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A Facile Synthesis of a, a'-bis(Substituted Benzylidene)cycloalkanones Catalyzed by bis(pethoxyphenyl)telluroxide(bmpto) Under Microwave Irradiation

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A FACILE SYNTHESIS OF α, α'-BIS(SUBSTITUTED BENZYLIDENE)CYCLOALKANONES CATALYZED BY BIS(*p*-ETHOXYPHENYL)TELLUROXIDE(BMPTO) UNDER MICROWAVE IRRADIATION

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Abstract: The bis(4-methoxyphenyl)telluroxide(BMPTO) catalyzed reaction of cyclopentanone or cyclohexanone with aldehydes brought about the cross-aldol condensation to give the corresponding 2,5-bis(substituted benzylidene) cyclopentanones or 2,6-bis(substituted benzylidene)cyclohexanones in high yield under microwave irradiation in mild conditions. The reaction needs only 5-10 min.

 α -Benzylidene cycloalkanones or α , α '-bis(substituted benzylidene) cycloalkanones are an interesting class of compounds because of their use as precursors to potentially bioactive pyrimidine derivatives^[1]. Cross aldol-type reaction is available for these preparation; however, traditional acid- or base-catalyzed reaction suffers from the reverse reaction^[2], and metal chlorides (TiCl₄ et al.) are reported to promote the self-comdensation of ketones and aliphatic aldehydes rather than the cross-aldol condensation^[3]. Ogoshi et al. reported a new

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practical method for the preparation of these cross-condesates^[4]. Whereas the obtained α, α' -bis (benzylidene)cyclohexanone in 30% yield by the Rh(III)-porphyrin complex-catalyzed reaction of cyclohexanone with aromatic aldehyde.

We had previously investigated the BMPTO-catalyzed condensation of active methylene compounds with aldehydes^[5], finding this kind of reaction. Using BMPTO as catalyst, we investigated the reaction of cycloalkanones with aromatic aldehydes under microwave irradiation, obtained α, α' -bis(substituted benzylidene) cycloalkanones in good yield. To obtain the α, α' -bis(substituted benzylidene) cycloalkanones, the mole ratios of alkanone to aromatic aldehyde we use



were 1:2, 1:3, or more and that's it. When the mole ratio of alkanone to aromatic aldehyde was 3:1, we hope to obtain α -benzylidene cycloalkanone, but unexpectedly, the only product we got was α, α '-bis(substituted benzylidene)cycloalkanones. For example, when the mole ratio of cyclopentanone to benzaldehyde was 1:3, 1:2, 3:1, α, α' -bis(benzylidene)cyclopentanone was the only product and the yield was 84.5%, 85% and 87%, respectively. The mole ratio of BMPTO to aromatic aldehyde was also investigated. The best ratio was 0.02:1 in the condensation of cyclopentanone with aromatic aldehyde, and was 0.08:1 in the condensation of cyclohexanone. The reactions and results were described in table 1.

As seen from the table 1, employing BMPTO as catalyst the present reaction condensation of cycloalkanone with aromatic aldehydes needs only 5-10 min, although the condensation of cyclopentanone with benzaldehyde catalyzed by BMPTO needs 3 days at room temperature in 30% isolated yield, obtaining α,α' bis(substituted benzylidene)cycloalkanones in high yield. Therefore, the present direct cross aldol condensation of cycloalkanones with aldehydes is a very attractive route to prepare α,α' -bis(substituted benzylidene)cycloalkanones and allows quick preparation of it.

α-BENZYLIDENE CYCLOALKANONES

		Reac.con.				
1/mmol	2 /mmol	BMPTO	Product	Yield(%) ^a	mp(℃) ^b	IR(KBr/cm-1) ^c
(mg)/t(min.)						
a/1	a/2	15/5	а	84.5	188-189	3052,2910,1690.1625
					(lit ^[6] .189)	1600,1446,765,676
a/1	b/2	15/5	b	81	230-231	3105,2847,1706,1605
					(lit ^[7] .233)	1521,1344,816
a/1	c/2	30/10	c	53.5	210-211	3030,2840,1696,1625,1615
					(lit ^[8] .212)	1596,1252,1030,836
a/1	d/2	15/5	d	93.4	222-224	3024,2925,1698,1625-1600
					(lit ^[9] .225)	1447,690
a/1	e/2	15/5	e	72.5	160-162	3131,2914,1680,1625
					(lit ^[10] .162)	1600,1290-1240,751
b/0.5	a/1	30/7	f	64.5	116-117	3030,2921,1660,1606
					(lit ^[11] .117)	1573,1465,770,694
b/0.5	b/1	30/7	g	71.4	159	3101,2962,1689,1600
					(lit ^[12] .159)	1585,1512,1342,858
b/0.5	c/1	30/7	h	69.5	203-204	2936,1634,1592,1450
					(lit ^[13] .205)	1249,1023,834
b/0.5	d/1	30/7	i	71	179-180	3028,2920,1653,1603-1549
					(lit ^[14] .180)	737,692
b/0.5	e/1	30/7	j	86	140-141	3149,2941,1643,1591-1546
					(lit ^[15] .145)	1165-1148,751

Table1. The cross-condensation of cycloalkanones with aldehydes catalyzed by BMPTO under microwave irradiation

a: Yield of isolated pure product.b: Mp were taken on a Buch 535 apparatus and uncorrected.c: The IR spectra were recorded on a Nicolet 740 FT-IR.

Experimental

TLC was carried out on silica gel GF254($20 \sim 40\mu$) Microwave assisted organic reactions were performed in MB20TFC-2 oven.

General procedure for the synthesis of 3 a.

A mixture of cyclopentanone (0.084 g , 1 mmol), benzaldehyde (0.214 g, 2 mmol) and BMPTO (0.015 g , 0.04 mmol) was dissolved in 1 mL acetonitrile in a

10 mL reaction flask. Then the flask was placed in a microwave oven for 5 min, leaving the mixture at room temperature to solidify, Recrystallization from 95% EtOH gave 0.254 g (85%) of α, α' -bis(benzylidene)cyclopentanone as pale yellow needles.

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