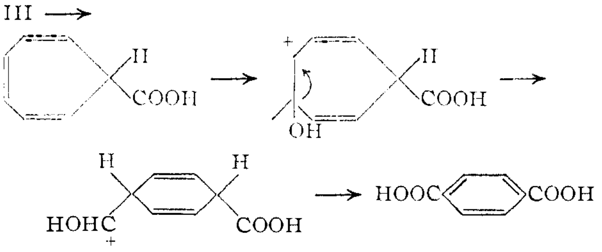
tonated norcaradienecarboxaldehyde. Oxidation of V gives norcaradienecarboxylic acid II which then forms the tropylium cation by a two electron transfer process as outlined earlier. The tropylium cation is further oxidized to benzaldehyde and benzoic acid.

The formation of terephthalic acid by oxidation of III with chromic acid in acetic acid probably is due to the formation of norcaradienecarboxylic acid as given above, followed by a second similar oxidation-rearrangement, thus



As mentioned previously we have found that chromic acid oxidation of norcaradienecarboxylic acid gave terephthalic acid and no tropylium salts could be isolated.

Acknowledgment.—We wish to thank Professor M. J. S. Dewar for valuable discussion and the D.S.I.R. for a maintenance grant to C.R.G.

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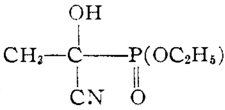
RECEIVED MARCH 8, 1957

A REARRANGEMENT TO FORM DIETHYL 1-CYANOETHYL PHOSPHATE

Sir:

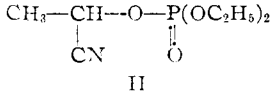
In a recent report[1] the preparation, some properties and pyrolysis of a compound believed to be diethyl 1-cyano-1-hydroxyethylphosphonate (I)



$$CH_2-\underset{CN}{\overset{OH}{C}}-\underset{O}{\overset{}{P}}(OC_2H_5)_2$$

I

were recorded. More recent analysis by the proton NMR method on a freshly distilled sample of this material, b.p. 91–92° (0.5 mm.), $n^{26}D$ 1.4130, showed a tertiary hydrogen and no hydroxyl hydrogen. The spectrum of the tertiary hydrogen consisted of two superimposed quadruplets which is the proper spectrum for a hydrogen adjacent to a methyl and a phosphate group. This coupled with the earlier observation[1] that the compound would not give an acetyl derivative and that its infrared spectrum showed no absorption in the hydroxyl region leads to the conclusion that the material in question is diethyl 1-cyanoethyl phosphate (II).

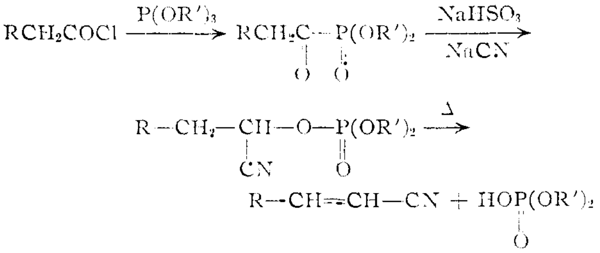


$$CH_3-\underset{CN}{CH}-O-\underset{O}{P}(OC_2H_5)_2$$

II

This conclusion is further strengthened by the isolation of acrylonitrile in high (83%) yield upon the pyrolysis of this material.[1] The formation of acrylonitrile would be expected from the pyrolysis of II far more logically than from the pyrolysis of I.

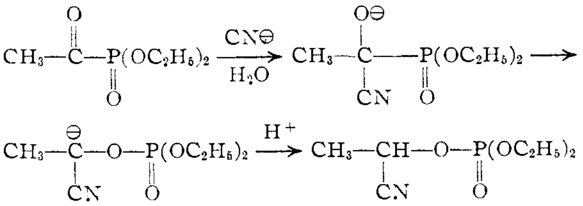
This series of reactions which led to acrylonitrile in excellent yield may demonstrate a general and useful route for the preparation of unsaturated nitriles (at least on a laboratory scale) starting with the readily available acyl halides provided a β-hydrogen atom is present



$$RCH_2COCl \xrightarrow{P(OR')_3} RCH_2\underset{O}{C}-\underset{O}{P}(OR')_2 \xrightarrow[NaCN]{NaHSO_3}$$
$$R-CH_2-\underset{CN}{CH}-O-\underset{O}{P}(OR')_2 \xrightarrow{\Delta}$$
$$R-CH=CH-CN + HO\underset{O}{P}(OR')_2$$

As was reported by earlier workers,[2] the expected product from the reaction of an α-keto phosphonate, sodium bisulfite and sodium cyanide would be a phosphonate, such as I.

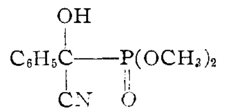
Apparently a rearrangement took place during its preparation under alkaline conditions; for example, as outlined below.



$$CH_3-\underset{O}{\overset{O}{C}}-P(OC_2H_5)_2 \xrightarrow[H_2O]{CN^{\ominus}} CH_3-\underset{CN}{\overset{O^{\ominus}}{C}}-\underset{O}{P}(OC_2H_5)_2 \longrightarrow$$
$$CH_3-\underset{CN}{\overset{\ominus}{C}}-O-\underset{O}{P}(OC_2H_5)_2 \xrightarrow{H^+} CH_3-\underset{CN}{CH}-O-\underset{O}{P}(OC_2H_5)_2$$

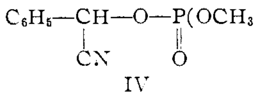
II

It is believed that the earlier Soviet workers[2] also had phosphate rather than phosphonate materials as products from their reactions. They reported preparation of III which on acid hydrolysis gave mandelic acid, $C_6H_5CHOHCOOH$. It is more likely that they had IV, from which the formation of mandelic acid upon acid hydrolysis would then be expected.



$$C_6H_5\underset{CN}{\overset{OH}{C}}-\underset{O}{P}(OCH_3)_2$$

III



$$C_6H_5-\underset{CN}{CH}-O-\underset{O}{P}(OCH_3)_2$$

IV

Recently Barthel, *et al.*,[3] and Lorenz, *et al.*,[3] reported the rearrangement of a hydroxyphospho-

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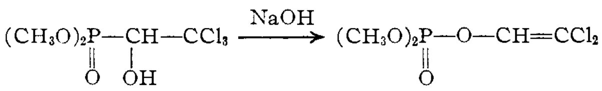
[1] L. A. R. Hall and C. W. Stephens, THIS JOURNAL, **78**, 2565 (1956).

[2] M. I. Kabachnik, P. A. Rossiiskaya and E. S. Shepeleva, *Bull. Acad. Sci. U.R.S.S., Classe Sci. Chim.*, 163 (1947); *C. A.*, **42**, 4133 (1948).

[3] W. F. Barthel, B. H. Alexander, P. A. Giang and S. A. Hall, THIS JOURNAL, **77**, 2424 (1955); W. Lorenz, A. Henglein and G. Schrader, *ibid.*, **77**, 2554 (1955).

nate (V) to a phosphate (VI) under alkaline conditions.



$$(CH_3O)_2\underset{\underset{O}{\|}}{P}-\underset{\underset{OH}{|}}{CH}-CCl_3 \xrightarrow{NaOH} (CH_3O)_2\underset{\underset{O}{\|}}{P}-O-CH{=}CCl_2$$

V VI

It appears that these alkaline induced rearrangements of α-hydroxyphosphonates to phosphates may be of a general nature when the α-carbon is substituted with electron withdrawing groups such as—CN,—CCl_3, etc.

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RECEIVED DECEMBER 28, 1956

A GENERAL METHOD FOR ESTABLISHING THE ABSOLUTE CONFIGURATION OF OPTICALLY ACTIVE BIPHENYLS BY ASYMMETRIC SYNTHESIS

Sir:

We wish to report a general and direct chemical method for correlating the configuration of a biphenyl with that of a centrally asymmetric compound, and hence for the establishment of absolute configuration in the biphenyl series. The method, which is illustrated in the following sequence, involves neither creation nor destruction of biphenylic (axial) dissymmetry.

Methyl *RS*-6,6′-dinitro-2,2′-diphenate[1] was reduced with $LiAlH_4$–$AlCl_3$ to *RS*-6,6′-dinitro-2,2′-bis-(hydroxymethyl)-biphenyl[2] (m.p. 142–144°; found: C, 55.5; H, 3.9; N, 9.0) which was converted to the dibromide (m.p. 183–185°; found: C, 39.0; H, 2.5; N, 6.3) with concd. HBr. Ring closure to the iminonitrile (m.p. 304° dec.; found: C, 59.8; H, 3.2; N, 17.1) with KCN, followed by acid hydrolysis, gave *RS*-4′,1″-dinitro-1,2,3,4-dibenz-1,3-cycloheptadiene-6-one (*RS*-DNDBCH-6-one), m.p. 234–236°; found: C, 60.4; H, 3.3; H, 9.2. Reduction with *i*-PrOH/Al(*i*-PrO)$_3$ gave *RS*-DNDBCH-6-ol, m.p. 199–200°; found: C, 60.0; H, 3.5; N, 9.2.

Treatment of *RS*-DNDBCH-6-one (951 mg.) with pinacolyl alcohol (14.0 g., $[\alpha]^{29}\mathrm{D}$ +7.73)[3] in the presence of Al(*t*-BuO)$_3$ (717 mg.) in dioxane (52.4 g.) at 63° for seven hours, followed by chromatographic separation of the resulting product, afforded 139 mg. of DNDBCH-6-one, $[\alpha]\mathrm{D}$ +136° (EtOAc), and 665 mg. of DNDBCH-6-ol, $[\alpha]\mathrm{D}$ −109° (EtOAc). Reduction of the (+)-ketone with *i*-PrOH/Al(*i*-PrO)$_3$ yielded DNDBCH-6-ol, $[\alpha]\mathrm{D}$ +498° (EtOAc). Finally, reduction of *RS*-DNDBCH-6-one with aluminum (+)-pinacoloxide for a twenty-five hour period gave only optically inactive DNDBCH-6-ol.

Inspection of a model of *S*-DBCH-6-one (Fig. 1 is a top view; the nitro groups are omitted for the sake of clarity) leads to the unambiguous prediction that hydrogen transfer to the carbonyl carbon *via* a Meerwein–Ponndorf–Verley type transition state[4] on *either* face of the carbonyl group will be rendered energetically unfavorable owing to the necessity of accommodating the bulky *t*-butyl group on the side of the jutting phenyl, whereas for the *R*-isomer only the much smaller methyl group need thus be crowded. It can therefore be anticipated that reduction of the *R*-isomer will proceed initially more rapidly than reduction of the *S*-isomer. The experimental results are completely compatible with this view. Accordingly we assign (+)-DNDBCH-6-one the *S*-configuration and (−)-DNDBCH-6-ol the *R*-configuration.

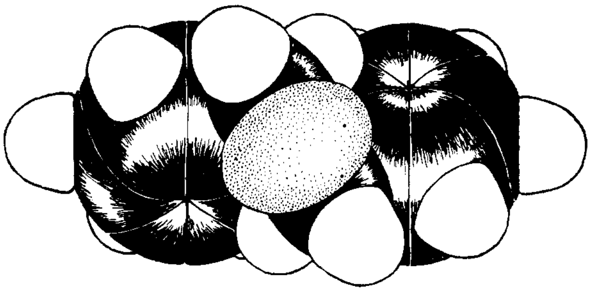

Fig. 1.

The above transformations represent the first example of a novel and general principle for the configurational correlation of hindered biphenyls with compounds possessing only central asymmetry.[5] Further related aspects are under active investigation in this Laboratory, as part of our program in biphenyl stereochemistry.[6]

This work was supported in part by a grant from The Trubek Laboratories.

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[1] We are here employing the nomenclature devised by R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia*, **12**, 81 (1956), although alternative designations are also possible (G. E. McCasland, private communication).

[2] Independently prepared by D. C. Iffland (private communication) through reduction of the acid chloride with sodium trimethoxyborohydride.

[3] This enantiomer has the *S*-configuration, as shown, for example, by asymmetric synthesis; H. S. Mosher and E. La Combe, THIS JOURNAL, **72**, 3994 (1950).

[4] W. von E. Doering and R. W. Young, *ibid.*, **72**, 631 (1950).

[5] J. A. Berson, *ibid.*, **78**, 4170 (1956), has pointed out that analysis of transition statesi n the particular case of the thebaine–phenyldihydrothebaine interconversion permits configurational correlation of starting material and product, leading to an absolute configuration of the (generated) biphenyl moiety in the latter.

[6] K. Mislow, *Trans. N. Y. Acad. Sci.*, in press.

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RECEIVED JANUARY 23, 1957

MODIFIED NICKEL CATALYST FOR THE HYDROGENOLYSIS AND ALKYLATION OF AROMATIC HYDROCARBONS

Sir:

It was found that when small amounts of sulfur-containing compounds are added to a nickel hydrogenolysis catalyst the latter is "modified" in such a way as to catalyze reactions which until now were associated with strong acid catalysts. Some of the following reactions were observed to occur in the presence of the "modified" nickel catalyst: dealkylation, transalkylation, alkylation and internal alkylation of benzenoid hydrocarbons.