cannot be characterized by XRD or other generally applicable techniques.

### ACKNOWLEDGMENT

The authors would like to acknowledge the help of Dr. John C. Helmer and Dr. Norbert H. Weichert of the Varian Company who obtained the ESCA spectra.

### REFERENCES

*1.* SIEGBAHN, K., NORDLING, C., FAHLMAN, A., NORDBERG, R., HAMRIN, K., HEDMAN, J., JOHANSSON, G., BERGMARK, T., KARLSSON, S. E., LINDGREN, I., AND LINDBERG, B., "ESCA, Atomic, Molecular, and Solid State Structure Studies by Means of Electron Spectroscopy." Almqvist and Wiksels Boktryckeri Ab, Uppsala, 1967.

*2.* PIERRON, E. D., RASHKIN, J. A., AND ROTH, J. F., *J. Catal.* **9,** 38 (1967).

*3.* BERGER, P. A., AND ROTH, J. F., *J. Phys. Chem.* **71,** 4307 (1967).

*4.* WOLBERG, A., AND ROTH, J. F., *J. Catal.* **15,** 250 (1969)

*5.* SELWOOD, P. W., AND DALLAS, N. S., *J. Amer. Chem. Soc.* **70,** 2145 (1948); JACOBSEN, P. A., AND SELWOOD, P. W., *J. Amer. Chem. Soc.* **76,** 2641 (1954).

*6.* HELMER, J. C., AND WEICHERT, N. H., *Appl. Phys. Lett.* **13,** 266 (1968).

*7.* SOKOLOWSKI, E., NORDLING, C., AND SIEGBAHN, K., *Phys. Rev.* **110,** 776 (1958).

*8.* BERTAUT, F., AND DELORME, C., *C. R. Acad. Sci.* **239,** 504 (1954).

*9.* Unpublished results on Ni and Co on alumina systems.

*10.* DELGASS, W. N., Ref. (*15*) *in* Hollander, J. M., Rep. UCRL-18972 (Lawrence Radiation Lab., Univ. of California, August, 1969).

A. WOLBERG
J. L. OGILVIE
J. F. ROTH

*Central Research Department,*
*Monsanto Company,*
*St. Louis, Missouri 63166*

*Received March 12, 1970*

---

# Deuteriumolysis of Benzophenone

Catalytic hydrogenolysis of ketones and alcohols at a benzylic position to yield hydrocarbons with unchanged carbon skeleton is well established as a useful technique in organic synthesis (*1, 2*). Hydrogenolysis of ketones related to acetophenone and benzophenone and their derivatives has been used to obtain pure hydrocarbons for the American Petroleum Institute (*3, 4*). Deuteriumolysis of ketones is in principle an elegant and economical means for introducing deuterium at the benzylic position. A possible limitation (depending upon catalyst and conditions) is the exchange of aromatic protium by deuterium (*5–9*). We report that the deuteriumolysis of benzophenone (**Ia**) to diphenylmethane-$\alpha,\alpha$-$d_2$ (**IIa**) may be accomplished without detectable exchange of aromatic protium.

## EXPERIMENTAL METHODS

### *Reduction of Benzophenone (**Ia**)*

**(a) Deuteriumolysis to diphenylmethane-$\alpha,\alpha$-$d_2$ (IIa).** To a dry 300-ml hydrogenation flask containing 10 ml of $CH_3CO_2D$ and 1.82 g of 10% Pd–C catalyst, prereduced with 60 ml of $D_2$, was added 9.1 g (0.05 mole) of **Ia** dissolved in 50 ml of $CH_3CO_2D$. Reduction at 25° at atmospheric pressure for 5.4 hr consumed 2535 ml of $D_2$. The catalyst was filtered out with Dicalite and the filtrate was made basic with 10% NaOH. Extracting with ether (2 × 200 ml), drying ($MgSO_4$), concentrating by rotary evaporation under reduced pressure, dissolving in 100 ml petroleum ether, bp 60–68°, and filtering through a 0.5-in. (o.d.) combination column (2 in. of silica gel on top and 1 in. of basic alumina at bottom) gave a colorless solution which was concentrated to 8.2 g of **IIa**.

**(b) Hydrogenation to diphenylmethane (IIb).** The procedure described under part (a) was repeated using $H_2$ to give **IIb**.

### *Chromic Acid Oxidation of Diphenylmethane (IIb) in Acetic Acid-O-d*

A 0.84-g sample of **IIb** dissolved in 21 ml of $CH_3CO_2D$ was oxidized by adding, at room temperature, 3 portions of 0.66 g of $CrO_3$ dissolved in 0.3 ml of $D_2O$ and 5.8 ml of $CH_3CO_2D$ at 24-hr intervals. The mixture was diluted with 100 ml of $H_2O$, made basic with 10% NaOH, extracted with ether, dried ($MgSO_4$), and concentrated to 0.5 g of a 70:30 **Ic**:**IIb** mixture. The mixture was separated by chromatography on a 0.5-in. (o.d.) combination column (2 in. of silica gel, 1 in. of basic alumina, and 1 in. of acidic alumina—top to bottom). Elution of **IIb** and **Ic** was accomplished with pentane and ether, respectively.

### *Oxidation of Diphenylmethane-α,α-$d_2$ (IIa)*

A 1.7-g (0.01 mole) sample of **IIa** was oxidized as described above except that sufficient oxidizing agent (5.28 g, 0.053 mole of $CrO_3$) was added over 81 hr to oxidize **IIa** to 1.3 g (72%) of colorless crystals free of **IIa**. Recrystallization from hexane gave benzophenone (**Ib**), mp 47–48°.

## RESULTS

The reduction of **Ia** was studied in acetic acid-*O-d*, Scheme I, and in acetic acid at atmospheric pressure with Pd–C at room temperature using deuterium and hydrogen, respectively.

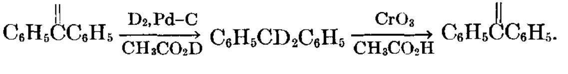
The deuterium content of the phenyl rings of **IIa** was determined by nmr integration using cyclohexane as the internal standard (*3*). The results of the integrations from four solutions of diphenylmethane, **IIb**, in cyclohexane and then solutions of **IIa** in cyclohexane are given in Table 1.

The standard deviations are ca. 1% for individual samples. These averages were weighted in proportion to the reciprocals of the squares of their standard deviations (*10*). The atom fraction of hydrogen in the aromatic rings of **IIa** is 10.569/10.498 or $1.0068 \pm 0.0052$, yielding $10.07 \pm 0.05$ atoms of aromatic hydrogen. These results were verified by use of the HR-60 spectrometer. As shown in Table 1, the deviation from 10 for the number of aromatic protons of **IIb** is less for HR-60 data than for A-60 data. The HR-60 data yields an atom fraction of aromatic hydrogen for **IIa** of 10.087/10.171 or $0.9918 \pm 0.087$. Thus the average number of atoms of aromatic protium in **IIa** is $9.99 \pm 0.09$.

The determination of the deuterium content of the aromatic rings of **IIa** by mass spectrometry is complicated by the observation that both methylene and aromatic hydrogens are involved in the loss of $C_6H_5$ from the molecular ion of diphenylmethane in forming *m/e* 91 (*11*).

This problem was resolved by reoxidation of **IIa** to benzophenone (**Ib**) with chromium trioxide in acetic acid. To establish the absence of exchange accompanying oxidation, **IIb** was oxidized to benzophenone (**Ic**) with chromium trioxide in acetic acid-*O-d*. The presence of an M − 1 ion at all values of the ionizing voltage great enough to produce a useful molecule ion intensity precluded determination of the deuterium content in **Ib** and **Ic**.

Since any isotope effect on loss of $C_6H_5$ from the benzophenone molecular ion producing the intense benzoyl ion, *m/e* 105, should be negligible, the atom percent deuterium in the benzoyl ion will equal that in the molecular ion. The absence of peaks at lower mass, at *m/e* 106 and 107 in excess of natural abundance peaks for *m/e* 105, and from *m/e* 108 through 110 was demonstrated. Comparison of the in-



$$C_6H_5\overset{O}{\overset{\|}{C}}C_6H_5 \xrightarrow[CH_3CO_2D]{D_2,Pd\text{-}C} C_6H_5CD_2C_6H_5 \xrightarrow[CH_3CO_2H]{CrO_3} C_6H_5\overset{O}{\overset{\|}{C}}C_6H_5.$$

SCHEME I

TABLE 1

NORMALIZED AROMATIC PROTON RATIOS FOR **IIa** AND **IIb**

| Sample | Compound in cyclohexane | Molar ratio[a] | No. of phenyl protons[b] | |
|---|---|---|---|---|
| | | | A-60 | HR-60 |
| 1 | Diphenylmethane | 1.1619 | 10.499 ± 0.101[c]<br>10.607 ± 0.096[d] | |
| 2 | | 1.1470 | 10.469 ± 0.118[c]<br>10.574 ± 0.103[d] | 10.150 ± 0.146 |
| 3 | | 1.3018 | 10.456 ± 0.097[c]<br>10.467 ± 0.091[d] | 10.201 ± 0.109 |
| 4 | | 1.2587 | 10.457 ± 0.091[c]<br>10.521 ± 0.136[d] | 10.153 ± 0.109 |
| Av | | | 10.498 ± 0.036 | 10.171 ± 0.068 |
| 5 | Diphenylmethane-$d_2$ | 1.1566 | 10.717 ± 0.142[c]<br>10.491 ± 0.088[d] | 10.029 ± 0.098 |
| 6 | | 1.0735 | 10.465 ± 0.096[c]<br>10.623 ± 0.091[d] | 10.086 ± 0.104 |
| 7 | | 1.1562 | 10.540 ± 0.114[c]<br>10.652 ± 0.091[d] | 10.139 ± 0.092 |
| Av | | | 10.569 ± 0.041 | 10.087 ± 0.056 |

[a] Molar ratio of **IIa**:cyclohexane or **IIb**:cyclohexane was chosen so that the absorptions of the phenyl: cyclohexyl protons were ca. equal.

[b] Normalized to a cyclohexane value of 12 with an average of 15–20 integrations of each sample at two different amplitudes. A 5% error in sample preparation was assumed in calculating standard deviations.

[c,d] Data obtained at different integral amplitudes.

tensities at *m/e* 106 and 107 from the spectra of **Ia** and **Ic** (Table 2, columns 2 and 3) shows that within experimental error, the oxidation of **IIb** in acetic acid-*O*-*d* proceeds without incorporation of deuterium in the aromatic ring.

In the mass spectrum of **Ib** (Table 2, column 4) small residual intensities which may be within experimental error equal to zero are observed at *m/e* 106 and 107. From these average values, the percentages of species containing 0, 1, and 2 atoms of

TABLE 2

ION INTENSITIES IN THE SPECTRA OF BENZOPHENONE **Ia**, **Ib**, AND **Ic**

| *m/e* | Residual ion intensities[a] | | | Species | % of total[d] |
|---|---|---|---|---|---|
| | **Ia** | **Ic** | **Ib**[b,c] | | |
| 105 | 100.0 | 100.0 | 100.0 | $d_0$ | $99.6_5$ |
| 106 | 8.15 | 8.00 | 0.287 ± 0.470 | $d_1$ | $0.29 \pm 0.4_7$ |
| 107 | 0.70 | 0.69 | 0.0645 ± 0.0499 | $d_2$ | $0.06 \pm 0.0_5$ |

[a] Average of data from 10 spectra each at 15 and 16 eV.

[b] Corrected for naturally occurring heavy isotopes.

[c] Derived by comparing with spectra of **Ia**.

[d] Applies only to spectra of **Ib**.

D were calculated (Table 2). The atom percent of aromatic hydrogen in **Ib** and consequently **IIa** is calculated to be 99.9 ± 0.4%.

Thus, both methods of analysis indicate that no more than 0.05% deuterium becomes incorporated in the aromatic rings of **Ia** during deuteriumolysis or in the aromatic rings of **IIa** during oxidation with chromic acid. Because of the relatively low cost of gaseous deuterium and the simplicity of the procedure, this method has a useful potential for specific introduction of deuterium at the benzylic position provided a process can be found which will obviate anticipated protium exchange adjacent to the carbonyl group (*12, 13*).

## ACKNOWLEDGMENTS

Financial assistance to J. W. Burnham and R. K. Mitchum from the American Petroleum Institute and Continental Oil Company, respectively, is gratefully acknowledged. We are also grateful to the Research Foundation of Oklahoma State University and the Petroleum Research Fund for financial assistance. We thank Dr. O. C. Dermer for having read the manuscript.

## REFERENCES

*1.* RYLANDER, P., "Catalytic Hydrogenation over Platinum Metals." Academic Press, New York, 1967.

*2.* AUGUSTINE, R. L., ed., "Reduction; Techniques and Application in Organic Synthesis." Dekker, New York, 1968.

*3.* Correspondence regarding API reference samples should be addressed to Mr. A. J. Streiff, American Petroleum Institute, Carnegie-Mellon University, Pittsburgh, Pa. 15213. We thank Mr. Streiff for a generous sample of high-purity cyclohexane.

*4.* MELTON, R. G., EISENBRAUN, E. J., FLANAGAN, P. W., AND HAMMING, M. C., *Org. Prep. Proc.* **2**, 37 (1970).

*5.* WEITKAMP, A. W., *J. Catal.* **6**, 431 (1966).

*6.* ANDERSON, J. R., AND KEMBALL, C., *Advan. Catal. Relat. Subj.* **9**, 51 (1957).

*7.* HORIUTI, I., AND POLANYI, W., *Trans. Faraday Soc.* **84**, 925 (1962).

*8.* TAYLOR, T. I., "Catalysis," Vol. 5, Chap. 5. Reinhold, New York, 1957.

*9.* HARPER, R. J., SIEGEL, S., AND KEMBALL, C., *J. Catal.* **6**, 72 (1966).

*10.* WORTHING, A. G., AND GEFFNER, J., "Treatment of Experimental Data," Chap. 9. Wiley, New York, 1943.

*11.* MEYERSON, S., HART, H., AND LEITCH, L. C., *J. Amer. Chem. Soc.* **90**, 3419 (1968).

*12.* KEMBALL, C., AND STODDART, C. T. H., *Proc. Roy. Soc. Ser. A* **241**, 208 (1957).

*13.* BOND, G. C., "Catalysis by Metals," Chap. 13. Academic Press, New York, 1962.

S. E. SCHEPPELE*
R. K. MITCHUM
J. W. BURNHAM
E. J. EISENBRAUN*

*Department of Chemistry*
*Oklahoma State University*
*Stillwater, Oklahoma 74074*

P. W. FLANAGAN

*Research and Development Department*
*Continental Oil Company*
*Ponca City, Oklahoma 74601*
*Received February 4, 1970*

* Address correspondence to these authors.