the products. In the second case, a mixture of benzaldehyde and m-chlorobenzaldehyde in various proportions was added rapidly to a solution of the ylid. In this competition experiment, some reaction of the ylid with benzaldehyde was always observed; however, the major product was still that arising from the more reactive aldehyde (Table V). In a typical experiment, 1.0 g. (0.00287 mole) of carbethoxymethylenetriphenylphosphorane was dissolved in 15 ml. of absolute ethanol, heated to reflux, and treated with an ethanolic solution of 0.305 g. (0.00287 mole) of benzaldehyde and 0.405 g. (0.00287 mole) of m-chlorobenzaldehyde. The solution was refluxed under nitrogen 16 hr., cooled, and the solvent removed *in vacuo* in the cold. The residue was then dissolved in 3 ml. of methylene chloride and the resulting solution analyzed with v.p.c.

Epoxide Ring Opening Reactions.—All of these experiments were performed in refluxing anhydrous ethanol. In a typical experiment, the epoxide (0.008 mole) and the appropriate amount of m-chlorobenzaldehyde (0.024 mole) were dissolved in 15 ml. of ethanol, and the solution was heated to reflux and a solution of the phosphine (0.008 mole) in 15 ml. of ethanol added. The solution was refluxed for a specified length of time. Nitrogen was passed through the solution throughout the period of reflux. When tributylphosphine was used, a reflux time of 20 hr. was utilized for the *trans*-epoxide and 42 hr. for the *cis*-epoxide. For triphenylphosphine it was necessary to reflux the *trans*-epoxide reaction 5 days and the *cis*-epoxide reaction 10 days. The extent of reaction was determined by periodically removing aliquots of the solution and adding these to an ethanolic solution of mercuric chloride.[33] When an aliquot showed the absence of unreacted phosphine, the solutions were cooled and analyzed with v.p.c.[34] Retention times for all of the products were compared with those of authentic samples. The products from one reaction were isolated with preparative v.p.c. and the aldehydes identified by oxidation to the corresponding acids and comparison *via* melting point and mixture melting point with authentic samples. The unsaturated esters were identified by comparison of their infrared spectra with those of authentic samples.

Acknowledgments.—We wish to thank Drs. K. W. Ratts and L. J. Taylor for many helpful discussions, and Dr. C. C. Tung for interpretation of the n.m.r. spectra of the epoxides.

(33) Triphenylphosphine and tributylphosphine form ethanol-insoluble complexes with mercuric chloride.

(34) A 5-ft. column of 20% Apiezon L on Chromosorb W maintained at 180° was used in all gas chromatographic analyses.

COMMUNICATIONS TO THE EDITOR

Aroylation at the Terminal Methyl Group of a 1,3,5-Triketone to Form a 1,3,5,7-Tetraketone[1]

Sir:

Although acetylacetone can be benzoylated at one of its terminal methyl groups with methyl benzoate by means of two equivalents of potassium amide in liquid ammonia to form I,[2] attempts in this Laboratory to further benzoylate I at its remaining methyl group by means of three molecular equivalents of this reagent to give II have been unsuccessful.

$C_6H_5COCH_2COCH_2COCH_3$ $C_6H_5COCH_2COCH_2COCH_2COC_6H_5$
I   II
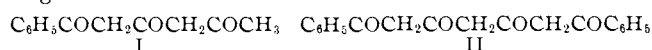
We now wish to report that not only the terminal benzoylation of acetylacetone[3] but also the terminal benzoylation of I to form II can be accomplished by means of sodium hydride in 1,2-dimethoxyethane.
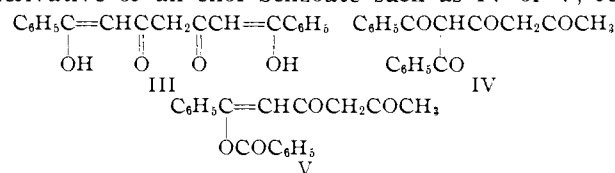
Thus, II, m.p. 91–93°, was obtained in 52% yield. *Anal.* Calcd. for $C_{19}H_{16}O_4$: C, 74.02; H, 5.22. Found: C, 73.83; H, 5.06. This appears to be the first example of an acyclic 1,3,5,7-tetraketone that has been isolated and characterized.

That the product was the terminal methyl derivative II (in an enol form such as III), not a methylene derivative or an enol benzoate such as IV or V, re-

$C_6H_5C\!\!=\!\!CHCCH_2CCH\!\!=\!\!CC_6H_5$ $C_6H_5COCHCOCH_2COCH_3$
  | ‖ ‖ | |
  OH   O   O   OH C_6H_5CO
       III   IV
          $C_6H_5C\!\!=\!\!CHCOCH_2COCH_3$
               |
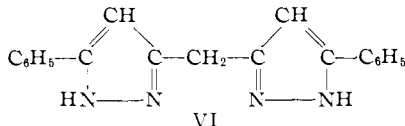 $OCOC_6H_5$
                V

spectively, was supported by its n.m.r. spectrum (in deuterated chloroform using tetramethylsilane as an internal standard), which showed peaks corresponding to the protons of the units $COCH_2$ (3.55 p.p.m.) and $C\!\!=\!\!CH$ (6.32 p.p.m.), but no peak indicative of a terminal methyl group as would be shown by IV or V.[4] An n.m.r. spectrum of the parent compound

I showed, in addition to peaks corresponding to the methylene and vinyl hydrogens, three peaks with chemical shifts of 2.02, 2.05, and 2.30 p.p.m. which were assigned to the terminal methyl protons.[5]

The structure of the tetraketone was further supported by its reaction with excess hydrazine to form the dipyrazole VI, m.p. 218–219°, in 88% yield. *Anal.* Calcd. for $C_{19}H_{16}N_4$: C, 75.97; H, 5.37; N, 18.66; mol. wt., 300. Found: C, 76.12; H, 5.24; N, 18.70; mol. wt., 312.

That the dipyrazole was VI, not the possible one from IV, was supported by its n.m.r. spectrum (in dimethyl sulfoxide using tetramethylsilane as an external standard) which showed peaks corresponding to the protons in the structural units NH (12.95 p.p.m.), C=CH (6.53 p.p.m.), and C—CH$_2$ (4.02 p.p.m.), but no peak indicative of the terminal methyl group as would be present in the dipyrazole of IV.

Studies are now in progress on other aroylations of 1,3,5-triketones and on the related acylations and carbethoxylations. The mechanism of the reaction and the properties of the products will be investigated. Such products should be of interest in connection with the biosynthesis of many plant and mould products by the acetate–malonate (polyketide) route.[6]

Acknowledgment.—The authors wish to thank Dr. Walter L. Meyer of Indiana University for obtaining and interpreting the n.m.r. spectra of the ketones prepared in this study.

same solution gave, besides the aromatic proton peaks, only two major peaks which were assigned as above.

(5) Apparently, in chloroform solution an equilibrium exists between three enolic forms.

(6) See A. J.Birch, P. Fitton, D. C. C. Smith, D. E. Steere, and A. R. Stelfox, *J. Chem. Soc.*, 2209 (1963); A. J. Birch and F. W. Donovan, *Australian J. Chem.*, **6**, 360 (1953); A. J. Birch, *Proc. Chem. Soc.*, 3 (1962).

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A Convenient Preparation of $B_{12}H_{12}{}^{2-}$ Salts[1]

Sir:

Studies of the $B_{12}H_{12}{}^{2-}$ anion have been severely hampered until now by the fact that it could only be prepared in poor yield from a halogenated decaborane.[2] The high stability of this anion and of its derivatives, considered together with the versatility of its substitution reactions,[3] makes the chemistry of this ion an intriguing area for research. We would therefore like to report a more convenient preparation of this anion from readily available starting materials by conventional techniques. At the same time this is a striking example of the formation of a highly stable end product by a quite unexpected route. Small yields of $B_{10}H_{10}{}^{2-}$ salts are produced as by-products.

In the course of carrying out ^{11}B n.m.r. spectral studies on the triborohydride anion it was found that heating a solution of NaB_3H_8 in diethylene glycol dimethyl ether (141) for 2 hr. on a steam bath caused the ^{11}B n.m.r. spectrum to change. The multiplet arising from $B_3H_8{}^-$ was completely replaced by a doublet of approximately the same over-all intensity with a chemical shift of 14.6 p.p.m. and a coupling constant of 126 c.p.s. This corresponded to the values for $B_{11}H_{14}{}^-$ and $B_{12}H_{12}{}^{2-}$ within experimental error.[3,4]

(1) Studies of Boranes IX. For paper VIII of this series see D. F. Gaines and R. Schaeffer, *Proc. Chem. Soc.*, 267 (1963).

(2) A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 3228 (1960).

A freshly prepared solution of NaB_3H_8 (18.5 g.) in 141 prepared by *in situ* hydroboration of sodium borohydride[5] was refluxed under a nitrogen atmosphere until colorless (16 hr.). When the resulting mixture was treated with a concentrated solution of $(CH_3)_3NHCl$ (30 g.) in water an exothermic reaction occurred which was accompanied by evolution of gaseous amine. The resulting mixture was cooled to room temperature, and the solid which separated was filtered and dried to yield 27 g. of crude products.

A fraction of the crude solid was dissolved in water and treated with a saturated solution of cesium chloride in water until no further precipitation took place. The precipitate was recrystallized three times from water to give a highly crystalline colorless solid. An X-ray powder diffraction pattern of this solid showed maximum reflections at d values of 3.59, 4.21, 2.16, and 2.60 and was identical with the diffraction pattern of a similar material prepared in similar fashion from an authentic sample of $(Et_3NH)_2B_{12}H_{12}$.[6]

The remainder of the crude product was recrystallized from a water–ethanol mixture to give $(Me_3NH)_2B_{12}H_{12}$ identified by its ^{11}B n.m.r. spectrum. Concentration of the mother liquor by conventional techniques gave further quantities of $(Me_3NH)_2B_{12}H_{12}$ and also in the last fractions some $(Me_3NH)_2B_{10}H_{10}$ (identified by its ^{11}B n.m.r. spectrum).[7]

Yields were not definitely established, since complete separation of $(Me_3NH)_2B_{12}H_{12}$ from $(Me_3NH)_2B_{10}H_{10}$ could not be readily achieved, but the yield of $B_{12}H_{12}{}^{2-}$ was at least 65%. The yield of $B_{10}H_{10}{}^{2-}$ was roughly 3%.

Thin layer chromatography carried out on the crude reaction product using silica gel and water as eluent showed that it consisted of at least three components with respective R_f values of 0, 0.3, and 1. The fraction with R_f 1 was shown to be $B_{12}H_{12}{}^{2-}$ and $B_{10}H_{10}{}^{-2}$. The other compounds present in the mixture are under investigation.

Acknowledgment.—The authors wish to thank Fred Tebbe for valuable discussions during this work. This work was supported by the Office of Naval Research.

(3) W. H. Knoth, *et al.*, *ibid.*, **84**, 1056 (1962).

(4) V. D. Aftandilian, *et al.*, *Inorg. Chem.*, **1**, 734 (1962).

(5) D. F. Gaines, R. Schaeffer, and F. Tebbe, *ibid.*, **2**, 526 (1963).

(6) (EtsNH)$_2$B$_{12}$H$_{12}$ was kindly supplied by Professor M. F. Hawthorne.

(7) A. R. Pitochelli, *et al.*, *J. Am. Chem. Soc.*, **84**, 1057 (1962).

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Synthesis of Polyhedral Boranes

Sir:

We wish to report a facile synthesis of polyhedral boranes, particularly $B_{12}H_{12}{}^{2-}$, directly from diborane.[1] The syntheses are based on two closely related reactions; (1) diborane and a metal borohydride, and (2) diborane and a base–borane complex. Other volatile boron hydrides may be used instead of diborane.

The $B_{12}H_{12}{}^{2-}$ syntheses are the most important, and nearly quantitative yields of salts of $B_{12}H_{12}{}^{2-}$ have been obtained from reactions 1 and 2 as follows.

$$2NaBH_4 + 5B_2H_6 \xrightarrow[100–180°]{(C_2H_5)_3N} Na_2B_{12}H_{12} + 13H_2 \quad (1)$$

$$2(C_2H_5)_3NBH_3 + 5B_2H_6 \xrightarrow{100–180°} [(C_2H_5)_3NH]_2B_{12}H_{12} + 11H_2 \quad (2)$$
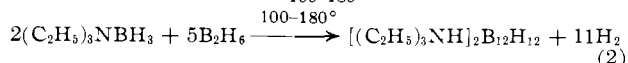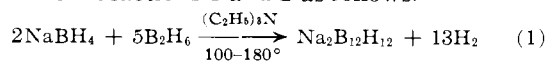
In the second case, the triethylammonium salt is obtained directly in analytical purity. These reactions

(1) (a) This ion was first reported by M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **82**, 3228 (1960); (b) we are indebted to Professor R. Schaeffer, who advised us of the synthesis of $B_{12}H_{12}{}^{2-}$ by pyrolysis of NaB$_3$H$_8$ in diethylene glycol dimethyl ether: I. A. Ellis, D. F. Gaines, and R. Schaeffer, *ibid.*, **85**, 3885 (1963).