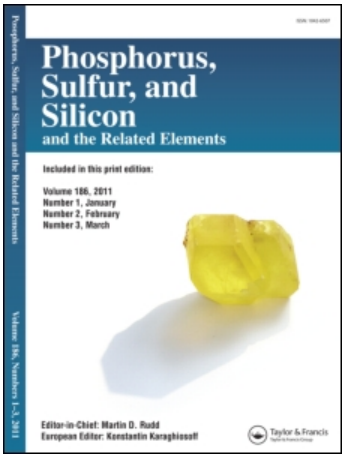

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Phase-Transfer Catalyzed Alkylation and Cycloalkylation of 3-Substituted-1*H*-pyrazol-2-in-5-ones in the Absence or Presence of Carbon Disulphide

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Phase-Transfer Catalyzed Alkylation and Cycloalkylation of 3-Substituted-1*H*-pyrazol-2-in-5-ones in the Absence or Presence of Carbon Disulphide

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*PTC-alkylation of 3-substituted-1*H*-pyrazol-2-in-5-ones by different organohalogen reagents at 25°C in the presence of tetrabutylammonium bromide as-catalyst was investigated either in the absence or presence of CS_2. This work aims to study the comparative reactivity of N-versus O-versus C-alkylation and cycloalkylation.*

Keywords 3-Substituted-1*H*-pyrazol-2-in-5-ones; alkylation; cycloalkylation; phase-transfer catalysis (PTC)

INTRODUCTION

Phase-transfer catalysis (PTC) is one of the promising methods in organic synthesis of specialty chemicals. In the last 20 years, a steadily increasing number of published articles and patents dealing with phase transfer catalysis topics and their applications. PTC is not merely important for substitution reactions, but nowadays it is being extensively applied in polymer chemistry, heterocyclic chemistry, organometallic and agrochemicals dyes, flavors, perfumes, and pharmaceutical manufacture.[1–3]

The technique of PTC has been extensively applied in the organic synthesis via substitution, displacement, condensation, elimination, redox, polymerization, and Ylide-mediated reactions. The most advantages of using the PTC technique to synthesize organic chemicals are the enhancement of the reaction rate, carrying out the reaction at

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moderate conditions, and obtaining high selectivity of the main product with high conversion of the reactants.[4,5]

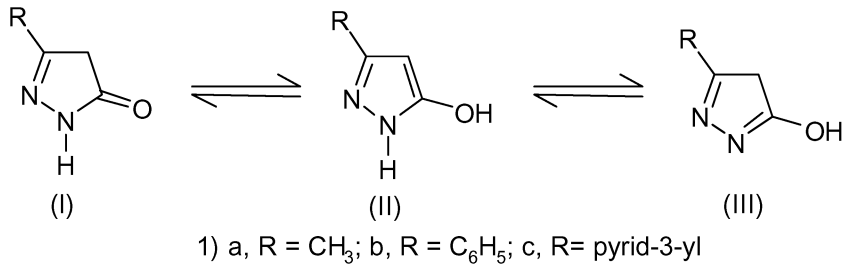
In continuation of our current research in the field of organic synthesis of some heterocyclic compounds under phase transfer catalysis conditions (PTC),[6–10] we aim here to study the reactivity of N-*vs.* O-*vs.* C-alkylation of 3-substituted-1*H*-pyrazol-2-in-5-ones.

5-Pyrazolones are very important class of heterocycles due to their biological and pharmacological activities[11,12] which exhibit an anti-inflammatory,[13] herbicidal,[14] fungicidal,[15] and bactericidal,[15] plant growth regulating properties[14] and antipyretic[16] and protein kinase inhibitors.[17] Also, they are used as a key starting for the synthesis of commercial arylazopyrazolone dyes.

RESULT AND DISCUSSION

The approach reported here is an extension and continuation of our interest in alkylation of some heterocycles under phase-transfer catalysis (PTC) conditions.[18,19] This work is aiming to study the phase-transfer catalyzed alkylation of 3-substituted-1*H*-pyrazol-2-in-5-ones and the comparative reactivity towards N-versus O-versus C-alkylation upon treatment with different organo–halogen reagents either under liquid-solid or liquid-liquid phases in the presence of tetrabutylammonium bromide (TBAB) as a catalyst in the absence or presence of CS_2 at 25°C.

3-substituted-1*H*-pyrazol-2-in-5-ones (**1a–c**) exist in three tautomeric forms (I–III) due to their keto-enol or lactam-lactime tautomerism, while the enol form (II) is the predominate one. This phenomenon is confirmed by spectral data in addition to our results of PTC-alkylation which are afforded O-monoalkylated products or O- and N-dialkylated or cycloalkylated products.



SCHEME 1 Tautomers of 3-substituted-1*H*-pyrazol-2-in-5-ones (1a–c).

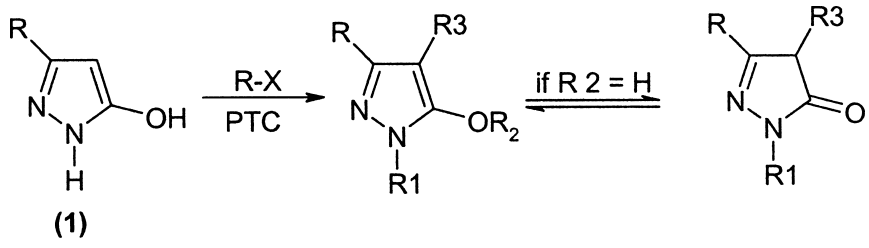
3-Substituted-1*H*-pyrazol-2-in-5-ones **(1a–c)** have been synthesized by heating a mixture of β-ketoesters with hydrazine hydrate.

The optimized reaction conditions of our PTC-alkylation are the treatment of 5-hydroxy-3-substituted-1*H*-pyrazoles (**1a–c**) with different organo-halogen compounds in a 1:3 molar ratio either in (a) acetonitrile as a liquid phase and anhydrous potassium carbonate as a basic solid phase in the presence of TBAB as a catalyst in the absence or presence of CS_2 at 25°C, and/or (b) acetonitrile as a liquid phase and a 30% aqueous sodium hydroxide solution as an immiscible liquid phase in the presence of TBAB as a catalyst at 25°C. In both conditions the reaction needs vigorous and efficient stirring for a limited short time where the reaction progress was monitored by thin-layer chromatography (TLC).

Methylation of 5-hydroxy-3-phenyl-1*H*-pyrazole (**1b**) under the optimized PTC conditions in solid-liquid phases by methyl iodide underwent O-methylation, predominantly to give 5-methoxy-3-phenyl-1*H*-pyrazole (**2**) (Scheme 2), while methylation of 5-hydroxy-3-methyl/or phenyl-1*H*-pyrazole (**1a**, **b**) by methyl iodide in the presence of carbon disulphide under the same liquid-solid PTC conditions afforded methyl 5-hydroxy-1,3-dimethyl-1*H*-pyrazole-4-carbodithioate (**3**) or methyl 5-hydroxy-1-methyl-3-phenyl-1*H*-pyrazole-4-carbodithioate (**4**), respectively (Scheme 3). The reaction proceeds via nucleophilic addition of C4 of pyrazolone to CS_2 followed by simultaneous N- and S-methylation of the intermediate carbodithioate anion.

PTC-alkylation of 5-hydroxy-3-phenyl-1*H*-pyrazole (**1b**) by allyl bromide using anhydrous K_2CO_3/acetonitrile as solid-liquid phases in the presence of TBAB as a catalyst underwent O-alkylation only to give 5-(allyloxy)-3-phenyl-1H-pyrazole (**5**) (Scheme 2).

Benzylation of 5-hydroxy-3-methyl-1*H*-prazole (**1a**) under the solid-liquid PTC conditions gave 1,4-dibenzyl-3-methyl-1*H*-2-pyrazolin-5-one (**6**) via C- and N-dibenzylations and 5-benzyloxy-3-methyl-1*H*-pyrazole (**7**) via O-benzylation that were separated by column chromatography using petroleum ether 60–80, ethyl acetate, chloroform (6:3:1) as eluent, while benzylation of 5-hydroxy-3-methyl-1H-prazole (**1a**) in the liquid-liquid PTC conditions gave three products are 1,4-dibenzyl-5-benzyloxy-3-methyl-1*H*-pyrazole (**8**) via C-, N- and O-benzylation, 1,4-dibenzyl-3-methyl-1*H*-2-pyrazolin-5-one (**6**) and 5-benzyloxy-3-methyl-1*H*- pyrazole (**7**) that are separated by column chromatography, using petroleum ether 60–80, ethyl acetate, chloroform (5:3:1) as eluent. Moreover, benzylation of 5-hydroxy-3-phenyl-1*H*-prazole (**1b**) using benzyl chloride in solid-liquid or liquid-liquid phases under the same PTC reaction conditions gave N- and O-monobenzylated products 1-benzyl-5-hydroxy-3-phenyl-1*H*-pyrazole (**9**) and 5-benzyloxy-3-phenyl-1*H*-pyrazole (**10)** that were separated by column chromatography using petroleum ether 60–80, ethyl acetate (2:3) as eluent.

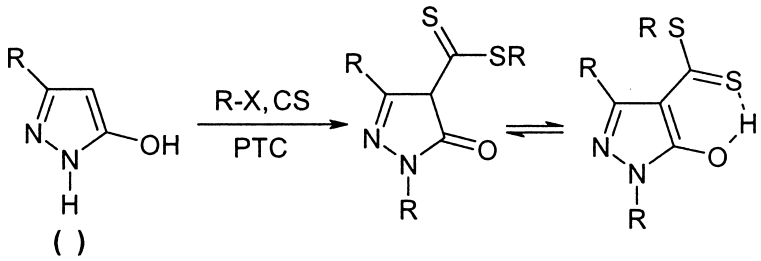


	R	R1	R2	R3
2	C_6H_5	H	CH_3	H
5	C_6H_5	H	CH_2-CH=CH_2	H
6	CH_3	CH_2Ph	-	CH_2Ph
7	CH_3	H	CH_2Ph	H
8	CH_3	CH_2Ph	CH_2Ph	CH_2Ph
9	C_6H_5	CH_2Ph	H	H
10	C_6H_5	H	CH_2Ph	H
11	C_5H_4N,3-	CH_2Ph	H	H
15a	C_6H_5	H	C_6H_{11}	H
15b	C_5H_4N,3-	H	C_6H_{11}	H
16a	C_6H_5	CH_2CN	CH_2CN	H
16b	C_5H_4N,3-	CH_2CN	CH_2CN	H
17a	C_6H_5	H	CH_2CN	H
17b	C_5H_4N,3-	H	CH_2CN	H
18	C_6H_5	CH_2CN	CH_2CN	CH_2CN
19a	CH_3	H	$CH_2COOC_2H_5$	H
19b	C_6H_5	H	$CH_2COOC_2H_5$	H
19c	C_6H_5	H	$CH_2COOC_2H_5$	H
20	CH_3	$CH_2COOC_2H_5$	$CH_2COOC_2H_5$	H

SCHEME 2 Alkylated products (2–20) of pyrazolones (1a–c) in the absence of CS2.

PTC-benzylation of **1c** by benzyl chloride using anhydrous K_2CO_3 as a solid phase and acetonitrile as liquid phase in the presence of TBAB as a catalyst underwent only N-monobenzoylation to give 1-benzyl-5-hydroxy-3-pyrid-3-yl-1*H*-pyrazole (**11**) (Scheme 2).

On the other hand, benzylation of 5-hydroxy-3-methyl-1*H*-pyrazole (**1a**) uses benzyl chloride in the presence of carbon disulphide TBAB as a catalyst and anhydrous K_2CO_3/dry acetonitrile as solid-liquid phases. The benzylation reaction was monitored by TLC and the



	R	R1	R2
3	CH_3	CH_3	CH_3
4	C_6H_5	CH_3	CH_3
12	CH_3	H	CH_2Ph
13	CH_3	CH_2Ph	CH_2Ph
14	C_6H_5	CH_2Ph	CH_2Ph

SCHEME 3 Alkylated products (3, 4 and 12–14) of pyrazolones (1a–c) in the presence of CS2.

products obtained were separated by column chromatography using petroleum ether 60–80 and ethyl acetate (7:6) as eluent. The benzylation reaction was believed to proceed via nucleophilic addition of C4 of pyrazolone to CS_2 followed by S-benzylation of the carbodithioate anion as intermediate to give benzyl 5-hydroxy-3-methyl-1*H*-pyrazole-4-carbodithioate (**12**) and benzyl 1-benzyl-5-hydroxy-3-methyl-1*H*-pyrazole-4-carbodithioate (**13**) via subsequent S- and N- benzylations. Moreover, Benzylation of **1b**, in the presence of carbon disulphide under the same PTC conditions afforded S- and N-dibenzylation to give benzyl 1-benzyl-5-hydroxy-3-phenyl-1*H*-pyrazole-4-carbodithioate (**14**) (Scheme 3).

PTC-cyclohexylation of 5-hydroxy-3-phenyl/or-3-(pyrid-3-yl)-1*H*-pyrazole (**1b**, **c**) by cyclohexyl bromide either in solid K_2CO_3/acetonitrile phases or NaOH solution/acetonitrile phases and TBAB as a catalyst affords O-alkylation only to give 5-cyclohexyloxy-3-phenyl/or-3(pyrid-3-yl)1*H*-pyrazoles (**15a**, **b**), respectively (Scheme 2).

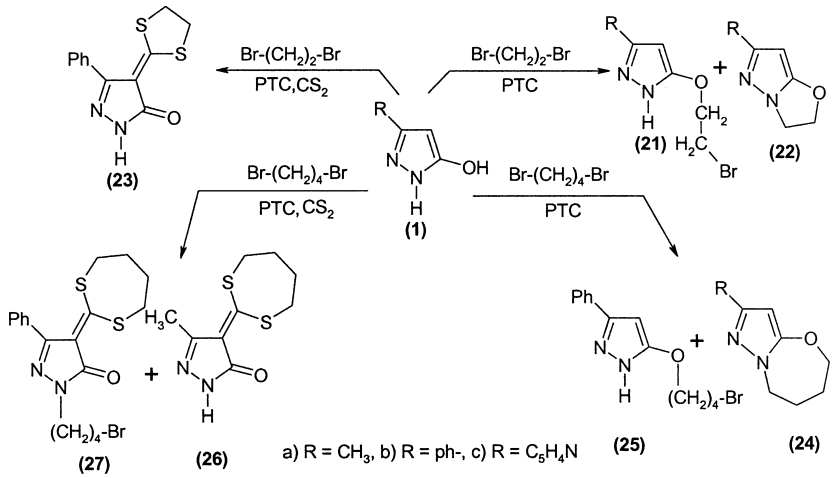
Alkylation of 5-hydroxy-3-phenyl/or-3-(pyrid-3-yl)-1*H*-pyrazoles (**1b**, **c**) by chloroacetonitrile in solid K_2CO_3 and acetonitrile as solid/liquid phases in the presence of TBAB as a catalyst at room temperature affords, simultaneous O- and N-dialkylations, 1-cyanomethyl-5-cyanomethyloxy-3-phenyl/or-3-(pyrid-3-yl)-1*H*-pyrazoles (**16a**, **b**) and O-alkylation, and 5-cyanomethyloxy-3-phenyl/or-3-(pyrid-3-yl)-1*H*-pyrazoles (**17a**, **b**), respectively. The products **16a** and **17a** are

separated by column chromatography using petroleum ether 60–80, ethyl acetate, chloroform (3:2:5) as eluent. However, products **16a** and **17a** are separated by column chromatography using petroleum ether 60–80 and ethyl acetate (3:2) as an eluent. Also, PTC-alkylation of 5-hydroxy-3-phenyl-1*H*-pyrazoles (**1b**) by chloroacetonitrile in NaOH solution/acetonitrile as liquid-liquid phases in the presence of TBAB at room temperature affords O-alkylation product (**17a**) with a simultaneous O-, N- and C4-trialkyled product 5-cyanomethyloxy-1,4-dicyanomethyl-3-phenylpyrazole (**18**) that is separated by column chromatography using petroleum ether 60–80, ethyl acetate, and chloroform (3:2:5) as eluent. However, alkylation of 5-hydroxy-3-(pyrid-3-yl)-1*H*-pyrazoles (**1c**) under the same PTC conditions affords the O-alkylation product, 5-cyanomethyloxy-3-(pyrid-3-yl)-1*H*-pyrazoles (**17b**) only (Scheme 2).

On the other hand, treatment of 5-hydroxy-3-phenyl/or-3-(pyrid-3-yl)-1*H*-pyrazoles (**1b**, **c**) with ethyl bromoacetate (1:3 molar ratio) under the same optimized PTC conditions of liquid-solid phases affords O-alkylated products only to give ethyl 3-phenyl/or-3-(pyrid-3-yl)-1*H*-pyrazol-5-yloxy acetate (**19b**, **c**). Treatment of 5-hydroxy-3-methyl-1*H*-pyrazoles (**1a**) with ethyl bromoacetate under the same PTC conditions affords O-alkylated product (**19a**) and the N-, O-dialkylated product, diethyl 3-methyl-1*H*-pyrazol-5-yloxy-1,5-diacetate (**20**), that separates by column chromatography using petroleum ether 60–80 and ethyl acetate (7:3) as eluent (Scheme 2).

Treatment of equimolar amounts of 5-hydroxy-3-methyl-1*H*-pyrazole (**1a**) and 1,2-dibromoethane in acetonitrile/anhydrous K_2CO_3 as liquid-solid phases and in the presence of TBAB as a catalyst at 25°C yielded 5-(2-bromoethoxy)-3-methyl-1*H*-pyrazole (**21a**) and 6-methyl-2,3-dihydropyrazolo[5,1-*b*]-oxazole (**22a**) which are separated by column chromatography using ethyl acetate:petroleum ether 60–80 (3:2) as eluent. Whenever under the same PTC reaction conditions, 5-hydroxy-3-phenyl-1*H*-pyrazole (**1b**) yields only 6-phenyl-2,3-dihydro-pyrazolo[5,1-*b*]-oxazole (**22b**). Moreover, 5-hydroxy-3-(pyrid-3yl)-1*H*-pyrazole (**1c**) yields a mixture of 5-(2-bromoethoxy)-3-(pyrid-3yl)-1*H*-pyrazole (**21c**) and 6-(pyrid-3-yl)-2,3-dihydro-pyrazolo[5,1-*b*]-oxazole (**22c**) which are separated by column chromatography using petroleum ether 60–80, ethyl acetate, and chloroform (2:8:1) as eluent (Scheme 4).

On the other hand, under the same PTC-reaction conditions, alkylation of pyrazole (**1a**) by ethylene dibromide in acetonitrile/NaOH solution as liquid-liquid phases affords the corresponding O-monoalkylation product (**21a**) while pyrazole (**1c**) yields a mixture of **21c** and **22c**.



SCHEME 4 Cycoalkylated products (21–27) of pyrazoles (1a–c) in the absence or presence of CS2.

On the other hand, treatment of 3-phenyl-2-pyrazolin-5-one (**1b**) with 1,2-dibromoethane in the presence of carbon disulphide in acetonitrile/anhydrous K_2CO_3 as liquid-solid phases and TBAB as a catalyst at room temperature affords 4-(1,3-dithiolan-2-ylidene)-5-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**23**) (Scheme 4).

PTC-Alkylation of 5-hydroxy-3-methyl/or-3-(pyrid-3-yl)-1*H*-pyrazoles (**1a**, **c**) by 1,4-dibromobutane in acetonitrile/anhydrous K_2CO_3 as liquid-solid phases or in acetonitrile/NaOH solution as liquid-liquid phases in the presence of TBAB as a catalyst at room temperature yields 2-methyl/or-3-(pyrid-3-yl)-5,6,7,8-tetrahydropyrazolo[5,1-*b*][1,3]-oxazepines (**24a**, **c**). However, liquid-liquid PTC-alkylation of 5-hydroxy-3-phenyl-1*H*-pyrazole (**1b**) with 1,4-dibromobutane yields either 2-phenyl-5,6,7,8-tetrahydropyrazolo[5,1-*b*][1,3]oxazepine (**24b**), while under solid-liquid PTC conditions affords 5-(4-bromobultyloxy)-3-phenyl-1*H*-pyrazole (**25**) only as O-monoalkylated product. It's worthy to mention that oily crude products of **24a**, **c** are first obtained and passed through a column using petroleum ether 60–80, ethyl acetate, chloroform (6:3:2), and petroleum ether 60–80, ethyl acetate (2:3) as eluents. Then the organic solvents are evaporated to give the pure crystalline solids.

On the other hand, treatment of 5-hydroxy-3-methyl/or phenyl-1*H*-pyrazole (**1a**, **b**) with 1,4-dibromobutane in the presence of carbon disulphide in dry acetonitrile/anhydrous K_2CO_3 as liquid-solid phases and TBAB as a catalyst at room temperature probably proceeds via nucleophilic addition of C4 of pyrazolone to CS_2 followed by alkylation

of the intermediate carbodithiolate anion to give 4-(1,3-dithiepan-2-ylidene)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (**26**) and 2-(4-bromobutyl)-4-(1,3-dithiepan-2-ylidene)-5-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**27**), respectively (Scheme 4).

EXPERIMENTAL

All melting points reported are uncorrected. IR spectra were recorded using Perkin Elmer's Spectrum RXIFT-IR spectrophotometer, USA (ν in cm^{-1}). The NMR spectra were recorded on Bruker Avance DPX400 spectrometer using deuterated chloroform ($CDCl_3$) as a solvent and TMS as an internal standard (chemical shifts in δ values in ppm. Elemental analyses were preformed on Perkin Elmer 2400, series II microanalyzer, USA. The used 1R, NMR spectrophotometers and CHN-microanalyzer are located at Chemistry Dept., Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia.

Condensation of β-Ketoester with Hydrazine Hydrate: Synthesis of 5-Hydroxy-3-substituted-1*H*-pyrazoles (1a–c)

A solution of ethyl acetoacetate, (0.01 mol, 1.54 g), ethyl benzoylacetate (0.01 mol, 1.92 mL) or ethyl nicotinoylacetate (0.01 mol, 1.94 g) and hydrazine hydrate (0.01 mol, 0.48 g, 100%) in ethanol (50 mL) is refluxed for 6 h then the solvent was evaporated. The solid residue is crystallized from ethanol to give the corresponding pyrazole (**1a–c**), respectively as white crystals. The results are listed in Tables I and II.

General Procedure of PTC-Alkylation

(A) Alkylation in the Absence of Carbon Disulphide

(1) In liquid-solid phases. In a 150 mL conical flask fitted with a rubber stopper, a suspension of 5-hydroxy-3-substituted-1*H*-pyrazoles (**1**, 0.01 mol), anhydrous potassium carbonate (0.02 mol, 2.76 g) and tetrabutylammonium bromide (TBAB, 0.003 mol, 0.9 g) in dry acetonitrile (50 mL) stirred at 25°C for 30 min, then the organo-halogen compound, and the alkylating agent, (0.03 mol) was added and the reaction mixture efficiently stirred at room temperature. The progress of the reaction was monitored by TLC during the entire reaction time. After the reaction completion, the organic layer was separated by filtration and the solvent was evaporated. The residue crystallizes from the proper solvent or separates by column chromatography using silica gel (80–120 mesh) and proper eluent to give one or more pure products. Also, the K_2CO_3 precipitate dissolves in water (100 mL) and acidifies by dilute

TABLE I The Physical Data of Alkylated Products Compounds 1–27

Compd no.	Reaction period (in h)	M. formula (m. wt.)	m. p.°C (color)	Solvent cryst. (yield %)	Elemental analysis calc./found %		
					C	H	N
1a	—	$C_4H_6N_2O$	218–220	E	48.97	6.16	28.55
		(98.10)		(60)	48.72	6.03	28.41
1b	—	$C_9H_8N_2O$	238–240	E	67.49	5.03	17.49
		(160.18)		(65)	67.31	4.96	17.33
1c	—	$C_8H_7N_3O$	260–261	E	59.62	4.38	26.07
		(161.16)		(55)	59.44	4.32	25.92
2	8	$C_{10}H_{10}N_2O$	188–120	P 80–100	68.94	5.78	16.08
		(174.20)	(White)	(37)	68.78	5.73	15.94
3	6	$C_7H_{10}N_2OS_2$	152–154	P 80–100	41.56	4.98	13.85
		(202.30)	(Yellow)	(57)	41.37	4.90	13.76
4	6	$C_{12}H_{12}N_2OS_2$	187–188	E	54.52	4.58	10.60
		(264.37)	(Yellow)	(66)	54.38	4.49	10.46
5	12	$C_{12}H_{12}N_2O$	141–142	P 80–100	71.98	6.04	13.99
		(200.24)	(Yellow)	(67)	71.90	6.00	13.81
6	24	$C_{18}H_{18}N_2O$	88–89	E	77.67	6.52	10.06
		(278.36)	(White)	(44)	77.46	6.49	9.97
7	24	$C_{11}H_{12}N_2O$	135–136	E	70.19	6.43	14.88
		(188.23)	(White)	(17)	70.03	6.41	14.67
8	24	$C_{25}H_{24}N_2O$	184–185	E	81.49	6.57	7.60
		(368.48)	(White)	(8)	81.33	6.52	7.51
9	26	$C_{16}H_{14}N_2O$	149–150	E	76.78	5.64	11.19
		(250.30)	(White)	(45)	76.67	5.53	11.02
10	26	$C_{16}H_{14}N_2O$	167–169	E	76.78	5.64	11.19
		(250.30)	(White)	(35)	76.69	5.60	11.07
11	24	$C_{15}H_{13}N_3O$	159–160	P 80–100	71.70	5.21	16.72
		(251.29)	(white)	(42)	71.53	5.19	16.58
12	18	$C_{12}H_{12}N_2OS_2$	208–210	E	54.52	4.58	10.60
		(264.37)	(Yellow)	(16)	54.38	4.50	10.47
13	18	$C_{19}H_{18}N_2OS_2$	149–150	E	64.38	5.12	7.90
		(354.50)	(Yellow)	(28)	64.19	5.08	7.72
14	12	$C_{24}H_{20}N_2OS_2$	155–156	E	69.20	4.84	6.72
		(416.55)	(yellow)	(28)	71.22	5.13	6.88
15a	48	$C_{15}H_{18}N_2O$	128–130	P 60–80	74.35	7.49	11.56
		(242.32)	(White)	(65)	74.27	7.43	11.49
15b	36	$C_{14}H_{17}N_3O$	140–141	P 80–100	69.11	7.04	17.27
		(243.31)	(White)	(35)	69.03	7.00	17.08
16a	24	$C_{13}H_{10}N_4O$	84–85	E	65.54	4.23	23.52
		(238.24)	(White)	(37)	65.41	4.20	23.42
16b	35	$C_{12}H_9N_5O$	123–124	E	60.25	3.79	29.27
		(239.24)	(White)	(34)	60.16	3.72	29.14
17a	18	$C_{11}H_9N_3O$	149–150	E	66.32	4.55	21.09
		(199.21)	(White)	(44)	66.17	4.50	21.00
17b	35	$C_{10}H_8N_4O$	152–153	E	60.00	4.03	27.99
		(200.20)	(White)	(25)	59.77	4.01	27.76

(Continued on next page)

TABLE I The Physical Data of Alkylated Products Compounds 1–27 *(Continued)*

Compd no.	Reaction period (in h)	M. formula (m. wt.)	m. p.°C (color)	Solvent cryst. (yield %)	Elemental analysis calc./found %		
					C	H	N
18	18	$C_{15}H_{11}N_5O$	142–143	E	64.98	4.00	25.26
		(277.29)	(White)	(23)	64.83	3.98	25.12
19a	36	$C_8H_{12}N_2O_3$	79–80	E	52.17	6.57	15.21
		(184.20)	(White)	(38	52.03	6.52	15.08
19b	6	$C_{13}H_{14}N_2O_3$	166–167	P 80–100	63.40	5.73	11.38
		(246.27)	(White)	(65)	63.28	5.64	11.19
19c	24	$C_{12}H_{13}N_3O_3$	120–121	E	58.29	5.30	16.99
		(247.25)	(Yellow)	(41)	58.11	5.25	16.74
20	36	$C_{12}H_{18}N_2O_5$	199–120	E	53.33	6.71	10.36
		(270.29)	(White)	(25)	53.17	6.68	10.23
21a	16	$C_6H_9N_2OBr$	171–172	E	35.15	4.42	13.66
		(205.06)	(White)	(35)	35.04	4.37	13.51
21c	36	$C_{10}H_{10}N_3OBr$	111–113	E	44.80	3.76	15.67
		(268.11)	(White)	(37)	44.68	3.71	15.43
22a	16	$C_6H_8N_2O$	162–163	E	58.05	6.50	22.57
		(124.14)	(White)	(25)	57.87	6.46	22.27
22b	12	$C_{11}H_{10}N_2O$	102–103	P 80–100	70.95	5.99	15.04
		(186.21)	White	(60)	70.37	5.87	14.93
22c	36	$C_{10}H_9N_3O$	139–140	E	64.16	4.85	22.45
		(187.20)	(White)	(24)	64.02	4.80	22.27
23	10	$C_{12}H_{10}N_2OS_2$	173–175	P 60–80	54.94	3.84	10.68
		(262.36)	(yellow)	(55)	54.77	3.78	10.41
24a	24	$C_8H_{12}N_2O$	—	E	63.13	7.95	18.41
		(152.20)	Oil	(55)	63.99	7.48	18.22
24b	14	$C_{13}H_{14}N_2O$	95–96	P 80–100	72.87	6.59	13.07
		(214.27)	(Yellow)	(60)	72.66	6.51	12.99
24c	36	$C_{12}H_{13}N_3O$	88–89	E	66.96	6.09	19.52
		(215.26)	(White)	(25)	66.74	6.02	19.37
25	18	$C_{13}H_{15}N_2OBr$	135–136	P 80–100	52.90	5.12	9.49
		(295.18)	(White)	(67)	52.73	5.04	9.27
26	6	$C_9H_{12}N_2S_2O$	195–196	P 80–100	47.34	5.30	12.27
		(228.34)	(Yellow)	(54)	44.26	5.53	12.73
27	6	$C_{18}H_{21}N_2OS_2Br$	173–175	P 60–80	50.82	4.98	6.58
		(425.41)	(Yellow)	(65)	50.68	4.90	6.40

P: petroleum ether; E: ethanol.

hydrochloric acid (10%) to separate and identify the acidic products in the solid phase, if any. The results are listed in Tables I and II.

(2) In liquid-liquid phases. A solution of 5-hydroxy-3-substituted-1*H*-pyrazoles (**1a–c**, 0.01 mol) in dry acetonitrile (50 mL) was mixed with sodium hydroxide solution (10 mL, 30% aqueous solution), and

TABLE II Spectral Data of Compounds 1–27

Compd. no.	IR (ν in cm^{-1})	^{1}H-NMR δ (ppm)	^{13}C-NMR δ (ppm)	MS (abundance %)
1a		DMSO: 2.09 (s, 3H, C$\underline{H}_3$), 3.35 (s, 1H, O$\underline{H}$), 5.21 (s, 1H, C_4-$\underline{H}$) 10.32 (broad, 1H, N$\underline{H}$).	DMSO: 11.84 (CH_3), 99.53 (C_4), 139.9 (C_3), 161.6 (C_5).	
1b	1590–1605 (C=C or C=N), 1650 (C=O of pyrazolin-one), 3320–3340 (OH or NH).	DMSO: 5.96 (s, 1H, C_4-$\underline{H}$), 7.34 (s, 1H, O$\underline{H}$), 7.40–7.73 (m, 5H, Ar-$\underline{H}$), 11.2 (broad, 1H, N$\underline{H}$).	DMSO: 87.59 (C_4), 125.4, 128.5, 129.5, 131.1 (phenyl carbons), 144.04 (C_3), 161.74 (C_5).	
1c		DMSO: 3.45 (s, 1H, O$\underline{H}$), 6.03 (s, 1H, C_4-$\underline{H}$), 7.44 (m, 1H, pyrid-C_5-$\underline{H}$), 8.08 (d, 1H, Pyrid-C_4-$\underline{H}$), 8.51 (d, 1H, Pyrid-C_6-$\underline{H}$), 8.99 (s, 1H, Pyrid-C_2-$\underline{H}$), 10.96 (s, 1H, N$\underline{H}$)	DMSO: 12.2 (CH_3), 34.3 (SCH_2), 60.9(OCH_2), 111.8(C_5), 127.6–136.5 (Ph-C), 157.6 (C_4), 159.7 (C_6),161.6(C_2), 166.3(CO, ester).	
2	1516 (C=C), 1551 (C=N), 2640 (CH, aliphatic), 3246 (OH).	$CDCl_3$: 3.75 (s, 3H, O-C$\underline{H}_3$), 5.72 (s, 1H, C_4-$\underline{H}$), 7.41–7.48 (m, 5H, Ar-$\underline{H}$), and 9.56 (broad s, 1H, N$\underline{H}$).	$CDCl_3$: 36.22 (O-CH_3), 91.12 (C_4), 125.6, 128.7, 129.5 and 130.3 (phenyl-carbons), 145.48 (C_3) 161.53 (C_5).	
3	1268 (C=S of carbodithioate), 1561 (C=C), 1623 (C=N), 2920 and 3057 (broad, OH).	$CDCl_3$: 1.02 (s, 1H, O$\underline{H}$), 2.45 (s, 3H, C_3-C$\underline{H}_3$), 2.58 (s, 3H, S–C$\underline{H}_3$), 3.67 (s, 3H, N–C$\underline{H}_3$).		
4	1274 (C=S), 1604 (C=C) 1615 (C=N), 2923 (broad, OH).	$CDCl_3$: 2.32 (s, 3H, N–C$\underline{H}_3$), 3.43 (s, 1H, O$\underline{H}$), 3.73 (s, 3H, S–C$\underline{H}_3$), 7.45–7.60 (m, 5H, Ar-$\underline{H}$).		

(*Continued on next page*)

TABLE I Spectral Data of Compounds 1–27 *(Continued)*

Compd. no.	IR (ν in cm^{-1})	^{1}H-NMR δ (ppm)	^{13}C-NMR δ (ppm)	MS (abundance %)
5	1566 (C=N), 2360 (CH, aliphatic), 3149 (NH).	$CDCl_3$: 4.57 (m, 1H, —C<u>H</u>=), 4.73 (d, 2H, C<u>H</u>$_2$=), 5.27 and 5.29 (dxd, 2H, OC<u>H</u>$_2$-), 5.99 (s, 1H, C_4-<u>H</u>), 7.36–7.54 (m, 5H, Ar—<u>H</u>), 10.23 (broad, 1H, N<u>H</u>).		
6	1606 (C=N), 1671 (C=O), 2850 and 2922 (CH, aliphatic), 3031 and 3088 (CH, aromatic).	$CDCl_3$: 2.08 (s, 3H, C<u>H</u>$_3$), 2.95 (d, 2H, C_4-C<u>H</u>$_2$), 3.26 (d, 2H, N—C<u>H</u>$_2$-), 7.12–7.24 (m, 10H, Ar—<u>H</u>), 7.93 (s, 1H, O<u>H</u>).		278 ($M^{+\cdot}$, 13), 187 (15, M—$C_6H_5CH_2$), 188 (24),115 (21), 91 (100 $C_6H_5CH_2^{+\cdot}$) 65 (12).
7	1544 (C=N), 2639 (CH, aliphatic), 3029 (CH, aromatic), 3430 (NH).	$CDCl_3$: 2.16 (s, 3H, C<u>H</u>$_3$), 5.08 (s, 2H, OC<u>H</u>$_2$-), 5.46 (s, 1H, C_4-<u>H</u>), 7.14–7.35 (m, 5H, Ar—<u>H</u>), 11.78 (broad, 1H, N<u>H</u>).		
8	1598 (C=N), 2639 (CH, aliphatic), 2920 and 3032 (CH, aromatic).	$CDCl_3$: 2.13 (s, 3H, C<u>H</u>$_3$), 3.00 (d, 2H, C_4-C<u>H</u>$_2$), 3.32 (d, 2H, N—C<u>H</u>$_2$-), 4.44 (s, 2H, O—C<u>H</u>$_2$—), 6.60–7.26 (m, 15H, Ar—<u>H</u>).		
9	1584 (C=C), 1605 (C=N), 1680 (C=O), 2623, 3030 (CH).	$CDCl_3$: 3.64 (s, 2H, N—C<u>H</u>$_2$), 5.00 (s, 2H, C_4-<u>H</u>$_2$), and 7.02–7.39 (m, 10H, Ar—<u>H</u>).		
10	1596 (C=C), 1610 (C=N), 2325 (NH), 2833 and 3034 (CH).	$CDCl_3$: 5.13 (s, 2H, O—C<u>H</u>$_2$), 5.74 (s, 1H, C_4-<u>H</u>), 7.06–7.40 (m, 10H, Ar—<u>H</u>).		
11	1578 (C=C, C=N), 1665 (C=O) and 3038 (CH).	$CDCl_3$: 1.87 (br, 1H, O<u>H</u>), 4.28 (s, 2H, NC<u>H</u>$_2$), 6.58–8.60 (m, 9H, Ar—<u>H</u> and C_4-<u>H</u>).	$CDCl_3$: 30.62 (t, <u>C</u>H$_2$Ph), 124.45, 132.54 (Ar—C), 146.7 (C_3), 149.1 (C=O).	
12	1280 (C=S), 1558 (C=C), 1612 (C=N), 1728 (C=O ester), 2818 and 3043 (CH) 3348, 3542 (NH or OH).	$CDCl_3$: 0.83 (b, 1H, O<u>H</u>), 2.68 (s, 3H, C<u>H</u>$_3$), 4.63 (s, 2H, SC<u>H</u>$_2$Ph), 7.28–7.44 (m, 5H, Ar—<u>H</u>), 12.44 (b, 1H, N<u>H</u>).		

13	1278 (C=S), 1570 (C=C), 1614 (C=N), 2582 and 3027 (CH) and 3221 (br. OH).	$CDCl_3$: 1.27 (b, 1H, O<u>H</u>), 2.63 (s, 3H, C<u>H</u>$_3$), 4.62 (s, 2H, SC<u>H</u>$_2$), 5.22 (s, 2H, NC<u>H</u>$_2$), and 7.19–7.41 (m, 10H, Ar–<u>H</u>).	
14	1256 (C=S), 1570 (C=C), 1607 (C=N), 2878 and 3052 (CH), 3185 (br., OH).	$CDCl_3$: 3.68 (s, 2H, SC<u>H</u>$_2$), 4.53 (s, 2H, NC<u>H</u>$_2$), 6.82–7.41 (m, 15H, Ar–<u>H</u>), 9.26 (br, 1H, O<u>H</u>).	
15a	1568 (C=C, C=N), 2856, 2923 (CH), 3337 (NH).	$CDCl_3$: 1.36 (m, 3H, cyclohexyl–<u>H</u>), 1.55 (m, 3H, cyclohexyl–<u>H</u>), 1.79 (m, 2H, cyclohexyl–<u>H</u>), 2.07 (m, 2H, cyclohexyl–<u>H</u>), 4.46 (m, 1H, O–C<u>H</u>$_2$-cyclohexyl), 5.96 (s, 1H, C$_4$-<u>H</u>), 7.25–7.55 (m, 5H, Ar–<u>H</u>).	242 (M^+, 3.4), 160 (100), 102 (12), 77 (12), 55 (29).
15b	1568 (C=C, C=N), 2856, 2923 (CH), 3337 (NH).		244 (M^+, 63), 163 (100), 161 (84), 160 (20), 105 (10).
16a	1550, 1590 (C=C, C=N), 2260 (C.≡N), 2957, 3145 (CH).	$CDCl_3$: 4.90 (s, 2H, N–C<u>H</u>$_2$), 4.99 (s, 2H, O–C<u>H</u>$_2$), 5.94 (s, 1H, C$_4$-<u>H</u>), 7.44–7.58 (m, 5H, Ar–<u>H</u>).	238 (M^+, 3.0), 199 (2), 167 (6), 149 (28), 105 (100), 91 (26), 81 (13) 77 (36), 69 (29), 57 (28).
16b	1550, 1590 (C=C, C=N), 2260 (C.≡N), 2957, 3145 (CH).	$CDCl_3$: 4.87 (s, 2H, N–C<u>H</u>$_2$), 4.98 (s, 2H, O–C<u>H</u>$_2$), 5.99 (s, 1H, C$_4$-<u>H</u>), 7.50, 7.80, 8.76 (m, 4H, pyridyl-<u>H</u>).	
17a	1571 (C=C, C=N), 2350 (C≡N), 2945, 3136 (CH), 3241 (NH).	$CDCl_3$: 4.99 (s, 2H, OC<u>H</u>$_2$), 6.10 (s, 1H, C$_4$-<u>H</u>), 7.32–7.58 (m, 5H, Ar–<u>H</u>), 9.82 (b, 1H, N<u>H</u>).	199 (M^+, 87), 159 (39), 131 (20), 103 (100), 77 (32), 63 (18)

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TABLE I Spectral Data of Compounds 1–27 *(Continued)*

Compd. no.	IR (ν in cm^{-1})	^{1}H-NMR δ (ppm)	^{13}C-NMR δ (ppm)	MS (abundance %)
17b	1571 (C═C, C═N), 2350 (C≡N), 2945, 3136 (CH), 3241 (NH).	$CDCl_3$: 4.98 (s, 2H, $OC\underline{H}_2$), 6.13 (s, 1H, C_4-$\underline{H}$), 7.42, 7.86, 8.66 (m, 4H, pyridyl-$\underline{H}$).		201 (M^+, 13), 200 (100), 160 (58), 132 (22), 105 (23), 104 (91), 103 (91), 78 (40), 77 (38), 76 (50), 75 (24), 51 (53).
18	1571 (C═C, C═N), 2235 (C.≡N), 2968, 3120 (CH).	$CDCl_3$: 3.41 (s, 2H, C_4-$C\underline{H}_2$), 4.83 (s, 2H, $NC\underline{H}_2$), 5.07 (s, 2H, $OC\underline{H}_2$), 7.43–7.65 (m, 5H, Ar—$\underline{H}$).		279 (M^+, 5), 238 (25), 213 (10), 167 (15), 149 (61), 127 (55), 113 (32), 102 (66), 97 (26), 95 (20), 91 (13), 85 (33), 71 (48), 69 (98), 57 (100), and 55 (62)
19a		$CDCl_3$: 1.28 (t, 3H, $C\underline{H}_3$ ester), 2.23 (s, 3H, C_3-$C\underline{H}_3$), 4.25 (q, 2H, $OC\underline{H}_2$ ester), 4.74 (s, 2H, C_5-$OC\underline{H}_2$), 5.55 (s, 1H, C_4-$\underline{H}$), 9.93 (br, 1H, N$\underline{H}$).		184 (M^+, 1.5), 177 (100), 149 (16), 107 (36), 77 (28), 53 (10).
19b	1575–1608 (C═C, C═N), 1737–1742 (C═O ester), 2931–3150 (CH), 3320–3351 (NH).	$CDCl_3$: 1.30 (t, 3H, $C\underline{H}_3$ ester), 4.27 (q, 2H, $OC\underline{H}_2$ ester), 4.81 (s, 2H, C_5-$OC\underline{H}_2$), 6.06 (s, 1H, C_4-$\underline{H}$), 7.35–7.51 (m, 5H, Ar—$\underline{H}$), 9.48 (br., 1H, N$\underline{H}$).		246 (M^+, 17), 149 (25), 129 (21), 105 (20), 102 (27), 97 (31) 85(36), 81(23),77 (28) 69 (78), 57 (74), and 55 (100).
19c		$CDCl_3$: 1.29 (t, 3H, $C\underline{H}_3$ ester), 4.26 (q, 2H, $OC\underline{H}_2$ ester), 4.81 (s, 2H, C_5—$OC\underline{H}_2$), 6.06 (s, 1H, C_4-$\underline{H}$), 7.34, 7.85, 8.55, 8.84 (m, 4H, pyridyl-$\underline{H}$).		248 (M^+, 58), 202 (34) 17 (68), 161 (61), 147 (43), 118 (48), 105 (100), 91 (23), 77(36), 63 (30).

20	1575, 1608 (C=C, C=N), 1737 (C=O ester), 2985, 3059, 3135 (CH).	$CDCl_3$: 1.26 (2xt, 6H, 2x$C\underline{H}_3$ ester), 2.15 (s, 3H, C_3-$C\underline{H}_3$), 4.20 (2xq, 4H, 2x$OC\underline{H}_2$ ester), 4.61 (s, 2H, N–$C\underline{H}_2$), 4.73 (s, 2H, C_5-$OC\underline{H}_2$), 5.58 (s, 1H, C_4-$\underline{H}$).	271 (M^+, 3), 256 (6), 185 (6), 149 (12), 129 (24), 113 (38), 97 (38), 83 (54),73 (69), 69 (75) 60 (64), and 55 (100).
21a	1588 (C=C, C=N), 2618, 2967, 3129 (CH), 3278 (NH).	$CDCl_3$: 2.25 (s, 3H, C_3-$C\underline{H}_3$), 3.65 (t, 2H, $C\underline{H}_2$Br), 4.21 (t, 2H, $OC\underline{H}_2$), 5.41 (s, 1H, C_4-$\underline{H}$).	
21c	1588 (C=C, C=N), 2618, 2967, 3129 (CH), 3278 (NH).	$CDCl_3$: 3.71 (t, 2H, $C\underline{H}_2$Br), 4.55 (t, 2H, $OC\underline{H}_2$), 6.09 (s, 1H, C_4-$\underline{H}$), 7.46, 7.84, 8.65, 8.88 (m, 4H, pyridyl-$\underline{H}$).	267 (M^+, 7), 187 (25), 161 (100), 149 (19), 103 (45), 76 (29).
22a	1570 (C=C, C=N), 2897, 2973, 3058, 3130 (CH).	$CDCl_3$: 2.19 (s, 3H, C_3-$C\underline{H}_3$), 4.18 (t, 2H, $NC\underline{H}_2$), 4.95 (t, 2H, $OC\underline{H}_2$), 5.15 (s, 1H, C_4-$\underline{H}$).	
22b		$CDCl_3$: 4.33 (t, 2H, $NC\underline{H}_2$), 5.03 (t, 2H, $OC\underline{H}_2$), 5.70 (s, 1H, C_4-$\underline{H}$), 7.25–7.75 (m, 5H, Ar–$\underline{H}$).	87 (M^+1, 12), 186 (M^+, 85),102 (100), 77 (10), 76 (15), 51 (28).
22c		$CDCl_3$: 4.36 (t,2H, $NC\underline{H}_2$), 5.08 (t, 2H, $OC\underline{H}_2$), 5.74 (s, 1H, C_4-$\underline{H}$), 7.31 8.02, 8.53, 8.95 (m, 4H, pyrid-$\underline{H}$).	
23	1656 (C=O, C=N), 2835, 3047, 3192 (CH), 3447 (OH or NH).	$CDCl_3$: 3.40 (t, 2H, $SC\underline{H}_2$), 3.55 (t, 2H, $SC\underline{H}_2$), 7.44–7.53 (m, 5H, Ar–$\underline{H}$), 9.17 (s, 1H, O$\underline{H}$ or N$\underline{H}$).	
24a			153 (M^+1, 100), 152 (M^+, 44), 111 (9), 67 (3), 55 (2).

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TABLE I Spectral Data of Compounds 1–27 *(Continued)*

Compd. no.	IR (ν in cm^{-1})	^{1}H-NMR δ (ppm)	^{13}C-NMR δ (ppm)	MS (abundance %)
24b		$CDCl_3$: 1.90 (m, 2H, N—C—C$\underline{H_2}$), 2.07 (m, 2H, O—C—C$\underline{H_2}$), 4.09 (t, 2H, N—C$\underline{H_2}$), 4.26 (t, 2H, O—C$\underline{H_2}$), 6.03 (s, 1H, C_4-$\underline{H}$), 7.26–7.74 (m, 5H, Ar—$\underline{H}$).		
24c	1548–1558 (C=C, C=N), 2873, 2956, 3064, 3142 (CH).	$CDCl_3$: 1.93 (m, 2H, N—C—C$\underline{H_2}$), 2.21 (m, 2H, O—C—C$\underline{H_2}$), 4.43 (t, 2H, N—C$\underline{H_2}$), 5.31 (t, 2H, O—C$\underline{H_2}$), 5.80 (s, 1H, C_4-$\underline{H}$), 7.32, 8.05, 8.98 (m, 4H, pyridyl-$\underline{H}$).		
25	1560 (C=C, C=N), 2878, 3038, 3126 (CH), 3319 (NH).	$CDCl_3$: 1.92 (m, 4H, 2,3-C$\underline{H_2}$-C$\underline{H_2}$), 3.42 (t, 2H, C$\underline{H_2}$-Br), 4.14 (t, 2H, O—C$\underline{H_2}$), 5.93 (s, 1H, C_4-$\underline{H}$), 7.36–7.58 (m, 5H, Ar—$\underline{H}$), 9.84 (s, 1H, N$\underline{H}$)	$CDCl_3$: 27.85 (C3-butyl-oxy), 29.25 (C4-butyloxy), 33.44 (C4-Br), 68.21 (O—C1-butyloxy), 87.49 (C4-pyrazole), 125.42, 128.57, 128.90 (aromatic-$\underline{C}$), 129.73 (C1-phenyl), 144.84 (C3-pyrazole), 163.82 (C5-pyrazole)	
26	1545 (C=C, C=N), 1657 (C=O, cyclic amide), 2917, 3050, 3153 (CH), 3318 (br. NH).	$CDCl_3$: 1.91 (m, 4H, 5,7-C$\underline{H_2}$-C$\underline{H_2}$ dithiapene), 2.42 (s, 3H, C_3-C$\underline{H_3}$), 3.17 (t, 2H, S—C$\underline{H_2}$), 3.36 (t, 2H, S—C$\underline{H_2}$), 8.72 (s, 1H, N$\underline{H}$).		
27	1659 (C=O, 5-pyrazol -one), 2883, 2962, 3060, 3145 (CH).	$CDCl_3$: 1.89-2.12 (m, 8H, 5,7-C$\underline{H_2}$-C$\underline{H_2}$ of dithiapene, 2,3-C$\underline{H_2}$-C$\underline{H_2}$ of bromobutyl), 3.01 (t, 2H, C$\underline{H_2}$Br), 3.36 (m, 4H, 2xS—C$\underline{H_2}$), 3.51 (t, 2H, C$\underline{H_2}$-N), 7.47–7.56 (m, 5H, Ar—$\underline{H}$).		

tetrabutylammonium bromide (TBAB, 0.003 mol, 0.90 g) was stirred for 30 min. Next, the organo-halogen compound (0.03 mol) was added and the reaction mixture was vigorously stirred at room temperature. The progress of the reaction was monitored by TLC over the entire reaction period. After completion of the reaction, the organic layer was separated, dried by anhydrous $MgSO_4$, and the solvent was evaporated. The residue was crystallized from the proper solvent or separated by column chromatography using silica gel and the proper eluent. The results are listed in Tables I and II.

(B) Alkylation in the Presence of Carbon Disulphide

In a round bottle flask (100) fitted with a condenser, a suspension of 5-hydroxy-3-substituted-1*H*-pyrazoles (**1**, 0.01 mol), anhydrous K_2CO_3 (0.02 mol, 2.76 g), tetrabutylammonium bromide (TBAB, 0.003 mol, 0.90 g) and carbon disulphide (10 ml) in dry acetonitrile (50 ml) was efficiently stirred at room temperature for 30 min. The organo-halogen compound (0.03 mol) was added and the reaction mixture was vigorously stirred at 25°C. The progress of the reaction was monitored by TLC over the entire reaction period. After the reaction completion, the organic layer was separated by filtration and the solvent was evaporated. The residue was crystallized from the proper solvent or separated by column chromatography. The results are listed in Tables I and II.

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