

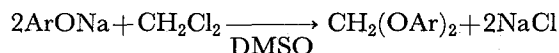
Syntheses of Formaldehyde Diaryl Acetals and Dithioacetals in the Presence of 18-Crown-6 Catalyst

Shigeo TANIMOTO,* Tamotsu IMANISHI, Shigeo JO, and Masaya OKANO

Received June 1, 1978

Dibromomethane was reacted with sodium phenolates and sodium thiophenolates in acetonitrile containing 18-crown-6 to form, respectively, the corresponding formaldehyde diaryl acetals (**1**) and formaldehyde diaryl dithioacetals (**2**) in very high yields.

It has previously been shown¹⁾ that the reaction of the appropriate sodium phenolates with dichloromethane in dimethyl sulfoxide (DMSO) provides formaldehyde diaryl acetals in moderate yields.



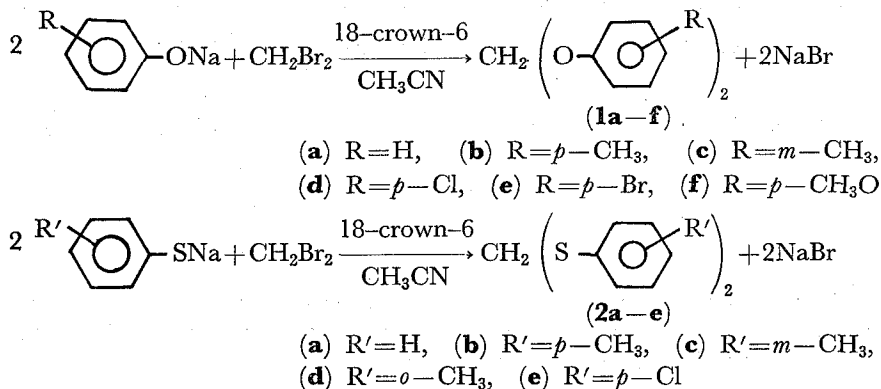
The achievement of this procedure is due to the nucleophilic enhancement of ArO^- by DMSO. In recent years, solid-liquid phase-transfer catalysis employing crown ethers has gained widespread use as a tool in organic synthesis.²⁾ The nucleophilic enhancement of anions by crown ethers in aprotic organic solvents is already well known. For instance, very interesting examples of crown ether catalyzed nucleophilic displacement by cyanide or carboxylate have been reported recently.²⁻⁶⁾ The use of crown ether to catalyze fluorine/halogen exchange with a wide variety of substrates has also been documented.^{7,8)}

We report here a new example of crown ether catalyzed nucleophilic displacement, in which dibromomethane is reacted with sodium phenolates and sodium thiophenolates in acetonitrile to form, respectively, the corresponding formaldehyde diaryl acetals (**1**) and formaldehyde diaryl dithioacetals (**2**) in very high yields. For these reactions, acetonitrile has been successfully used as a solvent. Though there is a comfortable fit between the crown and the centrally located ion, considering by the fact that the hole diameter of 1, 4, 7, 10, 13, 16-hexaoxacyclooctadecane (18-crown-6) has been estimated to be 2.6–3.2 Å and the ionic diameter of Na^+ is 1.90 Å,⁹⁾ 18-crown-6 was chosen as a phase-transfer catalyst in the reactions examined.

The reaction was conducted by refluxing a sodium phenolate (or a sodium thiophenolate) and an excess of dibromomethane in acetonitrile solution in the presence of 0.1 molar equivalents of 18-crown-6. In addition we have found that the same reactions proceed with yields ranging from 65 to 80% even in the absence of the crown ether under the same conditions covering the same period of time. The yields have

* 谷本重夫, 今西 保, 徐 重男, 岡野正彌: Laboratory of Petroleum Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

been, however, remarkably improved by the presence of catalytic amounts of the crown ether.



In comparison with the previous methods^{4,10,11)} employed for the synthesis of **1**, the synthesis using 18-crown-6 catalyst has some advantages: excellent yields, simple isolation and purification of products as well as the shortness of the reaction time.

Table I. Reactions of Sodium Phenolates with Dibromomethane in the Presence of 18-Crown-6

Run	R	Procedure	Reaction time (hr)	Product ^{a)}	Yield ^{b)} (%)
1	H	A	6	1a^{c)}	86
2	H	B	5	1a^{c)}	81
3	<i>p</i> -CH ₃	A	6	1b^{d)}	91
4	<i>m</i> -CH ₃	A	7	1c^{e)}	92
5	<i>p</i> -Cl	A	6	1d^{f)}	97
6	<i>p</i> -Br	A	6	1e^{g)}	90
7	<i>p</i> -CH ₃ O	A	7	1f^{h)}	94

a) All spectral data (nmr, ir, and mass spectral) of the isolated products were consistent with the assigned structures. b) Represents isolated yield. c) Bp 122–123°C/2.5 mmHg (lit,¹⁴⁾ 290–296°C). d) Mp 39–40°C (lit,¹⁵⁾ 40.2°C). e) Mp 49–50°C (lit,¹⁵⁾ 45°C). f) Mp 68–69°C (lit,¹⁶⁾ 70–70.5°C). g) Mp 72.5–73.5°C (lit,¹⁰⁾ 74–74.5°C). h) Mp 49–50°C (lit,¹¹⁾ 54°C).

Table II. Reactions of Sodium Thiophenolates with Dibromomethane in the Presence of 18-Crown-6

Run	R'	Procedure	Reaction time (hr)	Product ^{a)}	Yield ^{b)} (%)
1	H	B	5	2a^{c)}	91
2	<i>p</i> -CH ₃	B	5	2b^{d)}	92
3	<i>m</i> -CH ₃	B	5	2c^{e)}	85
4	<i>o</i> -CH ₃	B	5	2d^{f)}	90
5	<i>p</i> -Cl	B	5	2e^{g)}	93

a) All spectral data (nmr, ir, and mass spectral) of the isolated products were consistent with the assigned structures. b) Represents isolated yield. c) Bp 158–160°C/1 mmHg (lit,¹⁷⁾ 194°C/8 mmHg). d) Bp 168–169°C/1 mmHg (lit,¹⁷⁾ 213–215°C/8 mmHg). e) Bp 176–178°C/2 mmHg (lit,¹⁷⁾ 187–189°C/5 mmHg). f) A new compound. Bp 176–177°C/2 mmHg. g) Bp 193–194°C/2 mmHg (lit,¹⁷⁾ 221–223°C/7 mmHg).

The reaction temperature, however, is higher in the phase-transfer catalyst system.

A previously reported synthesis of bis(phenylthio)methane (**2a**) included heating dibromomethane with sodium thiophenolate in ethanol.¹²⁾ This method seems to be applicable to the preparation of other bis(substituted phenylthio)methanes. However, it is illustrated only by the formation of **2a**. More recently, a new synthetic method using methyltricaprylaminium chloride catalyst, which offers superior yields of **2**, was proposed by Herriott and Picker.¹³⁾ It has also been found that the phase transfer procedure using 18-crown-6 catalyst results in very high yields of **2**.

EXPERIMENTAL

The procedure are shown below: **Procedure A:** A dry 100 ml round-bottomed flask was charged with a dry sodium phenolate (25 mmol), acetonitrile (30 ml), dibromomethane (25 mmol), and 18-crown-6 (2.5 mmol). The mixture was refluxed, with protection from the atmospheric moisture by a calcium chloride drying tube, and stirring for 6–7 hr. The reflux condenser was then replaced with a short Vigreux column and the mixture was distilled under vacuum to remove the acetonitrile from the reaction mixture. Water was added, and the mixture was extracted with ether. The ether solution was washed with 0.5% NaOH aqueous solution, dried over MgSO₄, filtered, and concentrated under vacuum. The residue was vacuum distilled or was recrystallized to give the desired acetal.

Procedure B: A 100 ml round-bottomed flask was charged with a phenol (or a thiophenol) (25 mmol), acetonitrile (50 ml), NaOH (25 mmol) and water (6 ml). The mixture was then stirred to dissolve most of the NaOH. To this mixture were added dibromomethane (25 mmol) and 18-crown-6 (2.5 mmol). The reaction mixture was then refluxed for 5 hr. After which worked-up as in procedure A.

REFERENCES

- (1) S. Tanimoto, R. Taniyasu, and M. Okano, *Yūki Gōsei Kagaku Kyokai-shi (Journal of the Society of Organic Synthetic Chemistry, Japan)*, **29**, 166 (1971).
- (2) G. W. Gokel and H. D. Durst, *Synthesis*, 168 (1976).
- (3) J. W. Zubrick, B. I. Dunbar, and H. D. Durst, *Tetrahedron Lett.*, 71 (1975).
- (4) F. L. Cook, C. W. Bowers, and C. L. Liotta, *J. Org. Chem.*, **39**, 3416 (1974).
- (5) H. D. Durst, *Tetrahedron Lett.*, 2421 (1974).
- (6) C. L. Liotta, H. P. Harris, M. McDermott, T. Gonzalez, and K. Smith, *ibid.*, 2417 (1974).
- (7) T. A. Bianchi and L. A. Cate, *J. Org. Chem.*, **42**, 2031 (1977).
- (8) C. L. Liotta and H. P. Harris, *J. Am. Chem. Soc.*, **96**, 2250 (1974).
- (9) C. J. Pedersen, *ibid.*, **92**, 386 (1970).
- (10) S. Miron and A. Lowy, *ibid.*, **73**, 1872 (1951).
- (11) W. Baker, *J. Chem. Soc.*, 1765 (1931).
- (12) R. L. Shriner, H. C. Struck, and W. J. Jorison, *J. Am. Chem. Soc.*, **52**, 2060 (1930).
- (13) A. W. Herriott and D. Picker, *Synthesis*, 447 (1975).
- (14) L. H. Backeland and H. L. Bender, *Ind. Eng. Chem.*, **17**, 236 (1925).
- (15) M. Arnhold, *Ann.*, **240**, 202 (1887).
- (16) G. Jeminet and A. Kergomard, *Bull. Soc. Chim. France*, 3233 (1967).
- (17) I. I. Lapkin and N. S. Zelenina, *Chem. Abstr.*, **68**, 86950y (1968).