Notes

On the Dehydration of Bis-1,3- and Tetrakis-1,2,3,4-(α-hydroxydiphenylmethyl)cyclobutane

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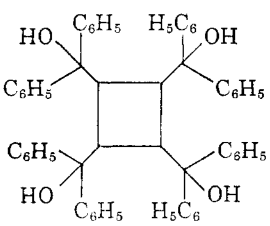
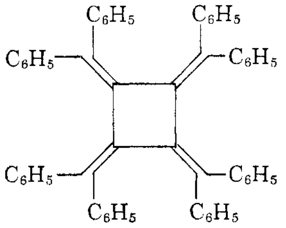
As part of a general study directed toward the synthesis of the unknown tetramethylenecyclobutane (I), for which some stability is indicated by molecular orbital calculations,[1] we have synthesized the tetracarbinol II[2] in the hope that subsequent dehydration to the related tetrakis(diphenylmethylene)cyclobutane (III)[3] might be achieved.



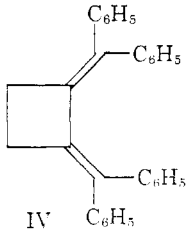
II



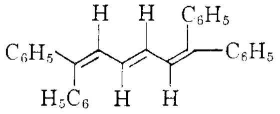
III

The alcohol II was prepared by the addition of phenylmagnesium bromide to either *trans, trans,-trans*-1,2,3,4-tetracarbomethoxycyclobutane[2] or *trans,trans,trans* - 1,2,3,4 - tetrabenzoylcyclobutane[4] and presumably because of steric interactions[5] has retained the *trans,trans,trans* stereochemistry. Treatment of II with iodine in xylene at 140° afforded a mixture of hydrocarbons. The mass spectrum[6] of this mixture established that only a trace of the desired product ($M/e = 712$) may have been formed.

The major component of the mixture (98%) was a yellow-green fluorescent product of mass 384 which after purification by recrystallization melted at 196–199°. The carbon-13 isotope abundance as determined from the mass spectrum as well as the elemental analysis and Rast molecular weight are in accord with an empirical formula of $C_{30}H_{24}$. The appearance of parent peaks at M/e 548 and 384 was not surprising in view of the *observed* formation of benzophenone during the reaction. The latter was isolated and characterized by direct comparison of infrared spectra and formation of benzophenone 2,4-dinitrophenylhydrazone. The $C_{30}H_{24}$ hydrocarbon showed ultraviolet absorption at λ_{max} 253 mμ (ε 18,980) and λ_{max} 367 mμ (ε 59,650).



IV



V

Although the ultraviolet spectrum of this material is qualitatively similar to that of the isomeric diene IV, [λ_{max} 258 mμ (ε 23,000); λ_{max} 351 mμ (ε 21,400)],[5] the melting points and infrared spectra of the two isomers are entirely different.

That the reaction product obtained on treating II with iodine in xylene was in fact the triene V became apparent from the results of catalytic hydrogenation and NMR analysis which showed no absorption above $\tau = 3.5$. The reduction, accomplished with copper chromite catalyst, at 150° (2200 p.s.i.), afforded a colorless compound having a melting point (120–122°) which is in agreement with the value reported for 1,1,6,6-tetraphenylhexane (m.p. 123–124°).[7a] A direct comparison of ultraviolet and infrared spectra of the unknown $C_{30}H_{24}$ hydrocarbon with those of an authentic sample[7b] of V confirmed our conclusion. Thus it appears that the reaction of II with iodine in xylene not only involves dehydration and loss of benzophenone, but in addition is accompanied by substantial cleavage of the cyclobutane ring. An investigation on the course of this reaction is in progress.

Under other conditions—*i.e.*, acid-catalyzed dehydration rather than reaction with iodine—II gives an oxygenated derivative (m.p. > 330°).

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[1] J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952).

[2] G. W. Griffin, A. F. Vellturo, and K. Furukawa, *J. Am. Chem. Soc.*, **83**, 2725 (1961).

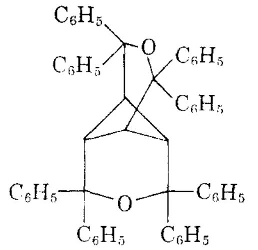
[3] During the course of our investigation, H. Shechter and R. O. Uhler (Dissertation Abstracts, **21**, 765 (1960)) reported evidence that the dimer obtained by sun-lamp irradiation of tetraphenylbutatriene possesses this structure.

[4] G. W. Griffin, R. Hager, and D. Veber, unpublished results.

[5] K. B. Alberman and F. B. Kipping, *J. Chem. Soc.*, 779 (1951). We are indebted to Professor Kipping for a sample of the hydrocarbon IV (m.p. 183–184°). The NMR spectrum of this material shows the expected split aromatic hydrogen peak ($\tau = 2.86$ and $\tau = 3.25$) as well as the —CH_2— peak at $\tau = 7.16$. It is assumed that the peak at $\tau = 3.25$ arises from the aromatic protons on the two proximal aromatic nuclei. We wish to thank R. B. Hager for obtaining the spectrum.

[6] We are indebted to Houston Research Laboratory, Shell Oil Co., Houston, Tex., for the mass spectrum of the dehydration mixture.

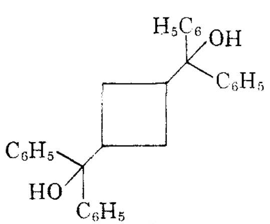
[7] (a) K. H. Bauer and H. Herzog, *J. prakt. Chem.*, **147**, 4 (1936). (b) J. Schmitt, *Ann.*, **547**, 103 (1941).



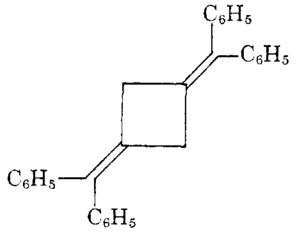
VI

This material is extremely insoluble in most organic solvents and has resisted catalytic hydrogenolysis in addition to cleavage with hydriodic acid. The infrared spectrum, as well as the elemental analysis and Signer-Barger molecular weight, is consistent with structure VI; however this assignment still remains to be firmly established.

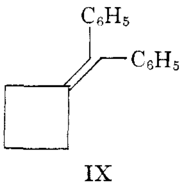
In contrast to II, bis-1,3-(α-hydroxydiphenylmethyl)cyclobutane (VII) under acid-catalyzed conditions is smoothly dehydrated in essentially quantitative yields to bis-1,3-diphenylmethylenecyclobutane (VIII, m.p. 252–253°) without formation of oxygenated by-products. The diol VII (presumably *cis*, m.p. 230–231°) was synthesized by addition of phenylmagnesium bromide to *cis*-1,3-dicarbomethoxycyclobutane.[8]



VII



VIII



IX

The ultraviolet spectrum of VIII (λ_{max} 266, ϵ 31,760) is consistent with two completely isolated diphenylmethylene groups such as the one present in diphenylmethylenecyclobutane[9] (IX) (λ_{max} 252, ϵ 16,130); however slight shoulders on either side of the band in the spectrum of VIII which are not present in that of IX may be indicative of some 1,3-π-type electronic interaction.[10] The NMR spectrum of VIII is in complete agreement with the proposed structure showing bands at $\tau = 2.77$ (aromatic) and $\tau = 6.21$ (—CH_2—) in an apparent ratio of 5:1 respectively. The results of a gas phase ultraviolet spectral study on IV, VIII, and IX and the ozonolysis of VIII will be reported at a later date.

Conditions are still being sought which will permit the conversion of the tetraalcohol II to tetrakis-(diphenylmethylene)cyclobutane.

EXPERIMENTAL[11]

Dehydration of 1,2,3,4-tetrakis(α-hydroxydiphenylmethyl)-cyclobutane (II). Three grams (0.0007 mole) of the dry carbinol was treated with 0.10 g. of iodine in 500 ml. of boiling xylene (dry). The heating was continued for a period of 48 hr., an additional crystal of iodine being added after 24 hr. The yellow-green fluorescent xylene solution was then cooled, washed with sodium thiosulfate solution, then with water, and finally dried. The xylene was then removed under vacuum at a temperature which did not exceed 60°. The yellow solid which was obtained was then extracted for 10 hr. with *n*-pentane from a Soxhlet thimble. Removal of the pentane provided 1.0 g. of a yellow solid which after recrystallization from ethanol afforded 0.16 g. (0.0004 mole) of a solid product, m.p. 194–197°. Sublimation of this solid at 175°/0.05 mm. followed by recrystallization from ethanol gave the pure hydrocarbon (50%), m.p. 196–199°. Ultraviolet spectrum: λ_{max} 253 mμ, ϵ 18,980; λ_{max} 366 mμ, ϵ 59,650.

Anal. Calcd. for $C_{30}H_{24}$: C, 93.71; H, 6.29; mol. wt. 384. Found: C, 94.05; H, 6.24; mol. wt. 357 (Rast).

Preparation of 1,3-bis-(α-hydroxydiphenylmethyl)cyclobutane (VII). One gram (0.006 mole) of *cis*-1,3-dicarbomethoxycyclobutane dissolved in 10 ml. of anhydrous ether was added dropwise to 0.08 mole of phenylmagnesium bromide prepared in 50 ml. of anhydrous ether. After heating under reflux for 1 hr. the reaction mixture was cooled and hydrolyzed by pouring it into a mixture of ammonium chloride (10 g.) and ice. The ether and diphenyl was then removed by steam distillation. The solid residue was collected and dried. Two recrystallizations from ethanol gave the carbinol in the form of needles (1.7 g., 67%), m.p. 230–231°.

Anal. Calcd. for $C_{30}H_{28}O_2$: C, 85.68; H, 6.71. Found: C, 85.77; H, 6.87.

Dehydration of 1,3-bis-(α-hydroxydiphenylmethyl)cyclobutane. (VII). A 0.10 g. (0.0002 mole) sample of the carbinol II was heated under reflux for 1 hr. in 10 ml. of acetic acid containing 1 ml. of concd. hydrochloric acid. The resulting suspension was filtered and the colorless solid melted at 251–252° after recrystallization from methylcyclohexane.

Anal. Calcd. for $C_{30}H_{24}$: C, 93.71; H, 6.29; mol. wt. 384. Found: C, 93.92; H, 6.07; mol. wt. 362 (Rast).

Acid-catalyzed dehydration of 1,2,3,4-tetrakis(α-hydroxydiphenylmethyl)cyclobutane (II). A suspension of the carbinol (1.0 g., 0.0002 mole) in 25 ml. of glacial acetic acid containing 2.5 ml. of concd. hydrochloric acid was heated for 1 hr. at 120°. The resulting suspended solid was then collected on a filter and subsequently crystallized from benzene-methylcyclohexane (m.p. > 330°). Ultraviolet spectrum: λ_{max} 259 mμ, ϵ 1880.

Anal. Calcd. for $C_{56}H_{44}O_2$: C, 89.80; H, 5.92; mol. wt. 748. Found: C, 90.02; H, 5.85; mol. wt. 698 (Signer-Barger in chloroform).

Acknowledgment. The authors are indebted to the Office of Ordnance Research (DA-ORD-31-124-61-

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(8) *cis*-1,3-Dicarbomethoxycyclobutane was prepared from a sample of the anhydride of *cis*-1,3-cyclobutanedicarboxylic acid generously supplied by Professor K. B. Wiberg and synthesized according to the procedure of D. H. Deutsch and E. R. Buchman. See Abstracts of the Meeting of the Organic Division of the American Chemical Society, Boston, April 1951, p. 35m.

(9) S. H. Graham and A. J. S. Williams, *J. Chem. Soc.*, 4066 (1959); we are grateful to these authors for a sample of diphenylmethylenecyclobutane for ultraviolet analysis.

(10) F. F. Caserio, Jr., S. H. Parker, R. Piccolini, and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 5507 (1958).

(11) All melting points are uncorrected.

G31) and the Research Corp. for mutual support of this work and to the National Institutes of Health for a graduate fellowship (GF 11801).

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Thermal Rearrangement of Tetrachloro-2*H*-pyran-2-one to Trichloro-2-furoyl Chloride

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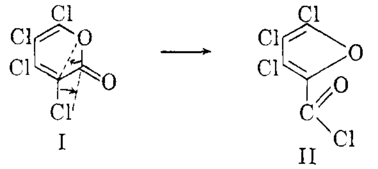
Prolonged heating of tetrachloro-2*H*-pyran-2-one (I)[1] was observed to yield a lower boiling product of the same empirical formula ($C_5Cl_4O_2$). This product has been proved to be the hitherto unreported trichloro-2-furoyl chloride (II). The structure was established by hydrolysis to the known acid, ammonolysis to the known amide, and alcoholysis to the known ethyl ester. Since these compounds have previously been accessible only in poor yield *via* chlorination of ethyl furoate,[2] the present method offers an advantageous route to trichloro-2-furoic acid and its derivatives.

The reaction, which does not require a catalyst, may be viewed as an intramolecular rearrangement favored by the formation of the aromatic furan ring. No evidence could be found (by infrared examination) for the reverse reaction in the temperature range used for the rearrangement.



I II

EXPERIMENTAL

The reaction was carried out in a 3-l. flask fitted with a 4-ft. fractionating column packed with glass helices and fitted with a still head having provision for control of the reflux ratio. In this apparatus, 3150 g. of tetrachloro-2*H*-pyran-2-one[1] (13.5 moles) was heated at reflux temperature for 1 hr. until the still head temperature dropped to about 177°. The reaction mixture was then distilled at 20:1 reflux ratio and the product taken off over the course of 36 hr. Except for a small foreshot distilling at 177°–228°, the vapor temperature was 228–234°. The distillation was stopped when the pot temperature reached 340°.

The colorless distillate, amounting to 2240 g., was found to contain 82% trichloro-2-furoyl chloride by comparison of its infrared spectrum with that of a purified specimen. Purification was effected by repeated recrystallizations from chilled hexane. The recrystallized trichloro-2-furoyl chloride melted at 34°.

Anal. Calcd. for $C_5Cl_4O_2$: C, 25.68; H, 0.00; Cl, 60.6. Found: C, 25.56; H, 0.11; Cl, 60.2.

Infrared bands (positions given in microns). Tetrachloro-2*H*-pyran-2-one (I): 5.59 (s), 5.66 (vs), 7.80 (w), 8.14 (s), 9.10 (w), 9.15 (w), 9.47 (w), 10.77 (m), 11.84 (m), 13.44 (m), 13.74 (m) in carbon disulfide; double bond stretching bands at 6.29 (m), 6.64 (m) in carbon tetrachloride.

Trichloro-2-furoyl chloride (II): 5.68 (s), 5.76 (m), 5.82 (m), 7.40 (s), 7.95 (m), 8.07 (w), 9.15 (m), 9.69 (w), 9.87 (w), 11.38 (w), 11.64 (vs), 14.49 (w), 14.89 (m) in carbon disulfide; double bond stretching bands at 6.30 (m), 6.42 (shoulder), 6.16 (shoulder) in potassium bromide disc.

Characterization of the acid chloride (II). The purified acid chloride was dissolved in aqueous acetone followed by partial evaporation of the acetone, to obtain a substantially quantitative yield of trichloro-2-furoic acid, m.p. 174–175°. By dissolving the acid chloride in excess ethanol followed by evaporation to dryness, there was obtained a nearly quantitative yield of ethyl trichloro-2-furoate, m.p. 63°. By passage of dry ammonia through a solution of the acid chloride in benzene for 1 hr. at room temperature, filtration of the precipitated solids, extraction of the ammonium chloride therefrom by water, and recrystallization of the remaining solid from ethanol, there was obtained a nearly quantitative yield of trichloro-2-furamide, m.p. 161°. These products were shown by infrared and mixed melting points to be identical to trichloro-2-furoic acid, ethyl trichloro-2-furoate, and trichloro-2-furamide prepared by the procedures of Hill and Jackson.[2]

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[1] A. Roedig and G. Märkl, *Ann.*, **636**, 1–18 (1960); H. M. Hill (to Eastman Kodak Co.), U. S. Patent 2,629,681 (1949); *Chem. Abstr.*, **47**, 5066 (1953).

[2] H. B. Hill and L. L. Jackson, *Am. Chem. J.*, **12**, 112–130 (1890).

Pyrolysis of β-Hydroxy Olefins. IV. The Synthesis of Long-Chain Unsaturated Ketones

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Previous publications[5-7] from this laboratory have demonstrated that β-unsaturated secondary alcohols can be pyrolyzed at temperatures in the range of 500° to yield olefinic substances and aldehydes. Cyclic alcohols yield ω-olefinic aldehydes. The cyclic transition state mechanism[6] invoked to rationalize these transformations predicts that β-unsaturated tertiary alcohols should yield ketones when pyrolyzed.

Specifically, 2-(1′-cyclohexenyl)cyclohexanone

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[5] R. T. Arnold and G. Smolinsky, *J. Am. Chem. Soc.*, **81**, 6443 (1959).

[6] R. T. Arnold and G. Smolinsky, *J. Org. Chem.*, **25**, 129 (1960).

[7] R. T. Arnold and G. Smolinsky, *J. Am. Chem. Soc.*, **82**, 4918 (1960).