de **5** (50°C, 24h, 0,5g de résine pour 1g de **5**) conduit à l'alkylidène-2 propanediol-1,3 **7** (71%). L'élimination de 2 groupements nitro vicinaux[7] sur **9** donne **10** (40%) qui est transformé en milieu acide en bis (hydroxyméthyl)-2,3 butène-2 diol-1,3 **11**[8] (75%). La préparation de **11** illustre une méthode générale de synthèse de dialkylidène-2 propanediol-1,3[10] dont l'extension à d'autres composés est en cours.

Tableau

C-alkylation des sels du diméthyl-2,2 nitro-5 dioxanne-1,3[a]

Nbre d'équivalent de **1**	Electrophile	Rendement % en C-alkylation[9]		
		4	**5**	**9**
2	**2**	85	5	
2	**2**[b]	88	traces	
1,5	**2**[c]	89		
2	**3**		89	
2	**8**			50
2	**8**			60[d]

a) Réactions effectuées à la lumière du laboratoire pendant 24h dans CH_3OH sous argon. b) Le mélange réactionnel est traité après 3h. c) **1** est formé à partir du diméthyl-2,2 nitro-5 dioxanne-1,3[5] par NBu_4OH 40% dans H_2O. d) La réaction est effectuée dans le DMSO.

La présence du groupement ylidène-2 propanediol-1,3 sur un nitro-5 imidazole[3] biologiquement actif accroît considérablement sa solubilité dans l'eau. D'autres applications dans le domaine de la chimie fine constituent les objectifs de la généralisation du mode de greffage de ce groupement polaire à différents substrats.

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REFERENCES ET NOTES

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2) M.P. CROZET et P. VANELLE, Tetrahedron Letters, 1985, 26, 323.

3) M.P. CROZET, J-M. SURZUR, P. VANELLE, C. GHIGLIONE et J. MALDONADO, Tetrahedron Letters, 1985, 26, 1023 et références citées sur les $S_{RN}1$.

4) G.B. LINDEN et M.H. GOLD, J. Org. Chem., 1956, 21, 1175.

5) H. PIOTROWSKA, T. URBANSKI et I. KMIOTEK, Rocz. chem., 1973, 47, 409.

6) a) Z. MATACZ, H. PIOTROWSKA et T. URBANSKI, Pol. J. Chem., 1979, 53, 187. b) L.C. GARVER, V. GRAKAUSKAS et K. BAUM, J. Org. Chem., 1985, 50, 1699.

7) N. KORNBLUM, S.D. BOYD, H.W. PINNICK et R.G. SMITH, J. Am. Chem. Soc., 1971, 93, 4316.

8) J.L. RIPOLL, Bull. Soc. Chim. Fr., 1974, 2567.

9) Les composés nouveaux décrits dans cette note ont des microanalyses et des analyses spectrales satisfaisantes.

10) **11** a été préparé pour l'étude comparative d'alkylation de divers polyols par catalyse par transfert de phase : R. NOUGUIER et M. MCHICH, J. Org. Chem., 1985, 50, sous presse.

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FACILE CONVERSION, USING A VASTLY IMPROVED GATTERMANN PROCEDURE, OF ACTIVATED THIOBENZOPHENONES INTO TETRAARYLETHYLENES.

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Abstract : A simple and inexpensive procedure is proposed for the title coupling, performed at room temperature in DMSO.

UNION of pre-existing trigonal carbons into an olefin is easily done : on paper. Achieving it in practice is more difficult, but it is feasible with an adjunct metal center or surface. The remarkable recent Mc Murry reaction uses Ti(0) : the glycol formed by the pinacol coupling of ketyls (radical anions) generated from the starting carbonyls dehydrates on the surface of the Ti(0) particles[1]. Olefin metathesis bears some conceptual resemblance to the desired goal, and it occurs via a metallocycle[2]. Thioketones, easily obtainable now[3] have been desulfurized into alkenes by Fe(II) chloride combined with sodium triethylborhydride on alumina[4]. As devised by Gattermann[5], olefin synthesis uses copper (0) and it requires high temperatures (180-200°). We saw in this venerable reaction a potential rival to Mc Murry's procedure, with the advantage of using the much cheaper copper instead of titanium. Low-valent titanium species can also reduce some of the substituents present in the substrate, for example the nitro group. Gattermann's procedure was modified once (xylene reflux)[6], but elevated temperatures continued to serve as a deterrent however.

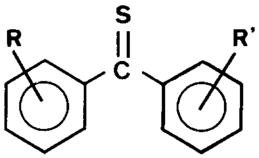
Formation of thioketyls, which would then couple, prior to extrusion of sulfur as copper sulfide, appears as a plausible path for the Gattermann reaction. Thus, our rationale here was to increase solvent polarity, since ion pairs presumably occur. In our hands, dimethyl sulfoxide gave the best results.

Indeed, reaction of thiobenzophenone with copper powder in DMSO leads to formation of the duplication olefin at room temperature within 30 hours. Reaction time is shorter in the presence of electron-withdrawing substituents (see the Table), whereas electron-releasing substituents retard the reaction. *Ortho*-substituted thiones do not react at elevated temperatures and, in the original Gattermann's procedure, give poor yields.

Standard procedure :

A mixture of 1 mM of thione, 0,25g of copper powder and 1 ml of dried DMSO is placed into the reaction flask, then flushed with nitrogen and stoppered. The reaction mixture is stirred at room temperature until disappearance of the blue color of the substrate, and for the time stated in the table. Products are isolated by several successive extractions with chloroform, followed by crystallization or by column chromatography.

Table : reaction of thiobenzophenones with copper in DMSO at room temperature.



entry	R	R'	reaction time	isolated yield(%)	ref.
1	H	H	31hrs	98	7
2	4-F	4-F	8hrs	93	8
3	4-Cl	4-Cl	15hrs	65	9
4	4-OMe	4-OMe	20hrs	73[a]	5
5	4-NO_2	H	4hrs	49[b]	10
6	4-CF_3	H	12hrs	98[b]	11
7	3-NO_2	H	22hrs	99[b]	10

Notes : a) reaction was run at 80°.

b) an equimolar mixture of the E and Z isomers was formed.

We believe that this renovated Gattermann synthesis, while being restricted in scope to thiobenzophenones activated by electron-withdrawing substituents, is nevertheless quite useful because of its good yields, simplicity, and low cost.

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REFERENCES

1. J.E. Mc Murry, Accounts Chem. Res., **16**, 405 (1983) ; **7**, 281 (1974).
2. T.J. Katz, Adv. Organometal. Chem., F.G.A. Stone and R. West, eds., Academic Press, New York, 1977, 283-317.
3. B.S. Pedersen, S. Scheibye, N.H. Nilsson, and S.-O. Lawesson, Bull. Soc. Chim. Belg., **87**, 223 (1978) ; J.W. Scheeren, P.H.J. Ooms, and R.J.F. Nivard, Synthesis, 149 (1973) ; for a review see also : D. Paquer, Int. J. Sulfur Chem. (B), **7**, 269 (1972).
4. H. Alper, S. Ripley, and T.L. Prince, J. Org. Chem., **48**, 250 (1983).
5. L. Gattermann, Ber., **28**, 2869 (1895).
6. A. Schönberg, O. Schütz, and S. Nickel, Ber., **61**, 1375 (1928).
7. L. Gattermann and H. Schultze, Ber., **29**, 2944 (1896).
8. D. Bethel and J.D. Callister, J. Chem. Soc., 3808 (1963).
9. J.F. Norris, R.Thomas, and B.M. Brown, Ber., **43**, 2947 (1910)
10. R. Kuhn and D. Blum, Chem. Ber., **92**, 1483 (1959).
11. E and Z isomers not separated, m.p. 152-181° ; IR (KBr, strong bands) 1325, 1170, 1120, 1110, 1070 cm^{-1} ; ^1H nmr ($CDCl_3$) δ 7,39-7,34 (m, 4H), 7,17-7,12 (m, 10H), 7,01-6,97 (m, 4H).

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