

filtrate was cooled and treated with 20 ml of ether, and the precipitated bromomethylpyrylium salts XXIII-XXXV were removed by filtration, washed with ether, and crystallized from glacial acetic acid.

LITERATURE CITED

1. G. N. Dorofeenko, E. I. Sadekova, and E. V. Kuznetsov, *The Preparative Chemistry of Pyrylium Salts* [in Russian], Izd. Rostovsk. Univ., Rostov-on-Don (1972), pp. 69, 160.
2. G. A. Reynolds and J. A. von Allan, *J. Org. Chem.*, **34**, 2736 (1969).
3. E. Gard and A. Vasilescu, *J. Lab. Comp.*, **3**, 196 (1967).
4. N. V. Khromov-Borisov and L. A. Gavrilova, *Zh. Obshch. Khim.*, **32**, 86 (1962).
5. L. G. Makarova and A. N. Nesmeyanov, *Methods of Heteroorganic Chemistry. Mercury* [in Russian], Nauka, Moscow (1965), p. 53.
6. M. Simalty, H. Strzelecka, and H. Khedija, *Tetrahedron*, **27**, 3503 (1971).
7. A. I. Tolmachev, G. G. Dyadyusha, E. F. Karaban, A. A. Ishchenko, and N. A. Derevyanko, *Khim. Geterotsikl. Soedin.*, No. 6, 739 (1978).
8. S. V. Krivun, S. V. Sayapina, and S. N. Baranov, USSR Inventor's Certificate No. 541848; *Byull. Izobret.*, No. 1, 108 (1977).
9. A. T. Balaban, I. Mateescu, and M. Ellian, *Tetrahedron*, **18**, 1083 (1962).
10. L. Bellamy, *Infrared Spectra of Complex Molecules*, Methuen, London (1958).
11. S. N. Baranov, V. F. Lipnitskii, and S. V. Krivun, USSR Inventor's Certificate No. 546614; *Byull. Izobret.*, No. 6, 74 (1977).
12. V. I. Boev and A. V. Dombrovskii, *Zh. Obshch. Khim.*, **50**, 467 (1980).
13. P. N. Fedoseev and N. P. Ivashova, *Zh. Anal. Khim.*, **11**, 233 (1956).

SYNTHESIS AND PROPERTIES OF BIS(PYRIDYLMETHYLENE)MERCURY

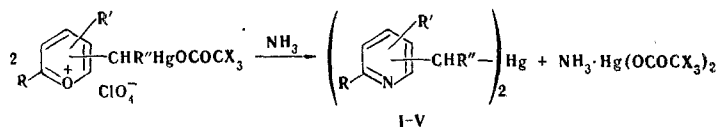
DERIVATIVES*

V. I. Boev and A. V. Dombrovskii

UDC 547.828.254.9

The action of ammonia on α - and γ -monomercurimethylenepyrylium perchlorates gave bis(pyridylmethylen)mercury derivatives, which undergo decomposition to the corresponding pyridine derivatives and mercuric chloride.

In our preceding communication [1] we described the syntheses of mercury-containing methylpyrylium perchlorates, which are of definite interest for the synthesis of various heteroorganic heterocyclic systems. It is known that under the influence of ammonia pyrylium salts are readily converted to the corresponding nitrogen-containing heterocyclic compounds [2]. We have found that bis(pyridylmethylen)mercury derivatives (I-V) can be obtained by the action of dry ammonia on α - and γ -monomercurimethylenepyrylium perchlorates [1] in anhydrous chloroform; in addition to conversion of the pyrylium cation to a pyridine ring, the starting substrates undergo symmetrization under the influence of ammonia [3] to give completely substituted organomercury compounds (I-V).



X=H, F; I R=CH₃, R'=2-C₆H₅, R''=H; II R=C₆H₅, R'=2-C₆H₅, R''=H; III R=C₆H₅, R'=2-C₆H₅, R''=C₆H₅; IV R=C₆H₅, R'=4-C₆H₅, R''=H; V R=p-C₆H₄OC₂H₅, R''=H

Compounds I-V are colorless or slightly colored crystalline substances that are quite soluble in organic solvents and mineral acids. The structure of I-V is confirmed by data

*See [1] for our preceding communication.

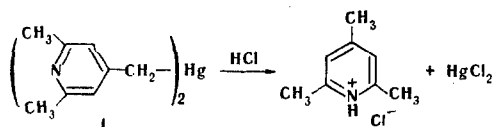
N. V. Gogol' Nezhin Pedagogical Institute, Nezhin 251200. Translated from *Khimiya Geterotsiklicheskich Soedinenii*, No. 7, pp. 887-888, July, 1981. Original article submitted May 5, 1980.

TABLE 1. Substituted Bis(pyridylmethylene)mercury Compounds (I-V)

Compound	mp, °C	IR spectrum, cm ⁻¹	Found, %		Empirical formula	Calc., %		Yield, %
			Hg	N		Hg	N	
I	144-145 ^a	2900, 1588, 1545, 1440, 1362, 1307, 1200, 1143, 1019, 980, 919, 849, 830	45,3	6,6	C ₁₆ H ₂₀ HgN ₂	45,5	6,4	78
II	201-202 ^b	2980, 1645, 1610, 1590, 1570, 1540, 1500, 1484, 1445, 1410, 1335, 1201, 1018, 990, 920, 864	28,8	4,0	C ₃₆ H ₂₈ HgN ₂	29,1	4,1	43
III	158-160 ^b	2970, 1665, 1640, 1588, 1569, 1483, 1440, 1381, 1305, 1203, 1015, 990, 910, 858	24,0	3,4	C ₄₈ H ₃₆ HgN ₂	23,8	3,3	48
IV	243-244	1585, 1525, 1490, 1440, 1388, 1355, 1200, 1020, 910, 865	29,0	4,1	C ₃₆ H ₂₈ HgN ₂	29,1	4,1	78
V	161-162 ^a	2940, 1645, 1593, 1500, 1468, 1410, 1381, 1275, 1200, 1164, 1038, 1000, 910, 890, 821	23,1	3,3	C ₄₄ H ₄₄ HgN ₂ O ₄	23,2	3,2	69

^aFrom absolute alcohol. ^bFrom hexane-ether (2:1).

from the IR spectra (Table 1), in which absorption bands of C-H stretching vibrations at 2900-3000 cm⁻¹ and pyridine ring C=C and C=N vibrations at 1500-1595 cm⁻¹ are observed. The vibrations of the pyridine ring itself are characterized by a strong absorption band near 1200 cm⁻¹, while characteristic frequencies between 1000 and 800 cm⁻¹ correspond to the deformation vibrations of the C-H bonds of both the pyridine ring and the aromatic rings. The absorption bands at 1640-1660 cm⁻¹ in the IR spectra of II-V are characteristic for the stretching vibrations of the C=C bonds of phenyl rings [4] and are absent in the spectrum of I.



When I-V are refluxed in concentrated hydrochloric acid, they undergo decomposition to give the corresponding pyridine derivatives and mercuric chloride. For example, collidine was isolated in the decomposition of bis(2,6-dimethyl-4-pyridylmethylene)mercury (I) under the indicated conditions, and the resulting Hg²⁺ ions were isolated quantitatively in the form of mercuric sulfide.

EXPERIMENTAL

The IR spectra of solutions of the compounds in chloroform were recorded with a Specord 71 IR spectrometer.

Bis(pyridylmethylene)mercury Derivatives (I-V, Table 1). A 1-mmole sample of the perchlorate of the corresponding mercury-containing methylpyrylium salt [1] was added to 25 ml of a saturated solution of dry ammonia in anhydrous chloroform, and the mixture was allowed to stand at room temperature for 24 h. The resulting precipitate was removed by filtration and washed with 20 ml of chloroform. The chloroform was removed from the filtrate by vacuum distillation, the residue was washed with ether, and crystalline I, IV, and V were removed by filtration, dried, and recrystallized. In the case of II and III the ether solutions were diluted with an equal volume of hexane, and the resulting precipitates were removed by filtration, dried, and recrystallized.

Reaction of Bis(2,6-dimethyl-4-pyridylmethylene)mercury (I) with Hydrochloric Acid. A mixture of 1.06 g of I and 20 ml of concentrated HCl was refluxed for 10 min, after which it was cooled and treated with 25 ml of water. Hydrogen sulfide was passed through the solution until it was saturated, and the resulting black precipitate of mercuric sulfide was removed by filtration, washed successively with water, alcohol, and ether, and dried to give 0.55 g (99.9%) of HgS. The aqueous filtrates were made strongly alkaline with KOH and extracted with ether (two 60-ml portions). The ether solutions were washed with water and dried with Na₂CO₃, the ether was removed by distillation, and the residue was distilled to give 0.2 g (34.5%) of collidine with bp 170-172°C [5].

LITERATURE CITED

1. V. I. Boev and A. V. Dombrovskii, *Khim. Geterotsikl. Soedin.*, No. 7, 881 (1981).
2. G. N. Dorofeenko, E. I. Sadekova, and E. V. Kuznetsov, *The Preparative Chemistry of Pyrylium Salts [in Russian]*, *Izd. Rostovsk. Univ., Rostov-on-Don* (1972), p. 127-131.
3. L. G. Makarova and A. N. Nesmeyanov, *Methods of Heteroorganic Chemistry. Mercury [in Russian]*, *Nauka, Moscow* (1965), p. 255.
4. L. Bellamy, *Infrared Spectra of Complex Molecules*, *Methuen, London* (1958).
5. G. N. Dorofeenko and S. V. Krivun, *Ukr. Khim. Zh.*, 29, 1058 (1963).

EFFECT OF THE NATURE OF THE SOLVENT ON THE RATE AND MECHANISM
OF THE CATALYTIC HYDROGENATION OF DIFURFURYLIDENEACETONE

R. Mat'yakubov and Yu. M. Mamatov*

UDC 541.12.038'127:542.93:547.723:724

It was established that the hydrogenation of difurfurylideneacetone on a skeletal Ni-Ti-Al catalyst at atmospheric pressure proceeds nonselectively. The rate of hydrogenation in both aprotic and protic solvents increases as their overall electrophilicity increases. The process is realized selectively under hydrogen pressure. By changing the type of solvent one can obtain a catalyzate enriched in various reaction products.

One of the most obscure problems in heterogeneous catalysis is the effect of the nature of the solvent on the rate and mechanism of the hydrogenation of organic compounds. It is known [1] that, depending on the type of solvent catalyst used, hydrogenation may lead to the formation of various reaction products.

The aim of the present research was to investigate the effect of the nature of various solvents on the rate and mechanism of hydrogenation of difurfurylideneacetone (I) on a skeletal nickel-titanium-aluminum catalyst and to determine the conditions for the selective hydrogenation of dienone I. It is known [2] that to characterize the nonspecific solvation capacity of solvents one uses two parameters, viz., the polarity and polarizability, which are expressed by functions of the dielectric constant or the refractive index. Scales of the overall acidity (electrophilicity) E of the solvents are used as the one-parameter characteristic of the polarities of solvents. The dependence of the rate of hydrogenation of dienone I on the electrophilicities of the solvents is shown in Table 1. It is apparent from the data presented for the hydrogenation of dienone I at 20°C in both aprotic and protic dipolar solvents that the reaction rate increases as the electrophilicity of the solvent increases. This dependence is displayed particularly distinctly in the hydrogenation of I at 50°C and atmospheric pressure.

The study showed that the hydrogenation of dienone I at atmospheric pressure in various solvents leads to the formation of a mixture of hydrogenated products.

It is apparent from the data presented that in the hydrogenation of dienone I at 20°C the reaction rate increases from 1.2 (in n-heptane) to 14 ml of H₂ per minute (in ethanol). As the temperature is increased to 50°C, the rate of hydrogenation ranges from 1.5 to 25 ml of H₂/min; the reaction rate increases in a different manner in various solvents. This phenomenon is evidently explained by the change in the coefficient of distribution of the substance undergoing hydrogenation between the solvent and the catalyst surface. The reason for the insignificant increase in the rate of hydrogenation of dienone I in n-heptane as the temperature is increased is the limited solubility of starting dienone I in this solvent. This also limits the hydrogenation process. After 300 min of hydrogenation of dienone I at

*Deceased.

"Plastmassy" Scientific-Industrial Union, Fergana 712001. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 7, pp. 889-893, July, 1981. Original article submitted September 10, 1979; revision submitted September 16, 1980.