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BIS(p-METHOXYPHENYL)TELLUROXIDE, A NOVEL ORGANOTELLURIUM ALDOL CATALYST

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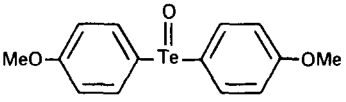
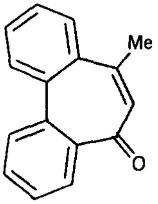
Summary: Bis(p-methoxyphenyl)telluroxide has been found to function as a mild catalyst for a variety of aldol condensations.

Although bis(p-methoxyphenyl)telluroxide (1) has been known since 1916,[1] it has been the subject of limited interest until the recent discovery by Barton and his coworkers of its mild and selective oxidizing properties.[2,3] We have now found that telluroxide 1 can also function as a new type of aldol catalyst under very mild aprotic conditions.

Condensations were generally carried out by refluxing a toluene solution of equimolar amounts of the aldol components with about 10 mole percent of 1 for 2 hours. A number of representative examples are shown in Table 1.



(1)



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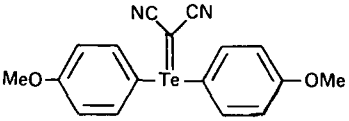

(3)

In a typical procedure, α-tetralone (0.50 g, 3.4 mmol), benzaldehyde (0.37 g, 3.5 mmol) and bis(p-methoxyphenyl)telluroxide (0.10 g, 0.28 mmol) were refluxed in toluene (10 ml) for 2 hours. Evaporation of the solvent followed by chromatographic separation (SiO_2, CH_2Cl_2/hexane 1:1) from a small amount of bis(p-methoxyphenyl)telluride, gave 0.77 g (96%) of 2-benzylidene-α-tetralone.

The smooth condensation of 2,2'-diacetylbiphenyl to the dibenzotropone 2[4] is remarkable in view of previous unsuccessful attempts to effect this cyclization using conventional catalysts.[5] On the other hand, the cyclization of acetonylacetone to 3-methyl-2-cyclopentenone and the condensation of benzil with dibenzyl ketone to give tetracyclone failed completely in the presence of 1, although these reactions proceed readily with conventional basic catalysts.

The relatively poor yields of condensation products in cases where very acidic methylene compounds were used (e.g. malononitrile and dimethyl malonate), may be attributed to a partial destruction of the catalyst due to formation of telluronium ylids. In fact, we at first believed that telluronium ylids might be intermediates in all these reactions, the observed products being formed in a Wittig-like reaction. In order to test this hypothesis, we prepared the telluronium ylide 3 by analogy to recent literature methods,[6] and heated it with benzaldehyde. No benzalmalononitrile was produced, however, thus ruling out an ylide mechanism for the condensation.

TABLE 1. Aldol condensations catalyzed by bis(p-methoxyphenyl)telluroxide

Substrates	Product	Yield (%)	mp	Lit.
benzaldehyde + acetophenone	chalcone	94	57-8	58-9 [9]
benzaldehyde + p-bromoacetophenone	benzal-p-bromoacetophenone	85	100-02	100-03 [10]
benzaldehyde + α-tetralone	2-benzylidene-α-tetralone	96	104-05	105 [11]
benzaldehyde + malononitrile	benzalmalononitrile	50	83-84	83.5-84 [12]
benzaldehyde + dimethyl malonate	benzalmalonic acid dimethyl ester	27	42-3	44-5 [13]
veratraldehyde + nitromethane	veratrylidenenitromethane	41 [b]	140-1	140-1 [14]
butyraldedhyde	2-ethyl-2-hexenal	85	116-18[a]	120 [15]
2,2'-diacetylbiphenyl	2	96	226-7[a]	252 [5]

[a] mp of 2,4-dinitrophenylhydrazone. [b] after 24 h reflux with an 8-fold excess of CH_3NO_2; a 54% yield of veratraldehyde was recovered.

The aldol condensation can be catalyzed by either acids or bases, the latter being most frequently employed.[7] To our knowledge, however, neither sulfoxides nor selenoxides have ever been observed to function as aldol catalysts. The greater polarization of the Te-O bond of a telluroxide may be sufficient to allow 1 to function as a mild and selective base catalyst.[8]

Further studies are in progress in our laboratories concerning the mechanism, as well as the scope and limitations of the telluroxide-catalyzed aldol reaction.

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References and Notes

1. K. Lederer, Ber. Dtsch. Chem. Ges., 49, 1076 (1916).
2. D. H. R. Barton, S. V. Ley and C. A. Meerholz, J.C.S. Chem. Comm., 755 (1979).
3. S. V. Ley, C. A. Meerholz and D. H. R. Barton, Tetrahedron Letters, 1785 (1980).
4. Oil. Satisfactory M.S. and analytical data were obtained on this compound. IR(neat) 1650 cm^{-1}. ^{1}H NMR ($CDCl_3$, Me_4Si) δ(ppm): 2.45 (s, 3 H), 6.63 (s, 1 H), 7.47-7.82 (several peaks, 8 H). The 2,4-dinitrophenyl hydrazone, mp 226-7°, also gave satisfactory NMR and analytical data.
5. D. M. Hall, J. E. Ladbury, M. S. Lesslie and E. E. Turner, J. Chem. Soc., 3475 (1956).
6. S. Tamagaki, R. Akatsuka and S. Kozuka, Bull. Chem. Soc., Jpn., 53, 817 (1980).
7. A. T. Nielsen and W. J. Houlihan, Org. React., 16, 1 (1968).
8. A pKa value of 14.9 was reported for this compound in acetonitrile. V. I. Naddaka, V. P. Garkin, I. D. Sadekov and V. I. Minkin, Zh. Org. Khim., 13, 220 (1977).
9. C. Weygand, Ann, 472, 143 (1929).
10. J. O. Ralls, J. Am. Chem. Soc., 62, 3485 (1940).
11. W. S. Rapson and R. G. Shuttleworth, J. Chem. Soc., 636 (1940).
12. B. B. Corson and R. W. Stoughton, J. Am. Chem. Soc., 50, 2825 (1928).
13. R. Anchütz, Ann, 354, 117 (1907).
14. C. Raiford and D. E. Fox, J. Org. Chem., 9, 170 (1944).
15. M. Häusermann, Helv. Chim. Acta, 34, 1482 (1951).

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