

The mechanism of the reaction is not known at present, but the following observations have been made. (1) The order of reactivity of the alkyllithium reagents for alkylation is tertiary > secondary > primary. This corresponds to presently accepted ideas concerning the reactivity of alkyl carbanions and also to the observations of Bartlett and co-workers⁷ on the addition of alkyllithium reagents to simple olefins. (2) Monoalkylation of naphthalene by *t*-butyllithium occurs at least 95% in the 1-position. Further alkylation appears to occur at the 3, 6 or 7 position. (3) Hydrogen is present in significant amounts in the gases evolved during hydrolysis of the reaction mixture.

A representative reaction was conducted as follows. The pentane in a commercial⁸ solution of *t*-butyllithium (0.11 mole) was replaced by decalin. To this was added naphthalene (0.11 mole), and the homogeneous mixture was heated at 165° for 41 hr.⁹ After hydrolysis, the organic products were separated by fractional distillation to give 5.69 g. of *t*-butylnaphthalene and 6.81 g. of a mixture of di-*t*-butylnaphthalenes. These represent 30 and 50% yields, respectively, based on *t*-butyllithium.

The n.m.r. spectrum of the presumed *t*-butylnaphthalene showed an aliphatic hydrogen singlet at 8.60 τ and an aromatic hydrogen multiplet at 1.70 to 3.15 τ . The ratio of the areas was 1.3 to 1.0. The calculated ratio for *t*-butylnaphthalene is 1.3 to 1.0.

The infrared spectrum had strong absorptions at 1395 cm^{-1} , 795 cm^{-1} and 767 cm^{-1} characteristic of alpha-substituted naphthalenes.¹⁰

Anal. Calcd. for $\text{C}_{14}\text{H}_{16}$: C, 91.25; H, 8.75. Found: C, 91.02; H, 8.99.

The n.m.r. spectrum of the mixture of presumed di-*t*-butylnaphthalene isomers exhibited three- CH_3 singlets at 8.13, 8.44 and 8.67 τ and an aromatic multiplet at 1.80 to 3.05 τ . The areas under the aliphatic and aromatic peaks were in the ratio 3.0 to 1.0; calculated for dibutylnaphthalene: 3.0 to 1.0.

Anal. Calcd. for $\text{C}_{18}\text{H}_{24}$: C, 89.94; H, 10.06. Found: C, 90.10; H, 10.15.

Research on the scope and limitations, optimum reaction conditions and mechanism of this reaction is being continued actively.

Acknowledgment.—The generous support of the American Petroleum Institute is gratefully acknowledged.

(8) Lithium Corporation of America.

(9) Later experiments indicate that the reaction probably is completed in a much shorter time.

(10) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 78.

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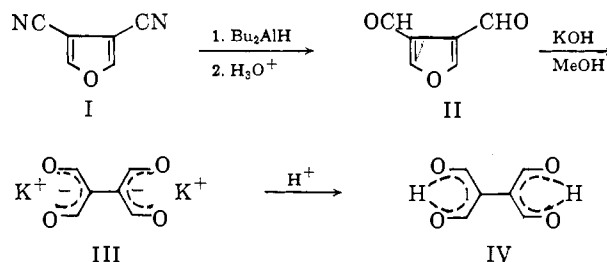
1,1,2,2-ETHANETETRACARBOXALDEHYDE
BY THE OPENING OF A FURAN RING WITH
HYDROXIDE ION

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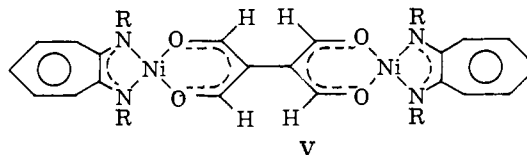
The furan ring system is normally stable toward base and labile to acid.¹ A dramatic reversal of this generalization was found in the case of 3,4-furandicarboxaldehyde (II). This compound (which may be regarded as the anhydride of 1,1,2,2-ethanetetracarboxaldehyde

(1) Under drastic conditions 2-phenyl-4-benzoylfuran was reported to be cleaved by KOH: R. C. Fuson, C. L. Fleming and R. Johnson, *J. Am. Chem. Soc.*, **60**, 1994 (1938). On the other hand, diethyl 3,4-furandicarboxylate was rapidly saponified by alcoholic KOH, the furan ring remaining intact: T. Reichstein, A. Grüssner, K. Schindler and E. Hardmeier, *Helv. Chim. Acta*, **16**, 276 (1933).

(IV)) reacted exothermally with hydroxide ion yielding the salt of IV, of interest as the simplest bifunctional 1,3-dicarbonyl chelating system suitable for the preparation of chelate polymers,² and as the only compound of this type where coplanarity with resultant electronic interaction between the quasiaromatic³ ring systems is feasible. The synthesis of IV by another route has been reported recently.⁴



Reduction of 3,4-furandicarbonitrile⁵ (I) with diisobutylaluminum hydride, followed by hydrolysis, afforded 3,4-furandicarboxaldehyde (II), m.p. 77–78° in about 50% yield ($\text{C}_6\text{H}_4\text{O}_3$: C, 58.1; H, 3.25; mol. wt. 124. Found: C, 58.5; H, 3.52; mol. wt. 129); its n.m.r. spectrum has two equal singlets at 1.88 (α -H) and -0.15 τ ($-\text{CHO}$). Treatment of II with freshly prepared methanolic KOH gave the salt III (ultraviolet: $\lambda_{\text{max}}^{\text{H}_2\text{O}}$ 270 $\text{m}\mu$, ϵ 39,800) which on acidification yielded IV, ($\text{C}_6\text{H}_6\text{O}_4$: C, 50.7; H, 4.26. Found: C, 50.8; H, 4.08). Its infrared shows broad absorption in the 1800–2800- cm^{-1} region, along with the expected broad band at 1560 cm^{-1} . The compound is sublimable and melts around 190°, being dehydrated,⁶ mainly to II and to polymeric products. Its saturated solution has a pH of 2.35. Salts of IV undergo a two-electron oxidation by bromine, iodine, ferric and mercuric ions, and readily form polymeric chelates with most transition metal ions. Mixed chelates of the type V were also prepared. For instance V (R = C_6H_5) was obtained as bronze-colored plates, m.p. 236–237° ($\text{C}_{32}\text{H}_{42}\text{N}_4\text{O}_4\text{Ni}_2$: C, 57.9; H, 6.33; N, 8.44; mol. wt. 663. Found: C, 57.2; H, 6.17; N, 8.35; mol. wt. 650).



The facile opening of a furan ring by alkali appears to be general (additional examples thereof will be reported later), and of synthetic utility for furans substituted in the 3 and 4 positions with electron-delocalizing, yet base-resistant groups. The driving force for this reaction is provided by the formation of a resonance-stabilized dianion, such as III.

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(3) (a) J. P. Collman, R. A. Moss, H. Maltz and C. C. Heindel, *J. Am. Chem. Soc.*, **83**, 531 (1961); (b) J. P. Collman and E. T. Kittleman, *ibid.*, **83**, 3529 (1961); (c) R. H. Holm and F. A. Cotton, *ibid.*, **80**, 5658 (1958); (d) M. Calvin and K. W. Wilson, *ibid.*, **67**, 2003 (1945).

(4) Z. Arnold, *Collection Czech. Chem. Commun.*, **27**, 2993 (1962).

(5) C. D. Weiss, *J. Org. Chem.*, **27**, 3514 (1962).

(6) Surprisingly, Arnold⁴ reports IV not to melt up to 250°.