appears at m/e 52 corresponding to $C_4H_4^+$. In the mass spectrum of IV, however, the m/e peak of 52 appears as the strongest peak. This peak is absent from the spectrum of N-methyl 2-pyridone (which evidently fragments to N-methylpyrrole and cyclopropenyl cations). The species $C_4H_4^+$ produced from IV by electron impact could well be the cyclobutadiene radical cation.

TABLE I

Compound	m/e (relative intensity)[a]
I	96(25), 68(58), 39(100), 29(25)
IV	109(15), 81(35), 52(100), 42(35), 39(30), 15(25)
N-Methyl-2-pyridone	109(100), 81(65), 42(38), 39(48)

[a] Intensity of strongest peak taken as 100; only peaks of intensity 25 are included.

The possibility of internal photoaddition reactions of 2-pyrones and 2-pyridones evidently has not been investigated seriously even though irradiations of both types of compounds have been reported.[10,11] We are currently extending these studies to related systems in addition to the heterocycles discussed above.[12]

(10) The irradiation of 4,6-dimethyl-2-pyrone in methanol solution affords methyl β-acetonylcrotonate, a reaction which has been interpreted as a cycloelimination proceeding *via* a ketene intermediate [P. de Mayo, "Advances in Organic Chemistry," Vol. II, Interscience Publishers, New York, N. Y., 1960, p. 394]. The intermediacy of a bicycle β-lactone would seem to be a reasonable alternative in view of our results.

(11) For the photodimerization of N-methyl-2-pyridone see: (a) E. C. Taylor and R. O. Kan, *J. Am. Chem. Soc.*, **85**, 776 (1963); (b) L. A. Paquette and G. Slomp, *ibid.*, **85**, 795 (1963); (c) W. A. Ayer, R. Hayatsu, P. de Mayo, and J. B. Stothers, *Tetrahedron Letters*, **No. 18**, 648 (1961); and (d) earlier papers by these authors.

(12) This work was supported by the National Institutes of Health.

(13) N. A. T. O. Postdoctoral Research Fellow.

DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASSACHUSETTS
E. J. COREY
JACQUES STREITH[13]

RECEIVED JANUARY 2, 1964

The Reductive Alkylation of Quinones with Trialkylboranes

Sir:

In the past, alkyl hydroquinones have been prepared through routes which involved the reaction of quinones with acyl peroxides[1] or electrophilic acylation[2] and alkylation[3,4] of hydroquinones. We wish to report a new method for the preparation of alkyl hydroquinones from 1,4-benzoquinone and the corresponding trialkylboranes. The latter materials may be conveniently prepared by the hydroboration of alkenes.[5] The reductive alkylation reactions are strongly exothermic and virtually quantitative. Triphenylborane did not react with 1,4-benzoquinone and triarylboranes may prove to be generally ineffective.

In all cases 0.10 mole of 1,4-benzoquinone dissolved in diethyl ether was added under nitrogen to a solution of 0.11 mole of trialkylborane in the same solvent at the reflux temperature. The trialkylboranes employed were crude products obtained by hydroboration[5] of the proper olefin. Following the addition (30 min.) the reaction mixture was maintained at the reflux temperature for 30 min. The reaction mixture was then steam distilled to remove solvent, boronic and borinic acids, and unused reagents. On cooling, the alkyl hydroquinone separated as a crystalline mass in the steam distillation flask. Each hydroquinone was characterized by conversion to the dibenzoate and corresponding 2-alky-1,4-benzoquinone. New compounds gave satisfactory elemental analyses. Yields and characterization data are presented in Table I.

TABLE I

Alkyl group	Crude yield, %	Hydroquinone, m.p., °C.	Quinone, m.p., °C.	Dibenzoate, m.p., °C.
1-Butyl	86	87–87.5[b]	34–35	97–98
1-Hexyl	98.5	84–84.5[b]	48–49	53–54
Cyclohexyl	99	163–165 (0.4)[a]	53–54[c]	106–108
2-Methylpropyl	91	111.5–112	35–36	120.5–121
2-Butyl	94	100–101	66 (1.0)[a]	92–93
Cyclooctyl	91	160–160.5	43.5–44.5	123–126
Benzyl	90	101–103[d]		151–153

[a] B.p. (mm.), °C. [b] J. Renz [*Helv. Chim. Acta*, **30**, 124 (1947)] reports m.p. 84–85° (1-butyl) and m.p. 79–80° (1-hexyl). [c] L. F. Fieser [*J. Am. Chem. Soc.*, **70**, 3165 (1948)] reports m.p. 53.5–54.5°. [d] R. Stolle and W. Moring [*Ber.*, **37**, 3486 (1904)] report m.p. 105°.

The reactions of representative trialkylboranes with other quinones and a mechanism study will be reported elsewhere.

Acknowledgment.—The authors wish to thank the Petroleum Research Fund administered by the American Chemical Society for generous financial support.

(6) Alfred P. Sloan Foundation Fellow.

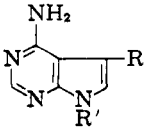
DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF CALIFORNIA
RIVERSIDE, CALIFORNIA
M. FREDERICK HAWTHORNE[6]
MARTEN REINTJES

RECEIVED JANUARY 9, 1964

Synthesis of 4-Amino-5-cyanopyrrolo[2,3-*d*]pyrimidine, the Aglycone of Toyocamycin[1]

Sir:

Two closely related antibiotics, Tubercidin (Ia) and Toyocamycin (IIa), have recently been reported from Japan and are the first naturally occurring derivatives of the pyrrolo[2,3-*d*]pyrimidine (7-deazapurine)



Ia, R = H; R′ = β-D-ribose
Ib, R = R′ = H
IIa, R = CN; R′ = D-ribose
IIb, R = CN, R′ = H

ring system. Tubercidin, first isolated by Anzai, Nakamura, and Suzuki,[2] was shown to possess structure Ia on the basis of degradation studies,[3–6] which led to the known 4-aminopyrrolo[2,3-*d*]pyrimidine (Ib).[7] It is active against *Mycobacterium tuberculosis* B.C.G. and *Candida albicans* and is reported to have strong antitumor activity.[2] Toyocamycin, isolated in crystalline form from a species of *Streptomyces*[8] and from the

(1) This work was supported in part by a research grant (CA-02551) to Princeton University from the National Cancer Institute, National Institutes of Health, Public Health Service.

(2) K. Anzai, G. Nakamura, and S. Suzuki, *J. Antibiotics* (Tokyo), **10A**, 201 (1957).

(3) S. Suzuki and S. Marumo, *ibid.*, **12A**, 360 (1960).

(4) S. Suzuki and S. Marumo, *ibid.*, **14A**, 34 (1961).

(5) Y. Mizuno, M. Ikehara, K. Watanabe, and S. Suzaki, *Chem. Pharm. Bull.* (Tokyo), **11**, 1091 (1963).

(6) Y. Mizuno, M. Ikehara, K. A. Watanabe, S. Suzaki, and T. Itoh, *J. Org. Chem.*, **28**, 3329 (1963).

(7) J. Davoll, *J. Chem. Soc.*, 131 (1960).

(8) H. Nishimura, K. Katagiri, K. Sato, M. Mayama, and N. Shimaoka, *J. Antibiotics* (Tokyo), **9A**, 60 (1956).

(1) L. F. Fieser and A. E. Oxford, *J. Am. Chem. Soc.*, **64**, 2060 (1942).

(2) E. C. Armstrong, R. L. Bent, A. Loria, J. R. Thirtle, and A. Weissberger, *ibid.*, **82**, 1928 (1960).

(3) C. C. Price, *Org. Reactions*, **3**, 70 (1949).

(4) L. F. Albright and R. N. Shreve, *Ind. Eng. Chem.*, **48**, 1551 (1956).

(5) H. C. Brown, "Hydroboration," 1st Ed., W. A. Benjamin, Inc., New York, N. Y., 1962.