N (15) are hydrogenobonded to their adjacent symmetry related (Fig. 1) nitrogen or oxygen atoms. There is one close intermolecular approach in this structure (2·939 Å) and that is between O (9) and its nearest symmetry related pyrimidinyl nitrogen N (15). The molecules are stacked together along the diagonals of the *ab* plane.

The authors (RKT and TPS) thank UGC, CSIR and DST (India) for liberal financial support.

Institute for Crystallography,
1000 Berlin 33
and
Department of Physics,
University of Indore,
Khandwa Road, Indore 452 001,
December 18, 1979.

R. REINHARDT.
R. K. TIWARI.
T. P. SINGH.*

---

* The author to whom correspondence to be addressed.

1. Singh, T. P. and Deo, N., *J. Sci. Ind. Res.*, 1978, **5**, 47.
2. Shin, S. H., Hn, H. G., Kim, H. S. and Koo, C. H., *Journal of Korean Chemical Society*, 1974, **18**, 329.
3. Koo, C. H., Kim, H. S., Yoon, Y. K. and Suh, I. H., *Journal of Korean Physical Society*, 1975, **8**, 37.
4. Cook, D. S. and Turner, M. F., *J. Chem. Soc. Parking*, *II*, 1974, p. 1021.
5. Kruger, G. J. and Gafner, G., *Acta Cryst.*, 1971, **B27** 326.

A SIMPLIFIED SYNTHESIS OF CHROMANONES

OXIMES of dichlorochromanones are reported to be useful as diuretics, in the control of blood pressure and as fungicides[1–3]. The methods described in literature[1] for their synthesis involve the use of hazardous reagents such as sodium hydride and hydrogen fluoride. General method for their synthesis is by the cyclisation of the corresponding O-propionic acids with PPA. The propionic acids could be obtained by the hydrolysis of the appropriate O-propionitriles or by the reaction of the dichlorophenols with *β*-chloropropionic acid. However, we have found that dichlorophenols do not undergo cyanoethylation even under different experimental conditions nor do they react with *β*-chloropropionic acid (with the exception of 2,4-dichlorophenol) to furnish the required O-propionic acids.

The method described here for the synthesis of dichlorochromanones involves the direct reaction of dichlorophenols with acrylic and crotonic acids in the presence of polyphosphoric acid (PPA) to afford the required chromanones in yields varying from 20–25%. The latter are about the same as obtained by known procedures but the simplicity of the procedure as also its usefulness in obtaining chromanones having alkyl substituents at the '2' position make this a very convenient method of synthesis. It is pertinent to mention here that in this reaction *α*-methylacrylic, *β*, *β*-dimethylacrylic and cinnamic acids did not yield the respective chromanones, but only tarry matter was obtained in all cases from which no pure product could be isolated.

The reaction of a dichlorophenol (0·005 mol) and acrylic (or crotonic) acid (0·05 mol) is carried out by heating the reactants in the presence of PPA [prepared from phosphorus pentoxide (15 g) and phosphoric acid (7·5 ml) preheated at 100° for 30 mins] at 120–130° for 5 hr, with occasional shaking. The resulting mass obtained after cooling with ice was kept overnight (at room temperature) and extracted with chloroform. The extract after washing with aqueous alkali and water was dried and the solvent removed to yield a dark red mass which was chromatographed over silica gel. From the alkaline solution about 30% of the dichlorophenol was recovered.

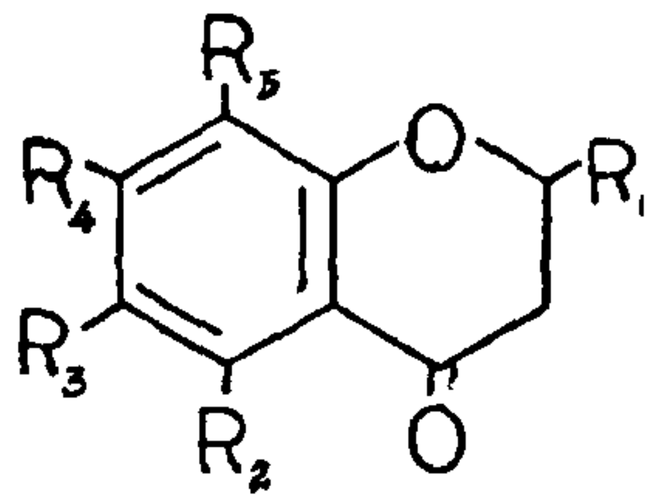
The various compounds obtained by elution are listed in Table I. In the reaction of 3,4- and 3,5-dichlorophenols with crotonic acid, besides the dichlorochromanones, the corresponding crotonates were also isolated in about 4% yield. They did not form 2,4-dinitrophenylhydrazone (2,4-DNP) derivatives. Their U.V. spectrum showed: λ_{max}^{MeOH} (log ϵ) : 215 (4·40), 335 (2·28) nm and I.R. ν_{max}^{KBr}: 1,750 (ester, C = O), 1,660 (C=C), 1,590 (aromatic) and 960 (–CH = CH–CH_3, trans), cm^{-1}.

All the dichlorochromanones crystallised as colourless solids from light petroleum (b.p. 40–60°) and formed crystalline 2,4-DNP derivatives, crystallised from alcohol. Their U.V. showed λ_{max}^{MeOH} (log ϵ) : 225 (4·40), 255 (4·10), 335 (3·64) nm whereas in I.R. (KBr) the carbonyl frequency was observed around 1,680–1,685 cm^{-1}.

In the case of 3,4-dichlorophenol, there is a possibility of two isomers but the compound isolated was a single substance (the single spot) and its nmr spectrum was in full agreement with the structure assigned. NMR spectrum of III : δ ($CDCl_3$) : 2·85 (*t*, 2H, J = 6·5 Hz), 4·60 [*t*, 2H, J = 6·5 Hz), 7·20 (*s*, 1H| aromatic proton], 8·00 (*s*, 1H, aromatic proton). NMR spectrum of IV : δ ($CDCl_3$) : 2·85 (*t*, 2H, J = 6·5 Hz), 4·58 (*t*, 2H, J = 6·5 Hz), 6·97 (*s*, 1H); 7·07 (*s*, 1H). NMR spectrum of VIII: δ ($CDCl_3$) : 1·5 (*d*, 3H, J = 6·5 Hz), 2·72 (*d*, 2H, J = 7·8 Hz), 4·48–4·84 (*m*, 1H); 6·95 (*s*, 1H); 7·07 (*s*, 1H).

All the compounds gave satisfactory elemental analysis.

TABLE I



No.	α,β-Unsaturated acid	Dichlorophenol	Dichlorochromanone					Elution solvents A : B	m.p. (°)	m.p. of 2,4,-DNP (°)
			R^1	R^2	R^3	R^4	R^5			
I	Acrylic	2,3-	H	H	H	Cl	Cl	40 : 60	69–70	269–70
II	Acrylic	2,4-	H	H	Cl	H	Cl	95 : 5	85–86	279–80
III	Acrylic	3,4-	H	H	Cl	Cl	H	50 : 50	131–32	247–48
IV	Acrylic	3,5-	H	Cl	H	Cl	H	25 : 75	141–42	255–56
V	Crotonic	2,3-	CH_3	H	H	Cl	Cl	90 : 10	117–18	231–32
VI	Crotonic	2,4-	CH_3	H	Cl	H	Cl	95 : 5	106–107	263–64
VII	Crotonic	3,4- (i)	CH_3	H	Cl	Cl	H	70 : 30	141–42	225–26
		(ii)			Crotonate			80 : 20	49–50	..
VIII	Crotonic	3,5- (i)	CH_3	Cl	H	Cl	H	5 : 95	94–95	230–31
		(ii)			Crotonate			26 : 75	61–62	..

A = Light petroleum ether (b.p. 40–60°)
B = Benzene.

We are thankful to Dr. K. Nagarajan, Ciba-Geigy Research Centre, Bombay, for the spectra and to Mrs. J. A. Patankar and Mr. D. S. More for micro-analyses.

Department of Organic Chemistry, J. R. MERCHANT.
Institute of Science, R. B. UPASANI.
Bombay 400 032, *March* 5, 1980.

1. Irasay, R. D., *Ger. Offen.*, **1**, 928, 027 ; *Chem. Abstr.*, 1970, **72**, 55261 *c*.
2. Du Pont de Nemours, E. I. and Co., *Brit.*, 1,265,212; *Chem. Abstr.*, 1972, **76**, 140531 *t*.
3. Moon, M. W., Sharp, J. C., *Ger. Offen.*, **2**, 513, 652; *Chem. Abstr.*, 1976, **84**, 30890 *s*.

EFFECT OF PHENACYL PYRIDINIUM BROMIDE ON GERMINATION AND SEEDLING EMERGENCE IN *CAJANUS CAJAN*

PHENACYL pyridinium bromides which are used as precursors for azomethine ylides*, have been utilized in the synthesis of a wide variety of cyclic and heterocyclic systems[1-3]; but their biological studies have not been reported so far.

For a better crop, a good knowledge of the seed germination behaviour is needed to devise suitable control measures. *Cajanus cajan* Sprang. is extremely nutritious and is consumed as a dal or flour. The leaves afford excellent fodder. Apart from these, the seeds and the leaves are of medicinal importance. The present investigation has been undertaken to ascertain whether the germination in this species is stimulated or retarded by the application of phenacyl pyridinium bromide.

The seeds were hand picked in May, 1979 from the field and were stored in glass stoppered bottles. Phenacyl pyridinium bromide was prepared by refluxing phenacyl bromide (40 m mole) with pyridine (40 m mole) in 100 ml of anhydrous benzene for 6 hrs and keeping overnight. The solid was filtered, washed with benzene and dried at room temperature. The white crystals of pyridinium salt was further recrystallized from $CHCl_3$-pet.ether (1 : 2), m.p. 190-92° C (Lit [4] m.p. 194-96° C).

Germination studies were carried out with 20 seeds by the wet filter paper method under laboratory conditions (23-37° C) in September, 1979. Seeds were treated with 10, 100, 200, 500, and 1000 ppm solutions of pyridinium salt. Three replicates of each treatment and three distilled water controles were maintained. A twelve hourly record of the number of seeds germinated in each petridish was made. The observations were continued upto 72 hours until the germination was constant in two sets of experiments. The length of the radicles was measured after complete germination.

The percentage of germination increases with increasing duration, but it decreases gradually as the concentration of pyridinium salt increases. In the beginning (in 36 hours) the changes in percentage germination are sharp, then gradual till the germination is completed[5,6]. The results are given in Table I.

* The ylides are the reactive intermediates in which a carbanion is directly linked to a heteroatom carrying a high degree of positive charge.

(M = N, P, As, S, Sb, etc.).

TABLE I

Changes in percentage germination of the seeds of Cajanus cajan *Sprang at different concentrations of phenacyl pyridinium bromide*

Time (hours)	Concentration (ppm)					
	0 (Control)	10	100	200	500	1000
0	..	..	..	..	..	..
12	17·0 ± 4·4	7·5 ± 2·0	6·6 ± 3·3	6·0 ± 2·2	5·7 ± 2·0	5·0 ± 2·2
24	62·3 ±14·2	55·0 ± 4·1	38·3 ± 1·7	33·3 ± 1·9	30·5 ± 2·1	27·5 ± 3·2
36	80·4 ± 8·6	78·0 ± 4·1	74·0 ± 3·9	67·0 ± 2·9	65·0 ± 3·1	63·0 ± 4·5
48	82·5 ± 6·3	80·0 ± 2·9	78·5 ± 4·4	70·5 ± 2·4	68·5 ± 2·6	66·0 ± 4·2
60	85·0 ± 5·1	82·0 ± 2·7	80·0 ± 5·0	73·0 ± 2·7	69·0 ± 2·9	66·5 ± 4·3
72	85·0 ± 5·1	82·0 ± 2·7	80·0 ± 5·0	73·0 ± 2·7	69·0 ± 2·9	66·5 ± 4·3