mixture was worked up after the reaction had gone 70% to completion (62 days). Infrared analysis (*vide supra*) of the phenolic material failed to reveal the presence of any *o*-benzyl-*p*-*t*-octylphenol, but a 94% yield of pure benzyl *p*-*t*-octylphenyl ether was isolated.

(b) **In Toluene at 25° (Heterogeneous).**—To 68.4 g. (0.30 mole) of sodium *p*-*t*-octylphenoxide was added 53.0 g. (0.31 mole) of benzyl bromide made up to 300 ml. with toluene at 25°. The initially heterogeneous mixture became much thinner and approached homogeneity after 7.5 hours when the reaction was *ca.* 60% complete. At this point all of the sodium bromide produced was found in the toluene solution. The reaction was complete in 2.5 days; 72% O- and 23% C-alkylation occurred.

(8) **Potassium *p*-*t*-Octylphenoxide and Benzyl Bromide at 25° (Heterogeneous).**—To 24.4 g. (0.10 mole) of potassium *p*-*t*-octylphenoxide suspended in 75 ml. of toluene was added 19.8 g. (0.11 mole) of benzyl bromide in 25 ml. of toluene at 25°. The initially heterogeneous reaction mixture became *completely* homogeneous in 50 minutes at which time the reaction was 60% complete. Incipient cloudiness appeared in 115 minutes by which time the reaction had gone 80% to completion. During these 65 minutes all of the potassium bromide produced could be titrated in the aqueous extract of the clear toluene solution. The reaction was complete in 12 hours; 84% O- and 15% C-benzylation occurred.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE CLAYTON FOUNDATION BIOCHEMICAL INSTITUTE AND THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Synthesis and Biological Activity of Some Cycloalkaneglyoxylic Acids

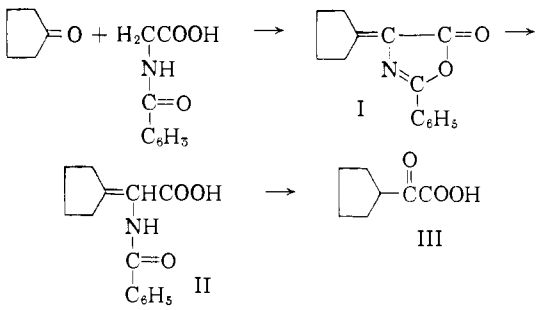
BY JOHN D. FISSEKIS,[1] CHARLES G. SKINNER AND WILLIAM SHIVE

RECEIVED NOVEMBER 25, 1958

Cyclopentane- and cyclohexaneglyoxylic acids were prepared from the corresponding cyclic ketones by condensation with hippuric acid to form the oxazolone followed by an initial alkaline hydrolysis to form the α-benzamido-β-cycloalkylideneacetic acids, and then acid hydrolysis to form the cycloalkaneglyoxylic acids. Cyclopentaneglyoxylic acid inhibits in a competitive manner the utilization of α-keto-β-methylvaleric acid in *Lactobacillus arabinosus* 17-5; whereas, the corresponding cyclohexane derivative is inactive. These biological effects are comparable to the results obtained with the corresponding amino acid analogs.

In biological systems, the inhibitory effect of an analog of a natural amino acid may frequently be circumvented by the corresponding natural α-keto acid. In the investigation of such effects, it is desirable to study the inhibitory properties of the α-keto acid analog corresponding to the amino acid antagonist.[2] Cyclopentaneglycine is an inhibitory analog of isoleucine,[3a] while cyclohexaneglycine does not exert any appreciable inhibitory effects upon biological utilization of amino acids.[3b] In order to study the mode of action of the keto acid (α-keto-β-methylvaleric acid) corresponding to isoleucine in preventing the toxicity of cyclopentaneglycine, its corresponding keto acid analog (cyclopentaneglyoxylic acid) was prepared as a potential antagonist of the natural keto acid. Further, in an effort to demonstrate the specificity of the cyclopentyl group in replacing the *sec*-butyl group of natural metabolites with the resultant retention of enzyme binding ability of the corresponding carbon skeleton, cyclohexaneglyoxylic acid was also prepared to demonstrate its inactivity in antagonizing the natural keto acid.

Two different approaches to the synthesis of cyclopentaneglyoxylic acid were examined in this study. One involved the initial preparation of 2-oxocyclopentaneacetonitrile by the interaction of cuprous cyanide with the acid bromide of cyclopentanecarboxylic acid. The subsequent reaction of this ketonitrile with anhydrous hydrogen chloride and ethyl alcohol gave an extremely hydroscopic and quite unstable product, presumably the corresponding imino ester hydrochloride. Hydrolysis of this intermediate product gave a reaction mixture containing the presumed keto derivative which was difficult to purify; therefore, an alternative procedure for the preparation of the keto acid was selected. The latter method involved the interaction of cyclopentanone with hippuric acid[4] to form 2-phenyl-4-cyclopentylidene-5-oxazolone (I). Upon alkaline hydrolysis, this oxazolone was converted to α-benzamido-β-cyclopentylideneacetic acid (II) which in turn was further hydrolyzed to yield cyclopentaneglyoxylic (III) as indicated in the accompanying equations.



Although the initial condensation step did not give good yields, most of the unreacted cyclopentanone could be subsequently recovered. Cyclopentaneglyoxylic acid was ultimately isolated by sublimation, and is a hygroscopic substance which was normally converted to its potassium salt for storage and subsequent biological study. Reaction of either the acid or its potassium salt with 2,4-dinitrophenylhydrazine gave identical 2,4-dinitrophenylhydrazones. Hydrogenolysis of the 2,4-dinitrophenylhydrazine derivative[5] produced cy-

(1) Rosalie B. Hite Fellow, 1957–1958.

(2) W. Shive and C. G. Skinner, *Ann. Rev. Biochem.*, **27**, 652 (1958).

(3) (a) W. M. Harding and W. Shive, *J. Biol. Chem.*, **206**, 401 (1954); (b) J. Edelson, J. D. Fissekis, C. G. Skinner and W. Shive, THIS JOURNAL, **80**, 2698 (1958).

(4) E. Erlenmeyer and J. Kunlin, *Ann.*, **316**, 145 (1901).

(5) C. H. N. Towers, J. F. Thompson and F. C. Steward, THIS JOURNAL, **76**, 2392 (1954).

clopentaneglycine as evidenced by paper chromatography. Also, interaction of cyclopentaneglyoxylic acid with pyridoxamine[6] produced cyclopentaneglycine which was similarly identified.

Cyclohexaneglyoxylic acid was prepared by the same general procedure as indicated above for the cyclopentane analog in that cyclohexanone was condensed with hippuric acid to yield the intermediate oxazolone which was subsequently hydrolyzed to form the corresponding keto acid. In contrast to the low conversions in the cyclopentane keto acid synthesis, the yields were routinely better for the intermediate condensation products as well as for the final keto acid in the preparation of the cyclohexane compounds.

Cyclopentaneglyoxylic acid inhibits in a competitive manner the utilization of α-keto-β-methylvaleric acid in *Lactobacillus arabinosus* 17-5 as indicated in Table I. The ratio of analog to the keto acid corresponding to isoleucine necessary for growth inhibition is approximately 20. In contrast, cyclohexaneglyoxylic acid is inactive under these conditions. The ability of the cyclopentane group, but not the cyclohexane group, to replace the *sec*-butyl group of isoleucine and produce an inhibitory amino acid analog is also true in the corresponding keto acid series. As anticipated, the utilization of isoleucine is not inhibited by cyclopentaneglyoxylic acid; however, if sufficient cyclopentaneglycine is present to inhibit the utilization of the exogenous isoleucine, a relatively small amount of the keto acid (corresponding to isoleucine) circumvents the inhibition and, under these conditions, a small amount of cyclopentaneglyoxylic acid relative to the amount of cyclopentaneglycine already present again inhibits the growth of the organism as indicated in Table II. These results indicate that separate competitively inhibited sites of utilization of keto and of amino acid are involved.

TABLE I

REVERSAL OF TOXICITY OF CYCLOPENTANEGLYOXYLIC ACID BY α-KETO-β-METHYLVALERIC ACID IN *Lactobacillus arabinosus* 17-5[a]

Cyclopentaneglyoxylic acid, γ/ml.	Supplement: γ/ml.: α-Keto-β-methylvaleric acid 10	20	50	100	DL-Isoleucine 10
	Galvanometer readings[b]				
0	48	55	60	66	51
40	39	55			
100	37	51	57		
200	6	23	56	65	53
400		3	40	64	51
1000			0	53	48
2000				19	46

[a] Incubated at 30° for 18 hours. [b] A measure of culture turbidity; distilled water reads 0, an opaque object 100.

Experimental[7]

Biological Assays.—The growth-assay procedure using *Lactobacillus arabinosus* 17-5 has previously been described[8,9]; however, the following changes were made in the media: isoleucine was omitted from the basal medium, calcium pantothenate was added at a concentration of 0.2 γ/ml., and the concentrations of adenine, guanine, uracil and biotin were decreased to 4, 4, 4 and 0.001 γ/ml., respectively. The α-keto-β-methylvaleric acid was prepared by hydrolysis of its ethyl ester, a sample of which was kindly supplied by Dr. H. E. Carter. All of the keto acids were weighed into sterile tubes, diluted with sterile water, and added aseptically to the sterile assay tubes without being heated. The assay tubes were incubated at 30° for about 18 hours, and the amount of growth was determined turbidimetrically in terms of galvanometer readings so adjusted that in a particular instrument distilled water read 0 and an opaque object 100.

TABLE II

INHIBITION OF SEPARATE SITES OF UTILIZATION OF α-KETO-β-METHYLVALERIC ACID AND DL-ISOLEUCINE

Test organism: *Lactobacillus arabinosus* 17-5, incubated 24 hours at 30°

Variable supplement, γ/ml.	Supplements to basal medium: DL-Isoleucine, 10 γ/ml.; cyclopentaneglycine, 1 mg./ml.: α-Keto-β-methylvaleric acid	Additional DL-isoleucine	DL-Isoleucine, 10 γ/ml.; cyclopentaneglycine, 1 mg./ml. α-keto-β-methylvaleric acid, 2 γ/ml.: Cyclopentaneglyoxylic acid	Additional cyclopentane glycine
	Galvanometer readings[a]			
0[b]	7	8	54	58
1	36			
2	53			
5		17		
10		34	24	
50		63	10	
100			6	48

[a] A measure of culture turbidity; distilled water reads 0, an opaque object 100. [b] DL-Isoleucine, 10 γ/ml., without cyclopentaneglycine reads 59.

Cyclopentanecarboxylic Acid.—The general procedure of Jackman, Bergman and Archer[10] was used with slight modifications which appreciably increased the percentage yield. A sample of 238.5 g. of 2-chlorocyclohexanone[11] was added to a well stirred solution of 82.5 g. of sodium in 1500 ml. of magnesium-dried ethanol over a two-hour period at room temperature. After stirring an additional 10 hours at room temperature, the reaction mixture was placed on a steam-cone for 12 hours to remove the excess alcohol; about 1000 ml. of water was added in small portions during this time to maintain the original volume. After cooling, the reaction mixture was washed with ether, after which the aqueous phase was acidified, and the resulting oil which separated was taken up in ether and dried over sodium sulfate. After removal of the solvent the residue was fractionally distilled to yield 140 g. of product, b.p. 120–123° (27 mm.).

Cyclopentanecarbonyl Bromide.—To a well stirred sample of 102.7 g. of cyclopentanecarboxylic acid was added 100 g. of phosphorus tribromide over a three-hour period while the reaction temperature was maintained below 10° with external cooling. After stirring in the cold an additional three hours, the reaction mixture was left at room temperature overnight. The cyclopentanecarbonyl bromide which separated from the cold reaction mixture was recovered, the residue was washed with ether, and the combined organic phases were fractionally distilled to yield 147 g. of product, b.p. 83–84° (27 mm.). A satisfactory elemental analysis could not be obtained due to the reactivity of the acyl bromide grouping; however, the anticipated cyclopentanecarboxamide was prepared in essentially quantita-

(6) D. E. Metzler and E. E. Snell, THIS JOURNAL, **74**, 979 (1952).

(7) All melting points are uncorrected. The R_f values were determined by the ascending technique. The authors are indebted to Mrs. Carole Baker for some of the biological assays, and to Mr. William H. Orme-Johnson and Miss Judith Morehead for the chemical analyses.

(8) J. M. Ravel, J. M. Estes, B. F. Molenhauer and W. Shive, *J. Biol. Chem.*, **229**, 93 (1957).

(9) J. M. Ravel, L. Woods, B. Felsing and W. Shive, *ibid.*, **206**, 391 (1954).

(10) M. Jackman, A. J. Bergman and S. Archer, THIS JOURNAL, **70**, 499 (1948).

(11) M. S. Newman, M. D. Earbman and H. Hipsher, "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p. 188.

tive yield from an aliquot portion of the distillate, m.p. 179°.[12]

2-Oxocyclopentaneacetonitrile.—To a carefully dried well stirred sample of 40 g. of cuprous cyanide heated to 70° was added 65 g. of cyclopentanecarbonyl bromide over a 1.5-hour period. After addition was complete, the reaction mixture was heated three more hours at 70°, followed by an additional 24 hours at a temperature of 40°. After filtration of the organic phase, the solid was washed with dry ether, and the combined organic phases were then fractionated under reduced pressure to yield 36 g. of product, b.p. 75° (22 mm.), 79.5%, $n^{25}D$ 1.4461, d^{25}_4 0.9993; *MR* calcd. 32.84 (32.17),[13] *MR* found 32.87.

Anal. Calcd. for C_7H_9NO: N, 11.37. Found: N, 11.31.

Several attempts to hydrolyze this nitrile using the procedure of Tschelinzeh and Schmidt[14] failed to yield a product which could be characterized by elemental analysis; however, the reaction mixture gave a positive test for carbonyl.

An attempt to prepare the corresponding imino ester hydrochloride using an equivalent weight of ethanol and hydrogen chloride mixed with the nitrile in dry ether resulted in the formation of a solid product. This latter material did not give an acceptable analysis for the anticipated imino ester hydrochloride salt, and was quite unstable. In view of the difficulties encountered in this sequence of reactions, an alternate preparative route to form the desired keto acid was initiated.

2-Phenyl-4-cyclopentylidene-5-oxazolone.—To a mixture of 71.5 g. of hippuric acid (dried *in vacuo* over phosphorus pentoxide), 36.9 g. of freshly fused sodium acetate and 230 g. of acetic anhydride, 380 g. of cyclopentanone was added dropwise over a four-hour period at room temperature. After the addition was completed, the reaction mixture was gently heated to 90–100° and allowed to remain there for 15 minutes. (A longer heating period resulted in the formation of 2-cyclopentylidenecyclopentanone which reduced the recovery yield of cyclopentanone.) The resulting clear, dark pink solution was then cooled to room temperature, and finally added slowly to 5 liters of cold water with vigorous stirring. After stirring an additional two hours, the resulting semi-solid material was recovered,[15] washed several times with cold water, and taken up in ethanol. After reduction in volume of the ethanol solution using an air jet, and cooling overnight in isopropyl alcohol–CO_2-bath, there was recovered 7.6 g. of product, m.p. 110°. A sample was recrystallized from ethanol for elemental analysis, m.p. 116°.

Anal. Calcd. for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.76; N, 6.16. Found: C, 74.36; H, 5.65; N, 6.19.

α-Benzamido-β-cyclopentylideneacetic Acid.—A 13.6-g. sample of 2-phenyl-4-cyclopentylidene-5-oxazolone was suspended in 100 ml. of 10% potassium hydroxide, and heated on a steam-cone for about 15 minutes to yield a clear yellow solution. The reaction mixture was then diluted with 200 ml. of water, cooled, washed with ether and acidified to a congo red end-point with concentrated hydrochloric acid. After standing in the cold for several hours, 12.75 g. of white solid separated which was filtered, washed several times with water, and dried *in vacuo* over potassium hydroxide, m.p. 206°. A sample was recrystallized from glacial acetic acid for elemental analysis, m.p. 216.5°.

Anal. Calcd. for $C_{14}H_{15}NO_3$: C, 68.55; H, 6.16; N, 5.71. Found: C, 68.76; H, 5.74; N, 5.80.

Cyclopentaneglyoxylic Acid.—A 9.2-g. sample of α-benzamido-β-cyclopentylideneacetic acid was suspended in 600 ml. of 6 *N* hydrochloric acid, and the reaction mixture was heated to reflux for about 5 hours to yield a clear solution. After cooling in an ice-bath, the precipitated benzoic acid was filtered, washed with cold water, and the combined filtrate and washings were extracted several times with ether. After drying the ether phase over calcium sulfate, the solvent was removed, and the residue was distilled *in vacuo* using a cold finger to collect 1.5 g. of hygroscopic product, m.p. 25–30°.

Anal. Calcd. for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 58.80; H, 7.26.

A cold aqueous suspension of the free keto acid was neutralized to *p*H 5 with 0.5 *M* potassium hydroxide, the solvent was removed *in vacuo*, and the product was precipitated with acetone to yield the potassium salt. A paper chromatograph of this latter material in butyl alcohol–ethyl alcohol–water (5:1:4) followed by development of the chromatogram with 2,4-dinitrophenylhydrazine reagent gave only one yellow spot, R_f 0.35.

Using the procedure of Metzler and Snell,[16] a sample of the keto acid isolated above was treated with pyridoxamine, and the resulting reaction mixture was examined by paper chromatographic techniques. There was produced a single amino acid which was identical with cyclopentaneglycine in several solvent systems.

2,4-Dinitrophenylhydrazone of Cyclopentaneglyoxylic Acid.—The interaction of cyclopentaneglyoxylic acid with 2,4-dinitrophenylhydrazine in the presence of 2 *N* hydrochloric acid yielded a yellow precipitate; which, after recrystallization from nitroethane, melted at 199° dec.

Anal. Calcd. for $C_{13}H_{14}N_4O_6$: C. 48.45; H, 4.38; N, 17.39. Found: C, 48.75; H, 4.34; N, 17.35.

A paper chromatograph of this material using isoamyl alcohol–ethyl alcohol–water (5:1:4) indicated only one hydrazone product was present, R_f 0.82. Hydrogenolysis of the 2,4-dinitrophenylhydrazone derivative using platinum oxide at room temperature in the presence of hydrogen gas under 50 lb./sq. in. pressure for 14 hours produced a reaction mixture which was ninhydrin positive. After separation of the catalyst, the reaction mixture was examined by paper chromatography, and there was found only a single ninhydrin spot which was identical with cyclopentaneglycine.

2-Phenyl-4-cyclohexylidene-5-oxazolone.—A mixture of 53.8 g. of hippuric acid (dried *in vacuo* over phosphorus pentoxide), 24.6 g. of freshly fused sodium acetate, 82 g. of acetic anhydride and 30 g. of cyclohexanone was heated on a steam-cone for 30 minutes to yield a dark pink solution. The warm reaction mixture was then reduced in volume *in vacuo* during which time a portion of the oxazolone precipitated as thin needles. The resulting residue was cooled for a few hours, suspended in ethanol, and poured into two liters of ice-water with continuous stirring. The aqueous phase was decanted, and the residue was taken up in hot ethanol. Upon cooling overnight in the refrigerator there was recovered 12.6 g. of pink needles, m.p. 140°. A sample was recrystallized from ethanol for elemental analysis, m.p. 142°.

Anal. Calcd. for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.80. Found: C, 74.95; H, 6.23; N, 5.99.

α-Benzamido-β-cyclohexylideneacetic Acid.—A mixture of 12 g. of 2-phenyl-4-cyclohexylidene-5-oxazolone and 100 ml. of 10% potassium hydroxide was heated for about one hour on a steam-cone to produce a clear yellow solution. The reaction mixture was cooled, diluted with 300 ml. of distilled water, washed with ether, and filtered to remove the insoluble residue. The clear filtrate was then acidified to a congo red end-point with concentrated hydrochloric acid and placed in the refrigerator. The resulting precipitate was filtered, washed with cold water and dried *in vacuo* over phosphorus pentoxide to yield 12 g. of product, m.p. 236°. A sample was recrystallized from glacial acetic acid for elemental analysis, m.p. 237°.

Anal. Calcd. for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.79; H, 6.62; N, 5.37.

Cyclohexaneglyoxylic Acid.—A mixture of 12 g. of α-benzamido-β-cyclohexylideneacetic acid and 500 ml. of 6 *N* hydrochloric acid was heated to reflux, with occasional shaking to prevent excessive foaming, for about 12 hours. Two portions of concentrated hydrochloric acid (50 ml.) were added at the end of 6 and 9 hours during this heating period. The resulting reaction mixture was diluted with 300 ml. of distilled water, cooled in an ice-bath, and the theoretical weight of benzoic acid was recovered. The filtrate was then extracted several times with ether, and the combined organic phase was dried over sodium sulfate.

(12) The reported m.p. is 179°; N. Zelinsky, *Ber.*, **41**, 2627 (1908).

(13) The first value was calculated using a value of 3.79 for the C≡N nitrogen (aromatic cyanide); the second value in parentheses was obtained using the aliphatic cyanide value for the C≡N nitrogen, 3.12.

(14) W. Tschelinzeff and W. Schmidt, *Ber.*, **62**, 2210 (1929).

(15) A continuous ether extraction of the aqueous phase at this stage after neutralization with sodium carbonate, followed by fractional distillation of the organic extract yielded 290 g. of recovered cyclopentanone.

(16) D. E. Metzler and E. E. Snell, THIS JOURNAL, **74**, 979 (1952).

After removal of the solvent *in vacuo*, a solid residue remained which was dried under vacuum over both potassium hydroxide and sulfuric acid to yield 4.4 g. of hygroscopic material, m.p. 45–50°. This product was then sublimed at 130° using a mercury-vapor vacuum pump to yield an analytical sample, m.p. 53°.

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.52; H, 7.74. Found: C, 61.60; H, 7.55.

A 2,4-dinitrophenylhydrazone derivative was prepared in the usual manner, and after recrystallization from chloroform–Skellysolve B, yielded fine yellow needles, m.p. 215–216°.[17]

(17) D. D. E. Newman and L. N. Owen, *J. Chem. Soc.*, 4713 (1952), report a m.p. of 211–212° for this derivative.

AUSTIN 12, TEXAS

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS CO.]

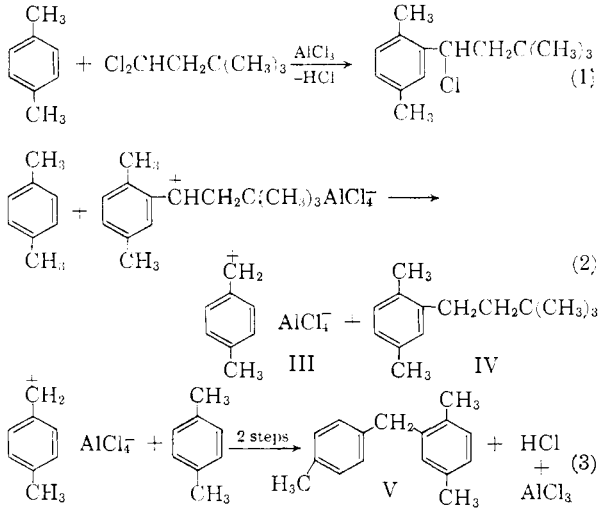
Hydrogen Transfer during the Alkylation of *p*-Xylene and of *p*-Chlorotoluene[1]

BY LOUIS SCHMERLING, J. P. LUVISI AND R. W. WELCH

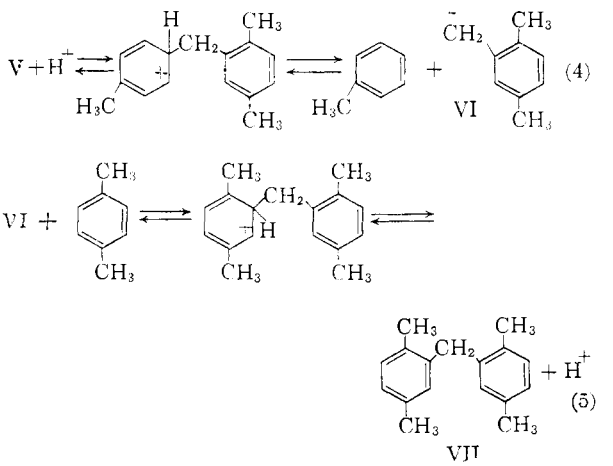
RECEIVED NOVEMBER 26, 1958

Hydrogen transfer involving benzylic hydrogen occurs when *p*-xylene or *p*-chlorotoluene is alkylated with a 1,1-dichloroalkane or a *t*-alkyl chloride in the presence of aluminum chloride. For example, the reaction of *p*-xylene with 1,1-dichloro-3,3-dimethylbutane yields (3,3-dimethylbutyl)-*p*-xylene (IV) and di-(*p*-xylyl)-methane (VII), production of the latter involving the intermediate formation of (*p*-methylbenzyl)-*p*-xylene (V), which then undergoes transaralkylation with excess *p*-xylene present. When the reaction is carried out in the presence of methylcyclohexane, the product consists chiefly of the hexyl-*p*-xylene (IV) and (methylcyclohexyl)-*p*-xylene, together with only a very minor amount of the dixylylmethane (VII), indicating that the saturated hydrocarbon containing a tertiary carbon atom furnishes the hydrogen necessary for the formation of the hexylxylene more readily than does the *p*-xylene. Aluminum chloride and zirconium chloride, but not ferric chloride, yield hydrogen transfer products in the reaction of *p*-xylene and *t*-butyl chloride.

It was previously shown that saturated hydrocarbons containing tertiary carbon atoms are involved in a hydrogen transfer reaction during the alkylation of benzene with polyhalides in the presence of aluminum chloride.[2] For example, excellent yields of a primary mono-alkylbenzene, 1-phenyl-3,3-dimethylbutane (I, 60%), and of a secondary cycloalkylbenzene, (x-methylcyclopentyl)-benzene (48%), together with only a minor amount (6%) of the expected disubstitution product, 1,1-diphenyl-3,3-dimethylbutane (II), are obtained by the reaction of benzene with 1,1-dichloro-3,3-dimethylbutane and methylcyclopentane at about 0°.[2a] In the absence of the saturated hydrocarbon, I and II are formed in approximately equal yields (26–28% and 19–20%, respectively).



Reaction of *p*-Xylene with 1,1-Dichloroalkanes.—It has now been found that hydrogen transfer is the principal reaction even in the absence of saturated hydrocarbon when *p*-xylene is alkylated with 1,1-dichloroalkanes, the source of the hydrogen being the benzylic hydrogens in the *p*-xylene (Table I). The reaction of 0.5 mole of 1,1-dichloro-3,3-dimethylbutane with 2.5 moles of the hydrocarbon in the presence of 0.04 mole of aluminum chloride at 1–20° yielded 0.14 mole of (3,3-dimethylbutyl)-*p*-xylene (IV, "neohexyl-*p*-xylene") and 0.095 mole of crystalline hydrogen transfer product, di-(*p*-xylyl)-methane (VII). There was no evidence of the formation of the disubstitution product, 1,1-di-(*p*-xylyl)-3.3-dimethylbutane; hydrogen transfer apparently occurred too readily.



The (*p*-methylbenzyl)-*p*-xylene (V) undergoes transaralkylation in the presence of excess *p*-xylene to yield the di-(*p*-xylyl)-methane (VII).[3]

(1) Presented before the Division of Organic Chemistry of the American Chemical Society at the Chicago Meeting, September, 1958.

(2) (a) L. Schmerling, J. P. Luvisi and R. W. Welch, THIS JOURNAL, **77**, 1774 (1955); (b) L. Schmerling, R. W. Welch and J. P. West, *ibid.*, **78**, 5406 (1956); L. Schmerling, R. W. Welch and J. P. Luvisi, *ibid.*, **79**, 2636 (1957).

(3) Alternatively, the transaralkylation may be formulated analogously to the transalkylation scheme of D. A. McCauley and A. P. Lien *ibid.*, **75**, 2411 (1953).