

TABLE I.

Fractional atomic coordinates for diaquanitratoglycinecalcium(II) nitrate.

Atom	x	y	z
Ca	0.0645	0.2288	0.0896
C(1)	0.582	0.186	0.147
C(2)	0.585	0.126	0.264
O(1)	0.722	0.218	0.103
O(2)	0.394	0.199	0.102
O(3)	0.470	0.067	0.019
O(4)	0.020	0.049	0.171
O(5)	0.016	0.082	0.054
O(6)	0.400	0.373	0.322
O(7)	0.579	0.460	0.458
O(8)	0.393	0.316	0.494
O _w (1)	0.050	0.405	0.134
O _w (2)	0.133	0.228	0.304
N(1)	0.428	0.065	0.283
N(2)	0.019	0.010	0.069
N(3)	0.466	0.385	0.427

dual index at present is about 0.12. Further refinement is under progress. The present fractional atomic coordinates are presented in table I. A view of the structure looking down the *a*-axis is shown in figure 1.

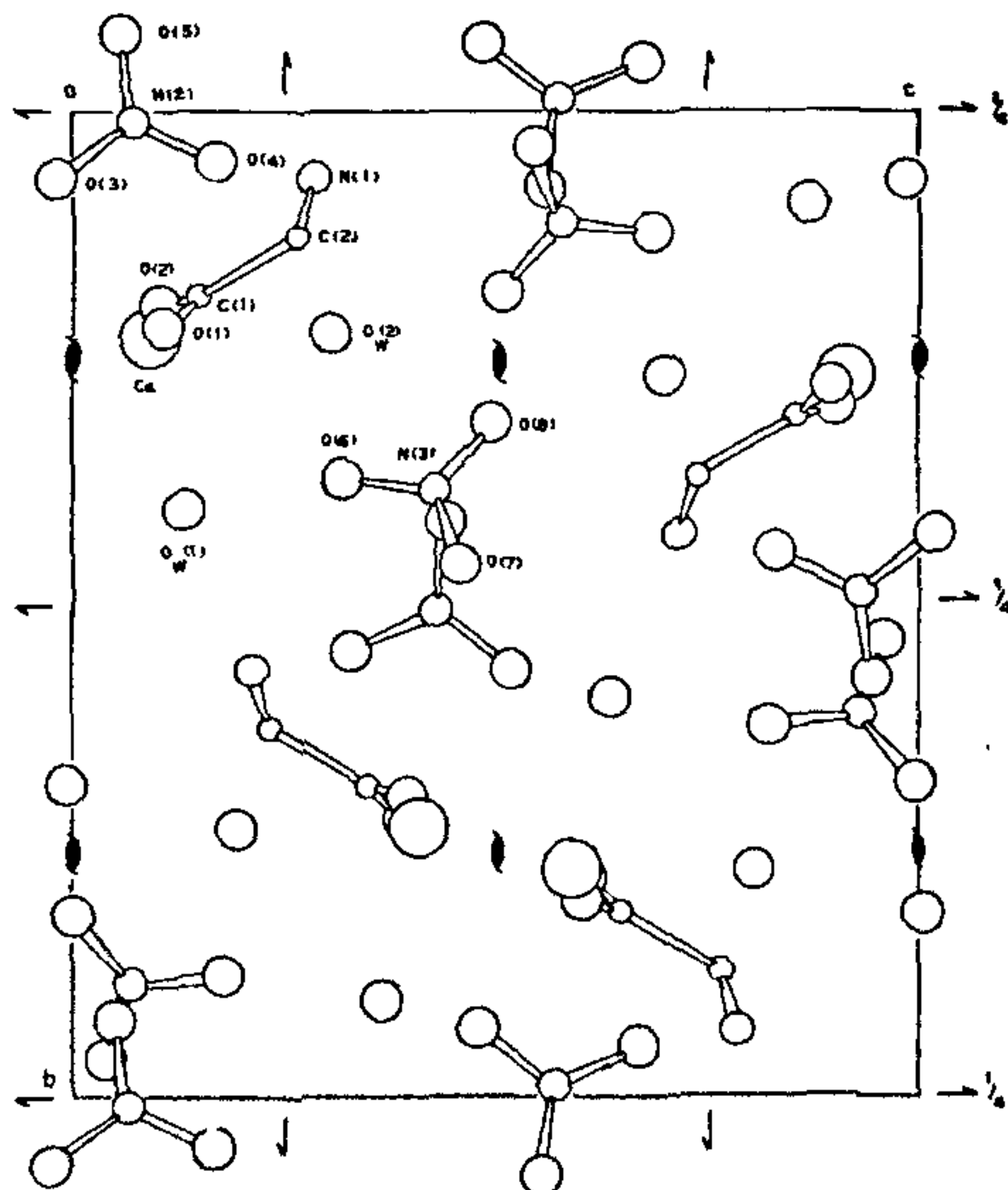


Figure 1. Projection of the structure of diaquanitratoglycinecalcium(II) nitrate down the *a*-axis.

Calcium is coordinated to eight oxygen atoms, two of them belonging to water molecules, another two belonging to a nitrate group and the rest to the carboxyl group of the glycine molecule. The Ca-O distance range from 2.3 to 2.64 Å. Glycine molecule and the nitrate groups have the normal bond distances and bond angles as found in other similar structures².

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A NEW ROUTE FOR SYNTHESIS OF 2,4,6-TRIARYLPYRIDINES VIA PHOSPHONIUM YLIDES

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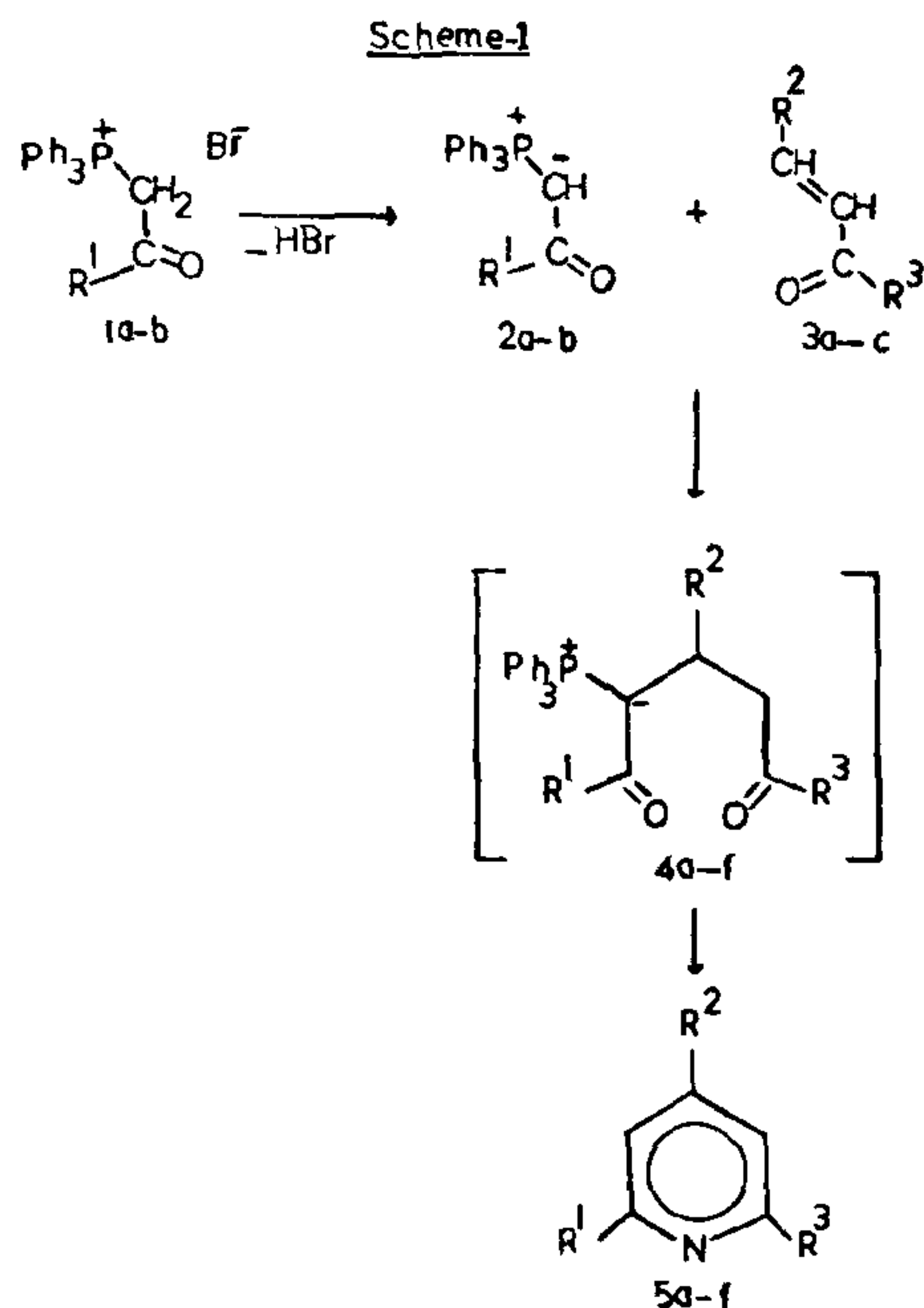
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A NEW route for the synthesis of 2,4, 6-triarylpyridines is reported. It involves the reaction of phenacylidetriphenylphosphoranes with α,β -unsaturated ketones with ammonium acetate as cyclization agent.

The intermolecular and intramolecular cyclization reactions of Phosphonium ylides find an extensive applications in the synthesis of a wide variety of cyclic systems¹⁻⁴. The reaction of phosphonium ylides with α,β -unsaturated carbonyl systems with simultaneous ring closure leading to the synthesis of pyridine nucleus is now reported.

Quaternization of triphenylphosphine with phenacyl bromide and 4-bromophenacyl bromide in benzene at reflux temperature gave phenacyltriphenylphosphonium bromide (1a) and 4-bromophenacyltriphenylphosphonium bromide (1b) in good yields^{5,6}. The reaction of these salts (1a-b) with substituted benzylideneacetophenones (3a-b) and benzylidene-3-acetophenanthrene (3c) in the presence of a mixture of ammonium acetate and acetic acid was carried out for 5-8 hr at reflux temperature to give 2, 4, 6-triarylpyridenes (5a-f) in 50-65% yields (scheme 1). The reaction was successful also when ammonium acetate in methanol was used as a cyclization agent but the yields were less.



The reaction presumably proceeds via the nucleophilic attack of phosphonium ylide carbanions (2a-b), formed by the dehydrohalogenation of the corresponding salts (1a-b), on β -carbon of α,β -unsaturated

ketones (3a-c) to form 1, 5-dionylphosphonium derivatives (4a-f) which undergo cyclization with ammonium acetate in acetic acid to give pyridines (5a-f) in 52-65% yields (scheme 1). Thus, the behaviour of these ylides (2a-b) towards α,β -unsaturated ketones is analogous to that reported for nitrogen ylides⁷.

The pyridines (5a-f) synthesized above gave satisfactory elemental analysis and the melting points are close to those reported in literature⁸⁻¹⁰. The structures of pyridines (5a-f) were confirmed by IR and NMR spectral analysis. The IR spectral data of 5a-f showed characteristic absorption band in the region 3020-3000 cm^{-1} , which is assigned to the C-H stretching mode of pyridine nucleus. The two bands in the region 1600 and 1500 cm^{-1} have been assigned to C=C and C=N vibration of pyridine rings. The NMR spectra of compounds (5a-f) in general exhibited two pyridyl protons in the range δ 6.83-7.00 and aromatic protons at δ 6.95-8.3.

Melting points were determined on Gallen Kamp apparatus and are uncorrected. The phosphonium salts (1a-b) were prepared by heating substituted phenacyl bromides with triphenylphosphine in benzene at reflux temperature according to the procedure cited in literature⁵⁻⁶.

To a stirred solution of 3 mmol of salt (1a-b) in 20 ml of glacial acetic acid and ammonium acetate (3 g), was added gradually a solution of α,β unsaturated ketone (3a-c; 3 mmol) in 10 ml of glacial acetic acid under nitrogen atmosphere. The reaction mixture was stirred at reflux temperature for 6-8 hr and kept overnight at room temperature. It was diluted with cold water (20 ml) and precipitate was separated, washed with methanol and crystallized from suitable solvents to give title compounds (5a-f) (table 1).

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TABLE I
Physical properties of 2,4,6-triarylpyridines (5a-f)

Compound	R ¹	R ²	R ³	Yield %	Recryst. Solvent	m.p. °C	Lit. m.p. °C
5a	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	50	A	135-37	(138) ⁸
b	C ₆ H ₅	3,4-O ₂ CH ₂ C ₆ H ₃	C ₆ H ₅	55	B	150-51	(152-53) ⁹
c	C ₆ H ₅	C ₆ H ₅	3-Phenanthryl	50	C	122-23	(120-21) ¹⁰
d	4-BrC ₆ H ₄	C ₆ H ₅	C ₆ H ₅	58	A	152-53	(150-52) ⁹
e	4-BrC ₆ H ₄	3,4-O ₂ CH ₂ C ₆ H ₃	C ₆ H ₅	60	C	133-35	(136-38) ⁹
f	4-BrC ₆ H ₄	C ₆ H ₅	3-Phenanthryl	65	B	140-41	(140-42) ¹⁰

A = C₅H₅N-EtOH (1:4); B = EtOH; C = CHCl₃-MeOH (1:4)

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EXCESS GRUNEISEN PARAMETER AND INTERMOLECULAR INTERACTION IN BINARY LIQUID MIXTURES OF TRICHLOROETHYLENE

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THE Gruneisen parameter (Γ), which is a dimensionless measure of change in entropy with volume or thermal pressure, has been extended to liquid state for investigating the internal structure, lustering phenomena and remaining quasicrystalline lattice nature¹⁻⁶. By using some thermodynamic relations, Γ can be expressed by the following relation:

$$\Gamma = C^2 \alpha / C_p = \gamma - 1 / T \alpha \quad (1)$$

where C , α , C_p and γ represent sound velocity, thermal expansion coefficient, principal heat capacity at constant pressure and heat capacity ratio respectively. The sum of exponents of Mies' equation has been determined⁷ for liquid mercury, using Gruneisen number, assuming a condensed system of molecules and consisting of harmonic oscillators. Attempts to study Gruneisen parameter in liquid mixtures have been rare⁸. In the present paper the Gruneisen parameter has been extended to binary liquid mixtures and the value of excess Gruneisen parameter has been calculated using the relation

$$\Gamma^E = \Gamma_{mix} - \sum_{i=0}^2 x_i \Gamma_i \quad (2)$$

TABLE I
Excess Gruneisen Parameter for various systems at 30° C

x_1	Γ^E
C ₂ HCl ₃ + benzene system	
0.1112	0.023
0.3679	0.024
0.5456	0.030
0.6064	0.026
0.7435	0.021
0.9459	0.006
C ₂ HCl ₃ + toluene system	
0.1256	-0.005
0.2537	-0.029
0.6721	-0.037
0.7233	-0.028
C ₂ HCl ₃ + <i>p</i> -xylene system	
0.2299	-0.028
0.3390	-0.045
0.5717	-0.080
0.6011	-0.077
0.7598	-0.067
C ₂ HCl ₃ + chloroform system	
0.2299	-0.001
0.3399	-0.002
0.4665	-0.001
0.6863	0.001
0.7221	0.099
0.8367	0.001
C ₂ HCl ₃ + CCl ₄ system	
0.1343	-0.002
0.2258	-0.007
0.3196	-0.002
0.4385	+0.003
0.6352	-0.007
0.7258	-0.008
0.8319	-0.010
0.9439	-0.005