

λ_{\max} 215¹⁰ and 227 $\mu\mu$,¹¹ respectively, whereas crotonic acid has λ_{\max} 208 $\mu\mu$.¹²

The absorption of α,β -unsaturated nitriles (Table II) is also very similar to that of the corresponding acids. Braude¹³ reported that 1-cyanocyclohexene had λ_{\max} 230 (ϵ 1,600) and 261 $\mu\mu$ (ϵ 60). These values seem most unlikely for a simple chromophore consisting of two unsaturated groups in conjugation. Frank, Berry and Shotwell¹⁴ reported that 1-cyano-4-isopropylcyclohexene has λ_{\max} 212 (ϵ 8,900) and 271 $\mu\mu$ (ϵ 102). The first maximum agrees with that found in the present work for 1-cyanocyclohexene (I, $n = 4$, R = CN) but a second maximum was not detected. The cyanoisopropylcyclohexene probably contained some aromatic¹⁵ impurities, since it was prepared by a pyrolytic method.

Experimental

The samples of acids and nitriles were those prepared in part III.^{1b}

The acid amides were prepared by heating the acids under reflux with excess thionyl chloride for 0.5 hours, distilling

(10) K. Bowden, E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946).

(11) L. Crombie, *ibid.*, 2997 (1952).

(12) I. I. Rusoff, J. R. Platt, H. B. Klevens and G. O. Burr, *THIS JOURNAL*, 67, 678 (1945).

(13) E. A. Braude, *Ann. Rept. Chem. Soc.*, 42, 105 (1945).

(14) R. L. Frank, R. E. Berry and O. L. Shotwell, *THIS JOURNAL*, 71, 3889 (1949).

(15) Phenyl cyanide has λ_{\max} ca. 270 $\mu\mu$; G. Scheibe, *Ber.*, 59, 2617 (1926).

off the unreacted thionyl chloride, and adding the crude acid chloride carefully to excess ammoniacal ether solution. The amides were recrystallized from water or aqueous methanol.

β,β' -Dimethylacrylamide had m.p. 109° (lit. m.p. 110°¹⁶); tiglamide, m.p. 78° (lit. m.p. 77°¹⁷); cyclopentenylcarboxamide, m.p. 204° (lit. m.p. 205°^{18a}); cyclohexenylcarboxamide, m.p. 135° (lit. m.p. 136°^{18b}) and cycloheptenylcarboxamide, m.p. 158° (lit. m.p. 157°^{18b}). The ultraviolet light absorption determinations were carried out using freshly prepared solutions in 95% ethanol, with a Beckman DU spectrophotometer. The alcohol was purified by distilling from zinc dust, and had good transmission to 205 $\mu\mu$. The determinations were carried out in duplicate or triplicate, and no departure from Beer's law was observed. The error in wave length was ± 500 . The results⁹ for the cycloalkenyl acids are in better agreement with those of Ungnade and Ortega²⁰ than those of Braude and co-workers.

Acknowledgment.—This work was supported by grants from the Rockefeller Foundation, New York.

(16) R. Kuhn, F. Kohler and L. Kohler, *Z. physiol. Chem.*, 247, 197 (1937).

(17) H. Sutter, F. Rottmayrand and H. Porsch, *Ann.*, 521, 189 (1936).

(18) (a) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 1755 (1951); (b) *ibid.*, 2202 (1953); (c) E. A. Braude and J. A. Coles, *ibid.*, 2014 (1950).

(19) The discrepancy may be due to the fact that with the Hilger spectrophotometer the use of too large optical density intervals can give spurious "maxima"; E. A. Braude quoted by J. K. L. H. Allan, E. R. H. Jones and M. C. Whithing, *J. Chem. Soc.*, 1862 (1955). This cannot occur with photoelectric instruments, which were used by Ungnade and Ortega, and in the present work.

(20) H. E. Ungnade and I. Ortega, *THIS JOURNAL*, 73, 1564 (1951). MEXICO 20, D.F.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF STANFORD UNIVERSITY]

The Stereochemistry of Raney Nickel Action. VI. Functional Group Hydrogenolyses in the α -Substituted α -Phenylpropionic Acid Series

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Optically active methyl and ethyl 2-phenyl-2-hydroxypropionates were dehydroxylated to optically active 2-phenylpropionates by action of Raney nickel in refluxing ethanol. The reaction occurred with predominant configurational retention, but with not quite as high stereospecificity as previously suggested. Methyl *D*(+)-2-phenyl-2-methoxypropionate was demethoxylated under similar conditions to methyl *D*(+)-2-phenylpropionate, again with substantial retention of configuration. Ethyl (+)-2-phenyl-2-aminopropionate failed to suffer deamination, but underwent reduction to ethyl (+)-2-cyclohexyl-2-aminopropionate. Methyl 2-phenyl-2-formylaminopropionate failed to undergo any reaction whatever, suggesting that a free amino group is necessary for the observed facile ring reduction. 2-Chloro-2-phenylpropionamide was smoothly cleaved to 2-phenylpropionamide, providing a preliminary example of carbon-chlorine bond hydrogenolysis.

Previous investigations on the stereochemistry of Raney nickel catalyzed hydrogenolyses have indicated that phenylmercapto,¹ benzenesulfinyl,² benzenesulfonyl¹ and hydroxyl groups³ are removed from the α -position of the 2-phenylpropionamide skeleton by the hydrogen adsorbed on Raney nickel⁴ with varying stereochemical consequences. Thus the former two functional groups suffer hydrogenolysis with complete racemization of the 2-phenylpropionamide moiety, whereas the benzenesulfonyl and hydroxyl groups are removed with substantial retention of optical activity in the adjacent asymmetric center. While the benzenesulfonyl group departs with apparent inversion of

the adjacent carbon atom, hydroxyl group removal results in retention of the starting configuration in the final product. In view of these divergent results it seemed pertinent to investigate other Raney nickel catalyzed functional group hydrogenolyses from, if possible, a stereochemical viewpoint. To this end we herein report new observations regarding hydrogenolyses of hydroxyl, alkoxy, amino and chlorine functions by the action of excess Raney nickel in refluxing ethanol.

It was previously stated³ that ethyl *D*(-)-2-phenyl-2-hydroxypropionate⁵ ($[\alpha]^{25D} - 20.0^\circ$, 87% optically pure) was dehydroxylated to produce ethyl *D*(+)-2-phenylpropionate, $[\alpha]^{25D} 45.5^\circ$ (ether), of over 90% optical purity, *i.e.*, with essentially no racemization. The latter figure was

(1) W. A. Bonner, *THIS JOURNAL*, 74, 1034 (1952).

(2) W. A. Bonner, *ibid.*, 74, 5089 (1952).

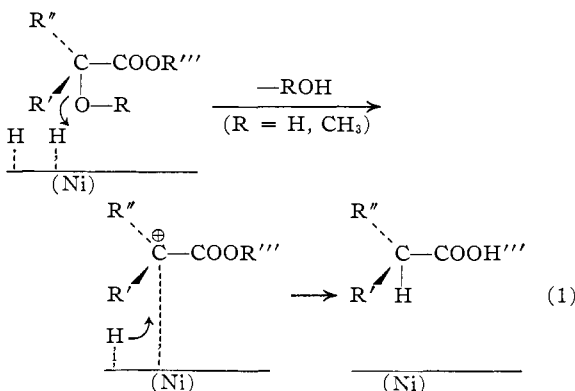
(3) W. A. Bonner, J. A. Zderic and G. A. Casaletto, *ibid.*, 74, 5086 (1952).

(4) W. A. Bonner, *ibid.*, 74, 1033 (1952).

(5) K. Freudenberg, J. Todd and R. Seidler, *Ann.*, 501, 199 (1933); E. Eliel and J. Freeman, *THIS JOURNAL*, 74, 923 (1952).

estimated from the value, $[\alpha]_D -51.0^\circ$ (ether), reported for ethyl L(-)-2-phenylpropionate by Levene.⁶ Unfortunately, Levene's rotation is not based on a completely resolved sample, as shown by the more recent report of Arcus and Kenyon.⁷ From the latter study it is possible to estimate a rotation of about 77° for optically pure ethyl D(+)-2-phenylpropionate, and to state that our previous product from the dehydroxylation of ethyl D(-)-2-phenyl-2-hydroxypropionate was actually only about 79% optically pure. Similarly, essentially completely resolved ethyl L(+)-2-phenyl-2-hydroxypropionate gave³ ethyl L(-)-2-phenylpropionate of 73% optical purity on treatment with Raney nickel for three hours. This product was reduced to 66% optical purity after further action of Raney nickel during 17 hours. The preparation of a sample of methyl D(+)-2-phenylpropionate of known optical purity now permits us to report also that the dehydroxylation of methyl D(-)-2-phenyl-2-hydroxypropionate occurred with 86% retention of optical configuration.³ The varying extent of racemization noted during the above reactions is at present unexplained and is under investigation.

Extension of our studies to hydrogenolytic dealkoxylations gave stereochemical results qualitatively similar to those observed during dehydroxylation. D(-)-2-Phenyl-2-hydroxypropionic acid was converted by repeated treatment with methyl iodide and silver oxide into methyl D(+)-2-phenyl-2-methoxypropionate. Treatment of the latter with Raney nickel in refluxing ethanol produced a sample of methyl D(+)-2-phenylpropionate 72% optically pure. Demethoxylation was complete after two hours reaction time, but appeared in complete after only 30 minutes, occurring with the same stereochemical consequences as dehydroxylation,³ namely, predominant retention of configuration. To explain this retention mechanistically, one may postulate either a stereospecifically adsorbed carbonium ion which abstracts a hydride ion from the catalyst surface from below its plane (1), or a concerted front side attack on the adsorbed



substrate by hydride ion. The racemization inherent in a free radical mechanism already has been discussed.^{1,8}

(6) P. A. Levene, L. A. Mikeska and K. Passoth, *J. Biol. Chem.*, **88**, 27 (1930).

(7) C. Arcus and J. Kenyon, *J. Chem. Soc.*, 916 (1939).

(8) H. Hauptmann and B. Wladislaw, *THIS JOURNAL*, **72**, 707, 711 (1950).

Attention was next turned to the stereochemistry of Raney nickel catalyzed deaminations, since Dahn has recently shown⁹ that certain substituted benzylamines undergo Raney nickel catalyzed replacement of the α -amino group by hydrogen. To this end 2-phenyl-2-aminopropionic acid was prepared¹⁰ and resolved¹¹ through its formyl derivative by the procedure of McKenzie and Clough. When ethyl (+)-2-phenyl-2-aminopropionate was treated with Raney nickel in refluxing ethanol under the usual conditions, no deamination was observed. Instead, ring reduction occurred producing ethyl (+)-2-cyclohexyl-2-aminopropionate. The latter compound was unambiguously characterized in the racemic series by its lithium aluminum hydride reduction to crystalline 2-cyclohexyl-2-aminopropanol, followed by cleavage of the latter with periodic acid to methyl cyclohexyl ketone and conversion of the ketone to solid derivatives. The facile reduction of ethyl 2-phenyl-2-aminopropionate to the cyclohexyl derivative finds some support in the work of Dahn,⁹ who reports that Raney nickel tends to reduce benzylamines, and contrasts to our earlier observations and those of Mozingo and co-workers¹² who comment upon the stability of aromatic rings under the reaction conditions employed. It is interesting to contrast the present behavior of Raney nickel with that of platinum catalyst, which failed to reduce ethyl 2-phenyl-2-aminopropionate during 48 hours at 25° and 4 atmospheres hydrogen pressure. Apparently the presence of a free amino group is essential to facile reduction of the aromatic nucleus, since methyl 2-phenyl-2-formylaminopropionate was recovered unchanged after treatment with Raney nickel under similar reaction conditions.

A preliminary study of carbon-chlorine bond hydrogenolysis has been undertaken using racemic 2-chloro-2-phenylpropionamide. Raney nickel under the usual conditions smoothly converts this substance into 2-phenylpropionamide, indicating that dechlorination of benzyl-type chlorides may occur under the same conditions as do desulfuration, dehydroxylation and dealkoxylation. Stereochemical investigations of catalytic dechlorination are presently in progress.

Experimental

Methyl 2-Phenyl-2-methoxypropionate.—The following preparation is an adaptation of the method of Freudenberg.⁵ A mixture of methyl iodide (20 ml.), silver oxide (6.00 g.) 2-phenyl-2-hydroxypropionic acid (4.00 g.), Drierite (5 g.) and glass beads (5 g.) was stirred vigorously under reflux during 24 hours, whereupon it was treated with anhydrous ether (20 ml.) and filtered. The filter cake was washed thrice with anhydrous ether, and the filtrate and washings were freed of solvent at reduced pressure. The infrared spectrum of the residual oil was examined, then the oil was re-treated in the above manner four additional times. Only after the fifth treatment did the hydroxyl band at 2.84μ completely disappear. The final oil, light yellow in color, was distilled at $68-71^\circ$ (1 mm.) to give 3.43 g. (73%) of colorless product, n_D^{20} 1.5029, d_4^{20} 1.081.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27; *MR*, 52.86. Found: C, 68.24, 68.39; H, 7.41, 7.52; *MR*, 53.04.

(9) H. Dahn and U. Solms, *Helv. Chim. Acta*, **35**, 1162 (1952).

(10) P. Levene and R. Steiger, *J. Biol. Chem.*, **76**, 308 (1928).

(11) A. McKenzie and G. Clough, *J. Chem. Soc.*, 101, 390 (1912).

(12) R. Mozingo, C. Spencer and K. Folkers, *THIS JOURNAL*, **66**, 1859 (1944).

Raney Nickel and Methyl 2-Phenyl-2-methoxypropionate.—One gram of the above ester and 6 g. of freshly prepared Raney nickel¹³ were heated in refluxing absolute ethanol (25 ml.) for a period of 25 minutes. The catalyst was filtered and rinsed with ethanol, and the solvent was removed at 100°, last traces at 1 mm. About 0.3 g. of clear oil was obtained, whose infrared spectrum was identical with that of methyl 2-phenylpropionate.

Methyl *D*(+)-2-Phenyl-2-methoxypropionate.—This material was prepared from *D*(-)-2-phenyl-2-hydroxypropionic acid (m.p. 114°, $[\alpha]_D^{25}$ -35.4° (*c* 3.5, abs. ether)) in the manner described above for the racemic modification. The final distilled oil had n_D^{20} 1.5023 and $[\alpha]_D^{22}$ 46.2° (neat). The literature⁶ reports $[\alpha]_D^{20}$ 51.6° (neat). On the basis of the acid used, the above material appears to be 97% optically pure.

Raney Nickel and Methyl *D*(+)-2-Phenyl-2-methoxypropionate.—The above optically active ester (1.42 g.) and Raney nickel (9 g.) were heated in refluxing ethanol (50 ml.) for two hours. Usual processing yielded 0.83 g. (69%) of oil, $[\alpha]_D^{25}$ 53.0° (*c* 5.5, ethanol), whose infrared spectrum coincided in all respects with that of methyl 2-phenylpropionate. When the reaction was duplicated during only a one-half hour reflux period, demethoxylation appeared incomplete in that several bands characteristic of the original methyl ether persisted in the infrared spectrum of the product.

***D*(+)-2-Phenylpropionic Acid and Derivatives.**—2-Phenylpropionic acid was resolved by the procedure of Arcus and Kenyon,⁷ giving a dextrorotatory enantiomer having $[\alpha]_D^{25}$ 67.8° (*c* 3.1, chloroform). These workers report $[\alpha]_D^{25}$ 74.8° (chloroform), but fail to record the temperature of measurement. Using their value as a maximum, the above resolved sample would be 96% optically pure.

A portion of the resolved acid was converted⁷ to *D*(+)-2-phenylpropionamide, $[\alpha]_D^{25}$ 57.9° (*c* 1.6, chloroform), m.p. 100.5°. Arcus and Kenyon report $[\alpha]_D^{25}$ 58.3° (chloroform, temp. unsp.) and m.p. 96–97° for this amide, and state that it may be recrystallized to m.p. 103–104°, giving no rotation for the higher melting sample.

A sample of the above resolved acid was converted to its methyl ester by action of diazomethane. The distilled reaction product had $n_D^{21.5}$ 1.4978, d_4^{25} 1.0409, $[\alpha]_D^{25}$ 108.7° (*c* 5.5, ethanol), $[\alpha]_D^{25}$ 92.4° (neat).

(+)-2-Phenyl-2-formylaminopropionic Acid.—2-Phenyl-2-aminopropionic acid was prepared from acetophenone, ammonium hydroxide and potassium cyanide by the method of Levene and Steiger,¹⁰ subl. pt. 269–271°. After unsuccessful attempts to resolve this acid directly using (+)-camphor-10-sulfonic acid, it was converted to its formyl derivative and the latter was resolved using quinine after the procedure of McKenzie and Clough.¹¹ The resolved product had m.p. 196–198° dec. and $[\alpha]_D^{25}$ 87.0° (*c* 3.3, ethanol); reported¹¹ m.p. 194–195°, $[\alpha]_D^{16}$ 91.9° (*c* 3.2, ethanol).

Methyl (+)-2-Phenyl-2-formylaminopropionate.—Approximately 0.25 g. of diazomethane was prepared in ether (100 ml.). The solution was added slowly to one of (+)-2-phenyl-2-formylaminopropionic acid (1.00 g.) in ethanol (15 ml.). The excess diazomethane was destroyed with a few drops of acetic acid, and the solvents were evaporated. The residue was recrystallized from a mixture of benzene and ligroin, giving 0.91 g. of product, m.p. 109–110°. Further recrystallization gave a sample m.p. 113.5–115°.

Anal. Calcd. for $C_{11}H_{13}O_3N$: C, 63.75; H, 6.32; N, 6.76. Found: C, 64.33, 64.37; H, 6.41, 6.50; N, 6.99, 7.16.

When a sample of this material was heated with Raney nickel in refluxing ethanol in the usual way, during a 6-hour period, it was recovered unchanged. Several recrystallizations of the crude product from a benzene–ligroin mixture gave platelets, m.p. 112–114°, $[\alpha]_D^{25}$ 25.3° (*c* 2.4, acetone), whose infrared spectrum was identical with that of the starting material.

Ethyl (+)-2-phenyl-2-aminopropionate was prepared by hydrolysis and esterification of (+)-2-phenyl-2-formylaminopropionic acid after the procedure of McKenzie and Myles.¹⁴ The resulting ester had b.p. 69–70° (0.1 mm.), n_D^{20} 1.5103, $[\alpha]_D^{25}$ 24.90 (*c* 2.61, abs. ethanol), α_D^{25} 5.48° (neat, *l* 0.5), in substantial agreement with the physical properties in the literature.¹⁴

Raney Nickel on Ethyl (+)-2-Phenyl-2-aminopropionate.—Two grams of the above ester, ca. 20 g. of Raney nickel and 50 ml. of absolute ethanol were heated under reflux for 5.25 hours. Customary processing gave 1.5 g. of colorless oil, b.p. 60–70° (0.5 mm.), n_D^{20} 1.4655. This was found to be almost completely soluble in 5% hydrochloric acid. The resulting acidic solution was extracted well with ether, made alkaline and re-extracted with ether. The latter extract yielded 1.07 g. of oil, b.p. 60–65° (0.5 mm.), $[\alpha]_D^{27}$ 18.66° (*c* 2.84, abs. ethanol), α_D^{27} 8.57 (neat, *l* 0.5). In contrast to methyl 2-phenylpropionate, the product was completely transparent in the 240–270 m μ ultraviolet spectral region. The sample was redistilled and a fraction, b.p. 60.5–61° (0.5 mm.), n_D^{20} 1.4639, taken for the analysis. The analytical data, as well as the observations below, indicate the product to be ethyl (+)-2-cyclohexyl-2-aminopropionate.

Anal. Calcd. for $C_{11}H_{21}O_2N$: C, 66.29; H, 10.62; N, 7.03. Found: C, 66.84, 66.89; H, 10.90, 10.72; N, 6.68, 6.75.

2-Cyclohexyl-2-amino-1-propanol.—Racemic ethyl 2-phenyl-2-aminopropionate (10.00 g.), Raney nickel (ca. 65 g.) and absolute ethanol (150 ml.) were heated in refluxing ethanol during 7 hours. The crude product, isolated as above, was 7.5 g. of oil. This was freed of neutral material by ether extraction of its hydrochloric acid solution. Evaporation of the solvent from this extract gave a negligible quantity of oil having the odor of ethyl 2-phenylpropionate. Treatment of the acidic layer with alkali, followed by ether extraction, recovered 7.3 g. of the basic oil. The material was distilled twice, and a middle-cut fraction of the second distillation was found to have n_D^{20} 1.4670 and $d_4^{18.5}$ 0.9807; molecular refraction calculated for ethyl 2-cyclohexyl-2-aminopropionate¹⁵ 56.1, found 56.2.

The first three quarters (4.35 g.) of material from the second distillation was dissolved in anhydrous ether (25 ml.), and the solution was slowly stirred into a mixture of lithium aluminum hydride (1.73 g.) in ether (75 ml.). The mixture was stirred for 15 minutes, then slowly decomposed with water. Processing of the ether layer gave 3.50 g. of viscous oil, crystallizable from a 1:1 mixture of ether and ligroin. Five recrystallizations gave pure 2-cyclohexyl-2-amino-1-propanol.

Anal. Calcd. for $C_9H_{19}ON$: C, 68.74; H, 12.18; N, 8.91. Found: C, 69.00; 69.02; H, 12.21, 12.26; N, 8.80.

Periodic Acid Cleavage of 2-Cyclohexyl-2-amino-1-propanol.—The crude amino alcohol solute in the mother liquors from the recrystallizations in the preceding experiment was recovered, 3.30 g. of viscous oil. To this was added 50 ml. of water containing 4.90 g. of periodic acid. The heterogeneous mixture was treated with ethanol (10 ml.) until homogeneous, then with water (50 ml.) until opaque, then allowed to stand at room temperature for four hours. The mixture was steam distilled (75 ml.), and the distillate was extracted with ether. Drying of the extract and solvent evaporation produced 0.60 g. (22%) of crude methyl cyclohexyl ketone, characterized by similarity of its infrared spectrum to that of an authentic sample, through its *p*-nitrophenylhydrazone, m.p. 149–151° (recorded value¹⁶ 154°), and through its semicarbazone, m.p. after five recrystallizations from dilute ethanol 172–175°, mixed m.p. with authentic sample (m.p. 177¹⁷) 173–177°.

2-Chloro-2-phenylpropionamide.—2-Phenyl-2-hydroxypropionic acid (30 g.) and thionyl chloride (50 ml.) were heated under reflux for three hours. The excess thionyl chloride was removed at reduced pressure and the resulting dark red residue was distilled to give 11.9 g. (32%) of yellowish oil, 2-chloro-2-phenylpropionyl chloride, b.p. 58–60° (1 mm.). The still residue was a viscous tar. This procedure is a modification of the method of McKenzie and Clough.¹¹

The yellow distillate was added to a 9% solution of ammonia in methanol (140 ml.), and the solution was concentrated at reduced pressure to three-fourths of its original

(13) R. Mazingo, *Org. Syntheses*, **21**, 15 (1941).

(14) A. McKenzie and J. Myles, *Ber.*, **65**, 215 (1932).

(15) A. Vogel, "A Textbook of Practical Organic Chemistry," Lougmans, Green and Co., New York, N. Y., 1948, p. 898.

(16) J. Braun, *Ber.*, **40**, 3948 (1907).

(17) O. Wallach, *Ann.*, **389**, 192 (1912).

volume. Water (100 ml.) was added, and the solution was chilled 12 hours, producing 6.1 g. (56%) of crude solid. This was recrystallized several times from a mixture of benzene and ligroin, then vacuum sublimed (75–85° (1 mm.)) to produce pure 2-chloro-2-phenylpropionamide, m.p. 100–101°.

Anal. Calcd. for C₉H₁₀ONCl: C, 58.84; H, 5.49. Found: C, 58.96, 59.12; H, 5.60, 5.63.

Raney Nickel and 2-Chloro-2-phenylpropionamide.—The above amide (0.57 g.) and Raney nickel (4 g.) were heated for four hours in refluxing absolute ethanol (20 ml.). Customary work-up gave 0.20 g. (43%) of crude solid, m.p. 80–86°. Recrystallization from benzene gave a sample, m.p. 88–93° undepressed on admixture with pure 2-phenylpropionamide.

STANFORD, CALIFORNIA

[CONTRIBUTION NO. 2080 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Small-Ring Compounds. XIV. Radioactive Cyclobutanone from Ketene and Diazomethane-¹⁴C¹

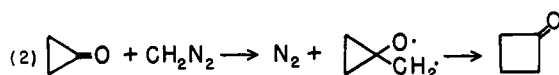
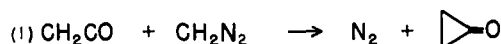
BY DOROTHY A. SEMENOW, EUGENE F. COX AND JOHN D. ROBERTS

RECEIVED JANUARY 23, 1956

It has been shown by the ¹⁴C-tracer technique that cyclobutanone is formed from the reaction of ketene with diazomethane-¹⁴C via an intermediate possessing the symmetry properties of cyclopropanone.

Introduction

The formation of cyclobutanone from ketene and diazomethane at –70° was discovered by Lipp and Köster² in the course of research on possible syntheses of cyclopropanone. They formulated the reaction as proceeding via cyclopropanone as an inter-



mediate. In support of this mechanism, it was cited² that step 2 was similar to the path previously proposed for the formation of methyl ethyl ketone from acetone and diazomethane³ and that cyclic ketones such as cyclopentanone and cyclohexanone react with diazomethane to form higher homologs.⁴

Subsequent workers⁵ have questioned the cyclopropanone intermediate on the grounds that it was considered unlikely that cyclopropanone would react smoothly with diazomethane in ether at –70° while cyclobutanone is stable under these same conditions.

The present research involved the determination of the ¹⁴C-distribution in cyclobutanone prepared from ketene and diazomethane-¹⁴C in order to obtain direct experimental evidence bearing on the reaction mechanism.

Synthetic and Degradative Procedures

Cyclobutanone-*x*-¹⁴C (I) was prepared from ketene and diazomethane-¹⁴C as described previously.^{2,5} The location of the ¹⁴C in the cyclobutanone (I) was achieved by ¹⁴C-analyses of the products of the following degradative scheme.

Results and Discussion

Inspection of the results of the ¹⁴C-analyses given in Table I reveals that the several ways of

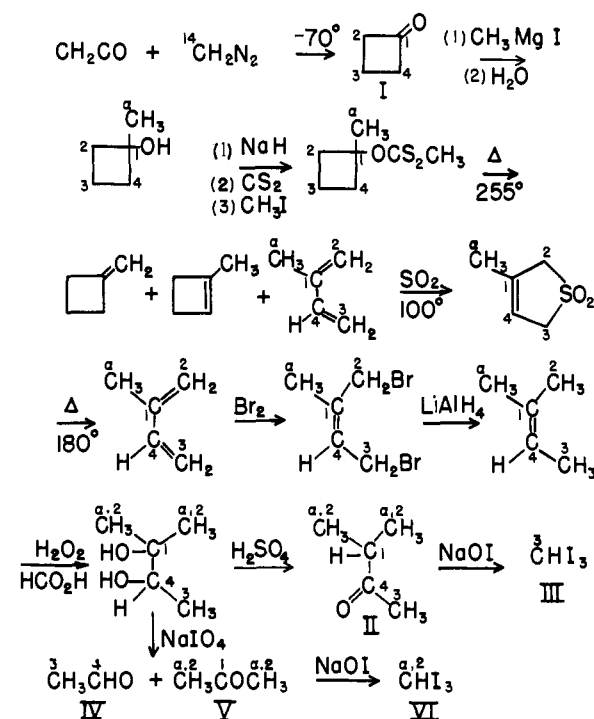
(1) Supported in part by the Petroleum Research Fund of the American Chemical Society.

(2) P. Lipp and R. Köster, *Ber.*, **64**, 2823 (1931).

(3) H. Meerwein and W. Burneleit, *ibid.*, **61**, 1840 (1928).

(4) E. Mosettig and A. Burger, *This Journal*, **52**, 3456 (1930).

(5) S. Kaarsemaker and J. Coops, *Rec. trav. chim.*, **70**, 1033 (1951).



adding and subtracting the various activities give agreement within the limits of error. Thus, the

TABLE I
RADIOACTIVITY ANALYSES OF DEGRADATION PRODUCTS OF
CYCLOBUTANONE-*x*-¹⁴C

	Meas. act. ^d	Total act., %
3-Methyl-2-butanone (II) ^a	0.1062	(100.00 ± 0.43°)
Iodoform (III)	.02736	25.76 ± .01°
Acetaldehyde (IV) ^b	.06703	63.12 ± .06°
Acetone (V) ^c	.03896	36.69 ± .14°
Iodoform (VI)	.01956	18.42 ± .04°

^a 3-Methyl-2-butanone as the 2,4-dinitrophenylhydrazone. ^b Acetaldehyde as dimethone. ^c Acetone as 2,4-dinitrophenylhydrazone. ^d Average activities in microcuries per millimole (μc./mmole); determined using the vibrating-reed electrometer method as described by O. K. Neville, *This Journal*, **70**, 3499 (1948). ^e Standard deviation determined from three or more combustions.