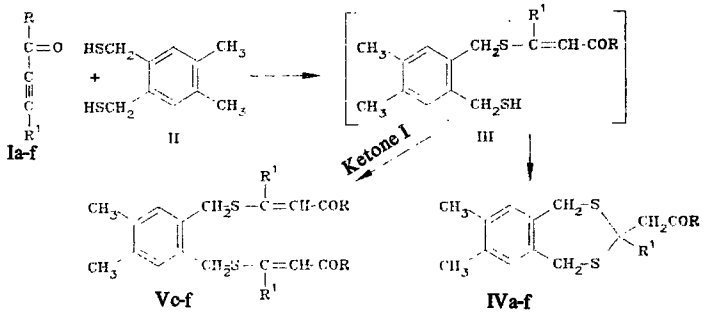
SYNTHESIS OF 3-ACYLMETHYL-1,5-DIHYDROBENZO[e]-2,4-DITHIEPINS AND 1,2-DI(ACYLVINYLTHIOMETHYL)-4,5-DIMETHYLBENZENES FROM α-ACETYLENE KETONES

A. S. Nakhmanovich, R. V. Karnaukhova,
V. N. Elokhina, and I. D. Kalikhman

UDC 547.892'536.4'379.1:543.422.4

Substituted 1,5-dihydrobenzo[e]-2,4-dithiepins and 1,2-di(acylvinylthiomethyl)-4,5-dimethylbenzenes were synthesized by the reaction between α-acetylene ketones and 1,2-dimethyl-4,5-di(mercaptomethyl)benzene in chloroform in the presence of K_2CO_3 or in methanol in the presence of triethylamine.

We have already described the reactions of certain dithiols (1,2-ethanedithiol, 1,5-pentanedithiol, o-phenylenedithiol, and 2,3-quinoxalinedithiol) with α-acetylene ketones [1-5] and 1-bromo-2-acylacetylenes [2, 4] that result in different sulfur-containing heterocyclic compounds. In the present work, we studied the reaction of α-acetylene ketones (Ia-d) with 1,2-dimethyl-4,5-di(mercaptomethyl)benzene (II), leading to the difficulty available 3-acylmethyl-7,8-dimethyl-1,5-dihydrobenzo[e]-2,4-dithiopins (IV), by the scheme



a, c, e R=α-C_4H_3S; b, d R=C_6H_5; f R=CH_3; a, b R^1=H; c, d, f R^1=C_6H_5; e R^1=p-$C_6H_4CH_3$

3-Acylmethyl-1,5-dihydrobenzo[e]-2,4-dithiepins (IVa-f) were exclusively obtained by the reaction of reagents I and II in an equimolar ratio in methanol in the presence of triethylamine at 20°C (method A).

The reaction of acylacetylenes Ia-f with dithiol II in an equimolar ratio of the reagents in chloroform in the presence of potassium carbonate as catalyst at 60°C (method B) led to the formation of benzo[e]-2,4-dithiepins (IVa-f) and 1,2-di(acylvinylthiomethyl)-4,5-dimethylbenzenes (Vc-f). The latter compounds could not be isolated in the reaction of terminal acylacetylenes Ia, b with dithiol II. When this reaction was carried out under the same conditions but in a 2:1 molar ratio of ketone Ic-f–dithiol II, the yield of compounds Vc,d increased considerably.

In the reaction with dithiol II by method B, terminal acetylene ketones Ia,b form compounds IVa,b in yields (77 and 53%) that are higher than those with substituted acetylene ketones Ic,d (the yields of compounds IVc,d are 56 and 36%, respectively). The yields of compounds IVa,b formed by method B are much higher than those obtained by method A (Table 1), while the yields of compounds IVc,d formed by the two methods are approximately the same.

In the IR spectra of the benzo[e]-2,4-dithiepins IVa-f there are absorption bands of the carbonyl group at 1670-1685 cm^{-1}, of the C–S bond at 690-705 cm^{-1}, intense absorption

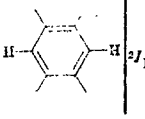
Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 203-205, February, 1985. Original article submitted April 18, 1984.

 0009-3122/85/2102-0166$09.50

TABLE 1. 3-Acylmethyl-7,8-dimethyl-1,5-dihydrobenzo[e]-2,4-dithiepins (IVa-f) and 1,2-Di(acylvinylthiomethyl)-4,5-dimethylbenzenes (V)

Compound	mp, deg C	Found, %			Empirical formula	Calculated, %			Yield (method)
		C	H	S		C	H	S	
IVa	156—157	61,3	5,3	28,8	$C_{17}H_{18}OS_3$	61,0	5,3	28,7	59 (A), 77 (Б)
IVb	184—185	69,8	6,2	19,2	$C_{19}H_{20}OS_2$	69,5	6,1	19,5	34 (A), 53 (Б)
IVc	184—186	66,4	5,4	23,1	$C_{23}H_{22}OS_3$	66,3	5,3	23,4	60 (A), 56 (Б)
IVd	147—148	73,8	5,9	15,8	$C_{25}H_{24}OS_2$	74,0	5,9	15,8	37 (A), 36 (Б)
IVe	146—148	67,6	5,6	22,7	$C_{24}H_{24}OS_3$	67,9	5,7	22,6	— 31 (Б)
IVf	130—131	70,2	6,6	18,4	$C_{20}H_{22}OS_2$	70,2	6,4	18,7	— 53 (Б)
Vc	200—201	69,6	4,9	20,8	$C_{36}H_{30}O_2S_4$	69,5	4,8	20,6	— 48 (Б)
Vd	170—171	78,6	5,5	10,3	$C_{40}H_{34}O_2S_2$	78,7	5,6	10,5	— 46 (Б)
Ve	162—163	70,1	5,1	20,0	$C_{38}H_{34}O_2S_4$	70,2	5,2	19,7	— 52 (Б)
Vf	50—51	73,9	6,5	13,2	$C_{30}H_{30}O_2S_2$	74,1	6,6	13,2	— 49 (Б)

TABLE 2. PMR spectra of 3-Acylmethyl-7,8-dimethyl-1,5-dihydrobenzo[e]-2,4-dithiepins (IV)

Compound	Chemical shift, δ, ppm						SSCC, J, Hz	
	CH_3	CH_2CO	SCH_2	R	R^1		$^2J_{HH}$	$^5J_{HH}$
IVa	2,16, s	3,25, d	3,89, d; 3,93, d	7,57, d, d; 7,26, d, d	4,81, t	6,87, s	14,7	7,0
IVc	2,12, s	3,52, s	3,81, d; 3,69, d	7,25, d, d; 6,81, d, d	7,99, d; 7,35, d 2,30, s;	6,81, s	15,0	—
IVe	2,13, s	3,50, s	3,89, d; 3,55, d	7,44, d, d; 6,90, d, d	7,11, d; 7,84, d	6,81, s	15,5	—
IVf	2,15, s	3,02, s	3,68, d; 3,72, d	1,77, s	7,35, m	6,75, s	15,4	—

bands of deformational vibrations of the CH_2 group at 1480-1485 cm^{-1}, and of tetrasubstituted benzene ring at 850-885 cm^{-1}.

A peak of molecular ion with m/z 404 (5%) is observed in the mass spectrum of IVd. The peak with maximal intensity corresponds to fragment $C_6H_5CO^+$ (105, 100%).† In the spectra there are also peaks of ions $[C_6H_5COCH_2CSC_6H_5]^+$ (240, 55%), $C_6H_5COCHCSC_6H_5$ (239, 95%), $[M-C_6H_5COCH_2CC_6H_5]^+$ (196, 40%), $[M-C_6H_5COCH_2CSC_6H_5]^+$ (164, 50%), $[M-C_6H_5COCH_2CS_2C_6H_5]^+$ (132, 40%), $C_6H_5COCH_2^+$ (119, 30%) and $C_6H_5^+$ (77, 15%).

In the IR spectra of compounds Vc-f there are absorption bands of the conjugated carbonyl group at 1630-1635 cm^{-1}, of the C=C bond at 1570-1585 cm^{-1}, of the C–S bond at 700-715 cm^{-1}, and of the CH_2 group at 1475-1485 cm^{-1}. The parameters of the PMR spectra of compounds IVa, c, e, f are given in Table 2.

Disulfone VI was obtained by the oxidation of benzo[e]-2,4-dithiepin IVb by 30% hydrogen peroxide in glacial acetic acid. The IR spectrum of VI contains absorption bands of the carbonyl group at 1685 cm^{-1}, and bands of asymmetric and symmetric stretching vibrations of SO_2 groups at 1330 and 1180, and of the CH_2 groups at 1442 cm^{-1}.

EXPERIMENTAL

The IR spectra were run on a UR-20 spectrophotometer in KBr tablets; the PMR spectra, on a Tesla B-487-C spectrometer (80 MHz) in CD_3OD or $CDCl_3$, with HMDS as internal standard. The mass spectrum was obtained on an MX-1303 mass spectrometer, with an ionization voltage of 70 eV, and the temperature of the ionization chamber of 100°C.

†The m/z values and peak intensity (in %) are given in parentheses.

The characteristics of the compounds synthesized are listed in Table 1.

3-Thernoylmethyl-1,5-dihydro-3H-benzo[e]-2,4-dithiepin (IVa). A. A 1.3-g portion (7 mmoles) of 1,2-dimethyl-4,5-di(mercaptomethyl)benzene (II) is added dropwise, with stirring, to a solution of 1 g (7 mmoles) of thenoylacetylene Ia in 15 ml of absolute methanol, and then 0.7 ml of triethylamine is added. The mixture is stirred at room temperature for 2 h, the solvent is partially evaporated *in vacuo*, and the residue is cooled to 0°C. The precipitate is filtered and reprecipitated from methanol. Yield 1.98 g (59%).

B. A solution of 1.9 g (0.01 mole) of dithiol II in 30 ml of chloroform is added, with stirring, to a solution of 1.3 g (0.01 mole) in 30 ml of chloroform. Then, 1 g of freshly calcined potassium carbonate is added, the mixture is heated to 60°C, and stirred for 2 h. The reaction mixture is cooled, K_2CO_3 is filtered, and the solvent is partially evaporated *in vacuo*. The reaction product is precipitated by a 20-fold amount of cold ether, the precipitate is filtered, and recrystallized from ethanol. Yield, 2.57 g (77%).

The remaining compounds IV are obtained in a similar way.

1,2-Di[5-(2-thienyl)-3-phenyl-2-thiapenten-3-yl]-4,5-dimethylbenzene (Vc). After isolation of benzo[e]-2,4-dithiepin IVc, as described for compound IVa, the chloroform–ether solution is partially evaporated *in vacuo*, the residue is cooled to 0°C, and the precipitate is filtered, and recrystallized from ethanol. Yield, 0.82 g (28%).

Compounds Vd-f are obtained in a similar way.

At a 2:1 molar ratio ketone I — dithiol II, the yield of compounds V is 48% (based on ketone), Vd 46, Ve 52, and Vf 49%.

3-Benzoylmethyl-1,5-dihydro-3H-benzo[e]-2,4-dithiepin Tetraoxide (VI). A 2.4-ml of 30% hydrogen peroxide is added dropwise slowly, with stirring, to a solution of 0.5 g (2 mmoles) of compound IVb in 5 ml of glacial acetic acid. The mixture is stirred for 2 h at 20°C, and left to stand overnight. The precipitate is filtered, washed with water, and recrystallized from ethanol. Yield, 0.36 g (46%). mp 255-256°C. IR spectrum (KBr): 708 (C–S), 858-900 (δ CH of tetrasubstituted benzene ring), 1180 ($\nu_s SO_2$); 1332 ($\nu_{as} SO_2$), 1452 (δ CH_2), 1710 cm^{-1} (C=O). Found: C 58.3; H 5.0; S 16.2%. $C_{19}H_{20}O_5S_2$. Calculated: C 58.2; H 5.1; S 16.3%.

LITERATURE CITED

1. A. S. Nakhmanovich, V. N. Blokhina, R. V. Karnaukhova, G. G. Skvortsova, and I. D. Kalikhman, Khim. Geterotsikl. Soedin., No. 11, 1489 (1982).
2. V. N. Elokhina, A. S. Nakhmanovich, R. V. Karnaukhova, I. D. Kalikhman, and M. G. Voronkov, Khim. Geterotsikl. Soedin., No. 3, 329 (1981).
3. A. S. Nakhmanovich, T. E. Glotova, M. G. Voronkov, Yu. M. Mansurov, T. N. Komarova, and V. Yu. Vitkovskii, Izv. Sib. Otd. Akad. Nauk SSSR, No. 9, 110 (1981).
4. A. S. Nakhmanovich, V. N. Elokhina, I. D. Kalikhman, and M. G. Voronkov, Khim. Geterotsikl. Soedin., No. 8, 1137 (1977).
5. V. N. Elokhina, R. V. Karnaukhova, A. S. Nakhmanovich, I. D. Kalikhman, and M. G. Voronkov, Zh. Org. Khim., 15, 57 (1979).