CONCLUSIONS

1. We studied the reaction of 1,3,3,5-tetrachloropentane, 1,1,1,3-tetrachloro-3-phenylpropane, and 2,2,4-trichloropentane with zinc in diverse solvents as the medium, which reaction leads to the formation of substituted cyclopropanes. In acetic acid the reduction of the chlorine-containing groupings to give alkanes becomes significant.

2. The reductive cyclization of 2,2,4-trichloropentane with Zn in ethanol, acetic acid, or DMF leads to the predominant formation of cis-1,2-dimethylcyclopropane.

3. On the example of 1,1-dichloro-2-phenylcyclopropane and 1-chloro-1-methyl-2-phenylcyclopropane it was shown that when these compounds are heated with Zn in ethanol the C–Cl bond is practically not reduced.

LITERATURE CITED

1. A. A. Kamyshova, E. Ts. Chukovskaya, and R. Kh. Freidlina, Dokl. Akad. Nauk SSSR, 233, 122 (1977).
2. A. A. Kamyshova, S. D. Polishchuk, E. Ts. Chukovskaya, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 185 (1977).
3. R. Kh. Freidlina, A. A. Kamyshova, N. N. Posledova, and E. Ts. Chukovskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 392 (1979).
4. R. E. Erickson, R. Annino, M. D. Scanlan, and G. Zon, J. Am. Chem. Soc., 91, 1767 (1969).
5. A. A. Kamyshova, E. Ts. Chukovskaya, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 896 (1974).
6. R. Kh. Freidlina, A. A. Kamyshova, E. Ts. Chukovskaya, and V. I. Dostovalova, Izv. Akad. Nauk SSSR, Ser. Khim., 859 (1975).
7. A. N. Nesmeyanov and V. A. Sazonova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 499, 511 (1941).

2-ALKYL-SUBSTITUTED OXAZOLES IN REACTION WITH ACETYLENEDICARBOXYLIC ESTER

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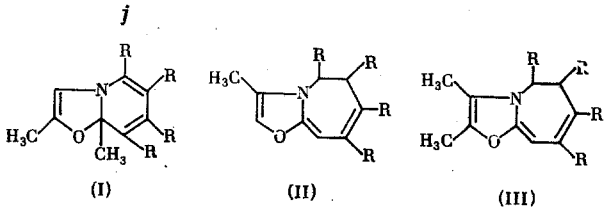
It is known that ethylenic dienophiles react with oxazole derivatives, including the 2-alkyl-substituted derivatives, on the type of 1,4-cycloaddition to give the corresponding pyridines [1]. Oxazoles with substituents in the 4 and 5 positions of the ring were used in the reaction with acetylenic dienophiles; this condensation also proceeds by the diene synthesis scheme and leads to functionally substituted furans [2].

While studying the condensation of some simple 2-alkyl-substituted oxazoles (2,4-dimethyl-, 2,5-dimethyl-, 2,4,5-trimethyl-, and 2-ethyl-4,5-dimethyloxazole) with acetylenedicarboxylic ester (ADE) we found that in this case the acetylenic addend does not add in the 1,4 position, but rather to the azomethine bond of the ring. As the result of adding 2 moles of ADE to 2,5-dimethyloxazole we obtained a crystalline substance $C_{17}H_{19}NO_9$(I), which, based on the PMR spectral data, contains a CH_3 group on the sp^2-hybridized C atom, a CH_3 group on the unsaturated C atom, and four $COOCH_3$ groups.



(I) (II) (III)

R = $COOCH_3$

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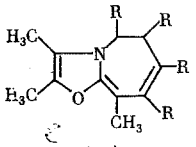
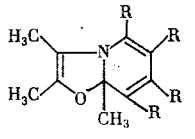
2,4-Dimethyloxazole under the same conditions forms a crystalline substance $C_{17}H_{19}NO_9$ (II), whose PMR spectrum had, besides the signals of one CH_3 group on C (sp^2) and four $COOCH_3$ groups, the signals of single protons with δ 4.24, 5.40, and 5.60 ppm. Compound (II) is formed if the 2-CH_3 group of the oxazole takes part in the condensation with ADE.

2,4,5-Trimethyloxazole when reacted with ADE behaves like 2,4-dimethyloxazole, and forms an adduct of composition $C_{18}H_{21}NO_9$ with a dihydroazepine structure (III). From the condensation products of 2-ethyl-4,5-dimethyloxazole were isolated the dihydroazepine $C_{19}H_{23}NO_9$ (IV) and a compound of composition $C_{19}H_{23}NO_9$, whose PMR spectrum contains the signals of three CH_3 groups on C (sp^2), four $COOCH_3$ groups, and a singlet with δ 3.38 ppm, which in intensity corresponds to two protons. Such a set of structural elements is in agreement with the formula of (V).


(IV)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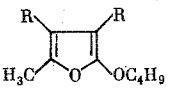
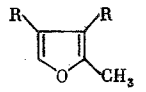

(VI)


(VII)

A similar type of transformation, with the formation and isomerization of bicyclic adducts with six- and seven-membered rings [3, 4], was observed previously on the example of the condensation of aromatic heterocycles, and specifically pyridines, thiazoles, benzimidazoles, and benzoxazoles with ADE.

Compounds (I)-(V) are formed in yields of 2-9%; the major portion of the starting oxazoles turns to a tar during synthesis. Together with (I)-(V), from the reaction mixtures were isolated, in an amount of 8-10%, crystalline substances with mp 130-160°C and mol. wt. 400-500, in whose PMR spectra can be seen the broad signals of CH_3 groups in the 2-2.4 ppm region and $COOCH_3$ groups in the 3.4-3.8 ppm region. These adducts when heated decompose into the starting oxazole and ester.

The specific effect of the 2-methyl group is apparently restricted to the gamut of alkyl-substituted oxazoles, since 2-methyl-4-phenyl- and 2-methyl-5-butoxyoxazole condense with ADE like ordinary azadienes. If these reactions are run under cooling, then the starting materials are recovered unchanged, and only furandicarboxylic esters (VI) and (VII) are formed when they are run in refluxing benzene or toluene; the 1,2-cycloaddition products were not detected.

EXPERIMENTAL

The PMR spectra were recorded on a Varian DA-60-IL spectrometer (60 MHz) relative to HMDS in $CDCl_3$.

Experimental Procedure. To a mixture of 0.041 mole of the oxazole and 0.017 mole of K_2CO_3 in 10 ml of benzene was added at 0°C, in drops, 0.041 mole of acetylenedicarboxylic ester (ADE), after which the mixture was kept at 0°C for 2-3 h, heated to 20°C, and chromatographed on a column packed with neutral Al_2O_3, with successive elution of the reaction products by diisopropyl ether, THF, and methanol.

Tetramethyl-2,7a-dimethylpyrido[1,2-b]oxazole-4,5,6,7-tetracarboxylate (I), red powder, mp 180-182°C (from methanol); yield 2.5%; mol. wt. (based on mass spectrum) 381. PMR spectrum (δ, ppm): 1.17 s (3H), 2.26 d (3H, J = 1 Hz), 3.7 m (12H), 6.7 q (1H, J = 1 Hz). Found: C 53.84; H 5.06; N 3.60%. $C_{17}H_{19}NO_9$. Calculated: C 53.60; H 4.98; N 3.68%.

Tetramethyl-3-methyl-4,5-dihydroazepino[1,2-b]oxazole-4,5,6,7-tetracarboxylate (II), yellow powder, mp 159-160°C (from methanol); yield 2%; mol. wt. (based on mass spectrum) 381. PMR spectrum (δ, ppm): 2.05 d (3H), 3.64 m (12H), 4.68 s (1H), 5.38 d (1H, J = 5 Hz), 5.60 d (1H, J = 5 Hz), 6.80 q (1H). Found: C 53.90; H 5.10; N 3.56%. $C_{17}H_{19}NO_9$. Calculated: C 53.60; H 4.98; N 3.68%.

Tetramethyl-2,3-dimethyl-4,5-dihydroazepino[1,2-b]oxazole-4,5,6,7-tetracarboxylate (III), yellow powder, mp 200-202°C (from methanol); yield 9%; mol. wt. (based on mass spectrum) 395. PMR spectrum (δ, ppm): 2.01 s (3H), 2.10 s (3H), 3.60 m (12H), 4.67 s (1H), 5.31 d (1H, J = 5 Hz), 5.45 d (1H, J = 5 Hz). Found: C 55.03; H 5.20; N 3.52%. $C_{18}H_{21}NO_9$. Calculated: C 54.70; H 5.32; N 3.54%.

Tetramethyl-2,3,8-trimethyl-4,5-dihydroazepino[1,2-b]oxazole-4,5,6,7-tetracarboxylate (IV), green powder, mp 170°C (from methanol); yield 3%; mol. wt. (based on mass spectrum) 409. PMR spectrum (δ, ppm): 1.76 s (3H), 1.96 s (3H), 2.09 s (3H), 3.62 s (12H), 5.28 d (1H, J = 5 Hz), 5.50 d (1H, J = 5 Hz). Found: C 56.12; H 5.56; N 3.38%. $C_{19}H_{23}O_9N$. Calculated: C 55.80; H 5.64; N 3.42%.

Trimethyl-2,3,7-trimethyl-7a-carbomethoxymethylpyrido[1,2-b]oxazole-4,5,6-tricarboxylate (V), white powder, mp 138-140°C (from chloroform); yield 4%; mol. wt. (based on mass spectrum) 409. PMR spectrum (δ, ppm): 2.10 s (3H), 2.15 s (6H), 3.38 s (2H), 3.60 m (12H). Found: C 56.12; H 5.58; N 3.40%. $C_{19}H_{23}NO_9$. Calculated: C 55.80; H 5.64; N 3.42%.

Experimental Procedure. A mixture of 0.03 mole of the oxazole and 0.03 mole of ADE in 10 ml of benzene (toluene) was refluxed for 3.5 h. The corresponding furandicarboxylic esters were isolated by distillation.

Dimethyl ester of 2-butoxy-5-methylfuran-3,4-dicarboxylic acid (VI), bp 160-165° (5 mm); yield 21%. PMR spectrum (δ, ppm): 0.9 t(3H), 1.48 q(2H), 1.9 n.m. (2H), 2.05 s(1H), 3.64 s(6H), 4.05 n.m.(2H). Found: C 57.40; H 6.58%. $C_{13}H_{18}O_6$. Calculated: C 57.80; H 6.68%.

Dimethyl ester of 2-methylfuran-3,4-dicarboxylic acid (VII), bp 115-117° (5 mm); yield 60%; cf. [5].

CONCLUSIONS

The condensation of simple 2-alkyl-substituted oxazoles with acetylenedicarboxylic ester proceeds at the azomethine bond of the oxazole ring.

LITERATURE CITED

1. G. Ya. Kondrat'eva, Khim. Nauka Prom., 2, 686 (1957); Izv. Akad. Nauk SSSR, Otd. Khim., 484 (1959).
2. G. Ya. Kondrat'eva, L. B. Medvedskaya, and Z. N. Ivanova, Izv. Akad. Nauk SSSR, Ser. Khim., 2276 (1971); Inventor's Certificate No. 298,586; Byull. Izobr., No. 11 (1971).
3. R. M. Acheson, M. W. Foxston, and G. R. Miller, J. Chem. Soc., 3200 (1965).
4. R. M. Acheson and W. R. Tully, J. Chem. Soc., 1623 C (1968).
5. K. Alder and H. F. Rickert, Ber., 70, 1354 (1937).

ALKYLATION OF SALTS OF AMIDES AND MIXED IMIDES OF ARYLSULFONIC, NITRIC, AND CARBOXYLIC ACIDS USING ETHYLENE GLYCOL α,α'-DICHLOROETHERS

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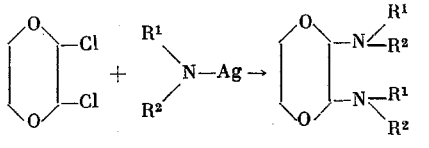
It is known that the chloromethyl ethers of monohydric alcohols alkylate the salts of N-alkylamides and imides of carboxylic acids at the nitrogen atom [1, 2], and the salts of the N-alkylamides of nitric acid (salts of primary nitramines) at both the nitrogen atom and the oxygen of the nitro group [3].

We studied the possibility and direction of alkylating a series of amides and imides using ethylene glycol α,α'-dichloroethers on the example of reacting 2,3-dichlorodioxane (I) and 1,2-dichloro-1,2-dimethoxyethane (II) with the Ag salts of N-methyltosylamide (IIIa), N-methylnitramine (IIIb),* ditosylimide (IIIc), N-nitrotosylimide (IIId), and N-nitrourethan (IIIe).

The N-alkylation products were isolated in low yields (10-25%) as the result of reacting (I) with the Ag salts of (IIIa), (IIIb), (IIId), and (IIIe). In the case of reacting (I) with the Ag salt of (IIIc) the yield of the alkylation product was 62%.



(I) (IVa—e)

R^1=Me, R^2=p-$MeC_6H_4SO_2$ (a); R^1=Me, R^2=NO_2 (b); R^1=R^2=p-$MeC_6H_4SO_2$ (c); R^1=NO_2, R^2=p-$MeC_6H_4SO_2$ (d); R^1=NO_2, R^2=CO_2Et (e).

*Compound (IIIb) was reacted with (II) as the triethylammonium salt.

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