LITERATURE CITED

1. L. P. Hammett, Physical Organic Chemistry, McGraw-Hill (1970).
2. W. P. Jencks, Catalysis in Chemistry and Enzymology, McGraw-Hill (1969).
3. M. O. Lidak and S. A. Giller, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 49 (1961).
4. L. Do Amaral, J. Org. Chem., 37, 1433 (1972).
5. J. Miller, J. Amer. Chem. Soc., 76, 448 (1954).
6. H. Bader, A. R. Hansen, and F. J. McCarty, J. Org. Chem., 31, 2319 (1966).
7. P. L. Noyak and K. K. Satpathy, J. Indian Chem. Soc., 49, 615 (1972).
8. V. N. Novikov, Z. N. Nazarova, L. D. Babeshkina, and T. F. Mikhailova, Summary of Papers on the Mechanisms of Heterolytic Reactions [in Russian], Leningrad (1974), p. 53.
9. V. N. Novikov and Z. N. Nazarova, Khim. Geterotsikl. Soedin., No. 1, 3 (1967).
10. Z. N. Nazarova and L. D. Babeshkina, Zh. Organ. Khim., 2, 1903 (1966).
11. Z. N. Nazarova and L. D. Babeshkina, Zh. Organ. Khim., 4, 176 (1968).
12. V. N. Novikov, V. Ts. Bukhaeva, F. T. Pozharskii, and A. M. Simonov, Khim. Geterotsikl. Soedin.. No. 2, 252 (1971).
13. Z. N. Nazarova, Zh. Obshch. Khim., 575 (1954).
14. Z. N. Nazarova, Yu. A. Babaev, and G. N. Natal'ina, Zh. Obshch. Khim., 1431 (1963).
15. R. Grigg, I. A. Knight, and M. V. Sargent, J. Chem. Soc., 6057 (1963).
16. Z. N. Nazarova and A. D. Garnovskii, Zh. Obshch. Khim., 1182 (1960).
17. Z. N. Nazarova, V. N. Novikov, and V. S. Pustovarov, Zh. Organ. Khim., 2, 161 (1966).
18. Experimental Methods in Chemical Kinetics [in Russian], Moscow (1971), p. 28.
19. K. J. Laidler, Kinetics of Organic Reactions [Russian translation], Mir, Moscow (1966).

SYNTHESIS OF γ-DIHYDROPYRONES AND β-DIHYDROFURANONES ON THE BASIS OF ACETYLENIC γ- AND δ-KETO ALCOHOLS AND ACETALS OF γ- AND δ-FORMYL ALCOHOLS

L. I. Vereshchagin, L. D. Gavrilov,
E. I. Titova, L. G. Tikhonova,
and S. R. Buzilova

UDC 547.722.3'724.812.5.07

Acetylenic γ- and δ-keto alcohols and acetals of acetylenic γ- and δ-keto alcohols and acetals of acetylenic γ- and δ-formyl alcohols undergo cyclization to γ-dihydropyrones and β-dihydrofuranones under the influence of acids.

Acetals (I) of acetylenic δ-hydroxy aldehydes [1] are potential sources of the corresponding δ-hydroxy aldehydes — they are converted to γ-pyrones (V) when the acetal protective group is removed by acidic reagents. It was found that this transformation is also common to other acetylenic carbonyl-containing compounds — γ- and δ-keto alcohols (II) and acetals (I) of acetylenic γ-formyl alcohols, which are converted, respectively, to γ-dihydropyrones (V) and β-dihydrofuranones (VII). This opens up a method for the preparation of compounds that have repellent properties. Thus 2,2-dimethyl-5-phenyl-4,5-dihydrofuran-3-one (VIIh) is a natural repellent.

The transformations found in this research can be explained by hydration of the triple bond of the above-indicated compounds to give hydroxydicarbonyl compounds (IV), which undergo cyclization with the loss of a water molecule to γ-pyrones V or β-furanones VII or are dehydrated to vinyl ketones or vinylketo aldehydes

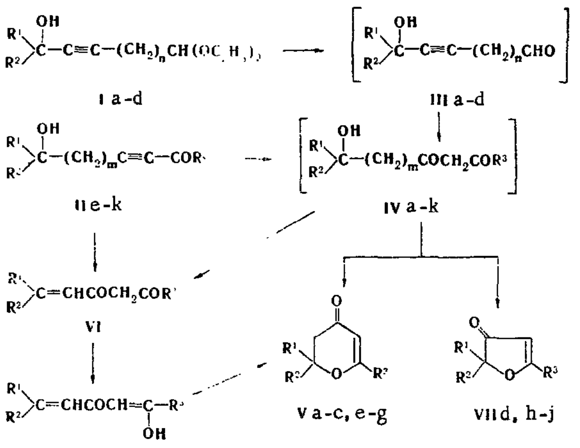
---

Institute of Petrochemical and Coal-Chemical Synthesis at Irkutsk State University, Angarsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1471-1473, November, 1976. Original article submitted November 24, 1975.

TABLE 1. 5,6-Dihydro-4-pyranones V and 1,2-Dihydro-3-furanones VII

Compound	R^1	R^2	R^3	bp, °C (mm), mp	Empirical formula	Found, %		Calc., %		Yield, %
						C	H	C	H	
Va	CH_3	CH_3	H	72–75 (10)[7]	—	—	—	—	—	24
Vb	CH_3	C_2H_5	H	80–85 (5)	$C_8H_{12}O_2$	68,0	9,0	68,5	8,6	40
Vc	$(CH_2)_5$		H	92–95 (1)	$C_{10}H_{14}O_2$	72,0	8,4	72,3	8,4	41
Ve	CH_3	CH_3	C_6H_5	126–129 (1)[5] 29–31	—	—	—	—	—	75
Vf	$(CH_2)_4$		C_6H_5	145–146 (1)	$C_{16}H_{18}O_2$	79,2	7,4	79,3	7,4	86
Vg	C_6H_5	H	n-C_3H_7	68–69	$C_{14}H_{16}O_2$	78,2	7,6	77,8	7,4	85
VId	CH_3	CH_3	H	44–45 (1)	$C_6H_8O_2$	64,0	7,4	64,2	7,1	59
VIIh	CH_3	CH_3	C_6H_5	65–68	$C_{12}H_{12}O_2$	76,2	6,4	76 6	6,4	93
VIIi	CH_3	CH_3	$C\equiv CC_6H_5$	38–39	$C_{14}H_{12}O_2$	79,3	5,9	79,2	5,7	80
VIIj	$(CH_2)_5$		C_6H_5	132–135	$C_{15}H_{16}O_2$	79,2	7,1	79,0	7,0	86

(VI). In fact, in a number of cases, a vinyl diketone was isolated – for example, vinyl diketone VIk, which, like other vinyl diketones [2], exists in the enol form in solution, was isolated when ketol IIk was treated with sulfuric acid in aqueous alcohol. Signals of vinyl protons (6.2, 6.52, and 7.63 ppm), as well as the signal of a hydroxyl group at 16.2 ppm, are recorded in the PMR spectrum of VIk. Enolization should promote intramolecular addition to the activated double bond.



I. III–V a $R^1=R^2=CH_3$, $R^3=H$, $n=1$; b $R^1=CH_3$, $R^2=C_2H_5$, $R^3=H$, $n=1$; c $R^1=R^2=(CH_2)_5$, $R^3=H$, $n=1$; I, III, IV, VII d $R^1=R^2=CH_3$, $R^3=H$, $n=0$; II, IV, V e $R^1=R^2=CH_3$, $R^3=C_6H_5$, $m=1$; f $R^1=R^2=(CH_2)_4$, $R^3=C_6H_5$, $m=1$; g $R^1=C_6H_5$, $R^2=H$, $R^3=n\text{-}C_3H_7$, $m=1$; II, IV, VII h $R^1=R^2=CH_3$, $R^3=C_6H_5$, $m=0$; i $R^1=R^2=CH_3$, $R^3=C\equiv CC_6H_5$, $m=0$; j $R^1=R^2=(CH_2)_5$, $R^3=C_6H_5$, $m=0$; II, IV k $R^1=R^3=C_6H_5$, $R^2=H$, $m=1$

One cannot exclude the possibility that anionotropic rearrangement of the type involved in the rearrangement of β-acetylenic [3] and α-acetylenic [4] alcohols leading to the corresponding vinyl diketones VI and vinylketo aldehydes also occurs in the case of δ-keto alcohols (IIe-g, k) and acetals (Ia-c) of δ-hydroxy aldehydes. The cyclization of compounds of this type to γ-pyrones under the influence of acids is well known [5].

The explanation of the conversion of γ-keto alcohols II and acetals of γ-hydroxy aldehydes to furanones through a step involving an ionotropic rearrangement is hardly acceptable. In this case, if the scheme of anionotropic rearrangement of α-acetylenic alcohols is followed [4], we should have isolated open-chain vinyl diketones or vinylketo aldehydes, the cyclization of which to β-dihydrofuranones VII is impossible. We are therefore inclined to suppose that the formation of γ-dihydropyrones V and β-dihydrofuranones VII is caused by hydration of the triple bond and subsequent cyclization of hydroxy dicarbonyl derivatives IV.

The IR spectra of V and VII contain intense absorption bands of a double bond conjugated with a carbonyl group (1570-1595 and 1570-1600 cm^{-1}) and of a carbonyl group (1640-1680 and 1690-1710 cm^{-1}). The PMR spectrum of γ-pyrone Vg contains signals of a vinyl proton (6.26 ppm) and of a proton attached to a saturated ring carbon atom (4.5 ppm), signals of a ring CH_2 group (2.6 ppm) and a propyl substituent (1.5 ppm), as well as a singlet of a methyl group (0.75 ppm) and a multiplet of aromatic protons at 7.05-7.7 ppm. The PMR spectrum of β-furanone VIId contains signals of vinyl protons at δ 5.52 and 8.20 ppm and protons of methyl groups (1.30 ppm). In addition to signals of aromatic protons at δ 7.11-7.86 ppm, the PMR spectrum of furanone VIIh contains the resonance of a vinyl proton (5.87 ppm) and of protons of gem-dimethyl groups (1.42 ppm).

EXPERIMENTAL

The IR spectra of thin layers or mineral-oil suspensions of the compounds were recorded with a UR-10 spectrometer. The PMR spectra were recorded with a Varian spectrometer (100 MHz) with tetramethylsilane as the external standard.

Acetylenic δ-keto alcohols IIe-g, k and formyl alcohol acetals Ia-c were obtained by the method in [1]; γ-keto alcohols IIh-j were obtained by the method in [6].

γ-Dihydropyrones (V) and β-Dihydrofuranones (VII). A solution of 0.05 mole of the appropriate acetal Ia-d or keto alcohol IIe-k was added to a solution of 12 ml of concentrated H_2SO_4 in 50 ml of ethanol and 50 ml of water, and the mixture was refluxed for 8 h. The ethanol was removed by distillation, the residue was extracted with ether, and the ether layer was washed with sodium carbonate solution and dried with $MgSO_4$. The solvent was removed by distillation, and the residue was vacuum fractionated. The physical constants of V and VII are presented in Table 1.

1,5-Diphenyl-4-pentene-1,3-dione (VIk). This compound, with mp 106-107°, was obtained in 89% yield by a similar method from 0.01 mole of 1,5-diphenyl-5-hydroxy-2-pentyn-1-one (IIk). Found: C 81.6; H 5.7%. $C_{17}H_{14}O_2$. Calculated: C 81.6; H 5.6%. IR spectrum, cm^{-1}: 1640 (C=O), 953, 970 (C=C).

LITERATURE CITED

1. L. I. Vereshchagin, L. D. Gavrilov, E. I. Tikhonova, and L. P. Vologdina, Zh. Organ. Khim., 9, 247 (1973).
2. C. Massyn, R. Pastor, and A. Cambon, Bull. Soc. Chim. France, 975 (1974).
3. T. K. Mamedov, N. E. Kolobova, K. N. Anisimov, and A. N. Nesmeyanov, Zh. Organ. Khim., 3, 1349 (1967).
4. R. Hansbrouck and A. Anderson, J. Org. Chem., 38, 2103 (1973).
5. I. N. Nazarov, Izv. Akad. Nauk SSSR, Ser. Khim., 107 (1948).
6. L. I. Vereshchagin, C. R. Gainulina, and L. P. Kirillova, in: Zh. Organ. Khim., "Biologically Active Compounds," 154 (1968).
7. E. Kosower and T. Sorensen, J. Org. Chem., 28, 687 (1963).
8. L. I. Vereshchagin, L. D. Gavrilov, E. I. Titova, and L. P. Vologdina, Zh. Organ. Khim., 9, 276 (1973).

CHEMISTRY OF HETEROANALOGS OF ISOFLAVONES

V.* REACTION OF FURAN AND BENZOFURAN ANALOGS OF ISOFLAVONES WITH ALKALIS AND HYDRAZINE

V. T. Khilya, L. G. Grishko,
and F. S. Babichev

UDC 547.814.5'728.1.778.2.3

It is shown that treatment of 3-hetarylchromones with alkalis and hydrazine hydrate leads to opening of the pyrone ring and subsequent conversion of the intermediate to α-hetaryl-2-hydroxyacetophenones and 2-hydroxyphenylpyrazole derivatives.

The reaction of chromones with alkalis can be used to establish the structure of compounds of this series [2]. We have studied the effect of alkalis on furan and benzofuran analogs [3] of isoflavones (Ia-c). It was es-

---

*See [1] for communication IV.

T. G. Shevchenko Kiev State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1474-1476, November, 1976. Original article submitted November 20, 1975.