was washed in succession with 3% HCl solution, 5% NaOH solution, and water, dried over $MgSO_4$, and the solvent was distilled off. Vacuum-distillation of the residue gave 0.71 g of (XVII), bp 100-102° (3 mm); n_D^{30} 4648 (see [4]).

CONCLUSIONS

Schiff bases that contain vinyl ether fragments were synthesized by the condensation of monoethanolamine vinyl ether with cyclohexanone, 2-methylcyclohexanone, and cyclopentanone. Their reaction with carboxylic acid halides in the presence of triethylamine gives the vinyl ethers of cycloalkenyl hydroxyethyl amides.

LITERATURE CITED

1. M. F. Shostakovskii, B. U. Minbaev, L. V. Kirilyus, and O. A. Aimakov, Izv. Akad. Nauk SSSR, Ser. Khim., 1978, 1217.
2. I. P. Chupp and E. R. Weiss, J. Org. Chem., 33, 2357 (1968).
3. U. S. Patents 3,574,746 and 3,586,496 (1971); Ref. Zh., Khim., 4N699, 10N591P (1972).
4. M. F. Shostakovskii, I. A. Chekulaeva, and I. V. Lipovich, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1963, 532.

THERMAL REACTIONS OF AZULENES WITH MALONIC, DIPHENYLACETIC, AND HALOACETIC ACIDS

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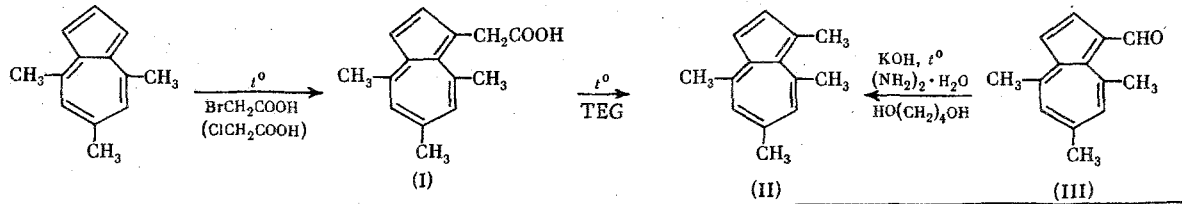
UDC 541.11:547.913.5:547.461.3:547.464.2

We found that the short heating at reflux of azulene with either diphenylacetic or malonic acid, without a catalyst, leads to the formation of mixtures of the corresponding 1-mono- and 1,3-diacylazulenes in respective yields of 55 and 1 or 22 and 5%. The acylation of 4,6,8-trimethylazulene (TMA) proceeds with the predominant formation of the 2-acyl derivatives (together with appreciable amounts of the 1-acyl-TMA in the reaction with malonic acid). The structure of the 1-acetyl derivatives of azulene and TMA (and also of 1,3-diacetylazulene) was proved by comparing their constants (melting point, R_f, and λ_{max}) with the data given in [1-3]. For the 2-acyl derivatives of TMA and all of the obtained ω,ω-diphenylacetylazulenes, after chromatographic purification, we determined the elemental composition and studied the UV and PMR spectra, which confirmed their structure. The thermal isomerization of the 1-acyl derivatives of TMA gives (to be sure, in lower yields) the above indicated 2-acyl derivatives, which can be considered as proof equivalent to counter synthesis, since similar 1—2 isomerization has been well studied [4-9].

The alkylation of azulene and its homologs under Friedel—Crafts conditions is directed to either the 1 or 3 position of the azulene ring, but because of the great sensitivity of azulenes to catalytic transformations [10, 11] these reactions always proceed to give low yields. For example, benzyl chloride under these conditions forms 1-benzylazulene in a total yield of 5.6% [11]. Alkyl halides give lower yields [1, 12]. The radical benzylation of azulene is also described [13].

It was shown by us that heating TMA with monobromo (or chloro-)acetic acid is accompanied by alkylation of the azulene ring in the 1 position, in which connection 4,6,8-trimethylazulenyl-1-acetic acid is formed in 30% yield.



(I) (II) (III)

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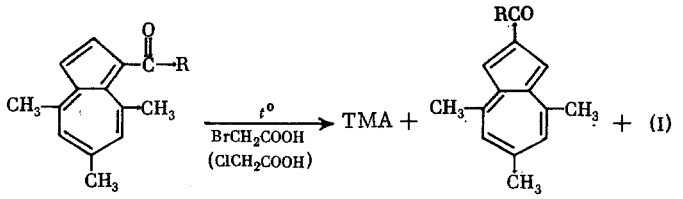
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 235-238, January, 1979. Original article submitted July 7, 1978.

The pyrolysis of acid (I) in refluxing triethylene glycol (TEG) leads to its decarboxylation and the formation of 1,4,6,8-tetramethylazulene (II), which we also obtained from 1-formyl-TMA (III) [14] by the Wolff—Kishner method. We postulate that this reaction is homolytic alkylation by either the carboxymethyl or carboxymethylene radical, which can be formed as intermediates by the thermal decomposition of the haloacetic acid.

Since all of the azulene derivatives are intensely colored, it was established by TLC that the thermal treatment of 1-acetyl- and 1-benzoyl-TMA [15] with haloacetic acids is accompanied mainly by cleavage of the acyl groups and their migration to the 2 position, in which connection the "substitutive alkylation" of the 1-acylazulenes* in the 1 position also occurs to slight degree.



$R_3 = CH_3$;Ph

The 1-nitro- [2] and 1-trifluoroacetyl-TMA [16] fail to undergo any transformations under similar conditions. 4,6,8-Trimethylazulen-1-yl phenyl sulfone when heated with bromoacetic acid gives the 2-phenylsulfonyl derivative in good yield, which is identical with the compound obtained by thermal cationotropic isomerization [17].

It proved that ferrocene, pyrene, anthracene, 6,6-diphenylfulvene, and 2-phenylbenzo[b]-cyclopenta[e]pyran (2-phenyl-BCPP) when heated neat with malonic acid give the corresponding monoacetyl derivatives, whereas 1,2,3-triphenyl-BCPP [18] fails to react. Consequently, the thermal acylation observed by us has a general character for compounds of the aromatic system where a high electron density is inherent to at least one carbon atom.

EXPERIMENTAL

Acylation of Azulene with Diphenylacetic Acid. A mixture of 640 mg of azulene and 7 g of diphenylacetic acid was heated to reflux, and here the color of the reaction mass changed from blue to crimson. After cooling, the melt was dissolved in 100 ml of 2% aqueous NaOH solution, extracted with benzene, dried over Na_2SO_4, and chromatographed on a silica gel column, using benzene as the eluant. The solvent was evaporated, and the residue was recrystallized from MeOH to give 880 mg (54.6%) of 1-ω,ω-diphenylacetylazulene: red needles with mp 106-107°C, R_f 0.36 (in benzene, Silufol), λ_{max} 530 nm, log ε 2.66 (benzene). Found: C 89.18; H 5.73%. $C_{24}H_{18}O$. Calculated: C 89.39; H 5.62%. Besides unreacted azulene, we isolated a small amount of the postulated 1,3-diacyl derivative. A part of the starting substance was converted to dark products that could not be eluted from the column.

Acylation of TMA with Diphenylacetic Acid. A mixture of 850 mg of TMA and 10 g of diphenylacetic acid was heated to reflex, in which connection the color of the melt changed from violet to blue-green. After cooling, the melt was worked up as indicated above; the blue zone was collected during chromatography, the eluate was evaporated, and the residue was recrystallized from EtOH using activated carbon to give 310 mg (18%) of 2-ω,ω-diphenylacetyl-TMA as blue needles with mp 172-173° (from EtOH), R_f 0.42 (in benzene, Silufol), λ_{max} 590 nm log ε 3.14 (benzene). Found: C 88.66, H 6.47%. $C_{27}H_{24}O$. Calculated: C 88.96; H 6.65%.

Acylation of TMA with Malonic Acid. A mixture of 680 mg of TMA and 12 g of malonic acid was refluxed until the color of the reaction mass changed from violet to dark blue, after which the melt was cooled, dissolved in 100 ml of water, extracted with benzene, and the extract was dried over Na_2SO_4 and chromatographed on a silica gel column, using benzene as the eluant. The blue zone, and then the red zone, were isolated. After evaporation of the solvent, the residue in each case was recrystallized from n-heptane. We obtained 216 mg (25.3%) of 2-acetyl-TMA as blue needles with mp 166-168°, R_f 0.33 (chloroform, Silufol),

*The term "substitutive alkylation" is given in order to emphasize the possibility of electrophilic displacement of the acyl groups.

λ_{max} 585 nm, log ε 2.87 (benzene). Found: C 84.77; H 6.71%. $C_{15}H_{16}O$. Calculated: C 84.89; H 7.60%. From the red eluate we isolated 192 mg (22.6%) of 1-acetyl-TMA, whose melting point and R_f agreed with the literature data [15].

4,6,8-Trimethylazulenyl-1-acetic Acid (I). A mixture of 5 g of monobromoacetic acid and 0.5 g of TMA was heated until the reaction mass began to boil, in which connection the color did not change from violet to dark blue. After cooling, the melt was dissolved in water and extracted with benzene. The extract was dried over Na_2SO_4, evaporated to minimum volume, and chromatographed on a silica gel column. The violet zone of the starting TMA was eluted first with benzene, and then the blue zone of 4,6,8-trimethylazulenyl-1-acetic acid was separated using a 1:1 benzene-chloroform mixture. The eluate was evaporated, and the residue was recrystallized from a 7:3 heptane—benzene mixture to give 180 mg (27%) of acid (I) as purple needles with mp 160-162°, R_f 0.15 (benzene, Silufol). When based on reacted azulene the yield of (I) was 38.4%. Most of the starting azulene was converted to dark-colored products that were eluted slowly from the column. Found: C 78.55; H 7.18%. $C_{15}H_{16}O_2$. Calculated: C 78.91; H 7.07%.

1,4,6,8-Tetramethylazulene (II). The compound was obtained by heating acid (I) in refluxing TEG for 15 min (the yield was 62% after cooling the reaction mass, treatment with water, extraction with heptane, and purification by chromatography). It was identified by the melting point, R_f, and UV spectrum by comparison with an authentic specimen, which was obtained by the reduction of 4,6,8-trimethyl-1-azulenecarboxaldehyde by the Wolff—Kishner method, mp 42-43° (from MeOH), λ_{max} 490 nm (n-heptane). Found: C 91.21; H 8.74%. $C_{14}H_{16}$. Calculated: C 91.26; H 8.75%.

CONCLUSIONS

1. The thermal acylation of azulene with diphenylacetic and malonic acids is structurally directed to the 1 and 3 positions. In 4,6,8-trimethylazulene the acylation is predominantly in the 2 position.

2. The thermal alkylation of 4,6,8-trimethylazulene with bromo(chloro)acetic acid leads to 4,6,8-trimethylazulenyl-1-acetic acid. The radical mechanism is postulated for the reaction.

3. The thermal reaction of the 1-acetyl-, 1-benzoyl-, and 1-phenylsulfonyl-4,6,8-trimethylazulenes with monohaloacetic acids is accompanied by cleavage, and also by the partial 1—2 migration of the substituents. 1-Nitro- and 1-trifluoroacetyl-4,6,8-trimethylazulene do not react under similar conditions.

4. Ferrocene, pyrene, anthracene, 6,6-diphenylfulvene, and 2-phenylbenzo[b]cyclopenta-[e]pyran when heated with malonic acid give monoacetyl derivatives.

LITERATURE CITED

1. A. G. Anderson and J. A. Nelson, J. Am. Chem. Soc., 72, 3824 (1950).
2. A. G. Anderson, J. A. Nelson, and J. J. Tazuma, J. Am. Chem. Soc., 75, 4980 (1953).
3. K. Hafner, A. Stephan, and C. Bernhard, Ann. Chem., 650, 42 (1961).
4. S. Kurokawa, Tetrahedron Lett., 1969, 3567.
5. S. Kurokawa, Bull. Chem. Soc. Jpn., 43, 509 (1970).
6. Yu. N. Porshnev, E. M. Tereshchenko, and K. Z. Ogorodnik, Zh. Org. Khim., 8, 2201 (1972).
7. Yu. N. Porshnev, N. A. Andronova, E. M. Tereshchenko, and K. Z. Ogorodnik, Zh. Org. Khim., 10, 2602 (1974).
8. S. Kurokawa, T. Sato, T. Noguchi, and K. Yano, Bull. Chem. Soc. Jpn., 48, 1559 (1975).
9. Yu. N. Porshnev and E. M. Tereshchenko, Zh. Org. Khim., 11, 462 (1975).
10. W. Treibs, K. Jost, C. Kurpjun, and G. Grunduke-Schroth, Chem. Ber., 94, 1728 (1961).
11. A. G. Anderson, E. J. Cowles, J. J. Tazuma, and J. A. Nelson, J. Am. Chem. Soc., 77, 6321 (1955).
12. J. Ohtani, K. Kawase, K. Nakamura, and J. Ogura, Yakugaku Zasshi, 91, 647 (1971); Chem. Abstr., 75, 63485 (1971).
13. J. F. Tilney-Bassett and W. A. Waters, J. Chem. Soc., 1959, 3123.
14. K. Hafner and C. Bernhard, Angew, Chem., 69, 533 (1957).
15. K. Hafner and K.-F. Bangert, Ann. Chem., 650, 98 (1961).

16. A. G. Anderson, R. G. Anderson, and G. T. Hollander, J. Org. Chem., 30, 131 (1965).
17. Yu. N. Porshnev, V. I. Erikhov, and M. I. Cherkashin, Zh. Org. Khim., 12, 2599 (1976).
18. Yu. N. Porshnev, V. A. Churkina, N. A. Andronova, and V. V. Titov, Khim. Geterotsikl. Soedin., 1977, 902.

FERROCENYLARYLPYRAZOLINES

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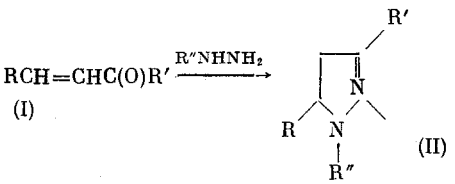
UDC 547.1'13:541.49:546.72:547.772.2

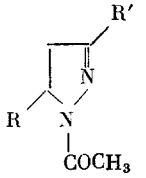
As a continuation of our studies on the chemistry of metallocenyl-substituted 2-pyrazolines [1] in the present paper we synthesized the isomeric 3- and 5-aryl-substituted pyrazolines with a ferrocenyl (Fc) group.



(I) (II)

R = Fc, R′ = *p*-$C_6H_4OCH_3$, R″ = H (a);
R = Fc, R′ = *p*-$C_6H_4OCH_3$, R″ = C_6H_5 (b)
R = *p*-$C_6H_4OCH_3$, R′ = Fc, R″ = H (c)
R = *p*-$C_6H_4OCH_3$, R′ = Fc, R″ = C_6H_5 (d)
R = Fc, R′ = *p*-C_6H_4Br, R″ = H (e)
R = Fc, R′ = *p*-C_6H_4Br, R″ = C_6H_5 (f)
R = *p*-C_6H_4Br, R′ = Fc, R″ = H (g)
R = *p*-C_6H_4Br, R′ = Fc, R″ = C_6H_5 (h)
R = Fc, R′ = R″ = C_6H_5 (k) [2]
R = R″ = C_6H_5, R′ = Fc (l)
R = Fc, R′ = C_6H_5, R″ = H (m) [2,
R = C_6H_5, R′ = Fc, R″ = H (n)

The 1-unsubstituted pyrazolines decompose easily in solution to the starting chalcones [1]. The 1-phenylpyrazolines, and especially the 1-acetylpyrazolines, are much more stable. The latter are easily obtained by the acylation of the N-unsubstituted pyrazolines.



(III)

R = Fc; R′ = *p*-$C_6H_4OCH_3$ (a)
R = *p*-$C_6H_4OCH_3$; R′ = Fc (b)
R = Fc; R′ = *p*-C_6H_4Br (c)
R = *p*-C_6H_4Br; R′ = Fc (d)
R = Fc; R′ = C_6H_5 (e) [2]
R = C_6H_5; R′ = Fc (f)

The PMR spectral data (Table 1) show that a greater $\Delta\delta$ value is characteristic for the 3-ferrocenylpyrazolines when compared with the 5-ferrocenylpyrazolines; this is apparently associated with the effect of the aryl substituent in the 5 position. In addition, a characteristic splitting of the signals of the protons of the substituted ferrocene ring is observed for the 3-ferrocenylpyrazolines (see Table 1, compounds (IId), (IIIb), (IIh), (IIId), (III1), (IIIf).

EXPERIMENTAL

3-p-Methoxyphenyl-5-ferrocenyl-2-pyrazoline (IIa). To 1.05 g of ferrocenal-p-methoxyacetophenone (Ia) [3] in 40 ml of ethanol was added 10 ml of hydrazine hydrate, and the stirred mixture was heated for 3 h. The obtained yellow crystals were washed with aqueous alcohol and dried over P_2O_5. Yield 0.93 g (86%), and mp 79°C (from alcohol). Found: C 66.90; H 5.56; Fe 15.41; N 8.10%. $C_{20}H_{20}FeN_2O$. Calculated: C 66.68; H. 5.60; Fe 15.50; N 7.78%.

M. V. Lomonosov Moscow State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 239-242, January, 1979. Original article submitted July 11, 1978.

 0568-5230/79/2801-0224$07.50