drogen-bonded chain. In the latter structure all the hydrogen atoms were directly located and the dihedral angle was found to be 146°.

Thus we have observed two examples of each of the enantiomorphic and racemate type of crystal structures in the four compounds we have studied. Which crystal forms, for any particular compound, will depend on whether the assemblage of like or of unlike molecules has the greater lattice energy at the temperature of the crystallization. No other crystal structure analyses of organic peroxides have been reported. It is interesting to note, however, that hydrogen peroxide itself has an enantiomorphic crystal structure in space group $P4_12_12$,[4] while the hydrogen peroxide dihydrate structure is centrosymmetrical.[5]

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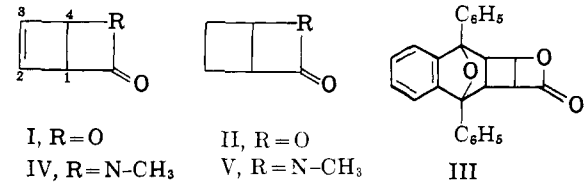
Internal Photoaddition Reactions of 2-Pyrone and N-Methyl-2-pyridone: A New Synthetic Approach to Cyclobutadiene

Sir:

Ultraviolet irradiation of a solution of 2-pyrone in ether (concentration 4–5 g./l.)[1,2] affords in almost quantitative yield an isomer to which structure I is assigned on the basis of chemical and physical data cited below. The photoproduct can be isolated in pure form by evaporation of solvent under reduced pressure (solutions of the product must be kept cold at all times) followed by evaporative distillation in a molecular still (below 0.05 mm.) at room temperature with the collecting surface maintained at −70°. It is a colorless, hygroscopic liquid which is pyrophoric in air at room temperature and which can explode on warming in air. *Anal.* Calcd. for $C_5H_4O_2$: C, 62.50; H, 4.20; mol. wt., 96. Found: C, 62.37; H, 4.20; mol. wt., 96 (mass spectral parent peak)[3]; mol. wt., 10[9] (osmometric in benzene). The n.m.r. spectrum shows four sets of peaks[4] (each due to one proton) centered at 6.73, 6.58, 5.30, and 4.40 δ, the multiplets approximating octet, quartet, quartet, and octet, respectively. The observed chemical shifts and coupling constants support structure I with the assignments of the above bands to the protons attached to C-3, C-2, C-4, and C-1, respectively (numbering as in I). The infrared spectrum (in CCl_4) of this photo 2-pyrone shows carbonyl absorption as a double peak at 5.41 and 5.50 μ (β-lactone) and a band at 6.48 μ which probably is due to C=C stretching (displaced to high wave length because of angle distortion[5]). The ultraviolet spectrum shows only end absorption (ϵ 1500 at 210 mμ). A yellow color develops with tetranitromethane, indicating the presence of an unconjugated olefinic linkage.



I, R=O II, R=O III
IV, R=N-CH$_3$ V, R=N-CH$_3$

As expected on the basis of formulation I, hydrogenation of the photoisomer (over palladium–charcoal) affords a mixture of cyclobutanecarboxylic acid[6] and a saturated β-lactone (II) (C, 61.26; H, 6.46); infrared maximum at 5.5 μ.; n.m.r. peaks (multiplets) at 4.8 (1H), 3.85 (1H), and 2.43 (4H) δ; no color with tetranitromethane. The amount of hydrogen absorbed and the ratio of products formed indicate that two molecules of hydrogen are required for the formation of the acid and one for formation of saturated lactone II.

The reaction of the photoisomer of 2-pyrone with 2,5-diphenyl-3,4-isobenzofuran[7] proceeds readily at 0° to give a 1–1 adduct, m.p. 212° dec. (C, 81.81; H, 5.10). The infrared spectrum of the adduct indicates that the β-lactone ring has been retained (band at 5.50 μ) and the n.m.r. spectrum shows (in addition to the expected aromatic proton peaks) a singlet at 3.42 δ (2H), doublets at 3.54 (1H, J = 2.6) and 4.62 δ (1H, J = 2.6), and no olefinic protons in accord with expression III for the adduct.

Photoisomerization of N-methyl-2-pyridone in ether (1.7 g./l.) under the same conditions as used for 2-pyrone follows a similar course, but at a slower rate. The product, isolated by molecular distillation at room temperature in 20% yield, is a colorless liquid (C, 65.86; H, 6.60; N, 12.92; mol. wt.,[3] 109) which is formulated as IV. The infrared spectrum shows absorption due to β-lactam carbonyl (5.74 μ) and C=C (6.49 μ) and the n.m.r. spectrum shows peaks due to two olefinic protons centered at 6.71 δ, two protons attached to saturated carbon at 4.38 and 4.18 δ, and three protons of N-CH$_3$ at 2.82 δ. The ultraviolet absorption spectrum of photo N-methyl-2-pyridone[8] shows a maximum at 237 mμ (ϵ 1500) in cyclohexane. Catalytic hydrogenation of IV produces the corresponding saturated β-lactam (V) which shows n.m.r. and infrared absorption in agreement with this structure.

Of special interest is the constitutional relationship of the internal addition products I and IV as adducts of cyclobutadiene with the stable molecules carbon dioxide and methyl isocyanate. Removal of these stable species from I and IV would seem to provide an approach to the synthesis of the elusive cyclobutadiene, either as an isolable substance or as a metastable intermediate, and this project is now under study in these laboratories. The mass spectra of I and IV provide information which is worthy of note in this regard (Table I). The photoisomer of 2-pyrone shows (in addition to the parent mass peak) m/e peaks corresponding to fragments $C_4H_4O^+$, $C_3H_3^+$, and CHO^+. These same peaks appear in the mass spectrum of furan[9] with about the same relative intensity, which suggests a pathway for fragmentation of I. Only a weak peak

(1) The irradiations were conducted using an internal water-cooled mercury arc lamp (Hanovia, Type L, 450-w.) with a Corex glass filter to eliminate wave lengths below 250 mμ. 2-Pyrone shows a maximum in the ultraviolet at 291 mμ (ϵ 7500) in ethanol. The temperature of the reaction mixture was maintained at −10 to −20° by external cooling, and the average time required for completion of the reaction was 15 hr.

(2) 2-Pyrone was prepared by pyrolysis of coumalic acid according to a procedure furnished by H. E. Zimmerman, G. L. Grunewald, and R. M. Paufler, *J. Am. Chem. Soc.*, **82**, 1514 (1960).

(3) Mass spectra were obtained using a Consolidated 21-103 C instrument.

(4) Measurements in carbon tetrachloride solution at 60 Mc., with chemical shifts given in p.p.m. downfield from tetramethylsilane as internal reference (δ).

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(6) Identified by infrared comparison with an authentic sample and conversion to the crystalline p-phenylphenacyl derivative.

(7) M. S. Newman, *J. Org. Chem.*, **26**, 2630 (1961).

(8) N-Methyl-2-pyridone in ether shows absorption maxima at 233, 238, 306, 317, and 332 mμ (ϵ 5000, 3800, 4000, 3750, 1700).

(9) Catalog of Mass Spectral Data, Vol. 2, No. 508, American Petroleum Institute, Project 44.

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.

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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.

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(6) Alfred P. Sloan Foundation Fellow.

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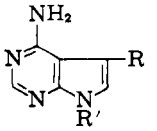
Synthesis of 4-Amino-5-cyanopyrrolo[2,3-*d*]pyrimidine, the Aglycone of Toyocamycin[1]

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.

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