

Notes

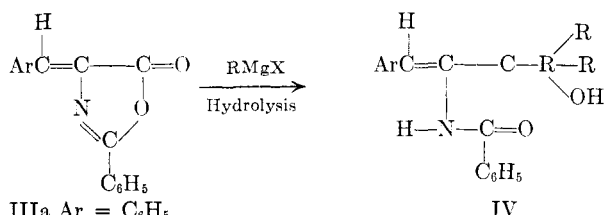
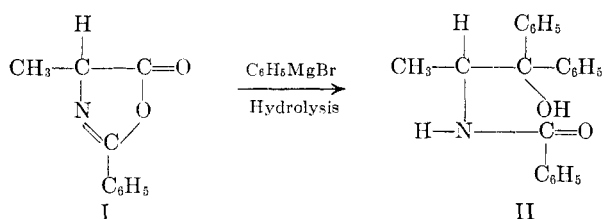
A department for short papers of immediate interest.

Action of Grignard Reagents IX. Action of Organomagnesium Compounds on 2-Phenyl-4-arylidene-2-oxazolin-5-ones and 2-Phenyl-4-benzylidene-2-imidazolin-5-one

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It has been shown¹ that the oxazolone ring in 2-phenyl-4-methyl-2-oxazolin-5-one (I) undergoes ring opening by the action of phenylmagnesium bromide, yielding 1,1-diphenyl-2-benzoylamino-1-propanol (II).

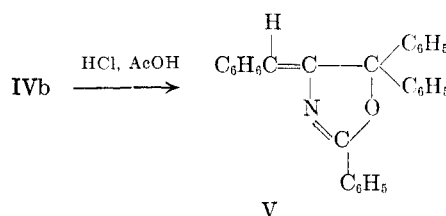


- IIIa Ar = C₆H₅
 b Ar = C₆H₄OCH₃-*p*
 IVa, Ar = C₆H₅, R = CH₃,
 b, Ar = C₆H₅, R = C₆H₅,
 c, Ar = C₆H₅, R = C₆H₄CH₃-*p*
 d, Ar = C₆H₄OCH₃-*p*, R = CH₃,
 e, Ar = C₆H₄OCH₃-*p*, R = C₆H₄CH₃-*p*

In extension of the work of one of us on the action of Grignard reagents on heterocyclic nitrogen compounds,² the action of these reagents on 2-phenyl-4-arylidene-2-oxazolin-5-ones (III) now has been investigated. Thus, when 2-phenyl-4-benzylidene-2-oxazolin-5-one (IIIa) and 2-phenyl-4-*p*-methoxybenzylidene-2-oxazolin-5-one (IIIb) are treated with an excess of methyl-, phenyl-, and *p*-tolyl-magnesium halides respectively, they undergo oxazolone ring opening with the formation of colorless products, believed to have structures IVa-f respectively.

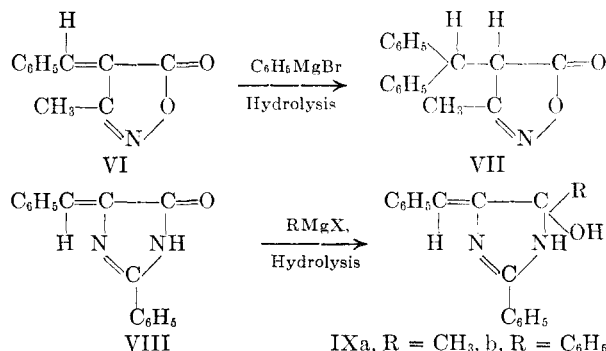
The structure of IVb, which was taken as an ex-

ample of compounds IVa-f, was inferred from the fact that it is colorless and contains two active hydrogen atoms. It was identical with the product obtained by the action of phenylmagnesium bromide on ethyl α -benzoylamino-cinnamate. IVb is readily transformed by the action of hydrochloric acid and glacial acetic acid into a yellow substance, believed to have structure V. Recently, Pourrat³ described the reaction between phenylmagnesium bromide and IIIa and has obtained a mixture of IVb and V, giving m.p. 174° for IVb and 151° for V. Our melting points differ from his.⁴



Whereas, the oxazolone ring in III is readily opened by the Grignard reagents, *e.g.*, phenylmagnesium bromide, Panizzi⁵ has shown that the isoxazolone ring in, *e.g.*, 3-methyl-4-benzylideneisoxazolone (VI) is stable toward the action of phenylmagnesium bromide and only the double bond of the lateral chain of VI enters into reaction, yielding 3-methyl-4-diphenylmethyl-5-isoxazolone (VII).

The nitrogen analog of IIIa, namely, 2-phenyl-4-benzylidene-2-imidazolin-5-one (VIII) also adds one molecule of methyl-, and of phenyl-magnesium halide, to yield colorless products, believed to have structures like IXa and IXb respectively; the structure of IX is not rigorously proved and is under further investigation. It seems that the imidazolone ring is comparatively stable toward Grignard reagents under the same experimental conditions which effect the opening of the oxazolone ring.



(1) Mustafa, Asker, Kamel, Shalaby, and Hassan, *J. Am. Chem. Soc.*, **77**, 1612 (1955); Mustafa, Asker, and Hishmat, *J. Am. Chem. Soc.*, **77**, 5127 (1955).

(2) Mohr and Stroschein, *Ber.*, **42**, 2521 (1909); Clarke, Johnson, and Robinson, *The Chemistry of Penicillin*, Princeton University press, Princeton, New York, 1949, p. 738.

(3) Pourrat, *Bull. soc. chim. France*, 828 (1955).

(4) Carter and Risser, *J. Biol. Chem.*, **139**, 255 (1941).

(5) Panizzi, *Gazz. chim. ital.*, **76**, 44 (1946).

TABLE I
ACTION OF GRIGNARD REAGENTS ON OXAZOLIN-5-ONES

Oxa- zolin- 5-one Derivs.	Grig- nard Reagent	Prod- uct	M.p., ^a °C.	Yield, %	Color with H ₂ SO ₄	Formula	Carbon		Hydrogen		Nitrogen	
							Calc'd	Found	Calc'd	Found	Calc'd	Found
IIIa	Methyl	IVa	118	65	Red	C ₁₈ H ₁₉ NO ₂	76.87	76.68	6.76	6.56	4.98	4.78
IIIa	Phenyl	IVb	156	73	Orange- red	C ₂₈ H ₂₃ NO ₂ ^b	82.96	82.75	5.68	5.48	3.46	3.27
IIIa	<i>p</i> -Tolyl	IVc	185	62	Red	C ₃₀ H ₂₇ NO ₂	83.14	82.94	6.23	6.13	3.23	3.18
IIIb ^c	Methyl	IVd	104	58	Orange	C ₁₉ H ₂₁ NO ₂	73.31	73.24	6.75	6.47	4.50	4.32
IIIb	Phenyl	IVe	106	63	Orange	C ₂₉ H ₂₅ NO ₂	80.00	79.68	5.74	5.66	3.22	2.98
IIIb	<i>p</i> -Tolyl	IVf	146	56	Orange	C ₃₁ H ₂₉ NO ₂	80.34	80.21	6.26	5.98	3.02	2.94

^a All melting points are uncorrected. ^b Active H, Calc'd: 0.49. Found: 0.42. Mol. wt.: 405. Found (micro-Rast) 391. ^c Henze, Whitney, and Eppright, *J. Am. Chem. Soc.*, **62**, 567 (1940).

EXPERIMENTAL

Action of Grignard reagents on 2-phenyl-4-arylidene-2-oxazolin-5-ones (III). The following illustrates the procedure: To an ethereal solution of phenylmagnesium bromide (prepared from 0.9 g. of magnesium, 8 g. of bromobenzene, and 40 ml. of dry ether) was added a suspension of 1 g. of IIIa⁶ in 30 ml. of benzene. The reaction mixture was refluxed (steam-bath) for two hours, set aside at room temperature overnight, and then decomposed with a cold, saturated aqueous ammonium chloride solution. The reaction mixture was extracted with ether; the ethereal layer was dried (Na₂SO₄) and allowed to evaporate slowly. The oily residue was washed several times with hot petroleum ether (b.p. 40–60°). The solid (IVa), so obtained, was crystallized from benzene, m.p. 156°. A mixture of benzene and petroleum ether (b.p. 50–60°) was used as a solvent for the products IVb–f.

Action of phenylmagnesium bromide on ethyl α -benzoylaminocinnamate. A solution of 1 g. of ethyl α -benzoylamino-cinnamate⁶ in 40 ml. of dry benzene was treated with phenylmagnesium bromide as described above. The oily residue that was obtained after the evaporation of the ethereal solution was washed several times with petroleum ether (b.p. 50–60°) and was crystallized from benzene, m.p. 156°. It was identified as IVb (m.p. and mixture m.p., and color reaction with sulfuric acid).

Behavior of 2-phenyl-4-benzylidene-2-imidazolin-5-one (VIII) toward: (a) *Methylmagnesium iodide.* To an ethereal solution of methylmagnesium iodide (prepared from 1 g. of magnesium, 7 g. of methyl iodide, and 40 ml. of dry ether) was added a suspension of 1 g. of VIII⁷ in 30 ml. of dry benzene. The reaction mixture was worked up in the usual manner and the solid obtained upon evaporation of the ethereal extract was crystallized from acetone, m.p. 188°. Yield, ca. 77%.

Anal. Calc'd for C₁₇H₁₆N₂O: C, 77.27; H, 6.06; N, 10.61. Found: C, 77.13; H, 5.87; N, 10.53.

Compound IXa is difficultly soluble in benzene and alcohol, and almost insoluble in aqueous sodium hydroxide solution (10%). It gives an orange color when treated with sulfuric acid.

(b) *Phenylmagnesium bromide.* A suspension of 1 g. of VIII in 40 ml. of dry benzene was treated with phenylmagnesium bromide as described for IIIa. The solid residue, obtained by evaporation of the ether extract, was crystallized from benzene, m.p. 216°.

Anal. Calc'd for C₂₂H₁₈N₂O: C, 80.98; H, 5.52; N, 8.59; Mol. wt., 326. Found: C, 80.77; H, 5.31; N, 8.24; Mol. wt. (micro-Rast), 311.

Compound IXb is difficultly soluble in boiling alcohol and benzene. It is almost insoluble in aqueous sodium hydroxide

solution (10%) and gives an orange color with sulfuric acid.

Action of hydrochloric acid and glacial acetic acid on IVb. A suspension of 0.5 g. of IVb in 20 ml. of glacial acetic acid and 10 ml. of hydrochloric acid (*sp. gr.* 1.18) was refluxed for 15 minutes. Compound IVb dissolved gradually giving a yellow solution. Compound V, which separated during the reflux period was filtered off, washed with water, and recrystallized from alcohol, m.p. 186°. The yield is almost quantitative.

Anal. Calc'd for C₂₈H₂₁NO: C, 86.82; H, 5.42; N, 3.62. Found: C, 86.67; H, 5.24; N, 3.55.

V is soluble in boiling benzene and acetic acid, readily soluble in cold chloroform. It is almost insoluble in aqueous sodium hydroxide solution (10%) and gives an orange-red color with sulfuric acid.

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The Preparation of 2-Methylthianaphthene and 2-Methylselenonaphthene and Their Ultraviolet Absorption Spectra

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The purpose of our investigations was the preparation of selenonaphthene with an alkyl group in α -position and the comparison of its spectrum with the spectra of the basic compound and the sulfur analog. As far as we are aware investigations of this compound have not been reported.

The synthesis of 2-methylthianaphthene (I) was carried out by the method of Hansch and Blondon¹ except that the 2-methyl-3-acetoxythianaphthene was isolated and the resulting ketone was subjected to a Clemensen reduction. The 2,3-dihydro-2-methylthianaphthene then was dehydrogenated by boiling with sulfur. We subjected our compound to this treatment so as to prove that the compound

(6) Erlenmeyer, *Ann.*, **275**, 11 (1893).

(7) Williams and Ronzio, *J. Am. Chem. Soc.*, **68**, 647 (1946).

(1) C. Hansch and W. Blondon, *J. Am. Chem. Soc.*, **70**, 1561 (1948).