REACTION OF ACETOACETALDEHYDE TETRAETHYLACETAL WITH QUATERNARY SALTS OF HETEROCYCLIC BASES AND SOME REACTIONS OF THE PRODUCTS

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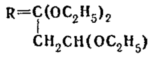
δ-Alkoxy-δ-methylbutadienyl salts were obtained by condensation of acetoacetaldehyde tetraethylacetal with quaternary salts of nitrogen-containing heterocyclic bases. δ-Methyl-substituted tetramethylidynehemicyanines were obtained by the reaction of the acetal with quaternary salts of heterocyclic bases and amines in pyridine. β-Methyl-substituted dicarbocyanine and α-methyl-substituted tetramethylidynemerocyanine dyes were synthesized.

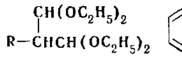
In our previous investigations we established that benzoylacetaldehyde tetraethylacetal (I) differs from 2-phenylmalonaldehyde tetraethylacetal (II) [1] in its peculiar chemical behavior. In contrast to II, acetal I, regardless of the nature of the salt anion, reacts with quaternary salts of heterocyclic bases in acetic anhydride to give alkoxybutadienyl salts [1] rather than a compound with a free aldehyde group.

It seemed of interest to study the behavior of acetoacetaldehyde tetraethylacetal (III) [2] in comparison with the acetals of 2-methylmalondialdehyde (IV) and I. One might have expected the formation of VI or VII or mixtures of them in the reaction of III with V in acetic anhydride. A salt-like substance, which, according to the results of elementary analysis, corresponded to structure VI or VII, was isolated from the reaction mixture.



$R{-}C(OC_2H_5)_2{-}CH_2CH(OC_2H_5)_2$

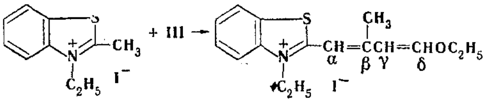
I, III



$R{-}CH(CH(OC_2H_5)_2){-}CH(OC_2H_5)_2$

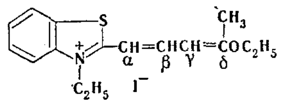
II, IV

I, II $R=C_6H_5$; III, IV $R=CH_3$

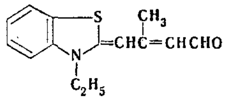


V

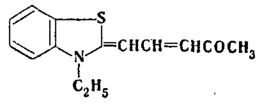
VI



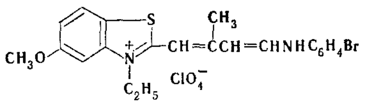
VII



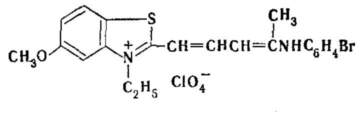
VIII



IX



X



XI

To determine the position of the methyl group, the salt obtained from III and V was dequaternized with an aqueous alcohol solution of potassium hydroxide. Aldehyde VIII or ketone IX might have been formed in the dequaternization. The dequaternization product proved to be identical (physical constants and IR spectrum) to a known [3] ketone (IX).* This structure VII should be assigned to the quaternary salt ob-

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*Compound IX was kindly given to us by N.N. Sveshnikov, to whom we are deeply grateful.

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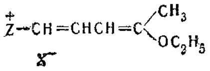
TABLE 1



$\overset{+}{Z}{-}CH{=}CHCH{=}C(CH_3)(OC_2H_5)\ X^-$

Z	X	Appear. (from ethanol)	Mp, °C	λmax, nm (log ε)	Empirical formula	Found, %			Calc., %			Yield, %
						C	H	N	C	H	N	
3-ethyl-2-benzothiazolium	ClO_4	Brown needles	132	434 (4,37)	$C_{16}H_{20}ClNO_5S$	51,1	5,2	3,90	51,3	5,3	3,7	81*
3-Ethyl-5-methoxy-2-benzothiazolium	I	Yellow prisms	178	438 (4,23)	$C_{17}H_{22}INO_2S$	47,2	5,3		47,3	5,1		54
3-Ethyl-5,6-dimethyl-2-benzothiazolium	ClO_4	Yellow plates	185	440 (4,32)	$C_{18}H_{24}ClNO_5S$	53,4	5,7	3,3	53,7	5,9	3,5	70
1-Ethyl-2-quinolinium	I	Yellow plates	175	440 (4,42)	$C_{18}H_{22}INO$	54,8	5,4	3,5	54,7	5,5	3,5	50

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*Obtained from 2-methyl-3-ethylbenzothiazolium tosylate in 70% yield.

tained from III and V. The δ-methyl-substituted butadienyl salt structure should apparently also be assigned to the products in the case of salts with other heteroresidues. The nature of the anion (tosylates, iodides, and perchlorates were investigated) does not alter the direction of the reaction (Table 1).

Thus, in contrast to 2-methylmalondialdehyde acetal (IV) [4], acetoacetaldehyde acetal, like benzoylacetaldehyde acetal (I) [1], forms alkoxybutadienyl salts regardless of the nature of the quaternary salt anion. However, the methyl group is in the δ position of the polymethine chain and the phenyl group is in the β position in the case of tetraethylacetal I.

We investigated the reaction of acetoacetaldehyde tetraethylacetal with quaternary salts of heterocyclic bases and amines in pyridine. It was found that acetoacetaldehyde tetraethylacetal, like benzoyl acetaldehyde tetraethylacetal [5], forms tetramethylidynehemicyanines, while 2-methylmalonaldehyde tetraethylacetal does not form γ-methyl-substituted tetramethylidynehemicyanine dyes under such conditions. For example, the formation of X or XI or a mixture of them might have been expected in the condensation of acetal III with 2-methyl-3-ethyl-5-methoxybenzothiazolium tosylate (XII) and p-bromoanaline in pyridine. However, only one compound was isolated from the reaction mixture. To determine the position of the methyl group, from 2-(δ-ethoxy-δ-methylbutadienyl)-5-methoxybenzothiazolium perchlorate (XIII) and p-bromoaniline, we obtained tetramethylidynehemicyanine dye XI, the physical constants and spectral characteristics of which were in agreement with those of the hemicyanine obtained in the condensation of III with XII and p-bromoaniline in pyridine.

The δ-methyl-substituted hemicyanine dye structure (Table 2) should apparently also be assigned to the hemicyanines in the other cases investigated.

We investigated the reactivity of the δ-ethoxy-δ-methylbutadienyl salts. The ethoxy group in these salts is labile, and they are capable of reacting with quaternary salts of heterocyclic bases to give symmetrical and unsymmetrical β-methyl-substituted dicarbocyanine dyes.

α-Methyl-substituted tetramethylidynemerocyanine dyes were obtained by the reaction of δ-ethoxy-δ-methylbutadienyl salts with 3-ethylrhodanine under the same conditions. These results indicate that the δ-ethoxy-δ-methylbutadienyl salts differ in reactivity from the δ-ethoxy-β-phenylbutadienyl salts, in which we observed the formation of α-phenylallylidene derivatives of rhodanine under similar conditions [6].

EXPERIMENTAL

The IR spectra of KBr pellets were recorded with a UR-10 spectrophotometer. The electronic spectra of 10^{-4} to $5 \cdot 10^{-5}$ N alcohol solutions were recorded with an SF-10 spectrophotometer.

2-(δ-Ethoxy-δ-methylbutadienyl)-3-ethylbenzothiazolium Iodide (VII). A mixture of 0.3 g (1 mmole) of 2-methyl-3-ethylbenzothiazolium iodide, 0.35 ml of acetoacetaldehyde tetraethylacetal (III), and 5 ml of acetic anhydride was heated at 80-90° for 4 h. The precipitate was removed by filtration and washed with ether to give 0.29 g (72%) of brown prisms with mp 136° (from ethanol); λ_{max} 434 nm (log ε 4.37). Found,%: C 47.7; H 4.7; N 3.4. $C_{16}H_{20}INOS$. Calculated,%: C 47.9; H 5.0; N 3.5.

The salts for which the characteristics are given in Table 1 were similarly obtained.

3-Ethyl-2-acetylallylidenebenzothiazoline (IX). A solution of 0.35 g of potassium hydroxide in 5 ml of water was added to a refluxing solution of 0.94 g (2.4 mmole) of iodide VII in 25 ml of alcohol, and the mixture was refluxed for 1 h. It was then treated with 200 ml of water and refluxed for another 2 h. The mixture was then extracted with benzene, and the extract was washed with water and dried with potassium carbonate. The benzene was removed by vacuum distillation, and the residue began to crystallize when petroleum ether was added to give 0.24 g (36%) of yellow prisms with mp 119-120° (after two crystallizations from ligroin); λ_{max} 440 nm (log ε 4.72); ν_{CO} 1665 cm^{-1}. Found,%: C 68.2; H 6.2; N 5.9. $C_{14}H_{15}NOS$. Calculated,%: C 68.5; H 6.2; N 5.7. No melting-point depression was observed for a mixture of IX with 3-ethyl-2-acetylallylidenebenzothiazoline [3].

3,3'-Diethyl-9-methylthiadicarbocyanine Iodide. A mixture of 0.2 g (0.5 mmole) of VII, 0.15 g (0.5 mmole) of V, 5 ml of absolute ethanol, and 0.16 ml of triethylamine was refluxed for 15 min. The resulting crystals were removed by filtration and washed with ether to give 0.22 g (80%) of green prisms (from ethanol) with mp 207°; λ_{max} 664 nm (log ε 5.45). Found,%: C 54.3; H 4.9; N 5.2. $C_{24}H_{25}IN_2S_2$. Calculated,%: C 54.1; H 4.7; N 5.3. According to [7], this compound has mp 210-211° and λ_{max} 664 nm (in ethanol).

3,3'-Diethyl-5-methoxy-9-methylthiadicarbocyanine Iodide. A mixture of 0.2 g (0.5 mmole) of VII, 0.21 g (0.5 mmole) of 2-methyl-3-ethyl-5-methoxybenzothiazolium iodide, 2 ml of absolute ethanol, and 0.16 ml of triethylamine was refluxed for 15 min. The crystals were removed by filtration and washed with alcohol to give 0.23 g (82%) of green prisms with mp 197° (from ethanol); λ_{max} 675 nm (log ε 5.39). Found,%: N 4.7; S 11.2. $C_{25}H_{27}IN_2OS_2$. Calculated,%: N 5.0; S 11.4.

3-Ethyl-5-(3'-ethylbenzothiazolinylidene-2'-α-methylbutenylidene)thiazolidine-2-thion-4-one. A mixture of 0.3 g (0.75 mmole) of 2-(δ-ethoxy-δ-methylbutadienyl)-3-ethylbenzothiazolium perchlorate, 0.12 g (0.75 mmole) of 3-ethylrhodanine, 4 ml of absolute methanol, and 0.2 ml of triethylamine was refluxed for 2 min. The crystals were removed by filtration, washed with methanol, dissolved in benzene, chromatographed on aluminum oxide (elution with benzene), and crystallized from alcohol to give 0.1 g (34%) of a product with mp 198-199°; λ_{max} 602 nm (log ε 4.83). Found,%: C 58.7; H 5.3. $C_{19}H_{20}N_2OS_3$. Calculated,%: C 58.7; H 5.2.

A similar procedure was used to obtain 3-ethyl-5-(3'-ethyl-5'-methoxybenzothiazolinylidene-2'-α-methylbutenylidene)thiazolidine-2-thion-4-one [33% yield, blue prisms with mp 211°; λ_{max} 616 nm (log ε 4.87). Found,%: C 57.2; H 5.3. $C_{20}H_{22}N_2O_2S_3$. Calculated,%: C 57.3; H 5.3], and 3-allyl-5-(3'-ethyl-5'-methoxybenzothiazolinylidene-2'-α-methylbutenylidene)thiazolidine-2-thion-4-one [45% yield, blue prisms with mp 188°; λ_{max} 628 nm (log ε 4.87). Found,%: C 58.3; H 5.2. $C_{21}H_{22}N_2O_2S_3$. Calculated,%: C 58.6; H 5.1.]

TABLE 2

$$\overset{+}{Z}\text{—CH=CHCH=C}\begin{matrix}\diagup CH_3\\ \diagdown NHR\end{matrix} \quad X^-$$

Z	R	X	Appearance (from ethanol)	Mp, °C	λ_{max}, nm (lg ε)	Empirical formula	Found, %			Calc., %			Yield, %.
							C	H	N	C	H	N	
3-Ethyl-5,6-dimethyl-2-benzothiazolium	*p*-BrC_6H_4	ClO_4	Red plates	145	514 (4,74)	$C_{22}H_{24}BrClN_2O_4S$	49,9	4,2		50,1	4,6		43
1-Ethyl-2-quinolinium	*p*-BrC_6H_4	ClO_4	Red needles	160	531 (4,70)	$C_{22}H_{22}BrClN_2O_4$	53,6	4,7		53,5	4,5		41
3-Ethyl-2-benzothiazolium*	C_6H_5	I	Red prisms	189—190	504 (4,77)	$C_{20}H_{21}IN_2S$	53,4	4,5	5,9	53,6	4,7	6,2	88

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*Obtained by condensation of 2-(δ-ethoxy-δ-methylbutadienyl)benzothiazolium iodide with aniline in alcohol (via method B).

3-Ethyl-2-[δ-(p-bromoanilino)-δ-methylbutadienyl]-5-methoxybenzothiazolium Perchlorate (XI). A. A mixture of 0.38 g (1 mmole) of XII, 0.3 g of p-bromoaniline, 0.3 ml of III, and 2 ml of pyridine was held at room temperature for 48 h. The dye was precipitated by the addition of ether and converted to the perchlorate. The perchlorate was crystallized from alcohol to give 0.17 g (32%) of dark red needles with mp 188-189°; λ_{max} 516 nm (log ε 4.77). Found,%: C 47.3; H 3.90. $C_{21}H_{22}BrClN_2O_5S$. Calculated,%: C 47.6; H 4.20.

B. A mixture of 0.80 g (2 mmole) of XIII, 0.6 g of p-bromoaniline, and 5 ml of methanol was refluxed for 2.5 h. The dye was precipitated by the addition of ether, and the crystals were removed by filtration and crystallized from alcohol to give 0.67 g (63%) of a substance that was identical to that described above.

LITERATURE CITED

1. A. V. Kazymov and E. P. Shchelkina, Khim. Geterotsikl. Soedin., 1378 (1971).
2. L. A. Yanovskaya, S. S. Yufit, and V. F. Kucherov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1246 (1960).
3. N. N. Sveshnikov, I. I. Levkoev, and N. S. Stokovskaya, USSR Authors' Certificate No. 115,839 (1957); Byull. Izobr., No. 1, 47 (1958).
4. A. V. Kazymov, E. P. Shchelkina, R. Kh. Khairusova, and N. N. Sveshnikov, USSR Authors' Certificate No. 172,333 (1965); Byull. Izobr., No. 13, 22 (1965).
5. A. V. Kazymov and E. P. Shchelkina, USSR Authors' Certificate No. 220,388 (1968); Byull. Izobr., No. 20, 45 (1968).
6. A. V. Kazymov and E. P. Shchelkina, Khim. Geterotsikl. Soedin., 780 (1972).
7. N. N. Sveshnikov and N. S. Stokovskaya, USSR Authors' Certificate No. 95,942 (1952); Byull. Izobr., No. 9, 36 (1953).