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STUDIES ON AROYLMETHYLENE-SULPHONIUM YLIDES: SYNTHESIS OF SOME NEW 1,2,3-TRIARYLSUBSTITUTED CYCLOPROPANES VIA SULPHONIUM YLIDES

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THE use of sulphonium ylides in the synthesis of heterocycles¹ and cyclopropanation reactions^{2,3} is documented. Utilizing this reaction with a view to exploring the synthetic potentialities of sulphonium ylides, we have studied the reactivity of these ylides (2a-c) towards α,β -unsaturated ketones (3a-f) and synthesized some new 1,2,3-trisubstituted cyclopropanes (4a-o).

Treatment of salts 1a-c with 10% aqueous sodium hydroxide generated an intense yellow colouration due to the formation of ylides (2a-c). The reactions of the ylides (2a-c) with α,β -unsaturated ketones (3a-f) at room temperature afforded trans-1,2,3-trisubstituted cyclopropanes (4a-o). The exclusive formation of trans-1,2,3-trisubstituted cyclopropanes 4a-o suggested that the addition of the ylide to the ketone was due to the additional delocalization of charge over the conjugated system in the transition state. The trans-geometry of the cyclopropane derivatives 4a-r was determined on the basis of NMR spectra in which the three cyclopropyl protons exhibited as expected AB₂ pattern and the trans-coupling constants observed were in the range of 5 CPS to 6 CPS.

All the cyclopropanes (4a-o) synthesized are listed in table 1. The structures of the compounds 4a-o were

determined on the basis of elemental analyses and IR and NMR spectral data.

Melting points were taken in a sulphuric acid bath and are uncorrected.

Phenacylidenedimethyl sulphurane (2a)

Phenacyldimethylsulphonium bromide (1a) (10 g) was dissolved in water (25 ml) and the coloured suspension was filtered. The clear filtrate was stirred with 10% aqueous sodium hydroxide (120 ml) for 3 hr and then extracted with CHCl₃, the CHCl₃ layer was dried over Na₂SO₄ and concentrated under reduced pressure to afford 2a as orange solid (10 g), m.p. 55-56° (Lit⁴ 56-57°).

3,4,5-Trimethoxybenzylidene acetophenone (3a)

A solution of sodium hydroxide (2 g in 10 ml of water) was added to a cooled solution of 3,4,5-trimethoxy benzaldehyde (9.8 g) and acetophenone (6 g) in ethanol (60 ml) dropwise. The reaction mixture was kept at 0-2° for 2.5 hr and left overnight in refrigerator. Water (150 ml) was added and the resulting precipitate was filtered. It was recrystallized from ethanol to give 4a (11.2 g, 75%), m.p. 144°; IR (nujol): 3000, 1665 (C=O), 1605 (C=C), 1230 and 1110 (OCH₃) and 820 cm⁻¹, PMR (CDCl₃; TMS): δ 3.85 (s, 3H, OCH₃), 3.9 (s, 6H, 2-OCH₃), 6.5 (d, J = 8Hz, 1H, olefinic proton), 7-8.2 (m, 7H, Ar-H); (Found: C, 72.5; H, 6.2; C₁₈H₁₈O₄ requires C, 72.5; H, 6.0%).

The following compounds were similarly prepared (m.p., yield %), 3b (117°, 75); 3c (108°, 76); 3d (125°, 78); 3e (154°, 73) and 3f (121°, 68).

1,2-Dibenzoyl-3-(3,4,5-trimethoxyphenyl)-cyclopropane (4a)

To a solution of 3a (2.98 g) in benzene (50 ml) was added 2a and the resulting solution was stirred for 15

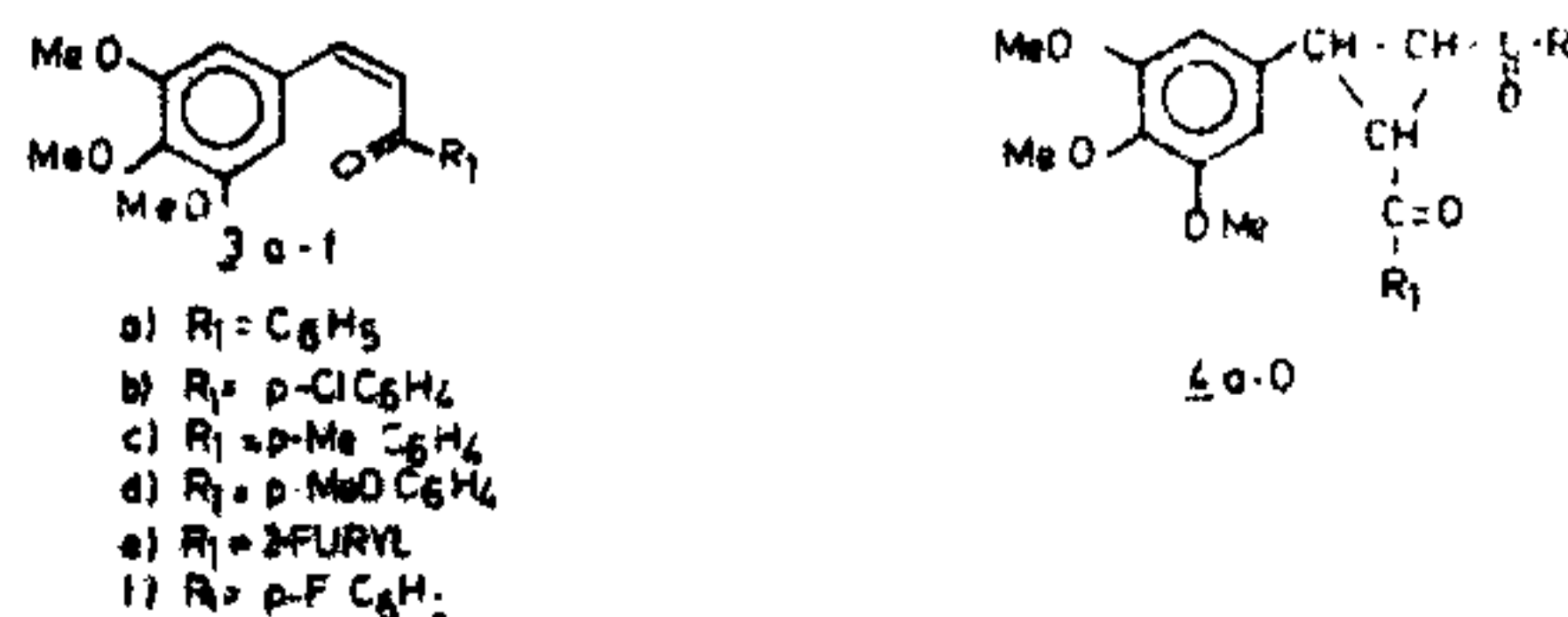
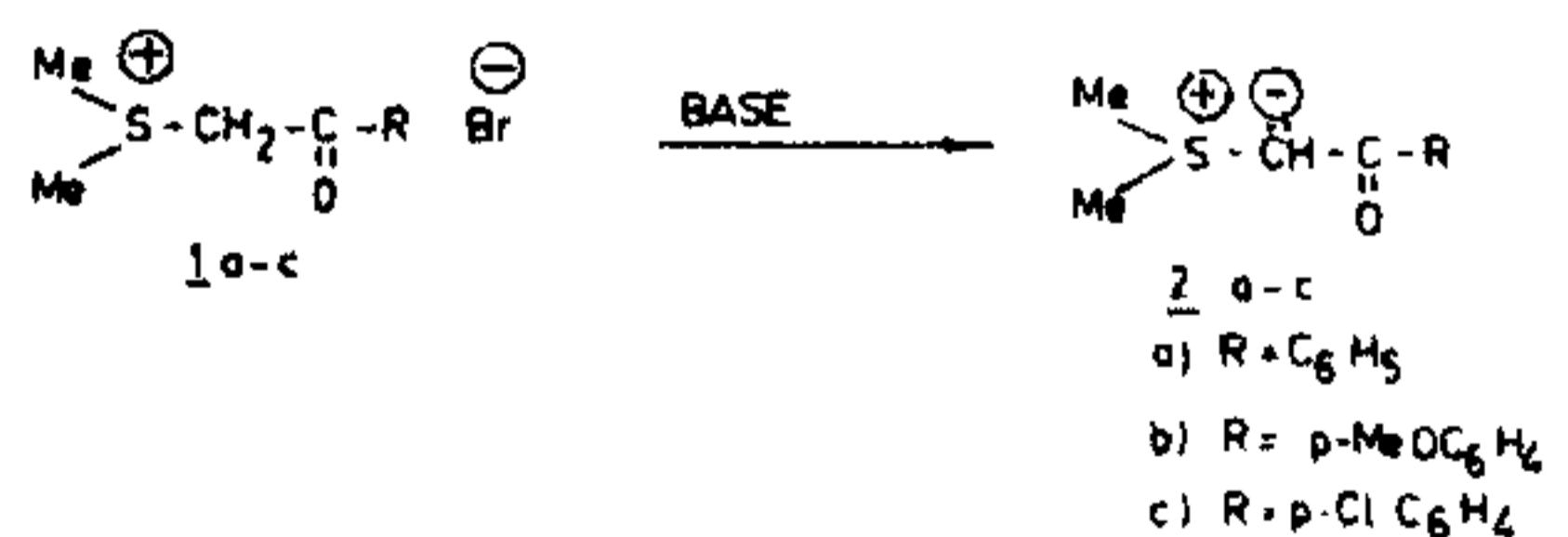


Table 1 Physical data of 1,2,3-trisubstituted cyclopropanes (4a-o)

Compound*	R ¹	m. p. (°C)	Mol. formula	C Found (Calc)	H% Found (Calc)
4a	C ₆ H ₅	115	R = C ₆ H ₅ C ₂₆ H ₂₄ O ₅	74.62 (74.98)	5.92 (5.80)
4b	p-ClC ₆ H ₄	105-06	C ₂₆ H ₂₃ ClO ₅	69.1 (69.25)	5.2 (5.14)
4c	p-MeC ₆ H ₄	98-99	C ₂₇ H ₂₆ O ₅	75.4 (75.32)	6.1 (6.08)
4d	p-MeOC ₆ H ₄	115—16	C ₂₇ H ₂₆ O ₆	72.2 (72.63)	5.3 (5.86)
4e	2-Furyl	146-47	C ₂₄ H ₂₂ O ₆	70.4 (70.74)	5.42 (5.69)
4f	p-FC ₆ H ₄	99	C ₂₆ H ₂₃ FO ₅	71.8 (71.87)	5.2 (5.33)
4g	p-ClC ₆ H ₄	136	R = p-MeOC ₆ H ₄ C ₂₇ H ₂₅ ClO ₆	67.5 (67.42)	5.4 (5.24)
4h	p-MeC ₆ H ₄	83	C ₂₈ H ₂₈ O ₆	73.2 (73.025)	6.0 (6.12)
4i	p-MeOC ₆ H ₄	113-14	C ₂₈ H ₂₈ O ₇	70.4 (70.57)	6.1 (5.92)
4j	2-Furyl	127	C ₂₅ H ₂₄ O ₇	68.82 (68.63)	5.51 (5.76)
4k	p-FC ₆ H ₄	94-95	C ₂₇ H ₂₅ FO ₆	69.5 (69.81)	5.5 (5.42)
4l	p-ClC ₆ H ₄	120	R = p-ClC ₆ H ₄ C ₂₆ H ₂₂ Cl ₂ O ₅	64.5 (64.33)	4.4 (4.54)
4m	p-MeC ₆ H ₄	78	C ₂₇ H ₂₅ ClO ₅	69.7 (69.75)	5.1 (5.38)
4n	2-Furyl	149	C ₂₄ H ₂₁ ClO ₆	65.38 (65.23)	4.77 (5.018)
4o	p-FC ₆ H ₄	110	C ₂₆ H ₂₂ FCIO ₅	66.7 (66.59)	4.6 (4.73)

*All the compounds were recrystallized from benzene-methanol.

hr at room temperature under nitrogen. The solvent was evaporated under vacuum and the residue was crystallized from methanol to afford 4a (2.5 g, 60%), m.p. IR (nujol): 3050 (Cyclopropane CH stretching), 1650 (C=O), 1603 (C=C), 1220 and 1130 (OCH₃) and 820 cm⁻¹; NMR (CDCl₃; TMS): δ2.5 (d, 2H, Cyclopropyl), 3.5 (q, 1H, cyclopropyl), 3.8 (s, 9H, methoxy); 6.65–8.2 (m, 12H, aromatic).

Compounds 4a–o recorded in table 1 were similarly prepared.

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