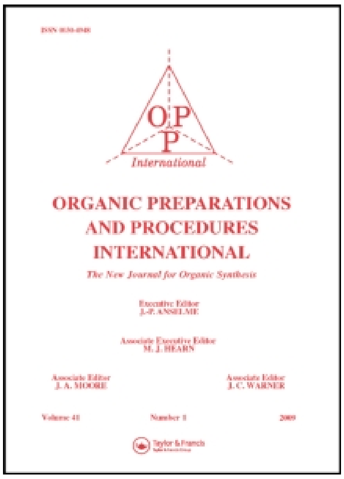

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O. Bhaskar Reddy[a]; V. M. Subramanyam[a]; V. Padmavathi[a]
[a] Department of Chemistry, Sri Venkateswara University, Tirupati, INDIA

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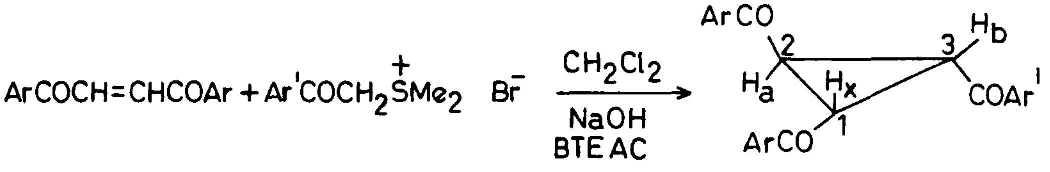
A FACILE METHOD FOR THE SYNTHESIS OF 1,2,3-TRIAROYLCYCLOPROPANES UNDER PHASE-TRANSFER CONDITIONS

D. Bhaskar Reddy*, V. M. Subramanyam and V. Padmavathi
Department of Chemistry
Sri Venkateswara University, Tirupati-517 502, INDIA

The cycloaddition of sulfur ylides, particularly non-stabilized ylides, to carbon-carbon multiple bonds constitutes one of the important route for the synthesis of cyclopropyl ketones.[1-5] However, the reactions of stabilized ylides, such as carbonyl stabilized sulfonium ylides $[RCO\bar{C}H-\overset{+}{S}(CH_3)_2]$ with carbonyl activated double bonds have not been well explored. The cycloaddition of sulfur ylides under usual conditions requires vigorous reaction conditions very often resulting in relatively poor yields. However, it has been reported that under milder reaction conditions of phase-transfer catalysis,[6] higher yields were achieved. There are very few reports about the utility of phase-transfer conditions for the addition of sulfur ylides to Michael acceptors.[7-9] This prompted us to explore the addition of carbonyl stabilized sulfur ylides to 1,2-diaroylethylenes.



1	2		3
a) Ar=C_6H_5,	Ar'=C_6H_5	g) Ar=4-ClC_6H_4,	Ar'=4-BrC_6H_4
b) Ar=C_6H_5,	Ar'=ClC_6H_4	h) Ar=4-BrC_6H_4,	Ar'=C_6H_5
c) Ar=C_6H_5,	Ar'=4-BrC_6H_4	i) Ar=4-BrC_6H_4,	Ar'=4-ClC_6H_4
d) Ar=C_6H_5,	Ar'=4-$CH_3C_6H_4$	j) Ar=4-BrC_6H_4,	Ar'=4-BrC_6H_4
e) Ar=4-ClC_6H_4,	Ar'=C_6H_5	k) Ar=4-$CH_3C_6H_4$,	Ar'=C_6H_5
f) Ar=4-ClC_6H_4,	Ar'=4-ClC_6H_4	l) Ar=4-$CH_3C_6H_4$,	Ar'=4-$CH_3C_6H_4$

TABLE 1. 1,2,3- Triarolycyclopropanes

Compound	Yield (%)	Obs. mp (°C)	lit. mp (°C)	Elemental Analysis (Calcd) C	Elemental Analysis (Calcd) H
3a	77	214-215	215[a]	81.40(81.33)	5.46(5.11)
3b	62	135-136		74.52(74.13)	4.08(4.40)
3c	74	153-154	153[b]	66.12(66.52)	4.23(3.95)
3d	61	120-121	122[b]	81.97(81.50)	5.83(5.47)
3e	66	118-119		68.50(68.09)	4.12(3.80)
3f	77	149-150		62.56(62.97)	3.64(3.30)
3g	80	165-166		57.92(57.40)	3.46(3.00)
3h	77	107-108		55.89(56.27)	2.80(3.14)
3i	80	167-168		53.10(52.73)	3.14(2.76)
3j	71	185-186		49.10(48.76)	2.86(2.55)
3K	73	152-153		80.95(81.65)	6.10(5.79)
3l	79	142-143		81.40(81.79)	6.39(6.10)

a) G.Maier, Chem. Ber., 95, 611 (1962). b) Ref. 3.

Cyclopropanation of the activated double bonds was carried out earlier by generating the ylide[10] in situ or by preparing the stable ylide first and then adding it to Michael acceptors.[11] But both the procedures are time consuming and require perfectly anhydrous conditions. These difficulties have now been overcome by carrying out the reaction under phase-transfer conditions using the dimethylphenacylsulfonium bromide salts directly. This method thus avoids the obvious problem of generation and preservation of the stable dimethylsulfoniumphenacylides. It was mentioned that the ylide 2 in the presence of moisture may be converted to 1,2,3-triaroylcyclopropane.[11] If such was the case, compounds 3a, 3f, 3j and 3l could have been formed from the respective ylides 2. It was also reported[11] that the ylide 2 undergo smooth Michael reaction with dibenzoylethylene in an atmosphere of nitrogen to give trans-1,2,3-tribenzoylcyclopropane in high yield. All our compounds have been obtained by the reaction of ylide 2 with diaroylethylenes under phase-transfer conditions. Thus it was obvious that the 1,2,3-triaroylcyclopropanes reported in the present work are not obtained directly from the ylide 2 but by the addition of the ylide 2 with diaroylethylenes 1. The later are considered to possess the trans-geometry as they were prepared from arenes and fumaroyl chloride.[12] Hence, the 1,2,3-triaroylcyclopropanes obtained by the cycloaddition of ylide 2 may be regarded to possess E-geometry with respect to diaroylethylenes. The IR spectra of these compounds displayed medium bands in the region 1015-995 and 880-860 cm^{-1}.[13] They also exhibited very strong carbonyl band at 1670-1660 cm^{-1}. The ^1H NMR spectra (δ ,ppm) of 3 exhibited complex multiplets in the regions 3.43-3.80 (H_b and H_x) and 3.90-4.32 (H_a). The carbonyl groups exert a deshielding effect on the cis-hydrogens in cyclopropanes. As a result the signal at the lowest field may be from the hydrogen (H_a) cis to two carbonyl groups while the signals at high field may arise from the two hydrogens cis to only one carbonyl i.e., H_b and H_x. The coupling constants of the vicinal hydrogens are in the range 5.60-6.00 cps ($J_{H_aH_x}$ and $J_{H_aH_b}$) and 10.00 H_z ($J_{H_bH_x}$).

TABLE 2. ^1H NMR of 1,2,3-Triaroylcyclopropanes(δ)

Compound	Cyclopropyl Hydrogens (abx) 2H	Cyclopropyl Hydrogens (abx) 1H	Aromatic Hydrogens o-hydrogens of Aroyl groups (6H)	Aromatic Hydrogens Other Aromatic hydrogens
3a	3.67-3.80	4.12-4.32	7.92-8.30	7.30-7.70
3b	3.56-3.70	3.96-4.15	7.76-8.24	7.18-7.52
3c	3.43-3.66	3.90-4.13	7.50-7.90	6.90-7.40
3f	3.60-3.72	4.05-4.20	7.85-8.25	7.25-7.62
3g	3.62-3.75	4.08-4.28	7.80-8.25	7.20-7.65
3h	3.60-3.74	3.95-4.12	7.95-8.32	7.15-7.45
3i	3.52-3.67	3.90-4.06	7.00-7.89	
3j	3.57-3.70	4.00-4.20	7.47-8.10	
3l	3.60-3.75	4.07-4.27	7.82-8.20	7.10-7.40

EXPERIMENTAL SECTION

Melting points were determined on a Mel-Temp apparatus and are uncorrected. The elemental analyses were performed by the Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow. The IR spectra were recorded on a Beckmann Infrared Spectrophotometer Model 18-A as KBr pellets. The wave numbers of the spectra were calibrated by using a standard polystyrene film. The ^{1}H NMR spectra were recorded in deuterochloroform at 90 MHz on Bruker spectrospin Nuclear Magnetic Resonance Spectrometer with TMS as an internal standard. The required dibenzoylethylenes were prepared by the condensation of different hydrocarbons with fumaroyl chloride.[12] Dimethylphenacylsulfonium bromides were prepared following the procedure of Speziale *et al*.[14]

1,2,3-Tribenzoylcyclopropanes. Typical Procedure.- A mixture of 2.36 g (0.01 mole) of 1,2-dibenzoylethylene, 2.87 g (0.011 mole) of dimethylphenacylsulfonium bromide[15,16] and 6 ml of methylene chloride in a 100 ml Erlenmeyer flask equipped with a magnetic stirrer was stirred with 4 ml of 50% aqueous sodium hydroxide until a clear two-phase mixture was obtained. Then 50 mg of benzyltriethylammonium chloride was added and the mixture stirred vigorously at room temperature for 3-5 hrs. The progress of the reaction was monitored by thin layer chromatography. After completion of the reaction the mixture was diluted with 50 ml of water. The organic layer was separated, washed with water, brine and dried over anhydrous magnesium sulphate. Evaporation of the solvent gave 1,2,3-tribenzoylcyclopropane which was purified by recrystallization from 95% ethanol. The purity of the products were checked by thin layer chromatography.

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