Related Thermal Data.—Table III lists the heats, entropies and free energies of formation at 298.16° K. of the two silicates from the elements and from the oxides. The entropy values are derived from the compilation of Kelley[13] and the work of Humphrey, King and Kelley,[14] and Todd and Bonnickson.[15]

---

(13) K. K. Kelley, U. S. Bureau of Mines Bull. 477 (1950).

(14) G. L. Humphrey, E. G. King and K. K. Kelley, U. S. Bureau of Mines, Report of Investigations 4870 (June, 1952).

(15) S. S. Todd and K. R. Bonnickson, This Journal, **73**, 3894 (1951).

BERKELEY 4, CALIFORNIA

NOTES

The Effect of Sodium Oxide on the Chromium Oxide Catalyzed Conversion of Aldehydes to Ketones[1]

By J. R. Coley[2] and V. I. Komarewsky

Received March 1, 1952

In the course of a study[3] of the action of metallic oxide catalysts on alcohols, it was found that alcohols and aldehydes of "n" carbon atoms undergo a complex dehydrogenation–condensation reaction when passed over a chromia catalyst at 400° to form ketones of "$2n - 1$" carbon atoms. It was noted that a sodium hydroxide precipitated catalyst was quite active in contrast to a comparatively inactive ammonia precipitated catalyst.

It has therefore been of interest to determine the effect of sodium content in a chromia catalyst upon this reaction.

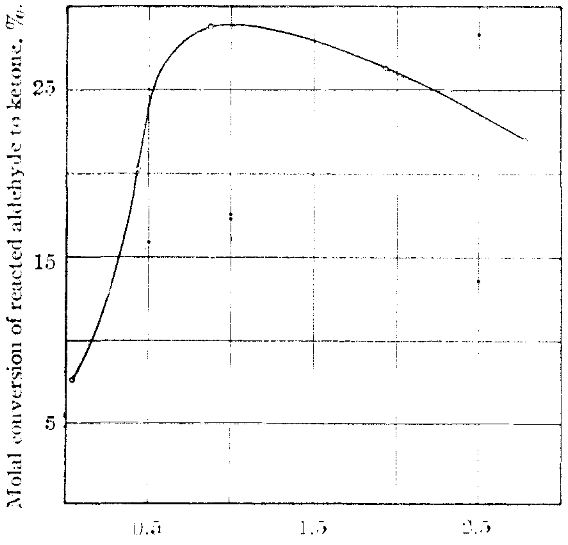


Fig. 1.—The effect of sodium oxide on the conversion of n-butyraldehyde to di-n-propyl ketone.

Experimental Part

Procedure.—The catalysts were prepared by redissolving a cold slurry of chromium hydroxide precipitate in cold excess sodium hydroxide. The chromite solution on standing overnight formed a chromium hydroxide gel. The gel was washed anion free, dried at 110°, screened to 8 mesh and heated in an atmosphere of hydrogen at gradually increased temperatures up to 500°. To vary the sodium content, portions of the catalyst, after washing but prior to drying, were agitated in sodium carbonate solutions of varying concentrations, filtered and dried. The method of sodium analysis was a modification of the triple acetate procedure devised by Kahane.[4]

The catalytic reaction procedure consisted of passing a three to one mixture of nitrogen and vaporized n-butyraldehyde over a granular (8–10 mesh) catalyst bed (volume 50 cc.), maintained at a temperature of 400° by an electrically heated furnace. A constant liquid space velocity of 0.1 was used for all runs. All products were distilled in a 20-inch super-cal Heli Grid Podbielniak Column.

Discussion of Results

The results obtained are given in Table I and Fig. 1.

TABLE I

DATA ON SODIUM CONTENT OF CHROMIA CATALYSTS *versus* YIELD OF KETONE

Weight % sodium	Molal conversion of reacted aldehyde to ketone,[a] %
0.04	7.6
.45	20.3
.88	28.8
1.93	26.3
2.79	22.1

[a] Dipropyl ketone, b.p. 144.18°.

These results indicate that the sodium content of a chromia catalyst has a definite effect on the catalytic activity for the dehydrogenation–condensation reaction discussed. This is consistent with the aldol mechanism proposed[3] for this ketone synthesis. The optimum sodium content was found to be approximately 1.0%.

---

(1) From the Senior Problems of B. M. Joseph and S. C. Mikszta.

(2) Research Dept., Standard Oil Co. (Indiana), Whiting, Indiana.

(3) V. I. Komarewsky and J. R. Coley, This Journal, **63**, 700 3269 (1941).

(4) E. Kahane, *Bull. soc. chim.*, **47**, 382 (1930).

DEPARTMENT OF CHEMICAL ENGINEERING
ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO, ILLINOIS

Preparation and Some Reactions of Indenyllithium

By Norman H. Cromwell and David B. Capps

Received March 24, 1952

In connection with a general project in this Laboratory concerned with the synthesis and reactions of cyclic ketones, methods of preparing β-(1-indanyl)-propionic acid have been under investigation. This acid had previously been prepared by v. Braun and co-workers[1] in a several step, side-chain building process starting with 1-indanone. It seemed desirable to develop a synthesis involving a readily prepared metallic derivative of the inexpensive indene. Although indenyllithium had been prepared previously[2] from indene using ethyllithium and diethylmercury, it seemed advisable to avoid this latter expensive and poisonous reagent.

Using a procedure similar to that employed in the synthesis of 9-fluorenyllithium and fluorene-9-carboxylic acid,[3] we have obtained indenyllithium and indene-1-(or 3)-carboxylic acid in good yields from the reaction of butyllithium with indene, followed by treatment with solid carbon dioxide.

Indenyllithium was found to react with ethyl β-bromopropionate to give a low (14%) yield of ethyl β-[1(or 3)-indenyl]-propionate. The major reaction probably involved the loss of hydrogen bromide from the β-bromo ester. The ester product on hydrolysis gave β-[1(or 3)-indenyl]-propionic acid which was readily hydrogenated to the β-[1-indanyl]-propionic acid.

Experimental

Indenyllithium and Indene-1(or 3)-carboxylic Acid.—Approximately 0.2 mole of *n*-butyllithium was prepared in 150 ml. of dry ether by the procedure of Gilman, *et al.*[4] To this solution 21.8 g. (0.188 mole) of indene (Eastman Kodak Co. Practical grade) was added over a period of 30 minutes with the evolution of butane. The rust colored mixture was refluxed for two hours and then poured in a thin stream onto solid carbon dioxide. One liter of water was cautiously added to the lithium-free ether mixture. The basic aqueous layer was acidified with hydrochloric acid to give 20.1 g. of indene-1(or 3)-carboxylic acid which was recrystallized from benzene, m.p. 159–160°; neut. equiv., calcd. 160.2, found 160 and 158.7.[5]

This experiment indicated that at least 67% of the indene had been converted into its lithium derivative.

β-[1(or 3)-Indenyl]-propionic Acid.—A solution of indenyllithium, prepared as in the previous experiment, was transferred through a glass wool filter into a nitrogen swept separatory funnel and added slowly in 30 minutes to a 160 ml. of dry ether solution of 34 g. (0.187 mole) of ethyl β-bromopropionate cooled to 3–5°. After the addition was complete the reaction mixture was allowed to stand at room temperature for 12 hours. The cooled solution was mixed with ice and ammonium chloride and the ether layer distilled to give 7.6 g. of the crude ethyl β-[1(or 3)-indenyl]-propionate, b.p. 155–163° (15 mm.). Hydrolysis of this ester with 20% sodium hydroxide produced 5.3 g. (14.7% yield based on the bromo ester) of β-[1(or 3)-indenyl]-propionic acid. Recrystallization from aqueous alcohol and then benzene gave colorless crystals, m.p. 129–130°.[6] Aqueous alkaline solutions of this unsaturated acid decolorized potassium permanganate instantly while aqueous acetone solutions gave a slower decolorization at 25°.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43; neut. equiv., 188.2. Found: C, 76.84; H, 6.38; neut. equiv., 188.5 and 190.2.

β-[1-Indanyl]-propionic Acid.—A sample of β-[1(or 3)-indenyl]-propionic acid (1.95 g.) in absolute alcohol was hydrogenated in the presence of palladinized charcoal under three atmospheres of hydrogen for seven hours. Isolation produced 1.45 g. of the crude acid, m.p. 45–48.5°. Recrystallization from petroleum ether gave a purer product, m.p. 49.5–51°.[1]

AVERY LABORATORY
UNIVERSITY OF NEBRASKA
LINCOLN, NEBRASKA

---

(1) (a) J. v. Braun and J. Reutter, *Ber.*, **59B**, 1922 (1926); (b) J. v. Braun and E. Danzinger and Z. Koehler, *ibid.*, **50**, 56 (1917).

(2) (a) W. Schlenk and E. Bergmann, *Ann.*, **463**, 227 (1928); (b) O. Blum-Bergmann, *ibid.*, **484**, 28 (1931).

(3) R. R. Burtner and J. W. Cusic, THIS JOURNAL, **65**, 264 (1943).

(4) H. Gilman, *et al.*, *ibid.*, **71**, 1499 (1949).

(5) W. S. Knowles, J. A. Kuck and R. C. Elderfield, *J. Org. Chem.*, **7**, 377 (1942). No evidence seems to be available to establish the location of the carboxy group with respect to the five-ring double bond. It seems probable that the correct structure is indene-3-carboxylic acid with C=O conjugated with the C=C bond.

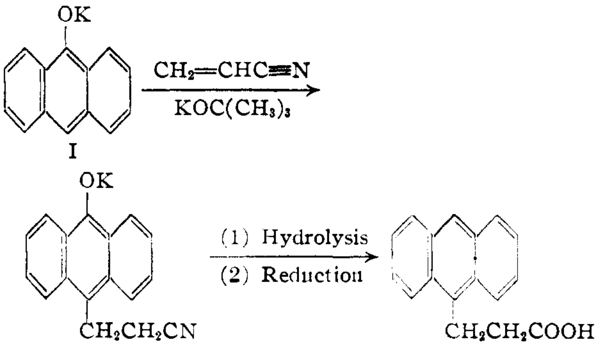
(6) Since completing our work we have noticed that G. R. Clemo *et al.*, *J. Chem. Soc.*, 863 (1951), have reported the preparation of β-[3-indenyl]-propionic acid, m.p. 120.5–121.5°, by four methods two of which start with indene and two starting with 1-indanone, all of which gave rather low yields. In spite of the difference in melting points we believe that our acid is essentially the same as that of Professor Clemo.

The Monocyanoethylation of Anthrone. An Improved Synthesis of β-(9-Anthranyl)-propionic Acid and β-(9,10-Dihydro-9-anthranyl)-propionic Acid[1]

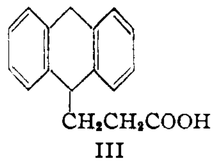
BY GUIDO H. DAUB AND W. CARTER DOYLE

RECEIVED APRIL 21, 1952

The cyanoethylation of anthrone as previously carried out by Bruson[2] gave 9,9-di-(β-cyanoethyl)-anthrone in 88% yield. Since it has been shown that certain phenols can be monocyanoethylated in excellent yield on a ring carbon[3] it was thought that anthrone as its potassium enolate salt could be monocyanoethylated in the 10-position. This has been carried out in excellent yield by allowing potassium anthranolate (I) to react with acrylonitrile in *t*-butyl alcohol using potassium *t*-butoxide as the condensing agent. The product was not isolated but was hydrolyzed and reduced with zinc dust in ammonium hydroxide to β-(9-anthranyl)-propionic acid (II) which was obtained in over-all yield of 90–95% from anthrone.



Reduction of the β-(9-anthranyl)-propionic acid (II) with sodium in *n*-amyl alcohol gave an 86% yield of β-(9,10-dihydro-9-anthranyl)-propionic acid (III). This synthesis of the dihydro acid (III) in 77.6% over-all yield from anthrone represents considerable improvement over its three-step syn-



III

---

(1) This work was supported in part by a grant from the National Cancer Institute, U. S. Public Health Service.

(2) H. A. Bruson, THIS JOURNAL, **64**, 2457 (1942).

(3) H. A. Bruson, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 94.