Anal. Calcd. for $C_{11}H_{17}OBrN_2S$: Br, 27.09. Found: Br, 26.4.

Summary

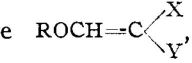
The formation of 2-aminothiazoles by action of iodine and thiourea on ketones has been examined as a preparative method.

EVANSTON, ILLINOIS RECEIVED FEBRUARY 2, 1950

[CONTRIBUTION FROM ROHM AND HAAS COMPANY]

Reaction of β-Alkoxyacrylic Esters with Secondary Amines

BY PETER L. DE BENNEVILLE AND JANE H. MACARTNEY

Replacement of an ether group with an amino group requires a particularly favorable structural condition in the molecule. Cook and Dixon[1] have succeeded in so replacing the ether group by heating β-alkoxypropionitriles with amines in an autoclave to temperatures generally in the neighborhood of 200°. This reaction can be attributed to the presence of the cyanide group in a neighboring position to the alkoxy group, with consequent weakening of the carbon–oxygen bond. A very labile system which has been known for some years is represented by the group of compounds of the structure  $ROCH{=}C\langle^{X}_{Y}$, where both X and Y are the customary labilizing groups —COR, —COOR and —CN.[2,3] Replacement of the alkoxy group with amino- and anilino- groups is readily carried out in these cases at temperatures ranging from room to 100°.

We have found that a single labilizing group, as found in the β-alkoxyacrylic esters, is sufficiently active to promote the replacement of the alkoxy group by a number of secondary amino groups, at temperatures generally no higher than 100°. At these temperatures no replacement of the ester alkoxy group was obtained; however, in reactions requiring higher temperatures, such a replacement might occur. The reaction did not take place with all secondary amines. A notable exception was the case of diisopropylamine, which gave no reaction. This would indicate that highly hindered bases or weak bases,[4] as in the aromatic series, would not react under such favorable conditions. Since the β-alkoxyacrylic esters are available from the reaction of acetylene and dialkyl carbonates,[5] this represents a superior method of obtaining the β-aminoacrylic esters.

The amination is readily carried out by heating molecular equivalents of the β-alkoxyacrylic ester and the amine at reflux or steam-bath temperature, depending on boiling point of the amine. A potassium carbonate catalyst was used in most of the reactions, but since omission of the catalyst gave only slightly lower yields in the one case where it was tried, the necessity for this catalyst is questionable. The alcohol may be removed by distillation as the reaction progresses, but this is unnecessary. The results of typical aminations are given in the accompanying table.

TABLE I

TRANSAMINATION REACTIONS,[a] $ROCH{=}CHCOOR' \rightarrow {>}NCH{=}CHCOOR'$

R	R′	Amine	Yield, %	B. p., °C. uncor.	at mm.	Nitrogen, % Found	Nitrogen, % Calcd.	Neutralization equivalent Found	Neutralization equivalent Calcd.	Sp. gr. 20/20	n^{20}_D
CH_3	CH_3	Morpholine	50[b]	M. p. 76–78°		8.20	8.18	174	171	....	....
C_2H_5	C_2H_5	Morpholine	69	138–142	0.8	7.67	7.57	185	185	1.1077	1.5309
C_2H_5	C_2H_5	Morpholine[c]	52	141–145	1.2	..	..	187	185	....	....
C_2H_5	C_2H_5	$(CH_3)_2NH$	53	84–85	1.4	9.32	9.78	145	143	0.9947	1.5114
C_2H_5	C_2H_5	$C_9H_{19}NHCH_3$	64	164–165	4.0	5.28	5.48	[d]	255	0.9196	1.4897
C_2H_5	C_2H_5	Piperidine	79	123–124	1.1	7.62	7.64	187	183	1.0293	1.5334
C_2H_5	C_2H_5	$(HOCH_2CH_2)_2NH$	82	Decomposed[e]		7.30	7.40	[d]	203	[e]	1.5021
C_4H_9	C_4H_9	Morpholine	26	165–175	2	5.94	6.59	230	213	1.0357	1.5056

[a] Anhydrous potassium carbonate used as catalyst except when indicated. [b] Product recrystallized from methanol. [c] No catalyst used. [d] Too weakly basic to titrate with indicator. [e] Product isolated by water wash to remove unreacted materials and stripping on the steam-bath under good water vacuum to remove low-boiling products. It was a thick almost glassy material at room temperature.

The β-dialkylaminoacrylic esters so produced were stable but very weak bases. For example, titration with hydrochloric acid to a brom phenol blue end-point led to a disappearing end-point which drifted back to the basic side until the neutral point was reached, which in almost all cases corresponded to the theoretical neutral equivalent for the compound. This basicity distinguishes these compounds from the other possible products of the reaction, the alkoxyacrylamides. Cold dilute hydrochloric acid slowly hydrolyzed ethyl

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[1] Cook and Dixon, U. S. Patent 2,425,693.

[2] Claisen, *Ann.*, **297**, 1 (1897).

[3] de Bollemont, *Bull. soc. chim.*, [3] **25**, 29 (1901).

[4] Methylaniline also did not give the expected product in this reaction (Dr. J. O. Van Hook, private communication).

[5] Croxall and Schneider, THIS JOURNAL, **71**, 1257 (1949).

β-dimethylaminoacrylate to ethyl trimesate, which is the end-product of the self condensation of ethyl formylacetate. This appears to be characteristic of the structure $R_2NCH{=}CH{-}$.[6]

Experimental

Raw Materials.—Alkyl β-alkoxyacrylates were supplied through the courtesy of Dr. W. J. Croxall of this Laboratory, and were prepared by the methods described by him.[5] The amines were commercial products used without purification.

General Procedure.—The following preparations are representative.

Ethyl β-Piperidinoacrylate.—To a mixture of ethyl β-ethoxyacrylate (57.6 g., 0.4 m.) and 20 g. of anhydrous potassium carbonate, heated on the steam-bath with stirring, piperidine (34 g., 0.4 m.) was added dropwise over a fifteen-minute period. The reaction mixture was heated on the steam-bath under reflux for four hours, filtered to remove potassium carbonate and distilled to yield 57.5 g. (79%) of ethyl β-piperidinoacrylate.

Ethyl β-Dimethylaminoacrylate.—To a mixture of ethyl β-ethoxyacrylate (144 g., 1 m.) and 50 g. of anhydrous potassium carbonate, contained in a flask equipped with gas inlet tube, stirrer and acetone–Dry Ice condenser. was added dimethylamine gas (45 g., 1 m.) at 25°. The mixture was stirred for several hours at room temperature, filtered to remove potassium carbonate and distilled. After removal of alcohol and unreacted ethyl β-ethoxyacrylate (31 g.) there was recovered 92 g. (53%) of ethyl β-dimethylaminoacrylate.

Hydrolysis of Ethyl β-Dimethylaminoacrylate.—Thirty grams of dilute hydrochloric acid (1:1) was added to ethyl β-dimethylaminoacrylate (21.5 g., 0.15 m.). The material formed a homogeneous solution which deposited an oily lower layer. After two weeks, crystals were present in this layer, and these were filtered off. The m. p. (132–135°) corresponded to that of triethyl trimesate and this was confirmed by a mixed m. p. with an authentic sample. Only a few grams of crystals were obtained; the remainder of the oil may have represented intermediate stages of condensation.

Acknowledgments.—To Dr. E. L. Stanley who directed the analytical work, and to Mr. E. J. Smialkowski for assistance in the experimental work.

Summary

A number of β-dialkylaminoacrylic esters have been prepared by the interchange reaction of β-alkoxyacrylic esters with secondary amines. The ease with which these reactions occur indicates a surprising degree of labilization by the single ester group.

Philadelphia, Pa. Received February 6, 1950

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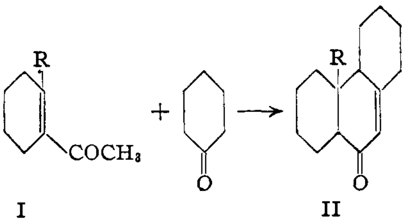
[6] Mannich and Davidsen, *Ber.*, **69B**, 2106 (1936).

[Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin]

The Condensation of 1-Methyl-2-acetylcyclohexene with 1-Decalone, and with 1,5-Decalindione

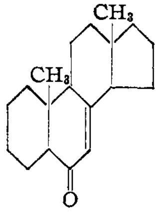
By William S. Johnson, Jacob Szmuszkovicz[1] and Max Miller[2]

The extension of the Robinson–Rapson synthesis[3]—typified by the base-catalyzed reaction between 1-acetylcyclohexene, I (R = H), and cyclohexanone to produce the ketododecahydrophenanthrene II (R = H)—to the production of fused ring systems containing the angular methyl group has been investigated by Huber,[4] who studied the condensation between 1-methyl-2-acetylcyclohexene, I (R = CH_3), and cyclohexanone. The product of this reaction was an oil, $\lambda_{max.}$ 238 mμ (in ether) (*E ca.* 2050), of expected composition which gave a semicarbazone in unspecified yield and on dehydrogenation with selenium afforded phenanthrene also in unspecified yield. From these observations Huber concluded that his product had the expected structure II (R = CH_3).

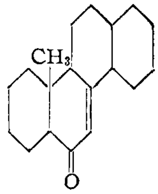


I II

On the basis of Huber's report, Bagchi and Banerjee[5] proposed the structure III for the product of the condensation of I (R = CH_3) with 8-methyl-4-hydrindanone, and Dimroth[6] similarly assigned the structure IV to the condensation product of I (R = CH_3) with 1-decalone. In the present paper we are reporting the results of some studies of condensations with 1-methyl-2-acetylcyclohexene, which force us to the conclusion that all of these structures II (R = CH_3), III and IV are open to question.



III



IV

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[1] Sterling-Winthrop Research Institute, and Wisconsin Alumni Research Foundation Postdoctoral Fellow 1948-1949; U. S. National Institute of Health Postdoctoral Fellow 1949-1950. On leave of absence from the Weizmann Institute of Science, Rehovoth, Israel.

[2] Wisconsin Alumni Research Foundation Research Assistant 1949-1950.

[3] Rapson and Robinson, *J. Chem. Soc.*, 1285 (1935); Crowfoot, Rapson and Robinson, *ibid.*, 757 (1936); Peak and Robinson, *ibid.*, 759(1936).

[4] Huber, *Ber.*, **71**, 725 (1938).

[5] Bagchi and Banerjee, *J. Ind. Chem. Soc.*, **23**, 397 (1946).

[6] Dimroth, *Angew. Chem.*, **59**, 215 (1947).