

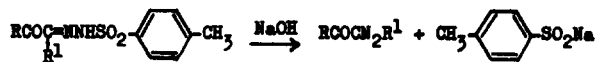
THE USE OF ALUMINA IN THE SYNTHESIS OF
 α -DIAZO CARBONYL COMPOUNDS

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The synthesis of α -dialzo carbonyl compounds via the base catalysed elimination of *p*-toluenesulfinate ion from α -dicarbonyl mono-*p*-toluenesulfonylhydrazones is usually accomplished with dilute sodium hydroxide in a two phase system (1).



We have found that aqueous sodium hydroxide can be advantageously replaced by a suspension of basic alumina (2) in dichloromethane or ethyl acetate. This method possesses some degree of generality and is complementary to the syntheses of α -dialzo carbonyl derivatives developed recently by Regitz (3,4), and Yates and Hendrickson (5). It constitutes a general approach to acyclic (I, R¹H) and cyclic α -dialzo ketones.

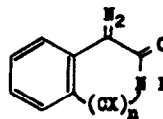
In addition, α -dialso esters of type II ($R=H$) and α -dialso lactams of type III ($R=H$, alkyl, aryl, etc., $X=O$, and $m=0$ or 1) are conveniently prepared in this manner.



I



II



III

When the requisite α -dicarbonyl compound is readily available this method is a useful alternative route to the corresponding α -dialso carbonyl derivative.

Simple aldehyde and ketone *p*-toluenesulfonylhydrazones do not decompose to dialsoalkanes under these conditions. Recently, however, Shechter, *et. al.* (6) have outlined a method whereby this decomposition can be effected at a relatively low temperature *in vacuo*.

When this work was nearing completion Van Leusen and Strating (7) reported that certain α -sulfonyl dialsoalkanes (IV, $R = \text{alkyl or aryl}$) are efficaciously prepared by passing a solution of the corresponding nitrosourethane over neutral alumina.



IV





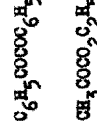
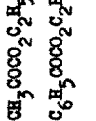
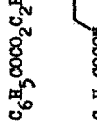
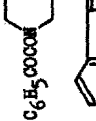
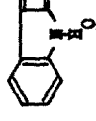
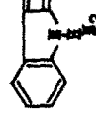
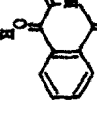
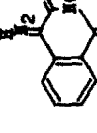
This, to our knowledge, is the only reported instance of the use of alumina in the synthesis of dialso compounds.

Some of the *p*-toluenesulfonylhydrazones and the dialso compounds derived therefrom are listed in the Table. The following is a typical procedure.

A solution of camphoquinone mono-p-toluenesulfonylhydrazone (334 mg., 1.00 m. Moles) in 50 ml. of dichloromethane was stirred with 10 g. of basic alumina for 2 hours. At the end of this time the yellow solvent layer was decanted and the residue was washed with two 25 ml. portions of dichloromethane. The solutions were combined, filtered to remove suspended alumina, and concentrated in vacuo at room temperature. A yellow, crystalline solid (177 mg., 99.3%) m.p. 75-76° (gas evolution) remained.

The author gratefully acknowledges the receipt of a generous gift of camphoquinone from Professor C. Richer, University of Montreal.

TABLE

P-Toluenesulfonyl- Hydrazone of:	Solvent	Reaction Time (hr.)	Diazo Compound (%)	Method of Characterization ^a
$\text{CH}_3\text{COCOCH}_3$ 	A ^c	16	$\text{CH}_3\text{COCN}_2\text{CH}_3$ (86) ^d 	Oil. Triphenylphosph- azine ^e , m.p. 136.5-141°
$\text{C}_6\text{H}_5\text{COCO}_2\text{C}_6\text{H}_5$ 	A	2	(99.3) 	m.p. 72-74°. Lit. (1) m.p. 75°
$\text{C}_6\text{H}_5\text{COCO}_2\text{C}_6\text{H}_5$ 	A	6	$\text{C}_6\text{H}_5\text{COCN}_2\text{C}_6\text{H}_5$ (83.8)	m.p. 73-76°. Lit. (6) m.p. 79°
$\text{CH}_3\text{COCO}_2\text{C}_6\text{H}_5$ 	A	4	$\text{CH}_3\text{CN}_2\text{CO}_2\text{C}_6\text{H}_5$ (0)	—
$\text{C}_6\text{H}_5\text{COCO}_2\text{C}_6\text{H}_5$ 	A	6	$\text{C}_6\text{H}_5\text{CN}_2\text{CO}_2\text{C}_6\text{H}_5$ (85)	Oil (9). Azine ^j m.p. 135.5-137.5°
$\text{C}_6\text{H}_5\text{COCO}_2\text{C}_6\text{H}_5$ 	A	12	$\text{C}_6\text{H}_5\text{CN}_2\text{CO}_2\text{C}_6\text{H}_5$ (0)	—
	B	15	 (83.7)	m.p. 162-164° Lit. (1) m.p. 168°
	A	2	 (90)	m.p. 147-148°

See next page for an explanation of the superscripts.

SUPERSCRIPTS

- (a) All compounds investigated had IR spectra in accord with their structure. The yields and melting points of the diazo compounds refer to those of the crude products.
- (b) M.p. 135-136°. Found: N, 11.16%.
- (c) A, dichloromethane; B, ethyl acetate.
- (d) IR analysis.
- (e) Found: C, 73.48; H, 5.97%.
- (f) We find m.p. 150-151.5° for this compound. Found: N, 8.44%.
Lit.(1) m.p. 110-113°.
- (g) Not characterized.
- (h) M.p. 116.5-118.5°. Found: N, 10.07%.
- (i) Mixture of two isomers. One isomer, m.p. 119.5-120.5°, was separated from the mixture. Found: C, 59.08; H, 5.03%.
- (j) Prepared in low yield by thermolysis of the diazo compound in cyclohexane. Found: C, 68.11; H, 5.56; N, 8.35%.
- (k) The α -keto amide, m.p. 104.5-105.5°, was prepared from ethyl benzoylformate and piperidine. Found: C, 72.19; H, 6.84%. The *p*-toluenesulfonylhydrazones had m.p. 189-192°. Found: N, 10.79%.
- (l) M.p. 192-195°. Lit.(1) m.p. 190-200°.
- (m) The diazo compound was liberated from the alumina by saturation of the solvent with carbon dioxide. The crude product was crystallized once from benzene.
- (n) The trioxo compound had m.p. 186.5-188.5°. Lit.(10) m.p. 186-188°. The *p*-toluenesulfonylhydrazone had m.p. 167.5-168.5°. Found: N, 11.50%.

- (o) Found: C, 59.49; H, 3.44; N, 20.85%. It was further characterized by hydroiodic acid reduction (11) to *N*-methylhomophthalimide, m.p. 121-122°. Lit.(12) m.p. 123°.

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