- 19. N. L. HOLDER. Unpublished results.
- 20. E. O. BISHOP. Ann. Reports, 58, 67 (1961).
- 21. G. M. WHITESIDES, D. HOLTZ, and J. D. ROBERTS. J. Am. Chem. Soc. 86, 2628 (1964).
- 22. J. P. PRITCHARD and F. G. A. STONE. J. Am. Chem. Soc. 83, 4138 (1961). P. R. SHAFER, D. R.

DAVIS, M. VOGEL, K. MAGARAJAN, and J. D. ROBERTS. Proc. Nat. Acad. Sci. U.S.A. 47, 49 (1961). J. S. WAUGH and F. A. COTTON. J. Phys. Chem. 65, 562 (1961).

 R. W. FESSENDER and J. S. WAUGH. J. Chem. Phys. 30, 944 (1959); J. D. SWALEN and C. A. REILLY. J. Chem. Phys. 34, 2122 (1961).

## Reaction of Iodine Azide with Cyclopentenone and Cyclohexenone

NOTES

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The addition of iodine azide to 2-cyclopentenone led to the formation of 2-iodo-2-cyclopentenone. A similar reaction with 2-cyclohexenone afforded the expected addition products in addition to 2-iodo-2-cyclohexenone.

L'addition d'azoture d'iode sur la cyclopentène-2 one conduit à l'iodo-2 cyclopentène-2 one. Une réaction similaire avec la cyclohexène-2 one conduit au produit d'addition attendu et à l'iodo-2 cyclohexène-2 one.

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In connection with other work, a sample of 3-aminocyclopentanone was required. From among many possible syntheses, the addition of iodine azide (1) to 2-cyclopentenone was selected. While this reaction was not expected to be regiospecific (2), separation of the reduction products 2-amino- and 3-aminocyclopentanone was not envisaged to be a problem of major proportions.

When 2-cyclopentenone (1) was treated with a solution of iodine azide in acetonitrile containing excess sodium azide according to the published procedure (1), the n.m.r. spectrum of the crude reaction mixture showed none of the expected absorptions for the addition products 3 (Scheme 1), but showed the product to be of the 2-substituted-2-cyclopentenone type. The i.r. spectrum showed strong azide and conjugated carbonyl absorptions (2120 and 1712 cm<sup>-1</sup> respectively). Chromatography afforded 2-iodo-2-cyclopentenone (4) and a compound A whose stability precluded identification. When a solution of 4 was treated under the reaction conditions with iodine azide, t.l.c. of the product indicated a partial conversion into A had occurred. When the reaction was carried out in an n.m.r. tube, a very weak and broad absorption appeared at ca. 5 p.p.m. which remained constant throughout the reaction. Whether this absorption is due to the addition products 3 which are subsequently converted into 4, or whether it is due to some small impurity is unclear. However, if the former is the case, the concentration of 3 cannot be more than 2% of the mixture at any time.

When the same reaction was applied to 2-cyclohexenone (5) (Scheme 2), the crude reaction mixture showed n.m.r. absorptions characteristic (2) of both of the two expected addition products 7a and b as well as of a 2-substituted-2-cyclohexenone in the ratio of 7:7:9 respectively. Chromatography afforded a mixture of 7a and b in the ratio of 1:1 (n.m.r.), and pure 2-iodo-2-cyclohexenone (8a). Treatment of the crude mixture with triethyl amine in ether resulted in the disappearance of the n.m.r. signals between  $\delta$  4 and 7. The i.r. spectrum showed conjugated carbonyl and azide absorptions indicating the presence of 8b, but chromatography afforded.

Comparison of the base-catalyzed rate of exchange of cyclopentanone and cyclohexanone (7:1) (4) provides a rationale for the relative amounts of 3 and 7 in the two reaction mixtures. If these relative acidities also apply to 2 and 6 or

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SCHEME 2

to 3 and 7, it is clear that loss of a proton from 2 or 3 will be more favorable than a similar deprotonation of 6 or 7.

The formation of 2-iodovinyl ketones from this reaction has not been reported previously. While Hassner *et al.* has reported (2, 3) the preparation of 2-azidovinyl ketones, either from the iodine azide adducts of conjugated ketones with sodium azide or from 2-bromovinyl ketones with sodium azide and hydrazoic acid in DMF, no mention of the presence of 2-iodovinyl ketones has been made. The reaction reported here, while not a general synthetic route, does provide a source of two members of this unusual class of compounds.

#### Experimental

The i.r. spectra were recorded on a Beckman IR 12 spectrometer in chloroform solution; n.m.r. spectra were obtained on a JEOLCO C6OHL spectrometer in deuteriochloroform and are reported in p.p.m. from an internal standard (TMS 0). Melting points are corrected. Microanalyses were performed by A. B. Gygli, Microanalysis Laboratory, Toronto, Ontario.

2-Iodo-2-cyclopentenone

To a slurry of 12.0 g (0.185 mol) of sodium azide in 45 ml of acetonitrile which had been cooled to  $-20^{\circ}$ , was added 4.5 g (0.027 mol) of iodine monochloride in 10 ml of the same solvent over a period of 30 min. 2-Cyclopentenone (2.0 g, 0.026 mol) was added all at once and the reaction mixture was stirred for 24 h and allowed to rise to ambient temperature. The dark brown mixture was poured into 100 ml of water and the aqueous solution was extracted with three 60 ml portions of ether. The combined ethereal extracts were washed with two 50 ml portions of 10% sodium thiosulfate solution and two 50 ml portions of water and were dried over sodium sulfate. Evaporation gave 3.4 g of a brown oil which showed no n.m.r. absorptions between 4 and 8 p.p.m., but did show a triplet at  $\delta$  8.15. The i.r. spectrum showed a very weak shoulder at 1745 cm<sup>-1</sup> and strong absorptions at 1720 and 2110 cm<sup>-1</sup>. The t.l.c. (alumina, 50% petroleum ether, 48% benzene, 2% ethanol) showed the presence of two components with  $R_{\rm f}$  values of 0.73 and 0.64.

Chromatography on silica gel using benzene – petroleum ether as eluent gave 1.53 g (30%) of 4, m.p. 70.5– 71.0° from petroleum ether: i.r. 3030, 2925, 1718, 1685 cm<sup>-1</sup>; n.m.r.  $\delta$  8.15 (1H, t, J = 3 Hz), 3.00–2.37 (4H, mult);  $R_{\rm f}$  0.73.

Anal. Calcd. for  $C_5H_5IO$ : C, 28.86; H, 2.24; I, 61.03. Found: C, 28.87; H, 2.46; I, 61.23.

Further elution gave 0.7 g of a very unstable yellow

oil (A) which exhibited strong azide and conjugated carbonyl absorptions in the i.r. spectrum (2100, 1719, 1590 cm<sup>-1</sup>) but no signals below  $\delta$  3.00 in the n.m.r. spectrum. This material decomposed to a black tar within minutes when solvent was removed. The t.l.c. indicated the presence of only the material with  $R_f$  0.64.

### 2-Iodo-2-cyclohexenone

The reaction was run in exactly the same manner using the same molar quantities of reactants. Evaporation of the dried solution gave 5.6 g of a dark brown oil; n.m.r.  $\delta$  7.90 (t, J = 6 Hz), 4.83 (br), 4.60 (br d), 4.24 (mult), 3.7–1.5 (mult); i.r. 3030, 2960, 2880, 2110, 1715, 1690, 1590, 1575 cm<sup>-1</sup>.

Assignment of the first three n.m.r. absorptions to 8a, 7b, and 7a (2) respectively gives a product distribution by n.m.r. integration of 9:7:7

Chromatography of the mixture on silica gel using benzene – petroleum ether as eluent gave a mixture of 7a and 7b in 20% yield

Anal. Calcd. for C<sub>6</sub>H<sub>8</sub>N<sub>3</sub>IO: C, 27.17; H, 3.02. Found: C, 27.31; H, 2.93.

Further elution of the column with benzene and benzene-ethanol afforded **8***a* (2.53 g, 44%) as white crystals from petroleum ether, m.p. 46.0–47.0°: i.r. 3030, 2960, 2940, 2890, 2870, 1690, 1593 cm<sup>-1</sup>; n.m.r.  $\delta$  7.90 (1H, t) 2.87–1.82 (6H, mult).

#### NOTES

Anal. Calcd. for  $C_6H_7IO$ : C, 32.46; H, 3.18; I, 57.16. Found: C, 32.76; H, 3.46; I, 56.76.

Crude adduct (3.0 g) was dissolved in 100 ml ether and 5 ml of triethyl amine was added. The mixture was stirred at room temperature for 18 h, filtered, washed with two 50 ml portions of water, dried, and evaporated to give a dark oil; n.m.r. blank between  $\delta$  4.0 and 7.5; i.r. 2110, 1695 cm<sup>-1</sup>. Purification as previously outlined afforded 1.65 g (55%) of 8a. A dark immobile band on the column may have been 8b or its decomposition products.

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- (a) A. HASSNER. Accts. Chem. Res. 4, 9 (1971). (b)
  F. W. FOWLER, A. HASSNER, and L. A. LEVY. J. Am. Chem. Soc. 89, 2077 (1967).
- 2. G. L'ABBÉ and A. HASSNER. J. Org. Chem. 36, 258 (1971).
- 3. A. HASSNER, G. L'ABBÉ, and M. J. MILLER. J. Am. Chem. Soc. 93, 981 (1971).
- 4. H. SCHECHTER, M. J. CULLIS, R. E. DESSEY, Y. OKUZUMI, and A. CHEN. J. Am. Chem. Soc. 84, 2905 (1962).

# Ozonation of Naphthalene with Water as Participating Solvent. Preparation of *o*-Phthalaldehyde

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The water in aqueous acetone solutions acts as a participating solvent in the reaction of naphthalene with ozone forming hydroperoxy intermediates which are reduced to *o*-phthalaldehyde by conventional agents. The results are markedly different from those obtained in anhydrous solvents. Yields of product requiring no purification are 63%.

Dans des solutions aqueuses d'acétone, l'eau agit comme solvant de participation dans la réaction de l'ozone avec le naphtalène. Il se forme des hydropéroxy intermédiaires que sont réduits en *o*-phthaladéhyde par les agents conventionnels. Les résultats sont très différents de ceux obtenus dans des solvants anhydres. Les rendements en produit (ne demandant aucune purification) sont de 63%.

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The profound effect that the presence of water in the solvent can have on the course of the reaction of a polycyclic aromatic hydrocarbon with ozone was first demonstrated some ten years ago (1) when yields of anthraquinone obtained directly from anthracene without the aid of reducing agents were improved from 28% in glacial acetic acid (2) to 73% in aqueous *t*-butanol (1). The anthracene reaction gave no useful isolable intermediate products and the mechanism of the ozonation reaction in aqueous media was studied first with phenanthrene (3) and later with pyrene (4). This is therefore the third in a series of reports devoted to the subject of ozonation in aqueous solvents.

The results of the work with anthracene,