SYNTHESIS OF SOME NEW BIS[1-(2-AROYL-3-ARYL)-CYCLOPROPYLCARBONYL]BENZENES AND PYRIDINES UNDER PHASE TRANSFER CATALYSIS (PTC) METHOD

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Some new bis[1-(2-aroyl-3-aryl)cyclopropylcarbonyl]benzenes and pyridines *IV* – *VI* have been prepared by the cycloaddition of dimethylsulfonium phenacylide to 1,1′-(1,3-, 1,4-phenylene, and 2,6-pyridylene)-bis(3-aryl-2-propen-1-ones) *I* – *III* by adopting two different methods. The advantages of the PTC method over the other have been discussed. The structures of the compounds have been confirmed by spectral data.

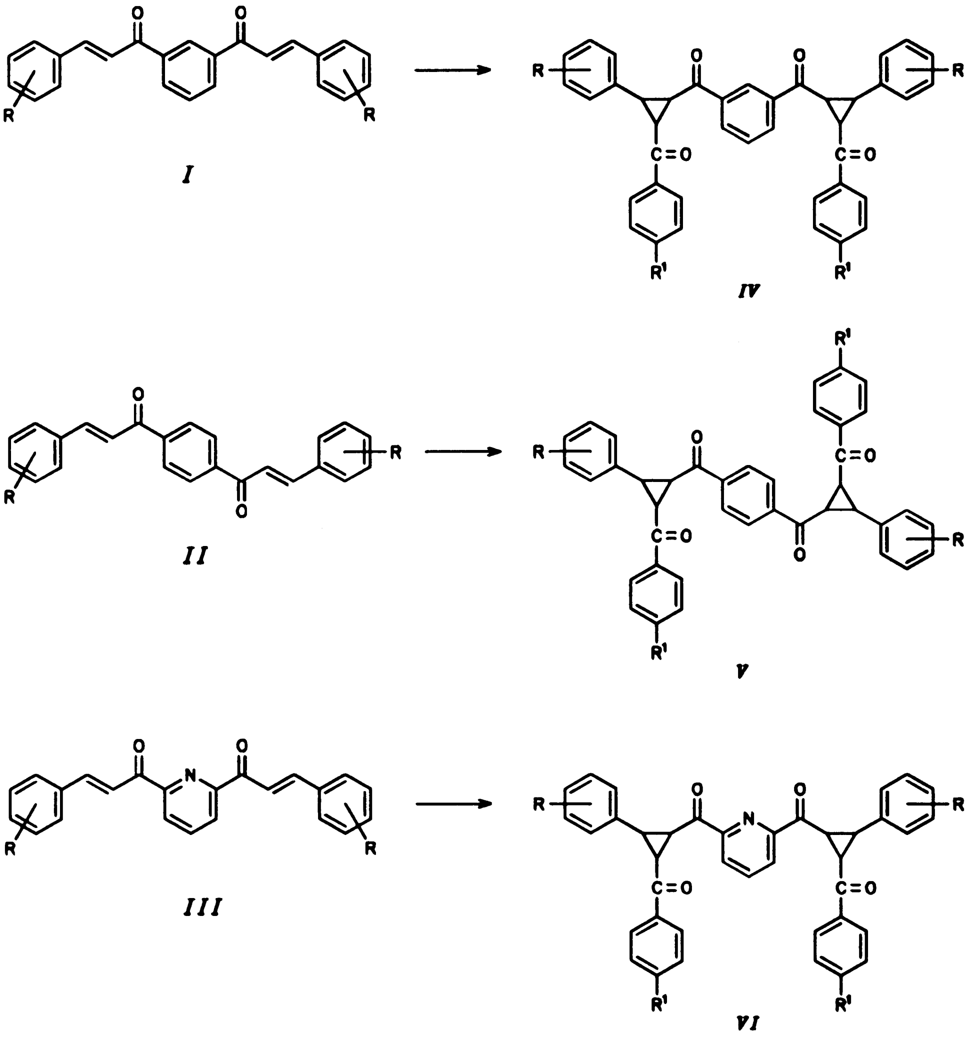
In our continued efforts to obtain more and more new cyclopropanes[1 – 4], we report in this paper the synthesis and structural elucidation of some new bis[1-(2-aroyl-3-aryl)cyclopropylcarbonyl]benzenes and pyridines *IV* – *VI*. Earlier, some α,β-unsaturated carbonyl compounds were cyclopropanated by the reaction of dimethylsulfonium phenacylides either by generating in situ[1 – 4] or by the direct addition of stable ylide under rigorous reaction conditions[5 – 7]. In order to focuss the efficacy of the PTC method over the other *IV*, *V*, and *VI* have been reported by the above mentioned two methods. In one method (*a*, PTC) the substrates (*I* – *III*) were treated with phenacyldimethylsulfonium bromide in dichloromethane and 50% aqueous sodium hydroxide by using benzyltriethylammonium chloride (BTEAC) as a phase transfer catalyst (Scheme 1). In this case dimethylsulfonium phenacylide is presumably generated in situ from the phenacyldimethylsulfonium bromide. However, the same reaction when carried out under identical conditions without the catalyst cyclopropanation did not occur. The other method involves the addition of dimethylsulfonium phenacylide to the same substrates in refluxing benzene. The phenacylide is obtained as a stable one from the salt by treatment with alkali. Relatively higher yields (*a*, 61 – 89%; *b*, 56 – 77%), (Table I) shorter reaction times (*a*, 10 – 12 h; *b*, 35 – 40 h) and milder experimental conditions are some of the advantages of method *a* over method *b*. Moreover, the PTC method, *a*, avoids the obvious problem of generation and preservation of the ylide since it is generated in situ from the salt.

TABLE I
Yields, melting points and IR data for compounds[a] *IVa* – *IVi*, *Va* – *Vj*, and *VIa* – *VIi*

Compound	R	R^1	Yield, %		M. p., °C	IR spectrum (cm^{-1})	
			Method *a*	Method *b*		C=O	ring deformation
IVa	H	H	71	62	158 – 159	1 660	1 015
IVb	H	Br	74	63	163 – 164	1 665	1 020
IVc	4-CH_3	H	80	–	171 – 172	1 655	1 010
IVd	4-CH_3	Cl	82	73	168 – 169	1 665	1 015
IVe	4-OCH_3	H	65	56	188 – 189	1 650	1 010
IVf	4-OCH_3	Br	68	–	185 – 186	1 655	1 010
IVg	4-Cl	H	78	65	235 – 237	1 660	1 020
IVh	4-Cl	OCH_3	74	64	241 – 243	1 665	1 020
IVi	4-Br	CH_3	77	–	238 – 239	1 660	1 020
Va	H	H	78	67	206 – 207	1 655	1 015
Vb	H	OCH_3	72	63	215 – 216	1 650	1 010
Vc	H	Cl	83	–	209 – 210	1 660	1 020
Vd	4-CH_3	H	85	76	220 – 221	1 655	1 010
Ve	4-CH_3	Br	81	–	241 – 242	1 665	1 015
Vf	4-OCH_3	H	67	59	222 – 223	1 655	1 010
Vg	4-OC_2H_5	Br	74	61	214 – 215	1 650	1 015
Vh	4-Cl	H	77	66	244 – 246	1 665	1 010
Vi	4-Cl	Cl	84	–	202 – 203	1 660	1 020
Vj	2,4-Cl_2	Br	89	77	248 – 250	1 665	1 020
VIa	H	H	70	61	179 – 180	1 655	1 025
VIb	H	Br	72	63	191 – 192	1 665	1 030
VIc	4-CH_3	H	75	64	216 – 218	1 660	1 020
VId	4-CH_3	Br	68	–	208 – 209	1 665	1 025
VIe	4-OCH_3	H	61	–	234 – 236	1 660	1 020
VIf	4-OCH_3	Cl	69	58	221 – 222	1 665	1 025
VIg	4-Cl	H	78	69	168 – 169	1 665	1 030
VIa	4-Cl	OCH_3	65	–	208 – 209	1 660	1 020
VIi	2,4-Cl_2	CH_3	73	62	256 – 258	1 665	1 030

[a] All the compounds gave satisfactory elemental analyses.

The products *IV* – *VI* were considered to possess trans-geometry as the ylide addition to Michael acceptors being stereoselective[6,7]. The satisfactory elemental analysis have been obtained for all these compounds. The IR spectra of *IV* – *VI* showed strong bands in the region 1 030 – 1 005 cm^{-1} confirming the presence of cyclopropane ring[2,4] (Table I). Bands with varying intensities have also been displayed by these compounds in the

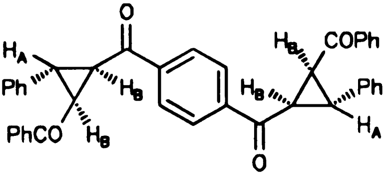


For R and R' in formulae *IV* – *VI* see Table I

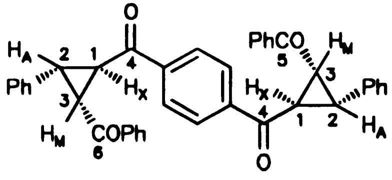
SCHEME 1

region 1 120 – 1 100 and 920 – 905 cm^{-1} indicating their trans-geometry[1,2]. A strong absorption band observed in the region 1 665 – 1 645 cm^{-1} is attributed to the carbonyl stretching frequency[1 – 4].

The addition of ylide to the substrates *I* – *III* offers a variety of possible isomeric forms with regard to structure of the products, *IV* – *VI*. The most reasonable and probable ones are shown below.



VI A



VI B

The protons H_B in *VIA* are magnetically equivalent and hence, methine protons of the cyclopropane ring should constitute an AB_2 pattern. However, in *VIB* all the three protons are magnetically non-equivalent although H_M and H_X are chemically equivalent. As a consequence of this, the three protons, exhibit an AMX pattern. Infact, the spectra of *IV* – *VI*, showed AMX pattern, and each proton appeared as a doublet of doublet. Therefore, they can be reasonably represented as shown in *VIB*. Further, the spectra showed that the two cyclopropyl rings are identical. These compounds are optically inactive as they possess centre of symmetry and alternating axis of symmetry. This was substantiated by the specific rotation $[\alpha]_D$ 0° measured in the polarimeter.

Although the three methine protons (H_A, H_M, and H_X) are deshielded, the H_A appeared at downfield region than H_M and H_X as a result of more deshielding effect exerted by the phenyl moiety[1,4]. The H_M appeared at downfield region relative to H_X because of the deshielding effect exerted by the phenyl moiety which is trans to it[4]. The δ values around 4.30, 3.75 and 3.50 ppm (Table II) are assigned to H_A, H_M and H_X, respectively. The coupling constant values are found to be $J(AX) = 5.8$, $J(MX) = 5.5$ and $J(AM) = 10.0$ Hz. Thus, it is evident that H_A, H_M are cis oriented, whereas H_A, H_X and H_M, H_X are trans.

The ^{13}C δ values around 38.0, 30.0 and 37.5 ppm are assigned to C-1, C-2 and C-3, respectively (Table III). The downfield absorption is attributed to C-1 and C-3 and upfield signals to C-2 since the carbonyl group exerts more deshielding effect than aryl group on the carbon to which it is attached[4,8]. The aryl moiety at C-2 is trans with respect to the substituent at C-1 and cis with the substituent at C-3 and hence C-1 and C-3 are magnetically non-equivalent and appear as two separate signals. Amongst C-1 and C-3 the former appears at relatively downfield region due to the steric interaction of the substituent at C-2 and C-3. The ^{13}C chemical shift values in the region 197.0 and 193.0 ppm are due to the carbonyl carbons at C-4 and C-5, respectively[8].

TABLE II
^{1}H NMR spectral parameters of compounds *IVa, IVd, IVe, IVg, IVi, Va, Vd – Vf, Vh, Vi, VIa, VIc, VIf*, and *VIg*. Chemical shifts in ppm (δ-scale), coupling constants (*J*) in Hz

Compound	Chemical shifts			Coupling constants		
	H_A	H_M	H_X	*J*(AM)	*J*(AX)	*J*(MX)
IVa	4.23	3.72	3.54	10.02	5.94	5.62
IVd	4.30	3.87	3.62	10.03	5.95	5.63
IVe	4.20	3.76	3.52	10.01	5.94	5.61
IVg	4.38	3.97	3.60	10.02	5.96	5.64
IVi	4.25	3.84	3.54	10.04	5.96	5.63
Va	4.28	3.84	3.58	10.00	5.85	5.56
Vd	4.15	3.60	3.45	9.98	5.86	5.55
Ve	4.22	3.73	3.54	10.01	5.87	5.57
Vf	4.20	3.66	3.48	10.01	5.86	5.56
Vh	4.28	3.79	3.61	9.99	5.87	5.58
Vi	4.30	3.82	3.64	10.00	5.85	5.56
VIa	4.38	3.66	3.48	10.09	5.91	5.62
VIc	4.30	3.55	3.39	10.08	5.93	5.64
VIf	4.41	3.69	3.52	10.10	5.92	5.63
VIg	4.43	3.72	3.54	10.08	5.90	5.62

TABLE III
Carbon-13 chemical shifts (δ, ppm) of compounds *IVa, IVc, IVe, IVf, IVh, Va, Vd, Vf – Vi, VIa, VId, VIe*, and *VIg*

Compound	C-1	C-2	C-3	C-4	C-5
IVa	38.43	30.16	37.89	197.84	193.98
IVc	38.32	29.71	37.20	197.56	193.52
IVe	37.87	29.74	37.21	197.63	193.56
IVf	38.92	30.45	38.26	198.23	194.47
IVh	38.59	30.27	37.96	197.99	194.22
Va	37.98	29.74	37.46	197.16	193.45
Vd	37.89	29.72	37.36	196.74	193.12
Vf	37.86	29.65	37.38	196.81	193.21
Vg	38.03	29.76	37.52	197.23	193.51
Vh	38.13	29.84	37.61	197.35	193.56
Vi	38.18	29.88	37.67	197.58	193.71
VIa	38.16	30.64	37.65	198.23	194.41
VId	38.35	30.82	37.78	198.59	194.63
VIe	37.52	30.35	37.09	197.78	193.95
VIg	38.68	31.08	38.04	198.60	194.86

TABLE IV
Mass spectra (m/z) of compounds *IVa, IVd, IVe, Va, Vc, Ve, Vh, VIa, VIf,* and *VIh*. Values in parenthesis indicate the percentage intensity

Compound	$M^{+\bullet}$	$[M-R^1C_7H_4O]^+$	$[M-RR^1C_{16}H_{11}O]^+$	$[RR^1C_{16}H_{11}O]^+$	$[RR^1C_{16}H_9]^+$	$[RR^1C_{15}H_{11}]^+$	$[R^1C_7H_4O]^+$	$[R^1C_6H_4]^+$
IVa	574 (3)	469 (15)	353 (9)	221 (18)	203 (15)	–	105 (100)	77 (78)
IVd	–	531 (10)	401 (32)	269 (15)	251 (26)	241 (20)	139 (100)	111 (48)
IVe	634 (6)	529 (16)	383 (14)	251 (19)	233 (8)	223 (14)	105 (100)	77 (55)
Va	574 (4)	469 (12)	353 (21)	221 (5)	203 (12)	193 (9)	105 (100)	77 (66)
Vc	642 (2)	503 (18)	387 (100)	255 (11)	237 (19)	227 (25)	139 (68)	111 (43)
Ve	–	575 (8)	445 (54)	313 (10)	295 (15)	285 (18)	183 (100)	155 (52)
Vh	642 (5)	537 (6)	387 (28)	255 (16)	237 (23)	227 (22)	105 (100)	77 (59)
VIa	575 (3)	470 (9)	354 (25)	221 (20)	–	193 (32)	105 (100)	77 (58)
VIf	–	564 (15)	418 (22)	285 (28)	267 (21)	257 (15)	139 (100)	111 (38)
VIh	–	568 (11)	418 (18)	285 (32)	267 (16)	257 (25)	135 (100)	107 (50)

A low intense molecular ion peak is observed in the 70 eV mass spectra of *IV* – *VI* confirming their molecular formulae (Table IV). Some of the compounds did not show $M^{+\cdot}$ ion peaks which indicate that they are unstable at 70 eV. However, $[M-ArCO]^+$ ion is observed with moderate abundance in such instances. The aroyl cation appeared as a base peak in all these compounds except in *Vc*, where it is $[M-RR^1C_{16}H_{11}O]^+$. Halogen substituted compounds exhibited isotopic peaks in their spectra. Molecular ions with odd mass value indicate the presence of a nitrogen in *VI*.

EXPERIMENTAL

Melting points were determined on a Mel-Temp apparatus and are uncorrected. The IR spectra (wavenumbers in cm^{-1}) were recorded on a Perkin–Elmer Grating Infrared Spectrophotometer Model 337 in KBr pellets. The ^1H NMR and ^{13}C NMR spectra were recorded at 500 MHz and 125 MHz on GE NMR Omega and Bruker spectrometers with tetramethylsilane as an internal standard, chemical shifts in ppm (δ-scale). The mass spectra were recorded on Krates MS-80 double focussing mass spectrometer. Purity of the compounds was checked by TLC using silica gel H (BDH) and hexane–ethyl acetate (3 : 2) as an eluant.

General Procedure for the Preparation of Bis[1-(2-aroyl-3-aryl)cyclopropylcarbonyl] Benzenes *IV*, *V* and Pyridines *VI*

a) A solution of *I* or *II* or *III* (refs[9,10], 5 mmol), phenacyldimethylsulfonium bromide[11,12] (11 mmol) in methylene chloride (40 ml) was stirred with 50% aqueous NaOH (20 ml) till a clear two-phase system was obtained. A catalytic amount (100 mg) of benzyltriethylammonium chloride (BTEAC) was added to this and the stirring continued for 10 – 12 h at room temperature. The progress of the reaction was monitored with TLC. After completion of the reaction the contents were diluted with water, the organic layer separated washed with water and brine and dried over anhydrous Na_2SO_4. The solid obtained after removal of the solvent was recrystallized from ethanol or benzene.

b) A mixture of *I* or *II* or *III* (refs[9,10], 5 mmol) and dimethylsulfonium phenacylide[5] (11 mmol) in dry benzene or toluene (20 ml) was refluxed for 35 – 40 h. The progress of the reaction was monitored by TLC. After completion of the reaction the solvent was distilled off. The crude product obtained was recrystallized from ethanol or benzene.

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