pyrazolidine is absorbed rapidly[7] from the gastrointestinal tract one can assume that this is due to the enolizable methine group that is lacking in the six-membered homologs and in the succinic dihydrazides.

Experimental[8,9]

α-(*n*-Propyl)-succinyl Chloride.—α-(*n*-Propyl)-succinic acid[10] (57 g., 0.36 mole) was placed in a three-necked flask with a stirrer, reflux condenser and a wide rubber tubing connected to an erlenmeyer flask containing phosphorus pentachloride (150 g., 0.71 mole). The phosphorus pentachloride was added slowly to the stirred acid and when the addition was complete the reaction mixture was warmed until all the solid acid was dissolved. The mixture then was distilled under water-pump vacuum through a 10-inch helix-packed column giving α-(*n*-propyl)-succinyl chloride, boiling at 102–106° at 15 mm., yield 37 g. (53%).

Anal. Calcd. for $C_7H_{10}O_2Cl_2$: C, 42.66; H, 5.11. Found: C, 42.80; H, 5.29.

α-(*n*-Butyl)-succinyl Chloride.—By a procedure similar to the above α-(*n*-butyl)-succinic acid[11] was converted to α-(*n*-butyl)-succinyl chloride, boiling at 118° at 14 mm., yield 45%.

Anal. Calcd. for $C_8H_{12}O_2Cl_2$: C, 45.51; H, 5.73. Found: C, 45.39; H, 5.62.

1,2-Diphenyl-4-methyl-3,6-diketohexahydropyridazine.—In a three-necked flask fitted with a stirrer, reflux condenser and dropping funnel there was placed hydrazobenzene (9.2 g., 0.05 mole), pyridine (10 ml.) and dry benzene (150 ml.); in the dropping funnel there was placed α-methylsuccinyl chloride[12] (8.4 g., 0.05 mole) dissolved in dry benzene (50 ml.). The acid chloride was dripped into the hydrazobenzene solution over a half-hour period at room temperature and then the mixture was heated at reflux for one hour. The cooled reaction mixture was shaken with an excess of 1 *N* hydrochloric acid to remove pyridine and the organic layer was separated and stripped of solvent under vacuum. The solid residue was crystallized from ethanol, yielding a material melting at 183–184°, yield 6.0 g. (43%).

Anal. Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.83; H, 5.75; N, 10.00. Found: C, 72.96; H, 5.91; N, 10.10.

1,2-Diphenyl-4-ethyl-3,6-diketohexahydropyridazine.—By a procedure similar to that used above, α-ethylsuccinyl chloride[13] was converted to 1,2-diphenyl-4-ethyl-3,6-diketohexahydropyridazine, in 40% yield, melting at 144–144.5°.

Anal. Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.60; H, 6.29; N, 9.56.

1,2-Diphenyl-4-(*n*-propyl)-3,6-diketohexahydropyridazine and α-(*n*-Propyl)-N,N′,N″,N‴-tetraphenylsuccinic Dihydrazide.—In a three-necked flask fitted with a stirrer, reflux condenser and a dropping funnel there was placed hydrazobenzene (25.3 g., 0.137 mole), pyridine (29 ml.) and dry ether (400 ml.) and in the dropping funnel there was placed α-(*n*-propyl)-succinyl chloride (27 g., 0.137 mole). The acid chloride was added slowly to the hydrazobenzene solution at room temperature and the resulting mixture was heated at reflux for two hours. The reaction mixture was cooled and shaken with excess of 1 *N* hydrochloric acid. The organic layer was evaporated to dryness and the solid residue was taken up in hot ethanol. On cooling, there were obtained crystals which weighed 6.5 g. (16%) and melted at 122.5–124.5°. A small sample, recrystallized from ethanol for analysis, melted at 126–127°.

Anal. Calcd. for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N, 9.09. Found: C, 74.18; H, 6.50; N, 9.10.

The mother liquor from the above crystals yielded a second crop of crystals weighing 7.5 g. (22%) and melting at 170–173°. A small sample was recrystallized from ethanol for analysis.

Anal. Calcd. for $C_{31}H_{32}N_4O_2$: C, 75.58; H, 6.55; N, 11.37. Found: C, 75.09; H, 6.52; N, 11.37.

α-(*n*-Butyl)-N,N′,N″,N‴-tetraphenylsuccinic Dihydrazide.—Following the same procedure used to prepare 1,2-diphenyl-4-methyl-3,6-diketohexahydropyridazine, α-(*n*-butyl)-succinyl chloride reacted with hydrazobenzene to give a 24% yield of material melting at 115–120°; this was recrystallized from ethanol to give a 16% yield of material melting at 122–124°; the material crystallized very slowly.

Anal. Calcd. for $C_{32}H_{34}N_4O_2$: C, 75.86; H, 6.76; N, 11.06. Found: C, 75.92; H, 6.83; N, 10.92.

WARNER–CHILCOTT RESEARCH LABORATORIES
113 WEST 18TH STREET
NEW YORK 11, N. Y.

(7) J. J. Burns, R. K. Rose, T. Chenkin, A. Goldman, A. Schubert and B. B. Brodie, *J. Pharmacol. Exptl. Therap.*, **109**, 346 (1953).

(8) All boiling points and melting points are uncorrected.

(9) Microanalyses were carried out by Miss Linda Einstein.

(10) G. Waltz, *Ann.*, **214**, 58 (1882).

(11) R. Fittig and A. Schmidt, *ibid.*, **256**, 105 (1889).

(12) E. Hjelt, *Ber.*, **16**, 2624 (1883).

(13) E. Carrière, *Ann. chim.*, [9] **17**, 60 (1922).

2,6-Di-*t*-butylbenzoquinone

BY S. J. METRO

RECEIVED AUGUST 18, 1954

During an evaluation of the antioxidant properties of 2,6-di-*t*-butyl-*p*-cresol in lubricating oils, a yellow crystalline substance, m.p. 65–66°, which was identified as 2,6-di-*t*-butylquinone, was formed in the condenser of the test apparatus after a few days. This substance has been shown to result from the action of 2,2′-azoisobutyronitrile on 2,4,6-tri-*t*-butylphenol in the presence of oxygen.[1] The quinone forms a mono-2,4-dinitrophenylhydrazone and like the 2,5-isomer[2,3] forms a monoöxime. Its ultraviolet spectrum resembles that of benzoquinone, but its maximum (256 mμ) occurs at longer wave lengths. It shows strong absorption at 6.0 μ in the infrared.[4]

A number of other oxidation products of 2,6-di-*t*-butyl-*p*-cresol, such as 3,5-di-*t*-butyl-*p*-hydroxybenzaldehyde,[1] 1,2-bis-(3,5-di-*t*-butyl-4-hydroxylphenyl)-ethane and 3,5,3′,5′-tetra-*t*-butylstilbene,4,4′-quinone have been reported.[5–8]

Experimental

2,6-Di-*t*-butyl-1,4-benzoquinone (I).—The apparatus used for the oxidation consisted of a glass tube 600 mm. long and 45 mm. in diameter. The tube had a water condenser which extended 100 mm. down into the tube. Three hundred ml. of a 0.4–0.8% solution of 2,6-di-*t*-butyl-*p*-cresol in lubricating oil was placed in the tube along with 60 ml. of water and a coil of copper–iron catalyst. Oxygen was bubbled through the solution at a rate of 3.5 ± 0.5 liters per hour while the temperature was maintained at 95 ± 0.5°. After two or three days approximately 100 mg. of II formed on the condenser, m.p. 65–66°, λ_{max} 256, ε 15,400.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.32; H, 9.10; O, 14.52; mol. wt., 220. Found: C, 76.61; H, 9.44; O, 14.43; mol. wt. (Rast), 219.

Monoöxime of 2,6-Di-*t*-butyl-1,4-benzoquinone.—Fifty mg. of 2,6-di-*t*-butyl-1,4-benzoquinone, 50 mg. of hydroxylamine hydrochloride, 3 ml. of pyridine and 5 ml. of absolute alcohol were refluxed for one hour on a steam-bath. The solvents were removed by evaporation in a current of nitro-

(1) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 3211 (1953).

(2) A. Gurewitsch, *Ber.*, **32**, 2424 (1899).

(3) E. Boedtker, *Bull. soc. chim.*, [3] **31**, 965 (1904).

(4) The infrared spectrum referred to in this paper has been deposited as Document number 4450 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints, or $1.25 for 35 mm. microfilm payable to Chief, Photoduplication Service, Library of Congress.

(5) T. W. Campbell and G. M. Coppinger, THIS JOURNAL, **74**, 1469 1952).

(6) C. D. Cook, *J. Org. Chem.*, **18**, 261 (1952).

(7) S. L. Cosgrove and W. A. Waters, *J. Chem. Soc.*, 388 (1951).

(8) G. R. Yohe, THIS JOURNAL, **75**, 2688 (1953).

gen under a hood. The pale yellow product was recrystallized from an ethanol–water mixture; m.p. 219–220°.

Anal. Calcd. for $C_{14}H_{21}O_2N_1$: O, 13.60; N, 5.95. Found: O, 13.43; N, 5.39.

2,4-Dinitrophenylhydrazone of 2,6-Di-*t*-butyl-1,4-benzoquinone.—Fifty mg. of I was dissolved in 10 ml. of 95% alcohol and to this solution was added 2 ml. of a freshly prepared sulfuric acid solution of 2,4-dinitrophenylhydrazine in alcohol. The red precipitate separated almost immediately and after recrystallization had m.p. 198–200°.

Anal. Calcd. for $C_{20}H_{24}O_5N_4$: C, 59.98; H, 6.04; N, 13.99; O, 19.98. Found: C, 60.79; H, 6.30; N, 13.90; O, 19.42.

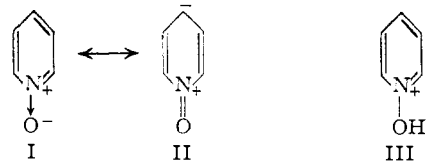
ESSO RESEARCH CENTER
P. O. BOX 51
LINDEN, NEW JERSEY

The Sulfonation of Pyridine-N-Oxide[1]

BY HARRY S. MOSHER AND FRANK J. WELCH

RECEIVED DECEMBER 27, 1954

Although pyridine undergoes nitration with considerable difficulty to give 3-nitropyridine,[2,3] pyridine-N-oxide (I) reacts with comparative ease to give a product substituted in the 4-position.[4–6] Ochiai[4,5] has attributed the susceptibility to nitration of the 4-position of the pyridine-N-oxide ring to the contribution of the resonance structure II to the activated state of the molecule. Linton[7] has shown by comparing the dipole moments of several tertiary amine-N-oxides that structures of the type II which increase the electron densities at the 2- and 4-positions of the ring are important to the activated state of the pyridine-N-oxide molecule. If the resonance structure II is responsible



I II III

for the location of the entering nitro group, it is to be expected that other electrophilic reagents as well will attack pyridine-N-oxide in the 4-position. However, there has been no report in the literature of the substitution of pyridine-N-oxide by electrophilic reagents other than in the case of the nitration reaction.[8] Formulas I and II, however, are an oversimplification of the states of the molecule under the conditions of the reaction since the nitration is conducted in sulfuric acid solution in which the pyridine-N-oxide must exist primarily as the salt form, III. This form, because of its positive charge, can hardly be readily susceptible to electrophilic attack. Thus if II is in reality the form of pyridine-N-oxide responsible for its ready nitration, then it must be formed from III on the approach of the nitronium ion with the simultaneous expulsion of a proton. Because of these considerations, an investigation of the action of other electrophilic reagents on this compound was undertaken.

The sulfonation of aromatic nuclei by fuming sulfuric acid is established as an electrophilic substitution.[9] When the conditions necessary for the sulfonation of pyridine-N-oxide were investigated, it was found that pyridine-N-oxide gave 3-pyridine-N-oxidesulfonic acid when treated with 20% fuming sulfuric acid in the presence of mercuric sulfate at 220–240°.[10] The structure of the product was determined by reducing it to 3-pyridinesulfonic acid and comparing this material with an authentic sample prepared by the sulfonation of pyridine. When the sulfonation was attempted at a temperature of 150° using the same reactants, no sulfonated product was isolated and 60% of the pyridine-N-oxide was recovered as the picrate. When the reaction was carried out at 220–240° in the absence of the mercuric sulfate, no sulfonated product was obtained. The conditions under which the sulfonation of pyridine-N-oxide was successful were the same as those necessary for the sulfonation of pyridine[11] and in both cases the 3-substituted derivative was obtained.

The action of several other electrophilic reagents on pyridine-N-oxide or on a suitably substituted pyridine-N-oxide was investigated, but in every case under the conditions employed no substituted product was isolated. Thus after treatment of pyridine-N-oxide with bromine at 110° in the presence of iron powder, the starting material was recovered as the picrate and no substitution product was isolated. Chlorosulfonation at 100° also failed to give a substituted product and 90% of the starting material was recovered as the picrate. The treatment of 3-methoxypyridine-N-oxide with *p*-nitrobenzoyl chloride and anhydrous aluminum chloride in refluxing carbon disulfide or in nitrobenzene at 90° was unsuccessful. Previous experiments[12] had shown that pyridine-N-oxide failed to undergo substitution with benzoyl chloride and aluminum chloride in nitrobenzene solvent at 190°; 75% of the pyridine-N-oxide was recovered as the picrate. Treatment of 3-hydroxypyridine-N-oxide with diazotized picramide failed to give a coupling product.

The results of these experiments seem to indicate that with the exception of nitration, pyridine-N-oxide is as resistant to electrophilic substitution as pyridine itself. The relative inertness of pyridine-N-oxide to electrophilic substitution is to be expected since the compound is basic and must exist

(1) Abstracted from the M.S. Thesis of Frank J. Welch, Stanford University, 1952.

(2) F. Friedl, *Ber.*, **45**, 428 (1912).

(3) A. Kirpal and E. Reiter, *ibid.*, **58**, 699 (1925).

(4) E. Ochiai and M. Ishikawa, *Proc. Imp. Acad.* (*Tokyo*), **18**, 561 (1942).

(5) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

(6) H. J. Den Hertog and J. Overhoff, *Rec. trav. chim.*, **69**, 468 (1950).

(7) E. P. Linton, THIS JOURNAL, **62**, 1945 (1940).

(8) Substitution does occur with sulfuryl chloride, but this presumably is not a simple electrophilic substitution reaction (B. Bobranski, L. Kochanska and A. Kowalewska, *Ber.*, **71**, 2385 (1938)). Since this investigation was completed, the mercuration of pyridine N-oxide in the 4-position has been reported by T. Ukai, Y. Yamamoto and S. Hirano, *J. Pharm. Soc. Japan*, **73**, 821 (1953); *C. A.*, **48**, 9946 (1954).

(9) C. M. Suter and A. W. Weston, "Organic Reactions," Vol. III, 1946, p. 142.

(10) Dr. T. Cislak in a private communication has reported that similar results have been obtained in the laboratories of Reilly Tar and Chemical Co.

(11) S. M. McElvain and M. A. Goese, THIS JOURNAL, **65**, 2233 (1943).

(12) These experiments were performed by Mr. Allen Carlsmith.