[CONTRIBUTION FROM THE WELLCOME RESEARCH LABORATORIES]

Catalytic and Chemical Hydrogenations of 2-Benzylidene- and 2-Benzylcyclopentanones. *cis*- and *trans*-2-Benzylcyclopentanols and Some Derivatives

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RECEIVED JULY 21, 1955

By application of appropriate catalytic and chemical hydrogenation procedures the *cis*- and *trans*-2-benzylcyclopentanols have been prepared by reductions of 2-benzylidene- and 2-benzylcyclopentanone. In this series the ketone carbonyl is resistant to reduction by either platinum or palladium catalysts in methanol solution in the absence of hydrochloric acid. When the ketones are hydrogenated with platinum in the presence of small amounts of hydrochloric acid, mixtures of nearly equal parts of ketone (or alcohol) and a hydrocarbon are obtained. These two products result, presumably, from simultaneous reductions proceeding along two alternate routes. The pure *cis*- and *trans*-2-benzylcyclopentanols are both hydrogenated readily by platinum in acidified methanol to the corresponding *cis*- and *trans*-hexahydrobenzylcyclopentanols.

Several years ago a series of investigations was initiated in these laboratories in which various mono- and dibenzylidenecycloalkanones served as the starting materials. This paper reports the results of one of these investigations, the reduction of 2-benzylidenecyclopentanone (I) and certain of its derivatives by various catalytic and chemical means.

The ketone I was prepared in good yield by the condensation of benzaldehyde with cyclopentanone in aqueous alkali in a modification of the method of Vorländer and Hobohm.[1]

Catalytic hydrogenation of I using palladized charcoal in methanol proceeded with an uptake of just one mole of hydrogen, and 2-benzylcyclopentanone (II) was obtained in 85–90% yield from the reduction mixture. This ketone, II, had been described previously both by Duff and Ingold[2] and by Treibs, *et al.*,[3] who had obtained it by alkylation of the sodium derivative of 2-carbethoxycyclopentanone with benzyl chloride, followed by hydrolysis and decarboxylation.

Catalytic hydrogenation of I using Adams catalyst in methanol resulted in the rapid uptake of 80% of the amount of hydrogen which would have been required to saturate both the carbon–carbon and carbonyl double bonds. This reduction gave about 70% of II and 15–20% of a 2-benzylcyclopentanol (III). Compounds II and III were not readily separated from this mixture by distillation but were isolated and identified from the reaction mixture as solid derivatives. Subsequently III was obtained in pure form by an alternative route, as will be described below. Compound III was assigned the structure of a 2-benzylcyclopentanol on the basis of analyses of the pure material, and from the formation and analyses of various suitable derivatives. In addition, oxidation of III with chromic acid gave II in high yield.

2-Benzylcyclopentanol can exist in *cis* (III) and *trans* (IV) forms, each a racemic mixture, unless resolved. 2-Benzylcyclopentanol has been reported earlier both by Duff and Ingold[2] and by Treibs, *et al.*,[3] but neither of these groups commented on the stereochemical possibilities, nor characterized their products by suitable derivatives. Since Duff and Ingold[2] prepared their alcohol by reduction of the benzyl ketone using sodium and moist ether, it undoubtedly was the *trans* isomer IV, though no distinguishing properties or derivatives were given. Thus the generalizations of Skita,[4] as well as the experience of Vavon and coworkers,[5] in reductions of numerous 2-alkylcyclopentanones lead to the expectation that catalytic hydrogenations of 2-alkylcyclopentanones with platinum in acidic media should give predominantly, if not exclusively, *cis* isomers, while reduction of these ketones using neutral or alkaline reagents should give almost entirely the *trans* isomers.

The 2-benzylcyclopentanol of Treibs and coworkers[3] also was not characterized by suitable properties or derivatives, thus allowing no clue as to its stereochemical nature. Their method of preparation, catalytic hydrogenation of the benzyl ketone over copper chromite at high temperatures and pressures, has not been commonly enough studied in similar cases to suggest what type of product might be expected. Furthermore, the boiling point given (b.p. 195–198° (14 mm.)) for their 2-benzylcyclopentanol by these workers[3] is quite out of line and much higher than has been found in the current investigation for either the *cis*-(III) or *trans*-(IV) alcohol.

The alcohol obtained by the hydrogenation of 2-benzylidenecyclopentanone over platinum was assigned the *cis* configuration III, tentatively, on the basis of the earlier work.[4,5]

The catalytic hydrogenation of I to give a mixture of II (70%) and III ($\leqslant$20%) suggests that the reduction of I under these conditions proceeds by two or more simultaneous pathways. Conjugated unsaturated systems such as I offer several possibilities for the initial steps of addition reactions such as hydrogenation: 1,2-, 3,4- or 1,4.

If 1,2-hydrogenation (of the carbonyl double bond) were one of the competing reduction steps, then the 2-benzylidenecyclopentanol[6] (V) thus formed must reduce further to III by the subsequent rapid addition of a second mole of hydrogen, since no V but only II and III were isolated from this reduction. That this process is quite reasonable is supported by the later finding that the best

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[1] D. Vorländer and K. Hobohm, *Ber.*, **29**, 1836 (1896).

[2] D. A. Duff and C. K. Ingold, *J. Chem. Soc.*, 87 (1934).

[3] W. Treibs, *et al.*, *Ber.*, **87**, 356 (1954).

[4] A. Skita, *ibid.*, **53**, 1792 (1920); **56**, 1014, 2234 (1923); *Ann.*, **427**, 255 (1922); **431**, 1 (1923).

[5] G. Vavon and A. Apchié, *Bull. soc. chim.*, **43**, 667 (1928); G. Vavon and J. Flurer, *ibid.*, **45**, 754 (1929); G. Vavon and A. Horeau, *ibid.*, [5] **1**, 1703 (1934); and many other papers before and since these.

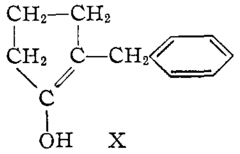
[6] The preparation and isolation of V by another method is described below.

method of preparation of relatively pure *cis*-alcohol III is by the platinum-catalyzed hydrogenation of the unsaturated alcohol V, preformed by another method of reduction.[6]

If primary 3,4-hydrogenation is used to account for the formation of the benzyl ketone II in this reduction, then, according to this hypothesis, it would appear that III was derived from V (or X) as an intermediate rather than from II. Since II was the main product in this rapid reduction, it is hard to argue why some, but not all, of II should have been reduced to III if this were the method of formation of III.

Attempts to reduce the pure benzyl ketone II using Adams catalyst in methanol failed. Only a small amount of hydrogen was taken up and this sluggishly. More than 85% of II was recovered unchanged from the reaction mixture. Attempts to isolate any alcohol (III or IV) from the reaction mixture as derivatives were unsuccessful.

A third mode of initial addition, 1,4-, would give 2-benzylcyclopenten-1-ol-1 (X) as an intermediate. Because of the endocyclic double bond, representing a strained configuration in the cyclopentane series, X should not be as stable an intermediate as either V or II. However, this relative instability of X could be relieved by further rapid reduction to III or by ketonization (it is an enol) to II.


X

These suggestions as to possible routes of hydrogen addition thus can account for the products obtained. The work of this paper does not seem to afford support for more detailed speculations as to how or why different paths should be followed in the reduction. Thus the differences may be attributed to different simultaneous reductions of a substrate: (1) adsorbed on the catalyst in the same way, or (2) adsorbed in two or more different ways. (3) A third possibility entails partial desorptions of the substrate from the catalyst during the course of the reduction. At any rate, in this and several subsequent hydrogenations over Adams catalyst, the products are mixtures of compounds seemingly not related as precursor–product, and multiple reduction routes, of origin still obscure, are suggested as the cause of these.

When II was hydrogenated over Adams catalyst in methanol acidified with a little concentrated hydrochloric acid, a rapid uptake of 4–5 moles of hydrogen occurred, and this reduction, also, seemed to proceed by at least two different reaction paths. Upon distillation of the reaction mixture *in vacuo* two products were separated and identified. The higher boiling one was the *cis*-hexahydrobenzylcyclopentanol (VII), whose preparation by reduction of pure *cis*-alcohol III will be described later. Compound VII was isolated in about 60–70% yield and was characterized by solid derivatives. The second, lower boiling product, not rigidly identified here, was the hydrocarbon hexahydrobenzylcyclopentane (VIII) which has been described previously.[7–9] After purification by several distillations *in vacuo*, analytical results on this material agreed well with the proposed structure VIII. The yield of VIII was about 20–25%.

Hydrogenation of 2-benzylidenecyclopentanone-(I) with Adams catalyst in acidified methanol proceeded rapidly with an uptake of a little over two moles of hydrogen per mole of I. Again a mixture of products resulted suggestive of multiple reduction pathways. In this case the products isolated were 30–40% of the benzyl ketone II, about 5% of the *cis*-alcohol III and 40–50% of lower boiling material, presumably mainly the known[3,7,8] benzylcyclopentane IX. Although satisfactory analyses were never obtained for IX, even after many redistillations *in vacuo*, this structure seems the only reasonable one for this low boiling material in view of the amounts of other materials isolated and the low hydrogen uptake. The mixture of products obtained in this reduction can be explained in the following way. As with the reduction of I by Adams catalyst in the absence of acid, both 1,2- and 3,4-addition presumably occur as the first steps to yield V and II, respectively, as intermediates. The presence of hydrochloric acid seems to have speeded up 1,2-addition at the expense of 3,4-addition as less II was formed. In this reduction, also, II was isolated in good yield and thus probably did not serve as an intermediate for further reduction. The presence of acid during the reduction seems not only to have speeded up 1,2-reduction, forming V as an intermediate, but to have accelerated a "debenzylative" carbon–oxygen cleavage of the allylic (resembling a benzylic) alcohol bond of V. This would explain the very poor yield of III obtained (5% ±) and the fairly high yield of IX (40–50%).

Preparation of the *trans*-2-benzylcyclopentanol (IV) was accomplished by reduction of 2-benzylcyclopentanone (II) with lithium aluminum hydride in ether solution. As an essentially basic reducing agent this should be expected to resemble in its behavior sodium in moist ether or alcohol and on the basis of the work of Skita,[4] Vavon[5] and others, should give predominantly a *trans* reduction product. That lithium aluminum hydride does, in fact, produce *trans*-alcohols as the principal products in related series has been demonstrated by the work of Russell[10] and of Cornubert, *et al.*,[11] on the reduction of 2-benzylcyclohexanones. The product IV, purified by distillation *in vacuo*, was obtained in about 95% yield. It boiled sharply, was free of ketone (gave no semicarbazone) and gave high yields of a 3,5-dinitrobenzoate and an α-naphthylurethan, the melting points of which were different from these derivatives of III. Oxidation of IV with chromic acid gave back II in high yield. Analysis of the reduction product itself and of its derivatives indicated it to be a 2-benzylcyclopentanol isomeric with III. On the basis of the methods of preparation of the two isomeric compounds, com-

[7] N. D. Zelinsky and I. N. Titz, *Ber.*, **64B**, 183 (1931).

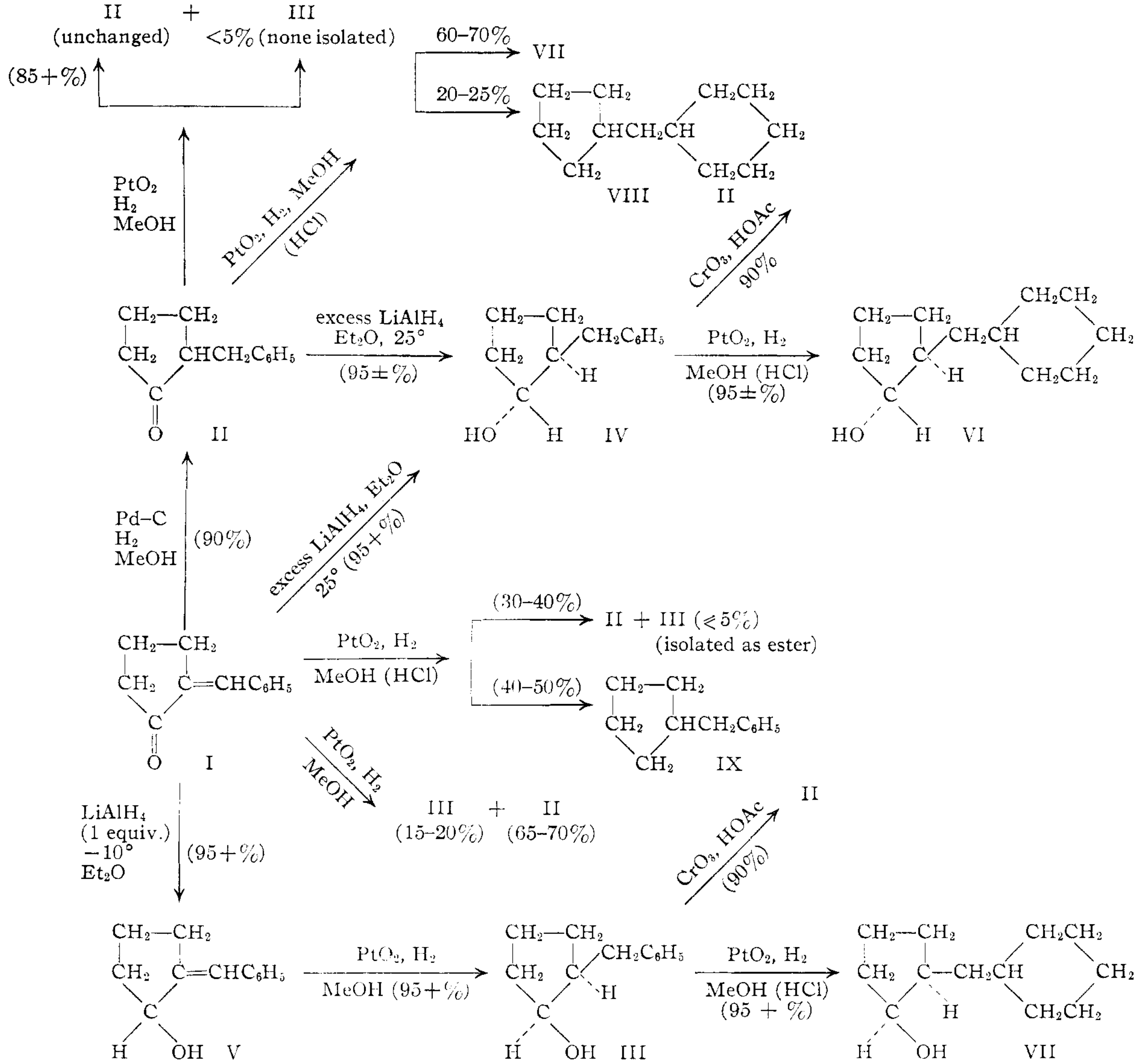
[8] J. I. Denissenko, *ibid.*, **69B**, 1668 (1936).

[9] C. D. Nenitzescu and E. Cioră̆nescu, *ibid.*, **69B**, 1820 (1936).

[10] P. B. Russell, *J. Chem. Soc.*, 1771 (1954).

[11] R. Cornubert, *et al.*, *Bull. soc. chim.*, 400 (1955).

Chart I



pound III has been assigned a *cis* and compound IV a *trans* configuration.

An attempt to reduce 2-benzylidenecyclopentanone (I) to 2-benzylidenecyclopentanol (V) using excess lithium aluminum hydride in ether at room temperature gave not V, but IV, again in 95% yield. The liquid nature of the product, its boiling point and analysis, the formation of melting points and analyses of suitable derivatives all established that this material was IV and not V. Furthermore, V is a known substance, a crystalline solid melting at 86°, which has been prepared by Braude and Forbes[12] by an entirely different route. The reduction of both the carbonyl and α,β-carbon–carbon double bond, in the case of I, was neither entirely unexpected nor without precedent. In certain cases of α,β-unsaturated carbonyl compounds even excess lithium aluminum hydride reduces only the carbonyl group. In other instances, as with cinnamaldehyde, it has been shown[13] that although reduction to cinnamyl alcohol is the first step, the usual conditions, using excess lithium aluminum hydride and ordinary temperatures, carry the hydrogenation further to hydrocinnamyl alcohol. In order to obtain the unsaturated alcohol it was necessary[13] to add slowly only a slight excess over the calculated amount of the hydride, in ether solution, to a solution of cinnamaldehyde in ether at −10°. Following this procedure[13] compound I gave V in nearly quantitative yield. Its melting point agreed with the product of Braude and Forbes[12] and analyses for carbon and hydrogen confirmed the formula assigned.

Catalytic hydrogenation of V using Adams catalyst in methanol at room temperature resulted in an uptake of one mole of hydrogen. This reduction gave a nearly quantitative yield of the same 2-benzylcyclopentanol (III) previously obtained, though in poor yields, by hydrogenation of I with Adams catalyst.

When the pure *trans*-2-benzylcyclopentanol (IV) or the pure *cis*-2-benzylcyclopentanol (III) was

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(12) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 1755 (1951).

(13) F. A. Hochstein and W. G. Brown, This Journal, **70**, 3484 (1948).

hydrogenated with Adams catalyst in acidified methanol (2 cc. of concentrated hydrochloric acid/150 cc. of methanol) each of these compounds took up an additional three moles of hydrogen with great ease. The products isolated in high yield were the 2-hexahydrobenzylcyclopentanols, the *trans* isomer VI from IV, the *cis* isomer VII from III. These isomeric alcohols VI and VII were characterized by analyses and by the preparation, melting points and analyses of the two sets of similar derivatives, the 3,5-dinitrobenzoates and α-naphthylurethans, which agreed in analyses for carbon and hydrogen, but which differed in melting points.

Chart I outlines all of the principal reactions described.

Experimental

2-Benzylidenecyclopentanone[1] (I).—2-Benzylidenecyclopentanone (I) was prepared by a modification of the method described by Vorländer and Hobohm.[1]

A mixture of 84 g. (1 mole) of cyclopentanone, 53 g. (0.5 mole) of benzaldehyde and 1 liter of water, containing 25 g. of dissolved sodium hydroxide, was stirred mechanically for 1 hour at room temperature. The alkali was then neutralized rapidly by the addition of hydrochloric acid. The oil and aqueous layer were shaken with ether and the aqueous layer was extracted several times with ether. After drying over anhydrous potassium carbonate, the combined ether layers were filtered and evaporated, leaving 130 g. of crude oil. Distillation *in vacuo* gave 60 g. (70%) of I, b.p. 165–168° at 10 mm., which crystallized on cooling. Recrystallizations from hexane and from methanol gave yellow crystals, m.p. 68–69°.

2-Benzylcyclopentanone[2,3] (II).—A solution of 26 g. (0.15 mole) of I in 150 cc. of methanol was shaken in a Burgess-Parr type hydrogenation machine at 2–3 atmospheres of hydrogen pressure and room temperature using 0.5 g. of a 5% palladized charcoal catalyst. Hydrogen uptake was rapid and stopped after the absorption of 0.15 mole. After removing the catalyst and evaporating the solvent, the product was distilled *in vacuo*. The product, II, boiled at 140–143° at 11 mm. (b.p. 130–133° at 7 mm., 87–90° at 2 mm.) and the yield was 22 g. (85%).

An aliquot gave 90–95% of 2-benzylcyclopentanone semicarbazone,[2] which was recrystallized from methanol and melted at 198–199°.

For certain reductions it seemed desirable to use 2-benzylcyclopentanone (II), free of the derived alcohols III or IV, which might be possible trace contaminants in the distilled product. The distilled ketone was shaken overnight (20 hr.) with a saturated aqueous solution of sodium bisulfite. The crystalline ketone bisulfite was collected and was washed first with a little saturated bisulfite solution and then with several portions of ether. Only about 50% of the calculated amount of ketone was obtained after liberation from the crystalline bisulfite. Since semicarbazone formation indicated a 90–95% yield of ketone, it is apparent that bisulfite addition is not complete under the conditions used.

Catalytic Hydrogenation of 2-Benzylidenecyclopentanone (I) with Platinum Oxide (No Acid). Preparation of II and III.—This reduction was repeated many times, always with the same results. The separation and isolation of the products as derivatives also has been duplicated many times. A typical run will be described in detail.

A solution of 17.2 g. (0.1 mole) of 2-benzylidenecyclopentanone (I) in 150 cc. of methanol was hydrogenated at 2–3 atmospheres of hydrogen pressure and at room temperature using 0.2 g. of Adams platinum oxide catalyst. Hydrogen uptake was rapid; 0.15 mole of hydrogen was absorbed in the first 10 minutes and the reduction came to a complete stop after an absorption of 0.17 mole of hydrogen in a total of 2.5 hours.

After removing the catalyst, solvent was evaporated and the product was distilled *in vacuo* and gave: A, 1 g. of foreruns, b.p. 35–128° at 9 mm.; B, 14 g. of main product, b.p. 133–140° at 9 mm.; and C, 2 g. distillation residue (high b.p. C was discarded).

The forerun A (1 g.) gave 1 g. of the semicarbazone[2] (melting at 194–196°) of II. This corresponds to a yield of at least 75% of II in fraction A.

The main fraction B (14 g.) was redistilled *in vacuo* and gave: B_1, 4 g., b.p. 36–134° at 8 mm.; B_2, 9.5 g., b.p. 134–137° at 8 mm., with little or no distillation residue.

Aliquots, 1 g. of each, of fractions B_1 and B_2 gave amounts of purified semicarbazone of II corresponding to 75–80% and 95–100% yields of II in the respective fractions.

An aliquot from fraction B above, before redistillation, on treatment with 3,5-dinitrobenzoyl chloride in benzene–pyridine gave the 3,5-dinitrobenzoate of *cis*-2-benzylcyclopentanol (III), m.p. 90–91°, yield 15–20%, after recrystallization from hexane, and from ethanol.

Anal. Calcd. for $C_{19}H_{18}N_2O_6$: C, 61.6; H, 4.9. Found: C, 61.7; H, 4.7.

Another aliquot from fraction B gave the phenylurethan of III, m.p. 108–109°, yield 20–25%, after several recrystallizations from hexane.

Anal. Calcd. for $C_{19}H_{21}NO_2$: C, 77.3; H, 7.2. Found: C, 77.4; H, 7.4.

Similarly an aliquot from B gave the α-naphthylurethan of III, m.p. 86–87°, yield 15–20%, after recrystallization from hexane.

Anal. Calcd. for $C_{23}H_{23}NO_2$: C, 80.0; H, 6.7. Found: C, 79.9; H, 6.6.

Catalytic Hydrogenation of 2-Benzylcyclopentanone (II) with Platinum Oxide. A. In the Absence of Acid.—A solution of 7 g. (0.04 mole) of II, purified through the sodium bisulfite adduct as described above, in 150 cc. of methanol was hydrogenated under the usual conditions described above, using 0.2 g. of Adams platinum oxide catalyst. Hydrogen absorption was extremely sluggish and incomplete. Over a period of 20 hours only 0.02–0.03 mole of hydrogen was taken up and the rate of uptake was so slow that it could not reliably be distinguished from normal leakage from the system. After removal of catalyst and solvent, the residual oil was distilled *in vacuo*. In this way 7 g. (100%) of colorless liquid was recovered, b.p. 133–137° at 8 mm.

An aliquot from this distilled material gave 85–90% of the semicarbazone[2] of II, m.p. 195–197°, after two recrystallizations from methanol.

Other aliquots were treated with 3,5-dinitrobenzoyl chloride and with α-naphthyl isocyanate in attempts to isolate any alcohol present as derivatives. No isolable amount of crystalline derivative was obtained from either of these experiments.

The above results show that 2-benzylcyclopentanone (II) is very little, if at all, reduced by hydrogen and platinum catalyst in the absence of acid.

B. In the Presence of Acid.—A mixture containing 17.4 g. (0.1 mole) of II, 150 cc. of methanol, 2 cc. of concentrated hydrochloric acid and 0.2 g. of platinum oxide was hydrogenated under the usual conditions. Hydrogen uptake was rapid and 0.4–0.5 mole of hydrogen was absorbed within 4–5 hours. After removing catalyst and solvent, the product in ether was washed with dilute alkali and with water. After drying and evaporating the ether, the residue was distilled *in vacuo* and gave: A, 5 g., b.p. 100–127° at 9 mm.; B, 10 g., b.p. 127–130° at 9 mm.

Neither fraction A nor B gave any semicarbazone, indicating that no ketone was present. Redistillation of fractions A and B gave: A_1, 3–4 g., b.p. 99–101° at 8 mm. (20–25% yield); B_1, 10–12 g., b.p. 127–130° at 8 mm. (60–70% yield).

Fraction A_1 proved to be the hydrocarbon hexahydrobenzylcyclopentane (VIII), from its much lower boiling point, from the large hydrogen uptake, from the non-formation of ketone or alcohol derivatives from it, and from analyses.

Anal. Calcd. for $C_{12}H_{22}$ (VIII): C, 86.7; H, 13.5. Found: C, 86.7; H, 13.5.

Fraction B_1 was believed to be a 2-hexahydrobenzylcyclopentanol, most likely of the *cis* configuration VII, from its boiling point, the high hydrogen uptake and the lack of ketone derivative formation. Analyses and the ready formation of appropriate alcohol derivatives supported the structure as a saturated alcohol. Comparison of the properties of these derivatives with those obtained later from the reduction of the pure *cis*- and *trans*-2-benzylcyclopentanols, confirmed that the alcohol product here was predominantly, if not entirely, the *cis* isomer VII.

Anal. Calcd. for $C_{12}H_{22}O$ (VII): C, 79.1; H, 12.2. Found: C, 79.2; H, 12.3.

This material when treated with 3,5-dinitrobenzoyl chloride in benzene–pyridine gave a white crystalline 3,5-dinitrobenzoate, yield 70–75%, m.p. 103–104° after several recrystallizations from ethanol.

Anal. Calcd. for $C_{19}H_{24}N_2O_6$: C, 60.6; H, 6.4. Found: C, 60.3; H, 6.4.

Fraction B_1 with α-naphthyl isocyanate gave the α-naphthylurethan in 80% yield, m.p. 111–112° after several recrystallizations from hexane.

Anal. Calcd. for $C_{23}H_{29}NO_2$: C, 78.6; H, 8.3. Found: C, 78.3; H, 8.2.

Catalytic Hydrogenation of 2-Benzylidenecyclopentanone (I) with Platinum Oxide in the Presence of Acid. Preparation of II and IX.—A solution containing 17.2 g. (0.1 mole) of I, 150 cc. of methanol, 2 cc. of concentrated hydrochloric acid and 0.2 g. of platinum oxide was hydrogenated under the usual conditions. Reduction was rapid and 0.2 mole of hydrogen was absorbed within 15 minutes; another 0.08–0.09 mole of hydrogen was taken up slowly and sluggishly over an 8-hour period before coming to a complete stop. In a duplicate run the reduction was interrupted after the rapid absorption of 0.2 mole of hydrogen (15–20 minutes), but the workup of the two runs gave essentially the same results.

After removal of the catalyst and solvent and after washing the product in ether with dilute alkali, distillation of the dried residue *in vacuo* gave two main fractions: A, 8 g., b.p. 98–120° at 8 mm.; B, 7 g., b.p. 120–145° at 8 mm.

Fraction A was believed to be chiefly 2-benzylcyclopentane because of its low boiling point and the low hydrogen uptake. However, even after repeated fractional distillations *in vacuo* it was still not obtained analytically pure. After these distillations, 4–5 g. of a colorless fluid liquid was obtained, b.p. 101–103° at 11 mm.

Anal. Calcd. for $C_{12}H_{16}$: C, 90.0; H, 10.0. Found: C, 88.5; H, 10.4.

Fraction B, because of its higher boiling point, but the low hydrogen uptake, was thought most likely to be 2-benzylcyclopentanone (II) or 2-benzylcyclopentanol (III or IV).

Refractionation of B gave no sharp separation: B_1, 1 g., b.p. 115–124° at 8 mm.; B_2, 2 g., b.p. 126–130° at 8 mm.; B_3, 3 g., b.p. 132–135° at 8 mm.

Fractions B_1, B_2 and B_3 each gave considerable amounts of the semicarbazone of II. The amounts of semicarbazone isolated indicated a 30–40% yield of II, while the lower boiling fractions A suggested the yield of hydrocarbon material (mostly IX) to be about 40–50%. The higher boiling fractions, B, may have contained small amounts of alcohol III, but only traces (<5%) of III were isolated as the 3,5-dinitrobenzoate, m.p. 88–90°.

Preparation of *trans*-2-Benzylcyclopentanol (IV). A. Lithium Aluminum Hydride Reduction of II.—A solution of 17.4 g. (0.1 mole) of 2-benzylcyclopentanone (II) in 100 cc. of dry ether was added slowly to a suspension of 4.2 g. (0.11 mole) of lithium aluminum hydride in 75 cc. of ether over a period of 2 hours with stirring at room temperature. After all the ketone had been added, the mixture was refluxed for 2 hours more. The reagent was decomposed with water, the ether solution was washed twice with water and dried over potassium carbonate (anhydrous). After removing the drying agent and ether the residual oil, 17 g. (95+%), was distilled *in vacuo*. The product boiled at 160–161° at 21 mm., yield 16 g. (90%).

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.8; H, 9.1. Found: C, 81.7; H, 9.1.

Treatment of this *trans*-alcohol IV with 3,5-dinitrobenzoyl chloride in the usual way gave 80–90% of the 3,5-dinitrobenzoate, m.p. 78–79°, after recrystallizations from ether–hexane and from alcohol.

Anal. Calcd. for $C_{19}H_{18}N_2O_6$: C, 61.6; H, 4.9. Found: C, 61.6; H, 5.0.

Treatment of this alcohol with α-naphthyl isocyanate gave the α-naphthylurethan of IV, m.p. 106–107°, crystallized from hexane, yield 80–85%.

Anal. Calcd. for $C_{23}H_{23}NO_2$: C, 80.0; H, 6.7. Found: C, 80.2; H, 6.7.

B. Lithium Aluminum Hydride Reduction of I.—A solution of 17.2 g. (0.1 mole) of 2-benzylidenecyclopentanone (I) in 100 cc. of dry ether was added to a suspension of 4.2 g. (0.11 mole) of lithium aluminum hydride in 75 cc. of ether over a 2-hour period with stirring at room temperature. The reaction mixture was refluxed for 2 hours longer, the excess reagent was decomposed with water and the ether layer was separated and washed with water. After drying the ether layer, solvent was removed and the product distilled *in vacuo*. The product boiled at 168–170° at 26 mm., yield 16 g. (90%), and was identical with the IV described just previously.

This product likewise gave a dinitrobenzoate melting at 77–78° and an α-naphthylurethan melting at 105–106°. Both of these derivatives gave carbon and hydrogen analyses in excellent agreement with the theory for these derivatives of the saturated alcohol IV. Thus the products from both of these lithium aluminum hydride reductions are the same saturated alcohol IV. The melting points of these derivatives differed significantly from the melting points of the corresponding derivatives from the alcohol III, obtained by platinum oxide catalyzed hydrogenation of I.

2-Benzylidenecyclopentanol[12] **(V).**—The lithium aluminum hydride reduction of the unsaturated ketone I using excess reagent at room temperature gave the saturated *trans* alcohol IV rather than the expected unsaturated alcohol V.[12] The reduction was thus repeated according to the procedure of Hochstein and Brown.[13]

A suspension of 1.1 g. (0.028 mole = 0.11 mole of H_2) of lithium aluminum hydride was added to a solution of 17.2 g. (0.1 mole) of 2-benzylidenecyclopentanone (I) in 100 cc. of dry ether kept at −10° during a period of 15 minutes, with stirring. After decomposing any excess reagent with water, the ether layer was washed with water, dried, and evaporated. The crystalline product V amounted to 18 g. (100%), m.p. 79–82°. After recrystallizations from hexane the yield was 16 g. (90–95%) of white crystals, m.p. 83–84°.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.8; H, 8.1. Found: C, 82.7; H, 8.1.

This unsaturated alcohol gave an α-naphthylurethan, white crystals from methanol, yield 95%, m.p. 130–131°.

Anal. Calcd. for $C_{23}H_{21}NO_2$: C, 80.5; H, 6.2. Found: C, 80.5; H, 6.2.

Preparation of *cis*-2-Benzylcyclopentanol (III). Catalytic Hydrogenation of V with Platinum Oxide.—Catalytic hydrogenation of a solution of 8.7 g. (0.05 mole) of V in 150 cc. of methanol containing 0.2 g. of platinum oxide proceeded rapidly. An uptake of 0.05 mole of hydrogen occurred within 2 hours. After removing catalyst and solvent, distillation *in vacuo* gave 8 g. (90%) of oil, b.p. 137–138° at 10 mm.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.8; H, 9.1. Found: C, 81.9; H, 8.9.

This product contained no ketone and gave no semicarbazone, but gave a 70% yield of a 3,5-dinitrobenzoate, m.p. 90–92°, by the usual procedure and after recrystallization from ethanol. The product here is thus the same *cis*-alcohol III, isolated only in the form of derivatives from the platinum oxide reduction of the unsaturated ketone I. The melting point of the 3,5-dinitrobenzoate obtained serves to distinguish the product here as different from, and thus *cis*, the product obtained by lithium aluminum hydride reduction of either II or I. The yield of 3,5-dinitrobenzoate obtained here indicates that this product must be nearly pure *cis* isomer.

Oxidation of the Isomeric *cis*-(III) and *trans*-(IV)-2-Benzylcyclopentanols with Chromic Acid.—Oxidation of aliquots of pure *cis*-2-benzylcyclopentanol (III) and of the pure *trans* isomer IV using chromic acid in aqueous acetic acid gave back in each case about 90% of 2-benzylcyclopentanone[2] (II). The recovered ketone was isolated and identified in each case as the semicarbazone,[2] m.p. 196–197°.

***trans*-Hexahydrobenzylcyclopentanol (VI).**—A solution of 17.6 g. (0.1 mole) of pure *trans*-2-benzylcyclopentanol (IV) in 150 cc. of methanol containing 2 cc. of concentrated hydrochloric acid and 0.2 g. of platinum oxide was hydrogenated under the usual conditions. The uptake of hydrogen proceeded at only a moderate rate and 0.3 mole was absorbed in from 5–8 hours before coming to a complete stop. After removing catalyst and solvent, the product in ether was washed with dilute alkali, and with water. After drying and removing ether, the residue was distilled *in vacuo* and gave 17 g. (95%) of liquid of b.p. 130–132° at 8 mm. with no forerun or distillation residue.

Anal. Calcd. for $C_{12}H_{22}O$: C, 79.1; H, 12.2. Found: C, 79.3; H, 12.0.

This product (VI) gave a 3,5-dinitrobenzoate which was very difficult to obtain crystalline, but which was eventually recrystallized several times from ethanol, yield 80–90%, m.p. 46–47°.

Anal. Calcd. for $C_{19}H_{24}N_2O_6$: C, 60.6; H, 6.4. Found: C, 60.7; H, 6.5.

The phenylurethan of VI was obtained in 90% yield, and after recrystallizations from hexane–pentane mixtures it melted at 84–85°.

Anal. Calcd. for $C_{19}H_{27}NO_2$: C, 75.8; H, 9.1. Found: C, 76.0; H, 9.2.

The α-naphthylurethan of VI, obtained in 85% yield, melted at 72–73° after recrystallization from hexane.

Anal. Calcd. for $C_{23}H_{29}NO_2$: C, 78.6; H, 8.3. Found: C, 78.8; H, 8.3.

***cis*-Hexahydrobenzylcyclopentanol (VII).**—Catalytic hydrogenation of a solution of 17.6 g. (0.1 mole) of pure *cis*-2-benzylcyclopentanol (III) in 150 cc. of methanol containing 2 cc. of concentrated hydrochloric acid and 0.2 g. of platinum oxide proceeded rapidly with an uptake of just 0.3 mole of hydrogen. After removing catalyst and solvent, the residue in ether was washed with a little dilute aqueous alkali to remove any acid. After drying the ether layer, the ether was removed and the product was distilled *in vacuo*. The yield of pure VII was 17 g. (95%), b.p. 130–131° at 10 mm., and with no observable foreruns or distillation residues.

This product gave a good carbon-hydrogen analysis, formed a 3,5-dinitrobenzoate melting at 103–104° in 80% yield, and gave an α-naphthylurethan melting at 111–112° in 85% yield. Analytical results and melting points for other samples of these compounds are reported under the description of one of the products of the catalytic hydrogenation of 2-benzylcyclopentanone (II) with platinum oxide in the presence of acid.

The further hydrogenation of the pure *cis-* and *trans-*2-benzylcyclopentanols (III and IV) in the presence of acid and platinum oxide leads only to the pure hexahydro derivatives, VII and VI, respectively, uncontaminated with any lower boiling (hydrocarbon), material. This strongly suggests that in the mixture of products obtained during the reduction, under similar conditions, of 2-benzylcyclopentanone (II) the lower boiling hydrocarbon product VIII must result in some other route from II, not mediated by the alcohol III. What this alternate pathway might be in this case still remains obscure.

Acknowledgment.—The authors are indebted to S. W. Blackman for the microanalytical results included here.

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Reactions with Diazoalkanes. V. Action of Diazoalkanes and of Aryl Azides on N-Arylmaleimides

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RECEIVED JUNE 27, 1955

Diazomethane and ethyl diazoacetate add to the C═C bond in N-arylmaleimides (Ia–f) at 0° to yield the corresponding bicyclic pyrazoline derivatives (II; *cf.* Scheme 1). The cyclopropane derivatives (IV) are obtained by the action of diphenyldiazomethane and of 9-diazofluorene on Ia–f in boiling benzene solution; the pyrazoline derivatives (III) are only obtained when these reagents are allowed to react with Ia and Ib at 0°, respectively (*cf.* Scheme 2). N-Phenylcitraconimide (VIIa) behaves similarly toward diazoalkanes (*cf.* Scheme 4). Δ^2-1,2,3-Triazoline derivatives (V) are readily obtained by the action of aryl azides on Ia–g and undergo loss of nitrogen with the formation of the corresponding aziridine derivatives (VI) (*cf.* Scheme 3). The behavior of 2,3-dichloro-N-phenylmaleimide (VIIb) toward sodium azide simulates that of 2,3-dichloro-1,4-naphthoquinone toward the same reagent, yielding 2,3-diazido-N-phenylmaleimide (XI).

In continuation of previous work,[1] the action of diazoalkanes on N-arylmaleimides has now been investigated. When Ia-f are allowed to react with ethereal diazomethane solution and/or ethereal solution of ethyl diazoacetate at 0°, the corresponding bicyclic pyrazoline derivatives (II) (*cf.* scheme 1) are obtained. The action of diphenyldiazomethane and of 9-diazofluorene on Ia and on Ib, respectively, in cold benzene solution leads to the formation of the pyrazoline derivatives (III), whereas their action on Ia-f in boiling benzene solution yields the corresponding cyclopropane derivatives (IV; *cf.* Scheme 2).

Similarly, N-phenylcitraconimide (VIIa) gives the pyrazoline derivatives (VIIIa or VIIIb) with diazomethane and with ethyl diazoacetate in the cold and the corresponding cyclopropane derivatives[2] (IX) with diphenyldiazomethane and with 9-diazofluorene in boiling benzene solution.

Whereas VIIa reacts readily with diphenyldiazomethane and with 9-diazofluorene (Scheme 4), 2,3-dichloro-N-phenylmaleimide (VIIb) is stable or almost stable toward the action of these reagents under the given experimental conditions.

The pyrazoline derivatives (II, III and VIIIa or VIIIb) are analogous. II (X = C_6H_5, R = H), which can be taken as an example, is colorless, melts with evolution of gas and gives the correct analytical values. When heated in vacuum above its melting point, it gives 2,3-cyclopropane-(N-phenyl)-dicarboximide (IV, X = C_6H_5, R = R′ = H). Similarly, the pyrolysis of II (X = C_6H_5, R = $COOC_2H_5$) gives a product believed, by analogy, to be 1-carbethoxy-2,3-cyclopropane-(N-phenyl)-dicarboximide (IV, X = C_6H_5, R = $COOC_2H_5$, R′ = H).

Reactions with Aryl Azides.—Similarities between diazoalkanes and their isoteric azides have been described. The addition of diazomethane and of phenyl azide to olefinic linkages in fumaric ester[3] and in toluoquinone[4] provides a good example.

We have now investigated the behavior of the C═C bond in Ia-g and in X toward the action of aryl azides. Whereas X failed to react with phenyl azide under the given experimental conditions, Ia-g react readily with aryl azides to give the addi-

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[1] For previous work on diazoalkanes see A. Mustafa, *J. Chem. Soc.*, 234 (1949); A. Mustafa and M. K. Hilmy, *ibid.*, 3254 (1951); 1434 (1952); A. Mustafa and A. H. E. Harhash, THIS JOURNAL, **76**, 1383 (1954).

[2] For the formation of cyclopropane derivatives by the action of diazoalkanes on olefinic compounds compare A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, 1434 (1952); L. Horner and L. Lingnau, *Ann.*, **591**, 21 (1955).

[3] L. Wolff, *Ann.*, **394**, 23, 59 (1912).

[4] G. Caronna and S. Palazzo, *Gazz. chim. ital.*, **82**, 292 (1952).