LITERATURE CITED

1. C. W. Muth, D. O. Streiniger, and Z. B. Papanstassion, J. Am. Chem. Soc., 77, 3393 (1955).
2. A. S. Pfan and P. A. Plattner, Helv. Chim. Acta, 23, 768 (1940).
3. A. G. Anderson, Jr., and I. I. Tazuma, J. Am. Chem. Soc., 75, 4479 (1953).
4. D. Bergmann and R. Ikan, J. Am. Chem. Soc., 78, 1492 (1956).
5. S. M. Makin, V. M. Likhosherstov, and Shelepina, Zh. Obshch. Khim., 35, 1809 (1965).
6. Yu. N. Porshnev, E. M. Tereshchenko, V. V. Titov, and V. B. Mochalin, Zh. Org. Khim., 8, 1942 (1972).
7. Yu. N. Porshnev, E. M. Tereshchenko, and V. B. Mochalin, Khim. Geterotsikl. Soedin., No. 10, 1329 (1974).
8. G. N. Dorofeenko, A. V. Koblik, B. A. Tertov, and T. I. Polyakova, Khim. Geterotsikl. Soedin., No. 11, 1580 (1972).
9. G. N. Dorofeenko, A. V. Koblik, B. A. Tertov, and T. I. Polyakova, Khim. Geterotsikl. Soedin., No. 8, 1016 (1973).
10. K. Hafner and H. Kaizer, Ann., 618, 140 (1958).
11. K. Hafner and C. Bernhard, Ann., 650, 35 (1961).
12. S. V. Krivun, S. N. Baranov, and A. I. Buryak, Khim. Geterotsikl. Soedin., No. 10, 1320 (1971).
13. A. D. Semenov, G. N. Dorofeenko, and V. I. Dulenko, Khim. Geterotsikl. Soedin., No. 1, 14 (1966).

SYNTHESIS OF SOME THIENYL-SUBSTITUTED α,β-UNSATURATED KETONES CONTAINING A NITRO GROUP

Yu. D. Churkin and L. V. Panfilova

UDC 547.732'733.07

A method for the condensation of nitroformylthiophenes with ketones of the aromatic and heterocyclic series by means of ammonium acetate in glacial acetic acid was developed. The method makes it possible to obtain thienyl-substituted α,β-unsaturated ketones with a nitro group in the heterocyclic ring.

Crotonic condensation is the most convenient and widely used method for the synthesis of α,β-unsaturated aromatic and heterocyclic ketones. Depending on the character of the reacting substances, either acids (usually H_2SO_4, HCl, or $AlCl_3$) [1, 2] or compounds with basic character (NaOH, KOH, amines, carbonates and bicarbonates of metals, or other compounds [3-5]) can be used as catalysts for this reaction. However, in a number of cases when nitro groups are present in the starting aldehydes and ketones, the known methods for crotonic condensation do not make it possible to obtain unsaturated carbonyl compounds. Thus, for example, the condensation of 5-nitro-2-formylthiophene with acetone cannot be realized in either alkaline or acidic media [1]. Unsaturated carbon 1 compounds that contain a system of conjugated C═C and C═O bonds display biological activity [6]. However, the introduction of a nitro group in the heterocyclic ring of unsaturated ketones markedly intensifies their specific biological action.

However, the direct introduction of a nitro group in unsaturated ketones is usually hindered both by the presence in the molecule of several reaction centers that decrease the selectivity of nitration significantly and by the relative instability of the double bond, which displays a capacity for hydrolysis and oxidation in acidic or alkaline media.

For the synthesis of thienyl-substituted α,β-unsaturated ketones that contain a nitro group in one of the positions of the heterocyclic ringwe therefore used crotonic condensation in glacial acetic acid. As the catalyst of this reaction we used for the first time ammonium

---

V. V. Kuibyshev Kuibyshev Polytechnic Institute, Kuibyshev 443645. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1048-1049, August, 1980. Original article submitted January 4, 1980.

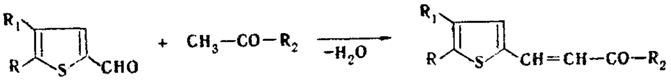
0009-3122/80/1608-0810$07.50

TABLE 1. Physicochemical Characteristics of New Nitrothienyl-Substituted α,β-Unsaturated Ketones

Compound	Reaction time, h	mp, °C	R_f	IR spectra (ν), cm^{-1}				Found, %				Empirical formula	Calc., %				Yield, %
				C=C	C=O	NO_{2as}	NO_{2s}	C	H	N	S		C	H	N	S	
I	50	237—238[a]	0,48	1595	1657	1550	1380	51,6	2,3	4,4	27,4	$C_{15}H_9NO_3S_3$	51,9	2,6	4,0	27,7	30
II	2	149—150[b]	0,31	1632	1684	1542	1335	51,4	4,5	6,2	16.0	$C_9H_9NO_3S$	51,2	4.3	6,5	15.6	94,6
III	20	171—172[a]	0,67	1597	1655	1556	1378	51,3	3.5	5,3	23,0	$C_{12}H_9NO_3S_2$	51,6	3,3	5,0	23.0	55,4
IV	10	158—159[a]	0,40	1610	1668	1556	1380	54.5	3.2	5,1	12,5	$C_{12}H_9NO_4S$	54,8	3,6	5,3	12,2	76,4
V	10	179—180[a]	0,59	1600	1667	1550	1378	61.2	3,9	5,4	11,4	$C_{14}H_{11}NO_3S$	61,5	4,1	5,1	11,7	73
VI	50	235—235,5[c]	0,61	1590	1643	1550	1355	53,5	2,8	3,5	26,4	$C_{16}H_{11}NO_3S_3$	53,2	3,1	3,9	26,6	14
VII	50	241—242[c]	0,63	1605	1670	1550	1380	69,0	4,7	4,4	9,4	$C_{20}H_{15}NO_3S$	68,8	4,3	4,0	9,2	12
VIII	2	72—73[d]	0,30	1615	1700	1555	1342	52,9	5,7	6,0	13,7	$C_{10}H_{11}NO_3S$	53,3	5,4	6,2	14,2	65
IX	8	139—140[a]	0,64	1600	1673	1550	1380	62,7	4,6	4,9	11,4	$C_{15}H_{13}NO_3S$	62,7	4,9	5,1	11,4	77
X	20	132—133[d]	0,7	1598	1658	1555	1380	53,6	3,9	5,1	22,0	$C_{13}H_{11}NO_3S_2$	53.2	3.8	4.8	21,8	34
XI	10	142—143[d]	0.37	1605	1665	1556	1378	56,5	4,2	5,2	11,8	$C_{13}H_{11}NO_4S$	56,3	4,0	5,1	11,6	18

[a] From isopropyl alcohol. [b] From ethanol. [c] From toluene. [d] From heptane.

acetate, which was previously used in the condensation of ketones with cyanoacetic acid [7] and in the Knoevenagel reaction [8].



I–XVI

I, XII—XVI $R=NO_2$; II—VII $R=CH_3$; VIII—XI $R=C_2H_5$; I, XII—XVI $R_1=H$; II—XI $R_1=NO_2$; I, VI, XVI $R_2=$ 2,2'-dithienyl-5-yl; VIII, XII $R_2=CH_3$; III, X, XIV $R_2=$2-thienyl; IV, XI, XV $R_2=$ 2-furyl; v, IX, XIII $R_2=C_6H_5$; VII $R_2=$ 4-biphenylyl.

The use of ammonium acetate as the catalyst enabled us to raise the yields of the known unsaturated nitro ketones by a factor of approximately two and to obtain a number of new previously undescribed compounds (Table 1). Ammonium acetate was also used to obtain α,β-unsaturated ketones from nitroformylthiophenes and methyl ketones of the biphenyl and 2,2'-dithienyl series. However, in this case the yields of desired products did not exceed 30%. The ratio of the condensing agent to the starting nitro aldehyde affects the yield of the final product. Better results are obtained at a molar ratio of 1:4. The reaction was carried out at the boiling point of acetic acid at reaction times ranging from 2 to 50 h. The reaction time depends on the nature of the R_2 in the ketone component of the reaction. The optimal condensation time for each specific case is presented in Table 1.

The structures of the compounds obtained were proved by their IR spectra, the results of elementary analysis, and by a comparison of the physicochemical constants obtained with the values described in the literature.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The purity of the compounds obtained was monitored on Silufol UV-254 plates in benzene.

Synthesis of Unsaturated Ketones I-XVI (General Method). A 0.01-mole sample of the nitroformylthiophene was dissolved in the minimum amount of glacial acetic acid, 0.01 mole of ammonium acetate and 0.01 mole of the aromatic or the heterocyclic ketone were added, and the reaction mixture was refluxed gently for 2-50 h. It was then cooled and maintained at 20°C for 3 days. If no precipitate formed, the reaction mixture was diluted to twice its original volume with water. The precipitate was removed by filtration and recrystallized from a suitable solvent. The yields and physical characteristics of ketones I-XI are presented in Table 1.

LITERATURE CITED

1. S. V. Tsukerman, V. M. Nikitchenko, and V. F. Lavrushin, Zh. Obshch. Khim., 32, 2324 (1962).

2. A. Gorvaisier, Bull. Soc. Chim. Fr., 528 (1962).
3. S. V. Tsukerman, I. K. Ginus, and V. F. Lavrushin, Zh. Obshch. Khim., 33, 2383 (1963).
4. I. Tirouflet and A. Gorvaisier, C. R., 250, 1276 (1960).
5. Yu. D. Churkin and V. I. Savin, Khim. Geterotsikl. Soedin., No. 1, 60 (1971).
6. S. Kushwaha, J. Indian Chem. Soc., 45, No. 8, 852 (1968).
7. A. C. Cope, J. Am. Chem. Soc., 63, 3452 (1941).
8. E. Knoevenagel, Ber., 37, 4461 (1904).

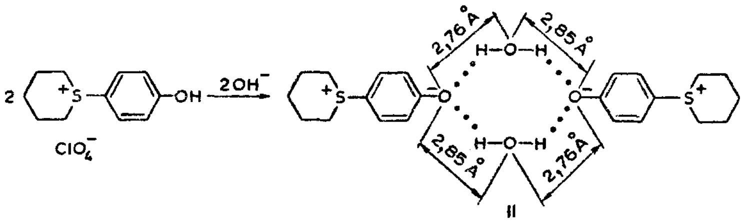
REACTIONS OF p-HYDROXYPHENYL- AND p-PHENOLATOTHIANIUM COMPOUNDS

E. N. Karaulova, L. P. Barykina,
T. S. Bobruiskaya, Yu. T. Struchkov,
G. D. Gal'pern, and M. A. Dzyubina

UDC 547.818

p-Hydroxyphenylthianium perchlorate reacts with OH^- to give bis(p-phenolatothianium) dihydrate, in which the oxygen atoms of the zwitter ions are tied up in an eight-membered ring by hydrogen bonds with the H_2O molecules. The unit cell of the perchlorate consists of two cations and two anions bonded by linear and forked hydrogen bonds. p-Hydroxyphenylthianium perchlorate reacts with a concentrated solution of KOH in methanol to give 1-(p-hydroxyphenyl)-1'-(p-phenolato)bisthianium perchlorate, which is also obtained by the reaction of p-hydroxyphenylthianium perchlorate with bis(p-phenolatothianium) dihydrate and of the latter with $HClO_4$. 1-(p-Hydroxyphenyl)-1'-(p-phenolato)bisthianium chloride hydrate and 1-(p-phenolato)thianiumbisphenol, respectively, were obtained by the reaction of bis(p-phenolatothianium) dihydrate with p-hydroxyphenylthianium chloride or with C_6H_5OH. Under the influence of picric or perchloric acid, 1-(p-h droxyphenyl)-1'-(p-phenolato)bisthianium perchlorate is converted to p-hydroxyphenylthianium picrate or its perchlorate, respectively, while reaction with OH^- gives bis(p-phenolatothianium) dihydrate, and heating with piperidine gives p-hhdroxyphenyl ω-piperidinoamyl sulfide. When bis(p-phenolatothianium) dihydrate is heated, it undergoes dehydration and polymerization to $[-OC_6H_4S(CH_2)_5-]_n$; depending on the conditions, n = 2, 3, 14, or 25. p-Hydroxyphenyl ω-piperidinoamyl sulfide is formed when II is heated with piperidine.

p-Hydroxyphenylthianium perchlorate (I) is converted to a base, viz., bis(p-phenolatothianium) dihydrate (II), when a soltuion of it in methanol, alcohol, or water is allowed to react with potassium hydroxide or when a methanol solution of I is treated with an anion-exchange resin (in the OH^- form):



II

This reaction is not a case of simple replacement of the anion, as assumed in [1], but rather involves proton transfer with the formation of p-phenolatothianium zwitter ions and water molecules that are bonded to them. According to data from x-ray diffraction analysis [2], the oxygen atom of the zwitter ion is tied up by hydrogen bonds simultaneously with two water molecules, which leads to the development of an eight-membered ring that is formed by four hydrogen bonds and four O–H bonds. The $O^-...O$ distance in two of the $O^-...H–O$ fragments

---

A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow 117909. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1050-1055, August, 1980. Original article submitted October 9, 1979.

0009-3122/80/1608-0812$07.50